

Generation, Direct Observation, and Kinetics of Triplet 9-(1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthryl)phenylcarbene

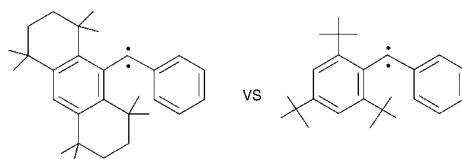
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Received May 1, 2002

ABSTRACT

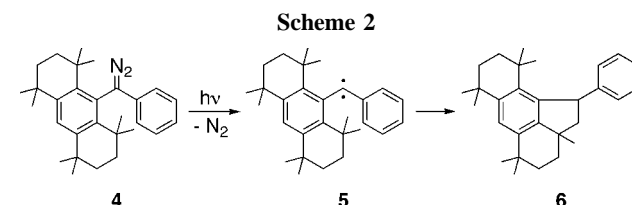
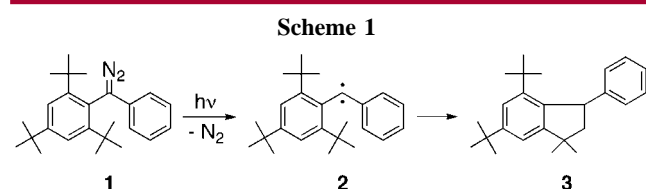


Reactivities of the title triplet carbene were compared with those of the “untied” counterpart, [2,4,6-tris(*tert*)butylphenyl](phenyl)carbene. An appreciable increase in the stability of triplet carbene is noted by tuning the distance between the *o*-hydrogen and the carbene center.

Triplet carbenes are highly reactive organic radicals that are also notoriously difficult to stabilize.¹ This is partly because they can abstract hydrogen even from very poor sources of electrons such as C–H bonds. For instance, the *tert*-butyl group is known as one of the most effective kinetic protectors and many reactive molecules have been stabilized and isolated by using this group. However, [2,4,6-tris(*tert*-butylphenyl)](phenyl)carbene (**2**) decayed due to intramolecular abstraction of hydrogen from the methyl group of *o*-*tert*-butyl to form indane (**3**) and the lifetime of **2** was estimated to be 125 μ s,² which is only 60 times longer than the “parent” diphenylcarbene (DPC) under identical conditions. The observations suggest that *tert*-butyl groups, which have been successfully used to protect many reactive centers, are almost useless to stabilize a triplet carbene center.

One way to retard intramolecular H transfer is to adjust the distance between hydrogen and the carbene center. We thus prepared a precursor (**4**) of hindered DPC in which the two *o*-*tert*-butyl groups have been “tied back” by incorporation into a six-membered ring.³ If the DPC (**5**) derived from **4** were to decay intramolecularly, a primary hydrogen would have to move in a different manner than that in **2** and the carbene should be more persistent than **2**. Inspection of the structure of triplet carbenes optimized by PM3 indicates that the carbene bond angle in **5** (166.8°) is smaller than that in **2** (179.5°) and that the distance between the methyl and carbene carbon in **5** (2.9 and 3.3 Å) is shorter than that in **2** (3.0, 3.1, and 4.4 Å).

9-(1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthryl)phenyldiazomethane (**4**)⁴ was prepared by the



treatment of the corresponding ketimine with N_2O_4 , followed by the reduction of the resulting *N*-nitrosoketimine with LiAlH_4 . An X-ray diffraction study of **4** confirmed the structure (Figure 1).⁵ Irradiation ($\lambda > 300$ nm) of **4** in a

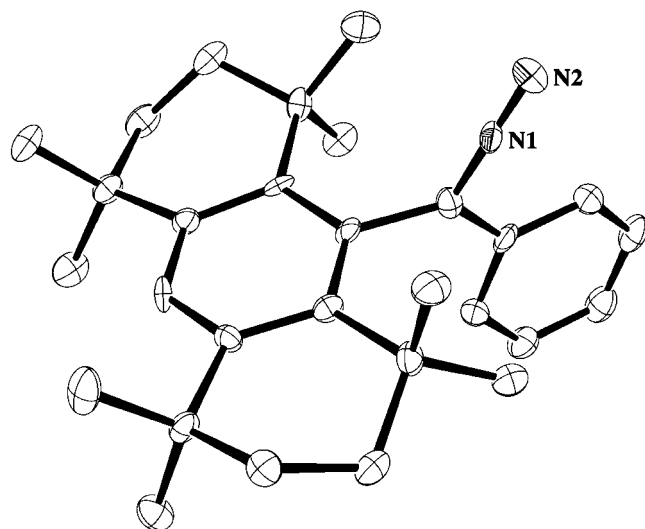


Figure 1. Molecular structure (ORTEP) of **4** as determined from X-ray diffraction analysis (see Supporting Information).

degassed benzene solution at room temperature gave indan derivatives (**6**)⁶ as a mixture of isomers. It is probable that **6** is produced from the photolytically generated carbene **5**, which underwent insertion into the C–H bonds of methyl groups at either the 1- and/or 8-position. A structural analysis was performed for **6** (Figure 2).⁵

The observation is essentially the same as that reported for *tert*-butylated DPC **2**. However, spectroscopic studies reveal the somewhat different nature between the two carbenes.

Irradiation ($\lambda > 300$ nm) of **4** in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave ESR signals with typical fine structure patterns for unoriented triplet species,⁷ i.e., **5** (Figure

(1) Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 175–214.

(2) (a) Hirai, K.; Komatsu, K.; Tomioka, H. *Chem. Lett.* **1994**, 503. (b) Tomioka, H.; Okada, H.; Watanabe, T.; Banno, K.; Komatsu, K.; Hirai, K. *J. Am. Chem. Soc.* **1997**, *119*, 1582. (c) Hirai, K.; Yasuda, K.; Tomioka, H. *Chem. Lett.* **2000**, 398.

(3) (a) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803. (b) Brunton, G.; Gray, J. A.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 4197.

(4) Red crystal; mp 133–150 °C dec; ¹H NMR (CDCl_3 , 300 Hz) δ 1.00 (s, 4H), 1.31 (s, 12H), 1.32 (s, 12H), 1.50–1.75 (m, 4H), 6.20 (d, $J = 8.08$ Hz, 1H), 6.87 (d, $J = 8.45$ Hz, 1H), 6.97 (t, $J = 7.90$ Hz, 1H), 7.11 (t, $J = 7.90$ Hz, 1H), 7.34 (d, $J = 7.72$ Hz, 1H), 7.48 (s, 1H); IR (KBr) 2046 cm^{-1} .

(5) See Supporting Information for full details of the X-ray crystal structure of compounds **4** and **6**.

(6) Major isomer: white crystal; mp 120–121 °C; ¹H NMR (CDCl_3 , 300 Hz) δ 0.861 (s, 3H), 0.96 (s, 3H), 1.16 (s, 3H), 1.23 (s, 3H), 1.30 (s, 3H), 1.33 (s, 3H), 1.41 (s, 3H), 1.51–1.67 (m, 7H), 1.96–2.06 (m, 1H), 2.09 (d, $J = 11.76$ Hz, 1H), 2.33 (dd, $J = 8.82, 11.76$ Hz, 1H), 4.77 (d, $J = 8.82$ Hz, 1H), 7.21 (s, 1H), 6.90–7.37 (m, 5H); EIMS m/z (%) 386.0 (M^+), 371.0 (100).

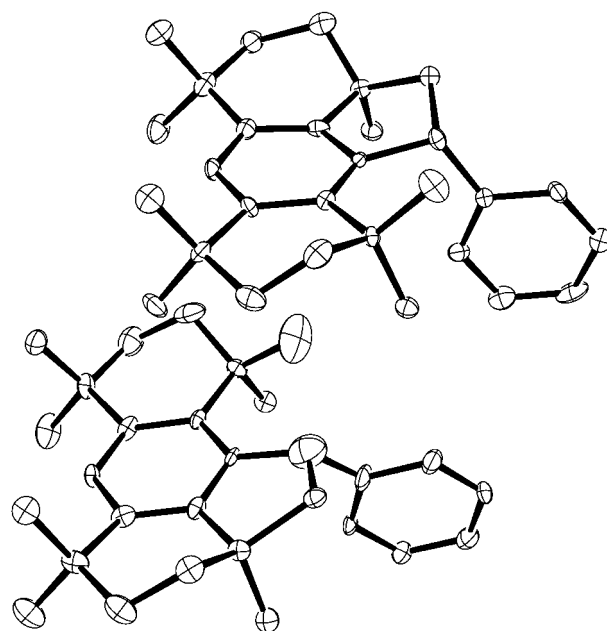


Figure 2. Molecular structure (ORTEP) of **6** as determined from X-ray diffraction analysis (see Supporting Information).

3). Signals at 4790, 4820, and 6850 G are assigned to a set of the high-field *x*, *y*, and *z* transitions from which the zero-field splitting (ZFS) parameters were obtained as $D = 0.332$ cm^{-1} and $E = 0.001$ cm^{-1} . Similar irradiation of **4** in 3-methylpentane (3-MP) at 77 K also gave ESR signals with essentially the same ZFS parameters ($D = 0.333$ cm^{-1} and $E = 0.001$ cm^{-1}). When sterically congested triplet DPCs are generated in a soft matrix, e.g., 3-MP, the *x* and *y* lines

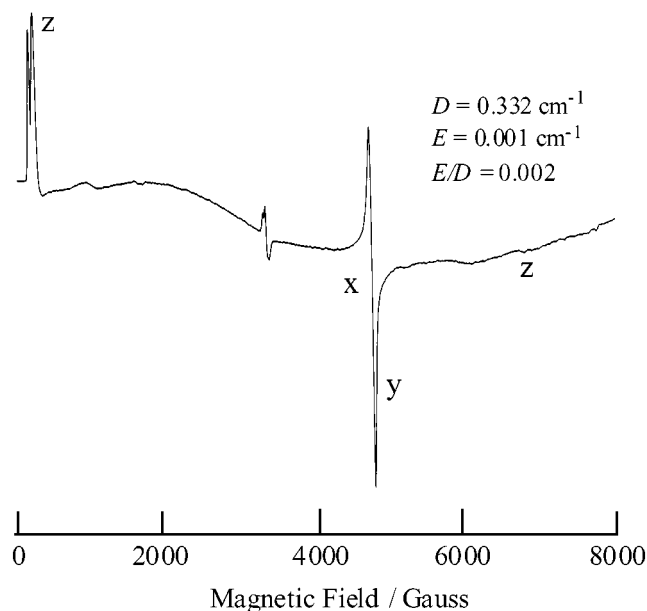


Figure 3. ESR signals obtained by photolysis ($\lambda > 300$ nm) of **4** in 2-methyltetrahydrofuran at 77 K.

of the spectrum become closer, thus resulting in a smaller E/D value than those in a harder matrix.

Since the E value, when weighted by D , depends on the magnitude of the central C–C–C bond angle,⁷ this is explained as an indication that the carbenes relax to a thermodynamically more stable structure with an expanded C–C–C angle, different from those of the nascent carbene, presumably to gain relief from steric compression.⁸ The small change in the parameters of **5** between two different matrices of significantly different rigidity suggests that in **5**, there is little change between the geometry at birth, which may be somewhat dictated by that of the precursor diazomethane, and the geometry of thermodynamically most stable form.

It is interesting to compare the results with that observed for **2**. The E/D value of **5** is larger than that of **2**, indicating that the carbene bond angle increases in going from **2** to **5**, which is in accord with the PM3 prediction.

To determine the thermal stability of these carbenes, they were generated in a more viscous matrix, i.e., propanetriol triacetate, and the matrix containing them was warmed gradually in 10 K increments. The ESR signals of **2** disappeared at around 170 K, while those of **5** started to decrease only at 190 K, suggesting that **5** is appreciably less reactive than **2**.

Irradiation of **4** in 2-MTHF 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 **4** (Figure 4). The new spectrum consists of two identifiable features, an intense UV band with a maximum at 281 nm and weak structured ones at 321 and 338 nm. These features are usually present in the spectra of triplet DPCs.⁹ Moreover, since strong ESR signals ascribable to a triplet carbene are observed under the identical conditions, the absorption spectrum can be assigned to triplet carbene **5**.

When the 2-MTHF matrix containing **5** was gradually warmed, the absorption bands due to **5** started to decompose at around 145 K. The bands due to **2** were shown to disappear at around 95 K under identical conditions. The greater thermal stability of **5** relative to that of **2** is again noted.

Laser flash photolysis¹⁰ of **4** in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl laser produced a transient species showing an apparent maximum at 335 nm (Figure 5). As the major absorption bands of carbene **5** are overlapping with the precursor diazo compound **4** and the samples were therefore not sufficiently transparent for adequate monitoring in this region, the whole spectrum was not observed. However, the band at 335 nm coincides with that observed during the

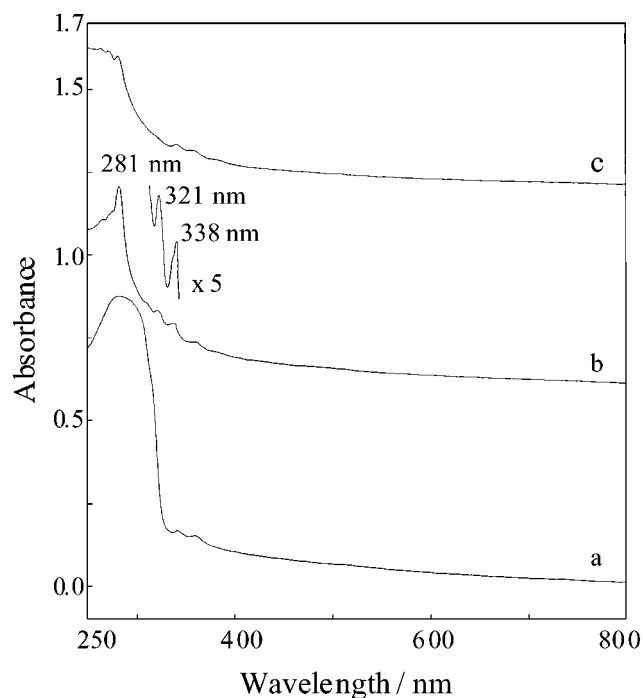


Figure 4. UV/vis spectra obtained by irradiation of **4** in 2-methyltetrahydrofuran. (a) Spectra obtained by irradiation ($\lambda > 300$ nm) of **4** at 77 K. (b) Same sample after 10 min of irradiation. (c) Same sample after the matrix was thawed to room temperature and refrozen to 77 K.

photolysis of **4** in a 2-MTHF matrix at 77 K. The decay of the transient band due to **5** was found to be first order ($k = 4.3 \times 10^3 \text{ s}^{-1}$), in accordance with the product analysis study, indicating that intramolecular H abstraction is the main decay pathway for **5**, and the lifetime was determined to be 233 μs .

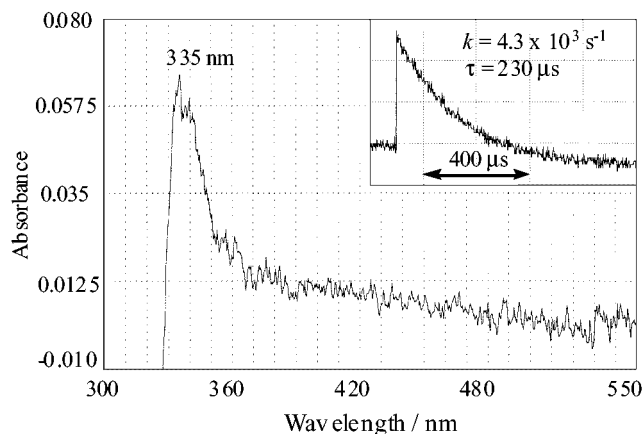


Figure 5. Absorption spectrum of transient products formed during the irradiation of **4** in degassed benzene recorded 1 μs after excitation. Inset shows the time course of the absorption at 335 nm (oscillogram trace).

(7) For reviews of the EPR spectra of triplet carbenes, see: (a) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1975; Vol. 2; pp 185–206.

(8) Tomioka, H. In *Advances in Strained and Interesting Organic Molecules*; Halton B., Ed.; JAI Press: Greenwich, CT, 2000; Vol. 8, pp 83–112.

(9) (a) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, p 185.

(10) Details of our LFT equipment are reported elsewhere; see ref 2b.

The increase in the stability of triplet DPC was achieved by tuning the distance between the *o*-hydrogens and the carbene center. The effect, however, is not large. Inspection of the X-ray structure of the precursor diazomethane **4** (Figure 1) and final product **6** (Figure 2) is expected to provide a more quantitative insight into the effect. Since the position of hydrogen in **4** cannot be determined absolutely, the bond distances between the 1- and 8-methyl and diazo carbons are used to roughly estimate the distance between hydrogen and the carbene carbon. As expected in the somewhat flexible octahydroanthracene structure, not all of the methyl groups in **4** are the same distance from the diazo carbon. The two methyl groups are noticeably closer (2.89 and 2.96 Å) than the other two (3.52 and 3.36 Å). As we have not determined the X-ray structure of **1**, we cannot evaluate the effect of fixation of one of the methyl groups into a six-membered ring. The most relevant compound we could find in the database¹¹ was 2-*tert*-butylbenzophenone.¹² The shortest bond distance between the methyl and carbonyl carbons in the benzophenone is 3.016 Å. This means that at least two methyl groups in **4** are forced to move close to the carbon that will become the carbene center. On the other hand, all bond lengths and angles in **6** are within the expected

(11) Cambridge Structural Data Base; Cambridge Crystallographic Data Center: Cambridge, UK, 2001.

(12) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.

limits for these types of compounds,¹³ but a slight distortion of the fused five-membered ring is noted by slight elongation of two bonds in this ring (1.55 and 1.56 Å). These observations mean that there might be a slight steric strain in a cyclic transition state for the H atom abstraction reaction of carbene **5** leading to **6**. Presumably, the stability of the carbene will be further increased if *o*-*tert*-butyl groups are tied back by incorporation into a smaller ring. Perdeuteration of all the primary hydrogens on the 1- and 8-methyl groups will also result in a more persistent triplet DPC. This research is currently in progress in our laboratory.

Acknowledgment. The authors are grateful to the Ministry of Education, Science and Culture of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (No. 12002007).

Supporting Information Available: X-ray structure determination for compounds **4** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) (a) Pitt, C. G.; Rector, D. H.; White, M. C.; McPhail, A. T.; Miller, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2374. (b) Ghosh, A. C.; Hazra, B. G.; Karup-Nielsen, I.; Kane, M. J.; Hawke, D.; Duax, W. L.; Weeks, C. M. *J. Org. Chem.* **1979**, *44*, 683. (c) Dobbs, T. K.; Hertzler, D. V.; Keen, G. W.; Eisenbraun, E. D.; Fink, R.; Hossain, M. B.; van der Helm, D. *J. Org. Chem.* **1980**, *45*, 4769. (d) Wilson, R. M.; Dietz, J. G.; Shepherd, T. A.; Ho, D. M.; Schnapp, K. A.; Elder, R. C.; Watkins, J. W., II; Geraci, L. S.; Campana, C. F. *J. Am. Chem. Soc.* **1989**, *111*, 1749.