Generation, Direct Observation and Kinetics of Triplet (2,4,6-Triisopropylphenyl)phenylcarbene

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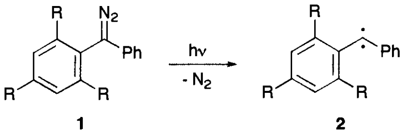
The title carbene (**2a**) was generated and studied not only by product analysis but also by spectroscopic means. The results are compared with those observed for the corresponding *tert*-butyl analogue (**2b**), which revealed intriguing and unique natures required for kinetic protectors of triplet carbene.

Since stable singlet carbenes have been synthesized and characterized in macroscopic scale,[1,2] the stabilization and isolation of a triplet counterpart has emerged as a next challenging target.[3] Recent growing interest in triplet carbenes as potential organic ferromagnets[4] adds more practical meanings on the project.

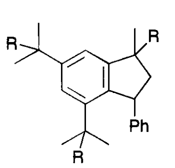
The stabilization of a triplet carbene is shown[3] to be better accomplished by steric protection than thermodynamic effects since the latter strategy not only result in the stabilization of the singlet but also poses the issue of electronic configuration as a pure carbene (one-centered diradical) as a result of conjugation. While steric protection (kinetic stabilization) is therefore a much better method of stabilizing the triplet, due to the highly reactive nature of carbenes, this strategy encounters a limitation when alkyl groups are employed as protecting groups. For instance, *tert*-butyl group, which has been recognized as one of the most effective protecting group, is shown to be ineffective in protecting triplet carbene center, since it is attacked by proximate carbene center instantaneously.[5]

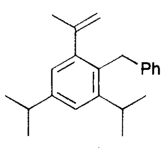
Isopropyl group appears to be an attractive kinetic protector for carbene since it is not expected to be in too much close contact with carbene center when introduced at ortho position of diphenylcarbene, but is still able to block the center from external reagents. Thus, we generated, characterized and studied the title carbene (**2a**) and compared its features with that of the *tert*-butyl counterpart (**2b**).



1 **2**

a: R = ^{i}Pr, **b**: R = ^{t}Bu





3 **a** : R = H, **b** : R = Me **4**

Irradiation of a degassed benzene solution of (2,4,6-triisopropylphenyl)phenyldiazomethane (**1a**)[6] at room temperature afforded phenylindan (**3a**)[7] and diphenylmethane (**4**)[7] in 10:1 ratio. It is probable that **3a** is produced from the photolytically generated carbene (**2a**), which underwent insertion into the C-H bonds of isopropyl methyl groups at the ortho positions. The formation of **4**, on the other hand, can be explained in terms of hydrogen abstraction of **2a** from the methine of *o*-isopropyl group, followed by H migration in the resulting diradical. It may be that **3a** is also formed by hydrogen-abstraction mechanism. Similar irradiation of **1a** in methanol, however, resulted in the exclusive formation of methyl ether at the complete expense of **3a** and **4**. This is not surprising since methanol is known[8] as a particularly excellent scavenger for most of the carbenes. These results are in contrast with that observed for the *tert*-butyl counterpart (**2b**) where the exclusive formation of the corresponding indan (**3b**) is observed even in methanol.[5]

Irradiation (λ>300 nm) of **1a** in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave a fine structured EPR line shape characteristic of randomly oriented triplet molecules with a large *D* value attributable to a one-center nπ spin-spin interaction at the divalent carbon of diarylcarbene.[9] The zero-field splitting (ZFS) parameters were $|D|$=0.4076 cm^{-1} and $|E|$=0.01495 cm^{-1}, showing unequivocally that the triplet signals are due to diphenylcarbene (^{3}**2a**) generated from **1a** as a result of N_2 elimination upon irradiation.

Similar irradiation of **1a** in a soft matrix, i.e., 3-methylpentane (3-MP) glass at 77 K also gave a structured EPR spectrum due to ^{3}**2a**. However, the *x* and *y* lines of the spectrum were closer than those observed in 2-MTHF matrix at 77 K and analysis of the signals gave markedly smaller ZFS parameters ($|D|$=0.3749 cm^{-1}, $|E|$=0.00935 cm^{-1}). Since the *E* value, when weighted by *D*, depends on the magnitude of the central C-C-C angle, it indicates that, in soft matrices, the carbene relaxes to a

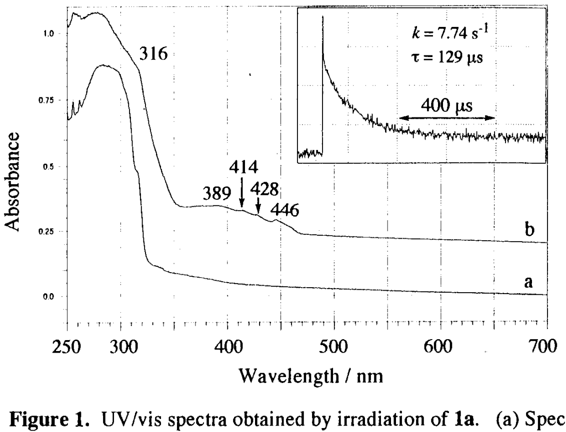


Figure 1. UV/vis spectra obtained by irradiation of **1a**. (a) Spectrum of **1a** in 2-MTHF at 77 K. (b) Same sample after 10 min irradiation (λ>300 nm) at 77 K. Inset shows a plot of the absorbance at 320 nm as a function of time in a degassed benzene at 20 °C.

structure with an expanded C-C-C angle presumably to gain relief from steric compression.[10]

The results are also to be compared with those observed for ^{3}**2b**, which exhibits essentially zero E value in both matrices at 77 K.[11]

Irradiation of **1a** in 2-MTHF glass at 77 K was then monitored by UV/vis spectroscopy, which revealed the rapid appearance of new absorption bands at the expense of the original absorption due to **1a** (Figure 1). The new spectrum consists of two identifiable features, intense UV band with maxima at 316 nm and weak, broad and structured ones with apparent maxima at 389, 414, 428, and 446 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic glasses at 77 K.[9b,12] The glassy solution did not exhibit any changes for several hours when kept at 77 K, but the characteristic bands disappeared irreversibly when the matrix was allowed to warm to 100 K. On the basis of these observations, coupled with the EPR data, the absorption spectrum can be safely assigned to triplet carbene **2a**.

Laser flash photolysis (LFP) of a degassed benzene solution of benzophenone (BP, 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 320 and 530 nm apparently due to triplet BP.[13] When LFP of BP was carried out in the presence of **1a**, essentially the same absorption was observed. However, the absorption band at 530 nm disappeared much faster than that at 320 nm and the rate of the 530 nm decay increased with the increasing concentration of **1a**.

This suggests that triplet BP is quenched by **1a**. The bimolecular rate constant for triplet BP quenching by **1a** was obtained from a plot of the rate of decay for triplet BP monitored at 530 nm vs. concentration of **1a** to be $k_{\rm BP}=4\times10^{9}$ M^{-1} s^{-1}, which is nearly diffusion-controlled. These observations indicate that energy transfer from triplet BP to **1a** occurs.

The residual spectrum around 320 nm is similar to that observed during the photolysis of **1a** in 2-MTHF glass at 77 K (vide supra). Thus, we assign the transient product showing the absorption maximum around 320 nm from the sensitized photolysis of **1a** to triplet carbene ^{3}**2a** which must be generated from triplet excited state of **1a**. The decay of the transient band due to ^{3}**2a** was found to be first order, in accordance with the product analysis data, showing that intramolecular H abstraction leading to **3** and **4** is the main decay pathway for triplet carbene (^{3}**2a**) under these conditions, and the lifetime was determined to be 129 μs, which is essentially the same with that of ^{3}**2b** (τ=120 μs).[5]

The comparison of the data between the two carbene systems reveals intriguing and unique natures required for kinetic protectors of triplet carbenes.

The significant E/D values of ^{3}**2a** as opposed to the essentially zero E value for ^{3}**2b** under the identical conditions clearly suggest that steric congestion around the carbene center in ^{3}**2a** is less severe than that in ^{3}**2b**, as expected. This suggests that the two methyls of *o*-isopropyl groups in ^{3}**2a** are directing opposite to the carbene center in order to avoid steric interaction at least in matrices at low temperature.

The observations reveal that *o*-isopropyl groups can act as kinetic protector of triplet carbene comparable to sterically more bulky *tert*-butyl group in the absence of efficient external reagents, although it can not protect the carbenic center from efficient trapping reagents such as methanol as opposed to *tert*-butyl groups.

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6 The diazomethane **1a** was prepared by the treatment of (2,4,6-triisopropylphenyl)phenylketimine with N$_2$O$_4$ followed by the reduction of the resulting *N*-nitroso ketimine with LiAlH$_4$; ^{1}H NMR (CDCl$_3$) δ 7.28 (t, J=7.26 Hz, 2 H), 7.01 (t, J=7.26 Hz, 1 H), 7.12 (s, 2 H), 6.79 (d, J=7.26 Hz, 2 H), 3.07 (sept, J=6.93 Hz, 2 H), 2.95 (sept, J=6.93 Hz, 1 H), 1.30 (d, J=6.93 Hz, 6 H), 1.19 (d, J=6.93 Hz, 6 H), 1.11 (d, J=6.93 Hz, 6 H); IR (NaCl) 2024 cm^{-1}.

7 **3a** (geometrical mixture): a colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.28-7.10 (m, 3 H), 6.99-6.82 (m, 4 H), 4.45-4.37 (m, 1 H), 3.33-3.12 (m, 1 H), 2.94-2.22 (m, 4 H), 1.30-0.83 (m, 15 H); HRMS for C$_{22}$H$_{28}$: Calcd *m/z* 292.2191; obsd 292.2182. **4**: a colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.20 (dd, J=7.35, 7.53 Hz, 2 H), 7.12 (t, J=7.53 Hz, 1 H), 7.00 (d, J=7.35 Hz, 2 H), 6.874 (s, 1 H), 6.868 (s, 1 H), 5.04 (s, 1 H), 4.74 (s, 1 H), 4.09 (s, 2 H), 2.95 (sept, J=6.80 Hz, 1 H), 2.90 (sept, J=6.98 Hz, 1 H), 1.91 (s, 3 H), 1.28 (d, J=6.98 Hz, 6 H), 1.07 (d, J=6.80 Hz, 6 H); HRMS for C$_{22}$H$_{28}$: Calcd *m/z* 292.2191; obsd 292.2097.

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11 ZFS parameters for ^{3}**2b** are; $|D|$=0.3408 cm^{-1}, $|E|\sim$0 cm^{-1} and $|D|$=0.3390 cm^{-1}, $|E|\sim$0 cm^{-1}, in 2MTHF and 3-MP at 77 K, respectively.

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