Anomalous Effects of Para Substituents on the Stability of Sterically Congested Triplet Diarylcarbenes. The First Triplet Carbene Surviving over Minutes under Normal Conditions

Hideo Tomioka,* Makoto Hattori, Katsuyuki Hirai, and Shigeru Murata

Chemistry Department for Materials
Faculty of Engineering
Mie University, Tsu, Mie 514 Japan

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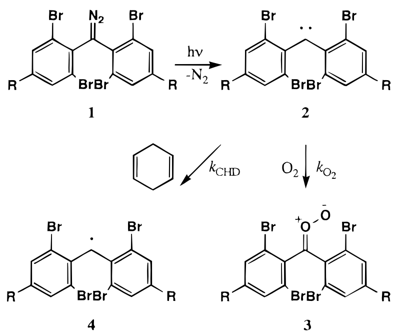
For a long time, carbenes were believed not to be stable enough to be isolated in macroscopic amounts at room temperature. However, the recent syntheses of stable singlet carbenes, i.e., phosphinocarbenes[1] and imidazol-2-ylidenes,[2] have upset this extreme view. Naturally, however, interpretation of these species as free carbene has been a topic of debate, especially concerning the possible contribution of the ylidic character as a result of $p\pi-p\pi$ delocalization.[3,4]

The stabilization of a triplet carbene emerges as a challenging target since triplet carbene is less susceptible to the conjugative stabilization causing the issue of electronic configuration as a pure carbene rather than the singlet manifold.[5] Moreover, steric protection (kinetic stabilization) is an ideal method of stabilizing the triplet since a protecting group when introduced near carbene center not only blocks the carbenic center from external reagents but also results in thermodynamic stabilization by increasing the central angle.[6] Attempts have been made along this line whereby triplet diphenylcarbenes (DPC) were stabilized by introducing a series of substituents at the ortho positions.[7,8] However stable triplet carbene is not realized yet partly due to a voracious appetite of carbene for electrons. Thus even the most persistent triplet carbene, i.e., 2,2′,4,4′,6,6′-hexabromodiphenylcarbene (**2a**), can survive no more than seconds under normal conditions, i.e., in a degassed benzene solution at room temperature.[8f] In this light it is crucial to develop a new strategy to stabilize this highly reactive center. During the course of our study to examine the effect of substituents on the reactivity of a series of polybrominated diphenylcarbenes (**2**), we found that the lifetime of these carbenes was dramatically affected by the remote para substituents whereby triplet carbene surviving over minutes was realized for the first time.

a : R = Br, **b** : R = Me, **c** : R = ^{t}Bu



Laser flash photolysis (LFP)[9] of (2,2′,6,6′-tetrabromo-4,4′-di-*tert*-butyldiphenyl)diazomethane (**1c**) in a degassed benzene solution at room temperature with a 308 nm pulse from a XeCl excimer laser (10 ns, 70−90 mJ) produced a transient species showing a strong absorption at 340 nm and a weak absorption extending from 380 to 400 nm, which appeared coincident with the pulse (Figure 1). On the basis of the low-temperature spectrum and ESR measurement (vide infra), we assigned the transient absorption to triplet carbene (**2c**). Support is lent to this assignment by trapping experiments using oxygen (vide infra). The oscillogram trace of the transient absorption due to **2c** was monitored at 340 nm is shown in the inset of Figure 1. *The transient signals decayed very slowly; it took more than 200 s before all the signals disappeared completely under these conditions*. The decay was found to be second order ($2k/\epsilon l = 0.36\ s^{-1}$). The rough lifetime of **2c** is estimated in the form of half-life, $t_{1/2}$, to be 16 s. These values clearly indicate that triplet **2c** is some 20 times longer-lived than triplet **2a** ($2k/\epsilon l = 8.9\ s^{-1}$, $t_{1/2} = 1$ s).[8f]

Anomalous stability of **2c** was also shown by monitoring the UV−vis spectra of **2** at low temperature as a function of temperatures.[10] Irradiation ($\lambda > 350$ nm) of **1c** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of new bands with maxima at 331 and 344 nm at the expense of the original absorption due to **1c**. The new bands exhibited no change when kept at 77 K but disappeared upon thawing the matrix to room temperature. On the basis of these observations coupled with EPR data (vide supra), the absorption spectrum can be attributed to triple **2c** generated by photodissociation of **1c**. Stability of carbene was examined then by warming the matrix containing **2c** slowly (5 °C/15 min) from 77 K. No appreciable changes were observed for the absorption bands due to **2c** in MTHF up to 160 K. Significant decomposition began only at 170 K where the "first-order" half-life was approximately 48 min. Similar measurement with **2a** showed that this carbene started to decompose at much lower temperature; at 120 K, $t_{1/2}$ was 40 min.[8e] Thus, the observations suggested that the replacement of bromine groups at the para positions with *tert*-butyl groups resulted in an unexpectedly large stabilizing effect on triplet carbene **2**.

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(10) Low-temperature spectra were obtained by using an Oxford variable-temperature cryostat (DN1704) with an Oxford Instrument intelligent temperature controller (ITC4).

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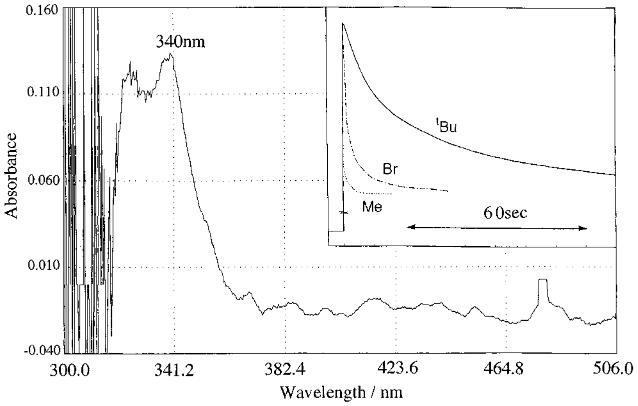

Figure 1. Absorption spectrum of the transient products formed during the irradiation of **1c** in degassed benzene, recorded 50 μs after excitation. The inset shows oscillogram traces monitored of transient absorption due to carbenes **2a** (— • —), **2b** (- - -) and **2c**(—).

Table 1. Kinetic and ESR Data for Carbenes **2**

carbenes	$2k/\epsilon l^a$ (s^{-1})	$t_{1/2}{}^a$ (s)	$k_{O_2}{}^b$ ($M^{-1}\,s^{-1}$)	$k_{CHD}{}^a$ ($M^{-1}\,s^{-1}$)	D^c (cm^{-1})	E^c (cm^{-1})
2a	8.9	1.0	1.1×10^7	7.4×10^2	0.3958	0.0295
2b	$(4.7)^d$	0.22	2.3×10^7	3.7×10^2	0.3957	0.0275
2c	0.35	16	2.1×10^7	5.3×10^2	0.3966	0.0311

[a] In degassed PhH at 20 °C. [b] In PhH at 20 °C. [c] In 2-MTHF at 77 K. [d] Unimolecular decay.

In marked contrast, the introduction of methyl groups at the para positions caused a significant destabilization in triplet carbene **2**. Thus, LFP of (2,2′,6,6′-tetrabromo-4,4′-dimethyldiphenyl)diazomethane (**1b**) in a degassed benzene also produced a transient absorption due to triplet carbene (**2b**), which decay rather rapidly within 1 s. The decay was found to be best fit to a first-order decay ($k = 4.7$ s^{-1}) and the lifetime (τ) is estimated to be 0.21 s ($t_{1/2} = 0.22$ s). In MTHF matrix, it decayed very fast even below 100 K.

The results clearly suggest that the lifetime of polybrominated DPC (**2**) was dramatically affected by the remote para substituents which are not expected to exert significant effect on the steric congestion around the carbenic center. In order to know the origin of these puzzling effects, the following studies were carried out. EPR spectra of carbenes (**2**) were obtained in MTHF glasses at 77 K by subjecting frozen solution of **1** to short periods of photolysis.[11] The spectra were persistent at this temperature and were analyzed in terms of D and E values, which are reported in Table 1. 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. Inspection of the data in Table 1 clearly indicates that there are no significant changes in E/D values as one changes the para substituents.[12] These observations indicate that the para substituents exhibit little effects on the geometries of triplet carbenes **2** as expected. PM3 calculations also indicate that both the central angle (α) and dihedral angle (θ) of the two aryl rings are essentially the same between the three carbenes (**2a**−**c**).

The reactivities of **2** toward typical triplet quenchers, i.e., oxygen and 1,4-cyclohexadiene (CHD) were then investigated by using LFP. Thus, LFP of **1** on a non-degassed benzene solution resulted in a dramatic decrease in the lifetime of triplet **2** and a concurrent appearance of a new absorption band at 410 nm. The rate of increase in the band at 410 nm is practically the same as that of the peak due to **2**, showing that triplet **2** is quenched with oxygen to form the carbonyl oxide (**3**).[13] The rate constant (k_{O_2}) for the quenching of **2** by oxygen is determined from a plot of the observed pseudo-first-order growth rate of **3** as a function of [O_2]. Similarly LFP of **2** on a degassed benzene solution in the presence of CHD generated a new signal attributable to the diarylmethyl radicals (**4**) as the signals of **2** decayed, showing that triplet **2** abstracts H from the diene.[14] The rate constant (k_{CHD}) of H abstraction of **2** from CHD is determined from a plot of the apparent build-up rate constant of the radical vs [CHD]. Inspection of the data summarized in Table 1 suggests that the reactivities of **2** toward those triplet quenchers are again not significantly affected by the para substituents.

Thus, these observations clearly support a naive idea based on intuition that the para substituents exert almost no steric effects around the remote carbenic center of **2** at least in terms of the sterically congestedness. Electronic effects, on the other hand, which usually affect the singlet state energy more effectively than the triplet, seem also not so important as to change the reactivity of **2**.[15] What is the origin of the marked para effect on the stability of **2** in benzene, then? Benzene is known to be one of the least reactive solvents toward triplet carbenes. Thus most persistent diphenylcarbenes undergo dimerization in benzene to form tetraarylethylenes as almost exclusive isolable product.[7,8] Carbene **2a** also underwent dimerization as evidenced by the second-order decay kinetic in benzene. However, product analysis of the spent solution showed that carbenic dimers were formed in surprisingly small amount. This suggests that simple dimerization of **2c** at the carbene center must suffer from severe steric repulsion and hence the carbene is forced to react at the other positions. The most probable reactive sites are the aromatic rings, where spin can be delocalized. In this light it is important to note that trityl radicals are known to undergo either methyl−para or para−para couplings depending on the substitution patterns.[16] Thus, it is likely that the brominated DPCs (**2**) also undergo similar coupling. The coupling reactions of trityl radicals are not suppressed by "reactive" substituents. The anomalous reactivity of halogen at the para position is noted, for instance, (p-bromophenyl)diphenyl undergoes methyl−para coupling.[17] On the other hand, tri-p-tolylmethyl undergoes rapid disproportionation to yield tri-p-tolylmethane and a quinoid structure which rapidly polymerizes.[18] However, the coupling at the para position is retarded by *tert*-butyl group at the para positions.[19] Thus, rather large stabilizing effects of *tert*-butyl groups at the para positions on the lifetime of **2** compared to that of bromo and methyl groups are compatible with effect of substituents observed in the coupling reaction of trityl radicals. The complexity of the products observed in the reaction of **2** must be partly due to the complexity associated with the coupling reactions. The α-para coupling of triplet carbenes, for instance, unlike that of trityls, does not lead to a final stable product and gives rise to an intermediate open-shell molecule whose subsequent reactions will be complicated by possible ambient reactivity.

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