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Reactions and Kinetics of (2,4,6-Tri-*tert*-butylphenyl)phenylcarbene

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The title carbene generated by photolysis of the corresponding diazo compound at room temperature gave 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan quantitatively. Triplet states of the carbene were observed by laser flash photolysis of the diazo compound in the presence of benzophenone as a triplet sensitizer.

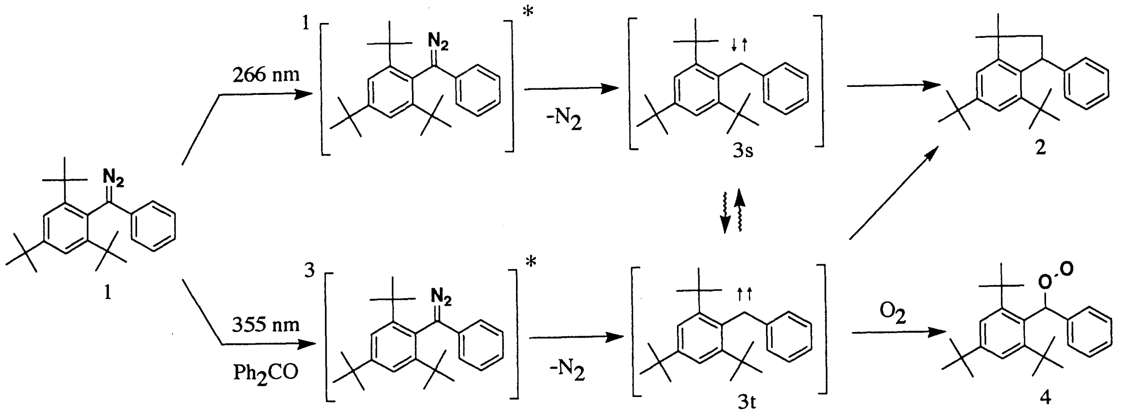
There have been continued and ever-increasing interests to persistent radicals since Gomberg in the year 1890 and many stable radicals have been synthesized and characterized.1) In a sharp contrast, almost no efforts have been made concerning persistent carbenes and it is only very recently that the isolation of "bottle-able" carbenes has been realized.2) However, these carbenes are stabilized by two heteroatom substituents directly attached to the carbenic carbon, which not only makes these carbenes have the singlet ground state but also causes a controversial situation concerning the electronic configuration as a pure carbene due to the ylidic character.3) Obviously, the isolation of triplet carbene is the next target which we must challenge. Stabilization of triplet carbene must be accomplished better by steric protection than thermodynamic effects which usually result in the stabilization of the singlet, and attempts were made in this line where diphenylcarbenes were shown to be stabilized by introducing four methyl or chloro substituents at the ortho positions.4-7) *tert*-Butyl group has been recognized as one of the most effective protecting group and successfully used to protect many reactive centers in organic molecules.8) Thus, we examined the reactivities of the title carbene not only by product analysis but also by using flash photolysis techniques in order to know the effect on *tert*-butyl group as protecting group toward the carbenic center.

Irradiation of a degassed benzene solution of (2,4,6-tri-*tert*-butylphenyl)phenyldiazomethane9) (**1**, 7.7 × 10^{-3} M) at room temperature afforded 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan (**2**)10) almost quantitatively. It is probable that this indan (**2**) must be produced from the photolytically generated 2,4,6-tri-*tert*-butyldiphenylcarbene (**3**), which underwent insertion into the CH bonds of *tert*-butyl groups at the ortho positions. Similar irradiation of **1** either in cyclohexane or in methanol also gave only **2**, no solvent adducts being detected. It is rather surprising to note that the carbene was not trapped even by methanol since methanol is well-known as an particularly excellent scavenger for most of carbene, and this indicates that the carbenic center in **3** is not only almost completely blocked toward external reagents but also trapped by the butyl group instantaneously.

Laser flash photolysis (LFP) of a degassed cyclohexane or acetonitrile solution of **1** (2.8×10^{-4} M) at room temperature with the fourth harmonic (266 nm) of a Nd/YAG laser (ca. 30 mJ, 4-5 nsec pulses) produced no transient species to the limit of time resolution of our LFP system (5 nsec). Similar LFP of **1** 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,11) 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 **1**, 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 was increased. Since it is now well-documented12) that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diarylketone oxides, which are easily observed directly either by matrix isolation techniques or by flash photolysis to show a rather broad absorption band centered at around 390-450 nm, the observation can be interpreted as indicating that the triplet carbene (**3t**) is trapped with oxygen to generate carbonyl oxide (**4**). The bimolecular rate constant for the reaction of 3t with oxygen, k_{O2}, is readily determined to be $(1.2 \pm 0.2) \times 10^8$ $M^{-1}s^{-1}$ by monitoring the pseudo-first-order growth rate of **4**, k_{obs}, at various oxygen concentrations by using equation 1,

$$k_{obs} = k_0 + k_{O2}\,[\text{oxygen}] \qquad (1)$$

where k_0 represents the rate of decay of **3t** in the absence of oxygen.



The above observations indicate that the nascent and therefore singlet carbene (**3**) generated by direct irradiation of **1** 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, triplet sensitized photolysis of **1** 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.11) When LFP of BP was carried out in the presence of **1**, the essentially similar absorption was observed (Fig 1). 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 the concentration of **1**. This suggests that triplet BP is quenched by **1**. The bimolecular rate constant for triplet BP quenching

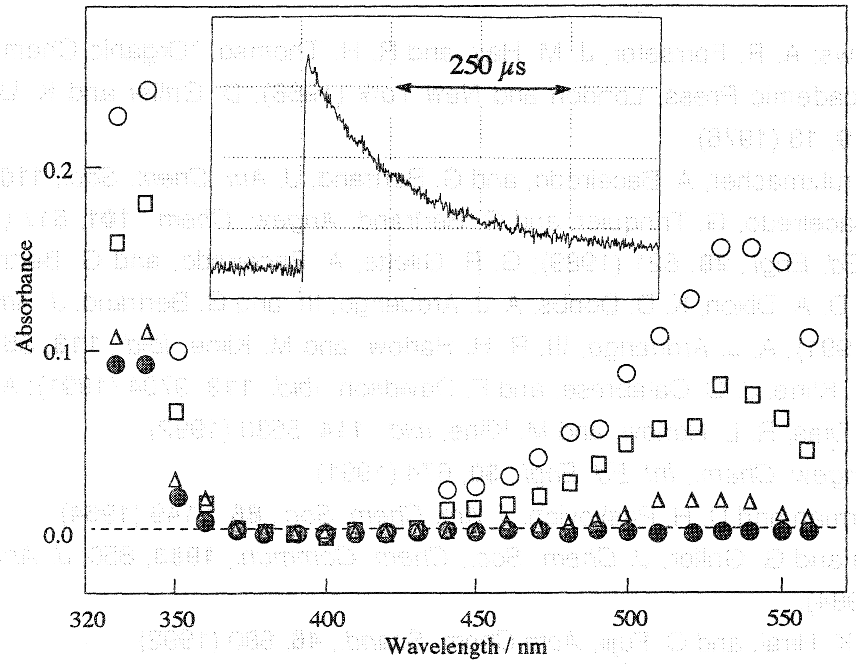


Fig.1. Absorption spectra observed on excitation of benzophenone(1.1×10^{-3} M) with a 355 nm laser pulse in the presence of (2,4,6-tri-*tert*-butylphenyl)phenyldiazomethane(6.7×10^{-4} M). Key is as follows:○,0.2 μs;□,0.4 μs;△ ,1.0 μs;●,3.0 μs after pulse. Insets show an oscillogram trace monitored at 340 nm.

by **1** was obtained from a plot of the rate of decay for triplet BP monitored at 530 nm vs. concentration of **1** to be $k_{BP} = (4.7 \pm 0.8) \times 10^9$ $M^{-1}s^{-1}$, which is nearly diffusion cotrolled, indicating that energy transfer from triplet BP to **1** occurs. The residual spectrum at 340 nm is similar to that obtained during the photolysis of **1** in a 2-methyltetrahydrofuran glass at 77 K. This absorption band was stable for hours at 77 K, but warming the sample to 110 K led to the disappearance. The product analysis of the spent solution showed the presence of the indan (**2**). On the basis of the low-temperature spectrum,[13)] the room temperature transient spectrum and the chemical analysis, we assign the transient product, showing the absorption maximum at 340 nm from the sensitized photolysis of **1** in benzene, to triplet carbene (**3t**) generated from triplet excited state of **1**. The oscillogram trace of the transient absorption due to **3t** monitored at 340 nm is shown in the inset of Fig 1. The decay was found to be first order, in accordance with the product analysis data, showing that intramolecular CH insertion to form **2** is the main decay pathway for triplet carbene (**3t**) under these conditions, and the lifetime was determined to be ca. 120 μs, which is some 60 times longer than that observed for diphenylcarbene.[14)]

In the light of the fact that half-lives of dimesitylcarbene[15)] and 2,2',4,4',6,6'-hexachlorodiphenylcarbene[6)] are determined to be 200 and 18 ms, respectively, the present observations suggest that *tert*-butyl group is much less effective in stabilizing the divalent center than methyl and even chloro groups. This is obviously due to a voracious appetite of carbenes for electrons by which they react even with very weak sources of electrons, e.g., C-H bond σ electrons.

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9) The diazomethane (**1**) was prepared by the treatment of (2,4,6-tri-*tert*-butylphenyl)phenylketimine with N_2O_4 followed by the reduction of the resulting N-nitroso ketimine with $LiAlH_4$. It was purified by gel permeation chromatography to afford a red crystal; mp 80-85°C; ^{1}H NMR (CCl_4) δ 7.60-6.88 (m, 7H, ArH), 1.40 (s, 9H, p-^{t}Bu), 1.34 (s, 18H, o-^{t}Bu); IR (NaCl) 2970, 2920, 2880, 2050, 1600, 1500, 1365 cm^{-1}. We wish to thank Professor R. Okazaki for advice in preparing the ketimine.

10) The indan (**2**) was obtained as a pale yellow oil; ^{1}HNMR (CCl_4) δ 7.72-7.28 (m, 7H, ArH), 4.76 (dd, J=10.0, 3.0Hz, 1H, ArPhCH-), 4.76 (dd, J=12.0, 10.0Hz, 1H, anti-$CHCMe_2$-), 2.44 (dd, J=12.0, 3.0Hz, 1H, syn-$CHCMe_2$-), 1.36 (s, 9H, ^{t}Bu), 1.24 (s, 3H, Me), 1.16 (s, 9H, ^{t}Bu), 1.04 (s, 3H, Me); MS m/e (relative intensity) 334 (24.0), 320 (25.7), 319 (95.9), 57 (100).

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