ORGANIC
LETTERS

2000
Vol. 2, No. 19
2995−2997

Generation and Characterization of Triplet Anthryl(aryl)carbenes

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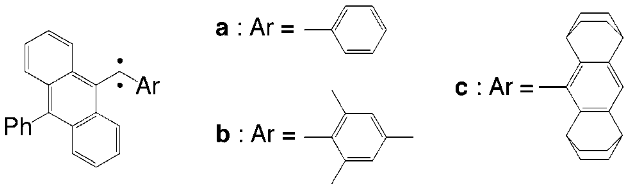
Received July 10, 2000

ABSTRACT



The title carbenes where aryl groups are phenyl, 2,4,6-trimethylphenyl, and octahydro-1,4:5,8-di(ethano)anthryl were generated for the first time by irradiation of the corresponding diazo precursors and fully characterized by ESR in a rigid matrix at low temperature. It has been demonstrated that anthryl groups can act as excellent reservoirs for the unpaired electrons as well as relatively effective kinetic protectors for carbene.

The unique role of the anthryl group on the structure and chemistry of triplet carbenes has been noted. Thus, triplet di(9-anthryl)carbene has been shown to have an almost linear and perpendicular structure with extensive delocalization of the unpaired electrons onto the anthryl portions.[1] In solution, it reacts with O_2 nearly 5 orders of magnitude slower than all other triplet carbenes, and the main mode of decay is self-quenching, which is diffusion-controlled.[2] Thus, the anthryl ring can be used as a reservoir of the unpaired electrons as well as a steric protector for the carbenic center. Despite its highly useful nature, the anthryl group has not been employed as a building block for persistent triplet carbenes.[3,4]

The reason for this lies mainly in the difficulty in preparing the nitrogenous precursors. The 10 position is usually attacked when 9-substituted anthracenes are subjected to the process necessary to prepare the diazo precursors. We found that this difficulty is overcome simply by introducing a phenyl group at the 10 position, which enabled us to prepare a series of anthryl(aryl)diazomethanes and generate and characterize the corresponding triplet carbene for the first time.

The desired diazo compounds **1a**−**c** were prepared by acyl cleavage of the corresponding *N*-alkyl-*N*-nitrosourethanes by potassium *tert*-butoxide according to the reactions summarized in Scheme 1 and obtained as rather stable orange solids[5] after repeated chromatography on a Shodex GPC H-2-1 column.

Irradiation of 9-(10-phenylanthryl)phenyldiazomethane

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(1) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Greene, F. D.; Abegg, V. P.; Weinshenker, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6335.

(2) Astles, D. J.; Girard, M.; Griller, D.; Kolt, J.; Wayner, D. D. *J. Org. Chem.* **1988**, *53*, 6053.

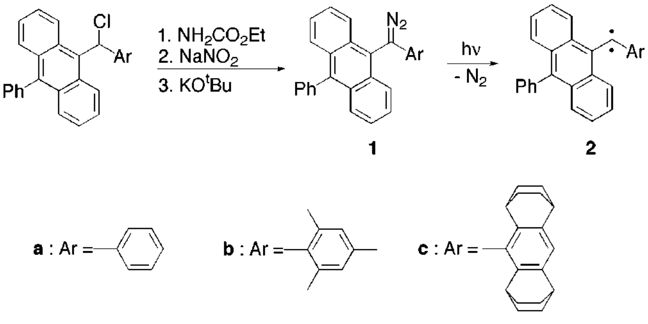
(3) For review of carbenes, see: (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (b) Regitz, M.; Ed. *Carbene-(oide), Carbine*; Houben-Weyl, Thieme: Stuttgart, 1989; Vol. E196. (c) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. I and II.

(4) See for reviews of persistent triplet carbenes: (a) Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 1315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 175−214.

(5) **1a**: orange solid; mp 122−126 °C (dec); ^1H NMR ($CDCl_3$) δ 6.91 (dd, $J = 7.3, 1.2$ Hz, 2 H), 7.03−7.09 (m, 1 H), 7.25−7.41 (m, 1 H), 7.46−7.52 (m, 4 H), 7.56−7.61 (m, 3 H), 7.73 (dd, $J = 8.6, 1.0$ Hz, 2 H), 8.14 (dd, $J = 8.8, 0.9$ Hz, 2 H); IR (KBr) ν 2032 cm^{-1}. **1b**: orange crystal; mp 142−146 °C (dec); ^1H NMR ($CDCl_3$) δ 2.17 (s, 6 H), 2.33 (s, 3 H), 6.97 (s, 2 H), 7.29−7.35 (m, 2 H), 7.40−7.46 (m, 4 H), 7.53−7.61 (m, 3 H), 7.67 (d, $J = 8.6$ Hz, 2 H), 8.06 (d, $J = 8.8$ Hz, 2 H); IR (KBr) ν 2032 cm^{-1}. **1c**: orange solid; mp 150−153 °C (dec); ^1H NMR ($CDCl_3$) δ 1.12−1.19 (m, 4 H), 1.35−1.50 (m, 4 H), 1.52−1.56 (m, 4 H), 1.65−1.73 (m, 4 H), 2.97 (bs, 2 H), 3.15 (bs, 2 H), 6.99 (s, 1 H), 7.29−7.45 (m, 6 H), 7.53−7.59 (m, 3 H), 7.69 (d, $J = 8.3$ Hz, 2 H), 8.16 (d, $J = 8.8$ Hz, 2 H); IR (KBr) ν 2032 cm^{-1}.

10.1021/ol006308c CCC: $19.00

Scheme 1



(**1a**) in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave EPR signals with typical fine structure patterns for unoriented triplet species, i.e., ^{3}**2a** (Figure 1).[6,7] Signals at 400, 410, and 500 mT 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 $|D| = 0.216$ cm^{-1} and $|E| = 0.00632$ cm^{-1}. The large signal at 130 mT is assigned to the low-field *z* transition. Other signals around 200 mT are assigned to the low-field *x* and *y* transitions and/or the signal due to $\Delta m = \pm 2$ transitions.

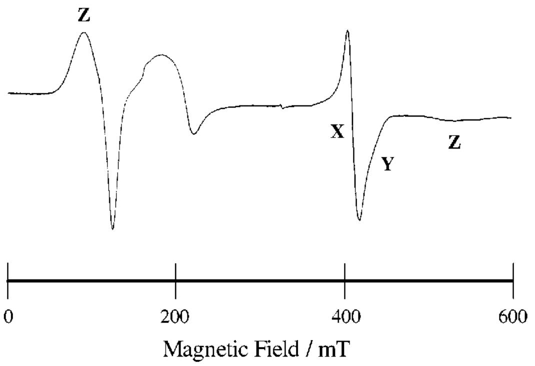


Figure 1. EPR signals obtained by photolysis of **1a** in 2-methyltetrahydrofuran at 77 K.

Similar signals were observed in the irradiation of the other diazo compounds (**1b** and **1c**) under identical conditions and were analyzed in terms of *D* and *E* values, which are reported in Table 1. The *D* values of typical diarylcarbenes are in the range of 0.41−0.32 cm^{-1}.[6] With the exception of di(9-anthryl)carbene,[1] the *D* value of ^{3}**2** is the smallest ever reported.

Table 1. ESR Data of Triplet Arylcarbenes (Ar−C−X)

	carbenes		*D*/hc	*E*/hc		
	Ar	X	cm^{-1}		*E*/*D*	Td[b]/K
2a	Ph-An	Ph	0.216	0.00632	0.0292	120
2b	Ph-An	Mes	0.201	0.00348	0.0173	130
2c	Ph-An	Dea	0.217	0.00289	0.0133	175
3[c]	Ph	H	0.515	0.0251	0.0485	
4[d]	An	H	0.3008	0.0132	0.0439	
5[e]	Ph-An	H	0.298	0.0133	0.0446	
6[f]	An	An	0.113	0.0011	0.0097	
7[g]	1-Np	Ph	0.363	0.016	0.0453	
8[h]	1-Np	1-Np	0.3157	0.0109	0.0345	

[a] In 2-methyltetrahydrofuran at 77 K unless otherwise noted. Abbreviations of substituents are the following: Ph-An, 9-(10-phenylanthryl); Mes, 2,4,6-trimethylphenyl; Dea, octahydro-1,4;5,8-di(ethano)anthryl; An, 9-anthryl; 1-Np, 1-naphthyl. [b] Temperature at which the ESR signals disappear upon thawing the 2-MTHF matrix containing triplet carbene. [c] Reference 8. In *p*-dichlorobenzene at 77 K. [d] Reference 9. In benzophenone at 77 K. [e] Reference 10. [f] Reference 1. In di(9-anthryl) ketone at 4 K. [g] Reference 11. [h] Reference 12.

The *D* value is related to the separation between the unpaired electrons, and the *E* value is a measure of the difference of the magnetic dipole interaction along the *x* and *y* axes. More plainly, the *D* value allows the determination of the amount of delocalization in carbenes with conjugated π-systems. The *D* value decreases with increasing delocalization of the unpaired electron, and the *E* value allows one to estimate the bond angle at the carbene center. For a linear carbene $E = 0$ is expected, while decreasing the bond angle leads to a larger value for *E*. The *E*/*D* ratio is frequently used to estimate the bond angle.[6,7]

To obtain more insight into the role of the anthryl group on the structure of triplet carbenes, it is useful to compare these values with the ZFS parameters observed for other related arylcarbenes, which are included in Table 1.[8−11] Inspection of the data in the table clearly revealed that the unpaired electrons are extensively delocalized onto both anthryl and phenyl rings. Thus, the *D* values of ^{3}**2a**−**c** are considerably smaller than the that of the "parent" 9-(10-phenylanthryl)carbene (**3**), indicating that the odd electron is delocalized also onto the phenyl ring at least to some extent. Taking into account the smaller loss of aromatization energy of the central aromatic ring of anthracene as opposed to that of the phenyl ring, it is obvious that the unpaired electrons are more extensively delocalized onto the anthryl ring. This is reflected by the fact that the *D* values of ^{3}**2a**−**c** are smaller than that of 1-naphthyl(phenyl)carbene ($D = 0.353$ cm^{-1})[11] and even than that of di(1-naphthyl)carbene ($D = 0.3157$ cm^{-1}).[12]

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(6) See for reviews of the ESR spectra of triplet carbenes: (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. (c) Tomioka, H. In *Advances in Strained and Interesting Organic Molecules*; Halton, B.; Ed.; JAI Press: Greenwich, CT, 2000; Vol. 8, pp 83−112.

(7) A large number of triplet carbenes have been characterized by ESR spectroscopy since the pioneering work of Wasserman et al. Wasserman, E.; Snyder, L. C.; Yager, W. A.; *J. Chem. Phys.* **1964**, *41*, 1763. Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27.

(8) Wasserman, E.; Trozzolo, A. M.; Yager, W. A. *J. Chem. Phys.* **1964**, *40*, 2408.

(9) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129.

(10) Itakura, H. Unpublished observation.

(11) Fujiwara, Y.; Sasaki, M.; Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett.* **1988**, *146*, 133.

(12) Tukada, H.; Sugawara, T.; Murata, S.; Iwamura, H. *Tetrahedron Lett.* **1986**, *27*, 235.

It is intriguing to examine the effect of the aryl group on the structure of the triplet anthrylcarbenes **2a**−**c**. The data in Table 1 clearly indicate that the aryl groups exert a considerable effect on the *E* value but have little effect on the *D* value. Consequently, the *E*/*D* value decreases rather significantly as more bulky groups are introduced on the phenyl group, suggesting that the central bond angle of ^{3}**2** expands as expected. One may expect that the unpaired electron can be more extensively delocalized as the carbene becomes more linear. Little changes in the *D* value on going from ^{3}**2a** to ^{3}**2b** to ^{3}**2c** may mean that the value of *D* is already too small to show a possible change or that the delocalizing abilities of aryl groups also vary.

It is very important to know the thermal stabilities of ^{3}**2a**−**c**. When 2-MTHF glass containing carbene ^{3}**2a** was warmed gradually in 10 K increments,[13] the ESR signals started to disappear at around 120 K. Since the ESR signals of most triplet diarylcarbenes disappear below 90 K, this means that ^{3}**2a** is thermally fairly stable. The ESR signals of ^{3}**2b** are persistent until 130 K, and those of ^{3}**2c** survive even up to 175 K, where the sample is fluid.

Anomalous thermal stability of ^{3}**2c** is obviously ascribable to the synergistic effects of thermodymanic and kinetic stabilization. Thus, the unpaired electrons are extensively delocalized onto the anthryl group while the carbenic center is effectively shielded by the bicyclohexyl groups along with the two peri hydrogens.

The present observations have revealed a useful role of the anthryl group as an excellent reservoir for unpaired electrons as well as relatively effective steric protectors in the chemistry of triplet carbenes. Our observations also suggest that the anthryl group can be employed as a very promising building block for constructing persistent triplet carbenes. Study along this line is in progress in this 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.

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(13) The sample temperature was raised in 10 K increments to the desired temperature, allowed to stand there for 1 min, and then recooled to 77 K to measure the signal.