

Bis[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbene. The first all-hydrocarbon triplet diphenylcarbene having a half-life over one second under normal conditions

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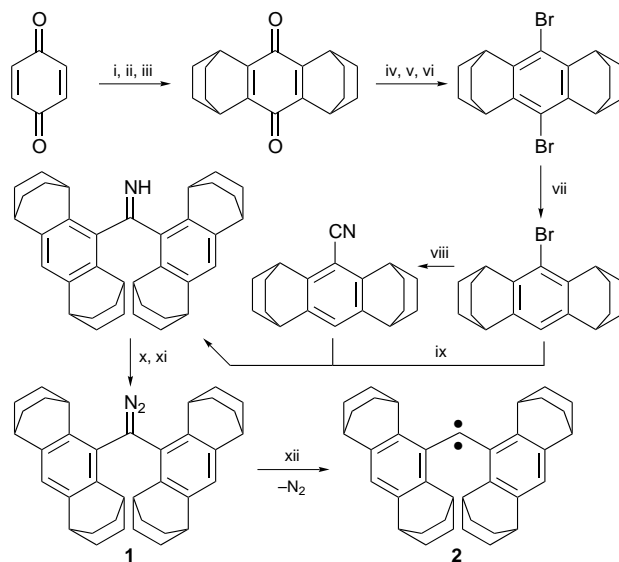
Bicyclo[2.2.2]octyl groups are demonstrated to be very effective kinetic protectors for triplet carbenes.

The stabilization of a triplet carbene¹ has emerged as a challenging target since the recent syntheses of stable singlet carbenes^{2,3} upset the long-standing view that carbenes are not stable enough to be isolated in macroscopic scale at room temperature.⁴ Steric protection is an ideal method for stabilizing the triplet since a protecting group when introduced near a carbene center not only blocks the carbene center from external reagents but also results in thermodynamic stabilization by increasing the carbene angle.^{5–7} However, due to the voracious appetite of carbenes for electrons, which they can abstract even from very poor sources of electrons such as C–H bonds, this strategy encounters a limitation when alkyl groups are employed as protecting groups. For instance, dimesitylcarbene was shown to decay by undergoing dimerization and to have a half-life of 160 ms, some five orders of magnitude longer lived than triplet diphenylcarbene. However, when more methyl groups are introduced on the phenyl rings, the carbenic center is more effectively blocked from external reagents due to a buttressing effect, but it becomes more easily trapped by the *ortho* methyl groups, which are brought closer to the carbene center, to form benzocyclobutene: didurylcarbene ($t_{1/2}$ 410 ms) was twice as long-lived as dimesitylcarbene, while decamethyldiphenylcarbene ($t_{1/2}$ 180 ms) decayed mainly unimolecularly by abstracting H from the *o*-methyl group and hence was shorter lived.^{5a,d}

In this light, it is crucial to develop a protecting group which is sterically congesting but unreactive toward triplet carbenes. Bicycloalkyl groups are very attractive since bridgehead C–H bonds are less susceptible to hydrogen abstraction, although not entirely unsusceptible,⁸ and thus the bridging chains will act as protectors. Thus, we generated diphenylcarbene protected by bicyclo[2.2.2]octyl groups and compared its reactivity with that of an open-chain ‘counterpart’, *i.e.* didurylcarbene (DDC).

The desired precursor diazomethane **1**[†] was prepared starting from a benzoquinone–cyclohexa-1,4-diene Diels–Alder reaction according to the reaction procedure as outlined in Scheme 1 and was obtained as a rather stable red solid with a mp of 183 °C (decomp.) after purification by gel permeation chromatography.

Irradiation of **1** in a 2-methyltetrahydrofuran (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 $n\pi$ spin–spin interaction at the divalent carbon of diarylcarbene. The fine-structure constants were $|D| = 0.3951 \text{ cm}^{-1}$ and $|E| = 0.0106 \text{ cm}^{-1}$, showing unequivocally that the triplet signals are due to diphenylcarbene **2** generated from **1** as a result of N_2 elimination upon irradiation. The EPR signals were persistent at this low temperature but disappeared irreversibly when the matrix was thawed. Since the E value 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 .⁹ Comparison of the E/D value (0.0269) of **2**



Scheme 1 Reagents and conditions: i, cyclohexa-1,4-diene, 120 °C; ii, H_2 –Pd/C; iii, Br_2 ; iv, NH_2OH ; v, SnCl_2 – Br_2 ; vi, NaNO_2 – HBr and Cu, 20 °C; vii, Bu^nLi and H_2O ; viii, CuCN ; ix, Bu^nLi ; x, N_2O_4 ; xi, LiAlH_4 ; xii, $h\nu$ ($\lambda > 300 \text{ nm}$)

with that observed for DDC ($E/D = 0.0279$),^{5c,d} an open chain ‘counterpart’ of **2**, indicates that carbene center of **2** is slightly more sterically congested than that of DDC.

Irradiation of **1** in 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 **1**. As shown in Fig. 1, the new spectrum consists of two identifiable features, two intense UV bands with maxima at 318 and 333 nm and a weak and broad one with an apparent maximum around 483 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic glasses at 77 K.¹⁰ The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm to room temp. and then cooled to 77 K, the characteristic bands disappeared. On the basis of these observations, coupled with the EPR data, the absorption spectrum can be attributed to triplet carbene **2**.

Again essentially the same spectral features were noted in the case of DDC. However, in this case, as the matrix thawed and carbene absorption bands decreased, a new broad absorption at 375 nm appeared. This secondary intermediate was assigned to *o*-xylylene presumably formed by an intramolecular 1,4 H shift from an *o*-methyl group to the carbene center and leading to benzocyclobutene.^{5a,d} The decay of the transient absorption of **2** was rather monotonous, no new band being detected even upon gradual warming, indicating that no intramolecular H abstraction occurs. This is in accord with the product analysis data.

Laser flash photolysis (LFP) of **1** in a degassed benzene solution at 20 °C with a 10 ns, 70–90 mJ, 308 nm pulse from a

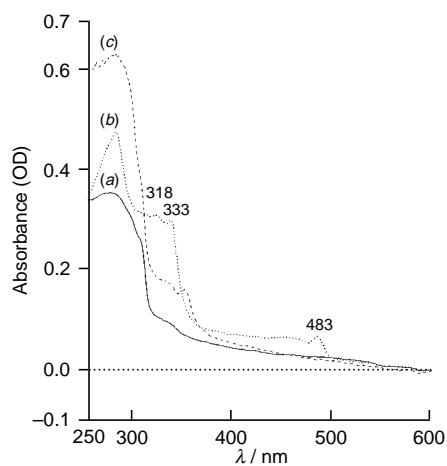


Fig. 1 UV-VIS spectra obtained by irradiation of **1** in MTHF. (a) Spectrum of **1** in MTHF at 77 K. (b) Same sample after warming the matrix to room temperature and refreezing to 77 K. OD = optical density.

XeCl excimer laser produced a transient species showing a strong absorption around 320–330 nm and a weak absorption around 480 nm, which appeared coincident with the pulse (Fig. 2). On the basis of the low-temperature spectrum, we assign the transient product to triplet **2**. The inset in Fig. 2 shows the decay of **2**, which is found to be second order ($2k/\epsilon l = 8.4 \text{ s}^{-1}$), suggesting that the carbene **2** decays mainly by undergoing dimerization. The approximate lifetime of **2** is estimated in the form of half-life, $t_{1/2}$, to be $1.5 \pm 0.1 \text{ s}$.

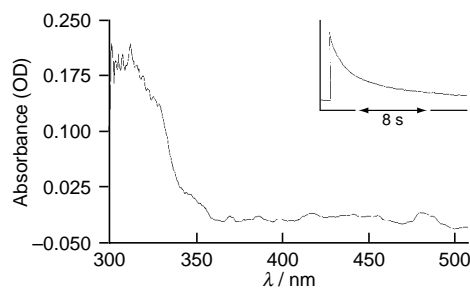


Fig. 2 Absorption spectrum of the transient products formed during the irradiation of **1** in degassed benzene, recorded 50 μs after excitation. The inset shows the time course of the absorption at 480 nm (oscillogram traces).

The reactivities of **2** toward typical triplet quenchers, *i.e.* oxygen and cyclohexa-1,4-diene (CHD), were then investigated by using LFP. Thus, LFP of **1** on a degassed benzene solution in the presence of CHD generated a new signal attributable to the diarylmethyl radicals as the signals of **2** decayed, showing that triplet **2** abstracts H from the diene.¹¹ 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]. Similarly the rate constant (k_{O_2}) for the quenching of **2** by oxygen was determined from a plot of the observed pseudo-first-order growth rate of the carbonyl oxide¹² as a function of $[\text{O}_2]$. The data are summarized in Table 1 along with those obtained in the reaction of DDC.

Table 1 Kinetic^a and EPR data^b for triplet diphenylcarbenes **1** and DDC

Carbenes	$(2k/\epsilon l)/$ s^{-1}	$t_{1/2}/\text{s}$	$k_{\text{CHD}}/$ $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{O}_2}/$ $\text{M}^{-1} \text{s}^{-1}$	$D/$ cm^{-1}	$E/$ cm^{-1}
2	8.4	1.5	3.6×10^2	2.3×10^8	0.3951	0.0106
DDC	—	0.41	3.4×10	7.1×10^7	0.3805	0.0106

^a In benzene at 20 °C. ^b In MTHF at 77 K.

Thus, these observations clearly support our original idea that bicycloalkyl groups are not delivering hydrogens to triplet carbenic centers while they are acting as a fairly good kinetic protector for the carbene. In this way, the formation of a hydrocarbon triplet carbene having a half-life over a second under normal conditions, *i.e.* in degassed benzene solution at room temperature, was realized for the first time. It should be noted here that the reactivity of **2** toward typical triplet quenchers is somewhat higher than that of DDC, while the half-life of **2** in benzene is distinctly longer than that of DDC. Comparison of the optimized geometries between DDC and **2** obtained by the AM1/UHF method¹³ reveals that there is slightly more space around carbene center in **2** compared to that in DDC, especially for a small particle such as hydrogen to attack, but that dimerization of the carbene center of **2** is obviously more severely retarded by the bulky rigid 'three-dimensional' bicyclic substituent compared to that of DDC which has more flexible methyl substituents.

The authors are grateful to the Ministry of Education, Science and Culture of Japan for support of this work.

Footnotes and References

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† Selected spectral data for **1**: $\delta_{\text{H}}(\text{CDCl}_3)$ 1.13–1.38 (16 H, m), 1.55–1.75 (16 H, m), 2.93 (4 H, b s), 3.16 (4 H, br s), 6.89 (2 H, s); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2032vs.

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Received in Cambridge, UK, 15th September 1997, 7/06663E