J. Am. Chem. Soc. **1995,** *117,* 11355−11356

Triptycyl(aryl)carbenes. A Remarkably Effective Kinetic Stabilizer of Triplet Carbenes

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Received June 27, 1995

While the history of persistent radicals is long and impressive, that of persistent triplet carbenes is short, and stable triplet carbenes are not attainable yet.[2] Two basic strategies, i.e., thermodynamic and kinetic stabilization, are possible for the stabilization of reactive species. However, each strategy encounters serious problems when applied to triplet carbenes. Thus, thermodynamic stabilization not only results in the stabilization of the singlet state but also poses the issue of electronic configuration as a pure carbene (one centered diradical) as a result of possible conjugation.[2,3] While steric protection (kinetic stabilization) is therefore a much better method of stabilizing the triplet,[4−6] a voracious appetite of carbenes for electrons makes it difficult to explore the usual protecting groups for this extremely reactive center. Carbenes react even with very poor sources of electrons, such as C−H bonds. In this light, it is crucial to develop a protecting group which is sterically much more congesting and unreactive toward triplet carbenes. We report here that the triptycyl group is exceptionally effective in protecting triplet carbenes, increasing the lifetimes of some arylcarbenes by a factor of ca. 10^5.

Irradiation[8] (λ > 300 nm) of 9-triptycyl-α-naphthyldiazomethane (**1a**)[7] in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of new absorption bands at 347 and 364 nm at the expense of the original absorption due to **1a**. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming it up to room temperature led to a disappearance of the characteristic absorption band (Figure 1). The transient absorption was assigned to triplet carbene **2a** generated by the photodissociation of **1a** on the basis of the similarity of the spectrum with that of other analogous triplet naphthylcarbenes.[9,10]

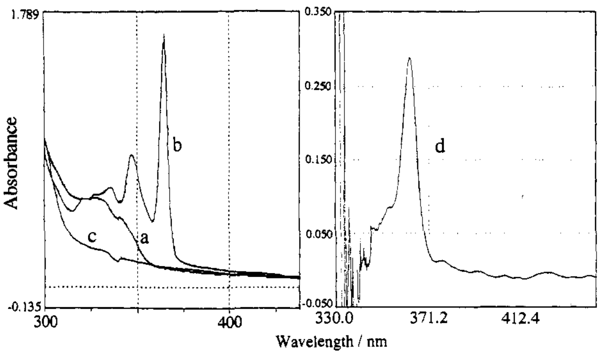
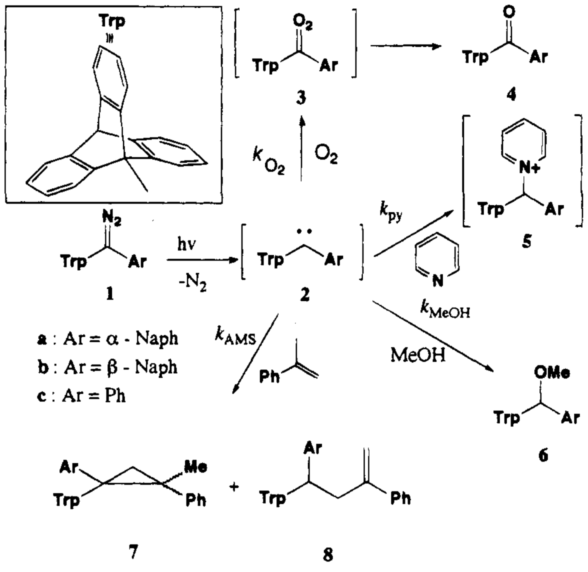


Figure 1. (a) UV/vis spectrum of **1a** in MTHF at 77 K. (b) Same sample after 5 min irradiation (λ > 300 nm). (c) Same sample after thawing the matrix. (d) Transient absorption formed during irradiation of **1a** in degassed benzene at room temperature, recorded after 50 μs.



Flash photolysis[8] of a degassed benzene solution of **1a** at room temperature with the output of a xenon lamp (pulse width of 10 μs) produced a transient species also showing absorption at 363 nm, which appeared coincident with the pulse and disappeared within ca. 100 ms (Figure 1). We assigned the transient absorption to triplet carbene **2a** on the basis of the low-temperature spectrum. The decay was found to be first order, and the lifetime was determined to be ca. 20 ms.

Trapping experiments using oxygen lend support to this assignment. When flash photolysis measurements were carried

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(1) (a) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Radicals;* Academic Press: London, 1968. (b) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13. (c) Ballester, M. *Ibid.* **1985**, *18*, 380. See also: Ballester, M.; Pascual, I.; Riera, J.; Cadtañer, J. *J. Org. Chem.* **1991**, *56*, 217.

(2) Phosphinocarbene and imidazol-2-ylidene were prepared as "bottle-able" carbenes in 1988 and 1991, respectively. See: Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, M. *J. Am. Chem. Soc.* **1988**, *110*, 6463. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. However, more recent studies demonstrate that the presentation of the phosphorus-containing compound is a phosphaacetylene, not a phosphinocarbene. See: Dixon, D. A.; Dobss, K. D.; Arduengo, A. J., III; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782. Soleilhavoup, M.; Baceiredo, A.; Treutler, O.; Ahlrichs, R.; Nieger, M.; Bertrand, G. *Ibid.* **1992**, *114*, 10959.

(3) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. Dagani, R. *Chem. Eng. News* **1991**, Jan 28, 19; **1994**, May 2, 20.

(4) The first attempts to isolate triplet carbenes by using steric protection strategies were made by Zimmerman. Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(5) (a) Tomioka, H.; Hirai, K.; Fujii, C. *Acta Chem. Scand.* **1992**, *46*, 680. (b) Tomioka, H.; Hirai, K.; Nakayama, T. *J. Am. Chem. Soc.* **1993**, *115*, 1285. (c) Tomioka, H.; Mizutani, K. Matsumoto, K. Hirai, K. *J. Org. Chem.* **1993**, *58*, 7128. (d) Hirai, K.; Komatsu, K.; Tomioka, H. *Chem. Lett.* **1994,** 503. (e) Tomioka, H.; Okada, H.; Watanabe, T.; Hirai, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 873. (f) Tomioka, H.; Watanabe, T.; Hirai, K.; Furukawa, K.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1995**, *117*, 6376.

(6) It has been reported that 9,9′-dianthrylmethylene is stable up to 160 °C in anthracene (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). However, the stability is due to the rigidity of the environment and not to an intrinsic lack of reactivity. For instance, flash photolysis studies show that it undergoes self-reaction at the diffusion-controlled limit in benzene at room temperature (Astles, D. J.; Girard, M.; Griller, D.; Kolt, R. J.; Wayner, D. D. M. *J. Org. Chem.* **1988**, *53*, 6053).

(7) Characteristic spectroscopic data for **1a**: mp 183 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.50 (d, J = 8.58 Hz, 1H), 8.02 (d, J = 7.92 Hz, 1H), 7.87−7.61 (m, 3H), 7.47−7.30 (m, 8H), 7.05−6.91 (m, 6H), 5.47 (s, 1H); IR (KBr) 2047 cm^{-1}. For **1b**: mp 178 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.80−7.75 (m, 2H), 7.70 (d, J = 8.58 Hz, 1H), 7.66−7.30 (m, 10H), 7.15 (d, J = 8.58 Hz, 1H), 7.06−6.85 (m, 6H), 5.47 (s, 1H); IR (KBr) 2045 cm^{-1}. For **1c**: red liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 7.26 Hz, 3H), 7.32 (d, J = 7.59 Hz, 3H), 7.28−6.95 (m, 8H), 5.43 (s, 1H); IR (KBr) 2050 cm^{-1}.

(8) For detail of the spectroscopic work, see refs 5b,c.

(9) See, for reviews: (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. 2, Chapter 5. (c) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.

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0002-7863/95/1517-11355$09.00/0

Table 1. Kinetic Data for Arylcarbenes

carbenes	lifetime (μs)[a]	k_{O_2}[b]	Kk_{py}[b]	Kk_{MeOH}[b]	k_{AMS}[b]
2a	20000	5×10^8	1.2×10^2	1.2×10^4	7.2×10
2b	1000	1.6×10^9	6.0×10^3	2.1×10^5	1.9×10^3
2c	840	1.6×10^9	1×10^4	3.2×10^5	3.3×10^3
α-naphthylcarbene[c]	~0.1[d]	3.5×10^9		1.6×10^7	
β-naphthylcarbene[e]	0.06			7.3×10^7	(4.3×10^7)[f]
di-α-naphthylcarbene[g]	70	1.7×10^9		3.1×10^5	
diphenylcarbene	2[h,i]	5×10^9[j]		1.2×10^7[h]	(1.4×10^6)[f,h]

[a] In degassed PhH. [b] In M^{-1} s^{-1}. [c] Reference 15. [d] In MeCN. [e] Reference 10b. [f] Reaction with styrene. [g] Reference 16. [h] Reference 17. [i] In cyclohexane. [j] Reference 11b.

out using the 308 nm pulses from a XeCl laser (~80 mJ, 10 ns pulse width) on a non-degassed benzene solution of **1a**, the lifetime of the absorption due to **2a** decreased dramatically (~1/10^5), and a broad absorption band with a maximum at 410 nm appeared as the band due to **2a** decayed. The rate of increase in the absorbance at 410 nm was practically the same as that of the decay of the peak at 363 nm, thereby indicating that triplet **2a** was quenched by dioxygen to form a new species. Subsequent analysis of the spent solution showed the presence of a large amount of ketone **4a**. It is well-documented[11] that arylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding aryl ketone oxides, which usually show a rather broad band centered around 390–450 nm. Thus, the observation can be interpreted as indicating that the triplet **2a** is trapped with oxygen to generate carbonyl oxide **3a**,[12] thus confirming that the transient absorption quenched by oxygen is due to **2a.** A plot of the observed pseudo-first-order rate of carbonyl oxide formation versus oxygen concentration yields the quenching rate constant $k_{O_2} = 5.0 \times 10^8$ M^{-1} s^{-1} which is somewhat smaller than those observed for ordinary diarylcarbenes.[11b]

On the other hand, laser flash photolysis[8] of **1a** in the presence of pyridine produced a transient absorption band peaking around 380 nm that was not observed in the absence of pyridine and was attributable to the pyridine ylide (**5a**) since it is also well-documented[13] that carbenes are readily trapped by pyridine (py) to form ylides which usually show rather intense absorption in the visible region. The apparent buildup rate constant, k_{obs}, of the ylide is essentially identical with that of the decay of the carbene and is given in eq 1,

$$k_{obs} = k_T + k_{py}K[py] \qquad (1)$$

where k_T is the total of all first-order and pseudo-first-order processes which consume the singlet and triplet carbene in the absence of pyridine, k_{py} is the absolute rate constant of reaction with pyridine, and K is the singlet–triplet equilibrium constant.[14] A plot of the observed pseudo-first-order rate constants for the growth of the absorption due to **4a** against [py] in the range 0.4–2.7 M is linear. The slope of this plot yields $k_{py}K = 1.2 \times 10^2$ M^{-1} s^{-1}, and the intercept yields $k_T = 4.7 \times 10$ s^{-1}. Thus, the lifetime ($1/k_T$ = 21ms) of **2a** determined by the pyridine method is in excellent agreement with that determined by the direct method (LFP).

Irradiation of **1a** in degassed methanol gave methyl naphthyl(triptycyl)methyl ether (**6a**) in 90% yield. LFP of **1a** (1×10^{-4} M) in degassed benzene containing methanol (0–1.2 M) formed the same transient species we detected in the absence of alcohol. The lifetime of this species decreased as the concentration of alcohol in the solution was increased. The transient decayed following a first-order rate law with a rate constant (k_{obs}) that depends linearly on the alcohol concentration. A plot of k_{obs} against the concentration of methanol is linear, and the slope gives a bimolecular rate constant of 1.2×10^4 M^{-1} s^{-1} for the reaction of the carbene (**2a**) with the alcohol (Kk_{MeOH}).

Photolysis of **1a** in α-methylstyrene, on the other hand, gave the appropriate cyclopropanes (**7a**) as a mixture of regioisomers as the main products along with 2-phenyl-4-naphthyl-4-(triptycyl)-but-1-ene (**8a**) in ca. 60% yield. When (*E*)-β-deuterio-α-methylstyrene was used, the NMR spectrum of the isolated cyclopropanes showed that the stereochemistry of the starting olefin was not retained. Laser spectroscopy showed that the transient product absorbing at 363 nm reacted with the styrene with a bimolecular rate constant (k_{AMS}) of 7.2×10 M^{-1} s^{-1}.

Essentially similar measurements were made for the other less congested triptycyl diazo compounds (**1b,c**),[7] and the data are summarized in Table 1, which also includes the data for the related carbenes. Inspection of the data clearly reveals that the triptycyl group exhibits a large kinetic effect on protecting the carbenic center. Thus, the lifetime of triplet **2a**, for instance, is some 10^5 times longer than that of triplet α-naphthylcarbene (τ ~0.1 μs),[15] and is 3×10^2 times longer even than di-α-naphthylcarbene (τ 70 μs).[16] Reactions with typical trapping reagents for triplet carbene are also highly retarded. Thus, k_{O_2} for triplet **2a** is approximately 1 order of magnitude smaller than that for most other triplet diarylcarbenes,[11b] including di-α-naphthylcarbene,[10,11b,15] which are usually trapped with a nearly diffusion-controlled rate constant. Similar effects, though less dramatic, are also noted for **2b** and **2c**. The remarkable longevity of these monoarylcarbenes is obviously ascribable not only to the steric bulkiness of the triptycyl group but also to its reluctance toward intramolecular reaction with the carbene center. For example, reactions in less reactive solvents such as benzene afforded complex product mixtures, but possible products arising from tribenzobicyclo[3.2.2]nonatetraene or -trienylidene as a result of rearrangement of **2** were detected.

Acknowledgment. This work was supported by a Grant-in-Aid for Priority Research from the Ministry of Education, Science and Culture, Japan.

JA952114U

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(12) For example, 1-naphthophenone oxide has a maximum at 405 nm.[11a]

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(14) We assume that **2a** has triplet ground states and that the low-lying singlet states are accessible at equilibrium and react with pyridine to form the ylides detected in this study.

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