

## Laser Flash Photolysis Study of Adamantanylidene

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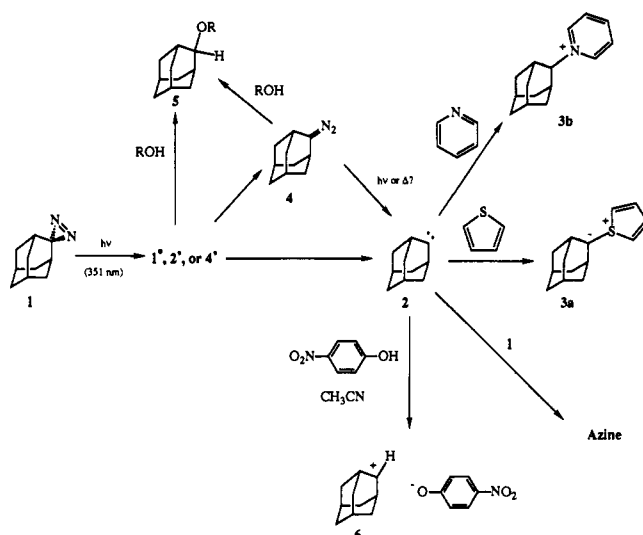
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Examples of bimolecular reactions of alkylcarbenes are rare due to the ease of intramolecular rearrangement.<sup>3</sup> A conspicuous exception to this rule is adamantanylidene,<sup>4</sup> which has been successfully intercepted by olefinic trapping agents. We and others have recently demonstrated that the dynamics of alkylhalocarbenes can be visualized by their trapping with pyridine to form ylides which absorb intensely in the UV-vis region.<sup>5</sup> This has prompted the present study of adamantanylidene by this technique.

Laser flash photolysis (LFP, XeF excimer laser, 351 nm, 60 mJ, 17-ns pulse width) of diazirine **1** in benzene fails to produce a UV-vis-active ( $\lambda > 300$  nm) transient intermediate. However, LFP of **1** in the presence of thiophene and pyridine produces intense transient absorptions centered at 320 and 390 nm, respectively. These transients are not observed upon LFP of thiophene or pyridine in the absence of **1** and are attributed to ylides **3a** and **3b**, respectively. The spectrum of pyridine ylide **3b** is quite comparable to the absorption spectra of ylides derived from alkylhalocarbenes and pyridine.<sup>5</sup> The absolute rate constant of formation of ylide **3a** is first order in thiophene concentration. The lifetime of adamantanylidene in benzene extrapolated to zero thiophene concentration is 2.2  $\mu$ s when  $[1] = 3.2 \times 10^{-2}$  M. We suspect that this lifetime is controlled principally by the reaction of **2** with diazirine precursor **1** (to form a known azine), as the rate of formation of thiophene ylide **3a** is a linear function of diazirine concentration. The kinetics of ylide **3a** are unaffected by the presence of molecular oxygen ( $\approx 10^{-3}$  M). This indicates that **2** is a ground state singlet carbene and that the ratio of triplet to singlet carbene at equilibrium is less than  $10^{-3}$ , assuming that triplet **2** reacts with oxygen at a diffusion-controlled rate, as is the case with other triplet carbenes.<sup>6</sup> The fact that photolysis (unfiltered Hg-Xe 1000-W arc) of **2** at 4-77 K in a variety of matrices, and in the presence and absence of triplet sensitizers, fails to produce an EPR spectrum of a triplet carbene is consistent

Scheme I



with this interpretation.<sup>7</sup> Presumably the singlet is the ground state of **2** because of its necessarily constricted bond angle at the carbene carbon.<sup>8</sup>

In principle one can obtain the absolute rate constants of reaction of **2** with scavengers by measurement of the yield of ylide (Stern-Volmer (SV) method) or the absolute rate of formation of **3a** (direct method) as a function of quencher concentration.<sup>9</sup> Generally a SV analysis of the data is more precise but the direct method provides more accurate rate constants. The effects of several quenchers on the ylide signal were determined and absolute rate constants deduced (Table I) by standard procedures.<sup>5a,9</sup> In a few cases (pyridine, *n*-butyl vinyl ether, acetic acid, acetic acid-*d*), the agreement between the direct and Stern-Volmer methods is acceptable, but with diethyl fumarate and the silanes as scavengers the Stern-Volmer analysis consistently gives apparent rate constants that are much larger than those obtained by direct kinetic analysis. In fact simple alcohols effectively quench the yield of ylide **3a** but have no effect on the observed rate constant of formation of **3a**. This requires that there be an extra trappable intermediate present in solution and that this species be a precursor to carbene **2**, the species that reacts with thiophene to produce ylide **3a**. The identity of this intermediate is not known with certainty but may be an excited state of either diazirine **1**,<sup>10</sup> diazo compound **4**, or carbene **2** as shown in Scheme I. The kinetics require that the lifetime of the second intermediate be much shorter than the carbene lifetime of 1-2  $\mu$ s. This effectively eliminates the ground state of diazo compound **4** as the transient carbene precursor<sup>11</sup> (on microsecond time scales) as the pink color

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(3) For excellent reviews, see: Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, NY, 1973; Vol. 1, p 1. Kirmse, W. *Carbene Chemistry*; Academic Press: New York, NY, 1968.(4) See: (a) Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* **1981**, *38*, 349 and references therein. (b) Adding, A. C.; Strating, J.; Wynberg, H.; Schlattmann, J. L. M. A. *Chem. Commun.* **1966**, 657. (c) Isaeu, S. D.; Yuchenko, A. G.; Stepanov, F. N.; Kolyada, G. G.; Novikov, S.; Karpentko, N. F. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 724. (d) Bayley, H.; Knowles, J. R. *Biochemistry* **1978**, *17*, 2420; **1980**, *19*, 3883.(5) (a) Jackson, J. E.; Platz, M. S. *Advances in Chemical Applications of Lasers*; Hilinski, E., Ed.; JAI Press: Greenwich, CT, in press. (b) Jackson, J. E.; Soundararajan, N.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 5595. (c) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H. *Tetrahedron Lett.* **1989**, *30*, 1335. (d) Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874. (e) Morgan, S. C. M.S. Thesis, The Ohio State University, 1989. (f) White, W. R.; Platz, M. S.; Chen, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 7794. (g) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. J. *Am. Chem. Soc.* **1989**, *111*, 5973. (h) Ho, G. J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (i) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298. (j) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638. (k) Chateaveuf, J. E.; Johnson, R. P.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217.(6) (a) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. (b) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623. (c) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (d) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 39028.(7) Similar results have been obtained by Professors Moss and Dowd (personal communication). Other dialkylcarbenes have been detected by matrix EPR spectroscopy and have unexceptional spectra; see: (a) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326. (b) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.(8) Hoffmann, R.; Zeiss, G. D.; VanDine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.(9) The pyridine probe method is based upon models developed by Scaiano to probe free-radical reactions. For examples, see: (a) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828. (b) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431; (c) **1978**, *59*, 246.(10) Liu has previously speculated that the excited state of benzylchlorodiazirine undergoes protonation reactions. See: Liu, M. T. H. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. 1, p 142. Reactions of diazirine excited states masquerading as carbene chemistry have been detected previously by noting large differences between product mixtures obtained by thermal and photochemical decomposition of diazirines. See: Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. Unfortunately, diazirine **1** does not fluoresce, hence, it is impossible to establish quenching of **1\*** by the fluorescence technique. We are also unaware of any fluorescence attributable to a dialkyl diazo compound.(11) The diazo compound **4** may well decompose to form carbene **2** in solution, but it happens too slowly to effect the yield of ylide **3a** on microsecond time scales.

**Table I.** Absolute and "Apparent" Rate Constants for the Reaction of Adamantanylidene with Various Quenchers, in Benzene at Ambient Temperature

quencher	precursor concn, M	$k$ , M <sup>-1</sup> s <sup>-1</sup> (direct meth, carbene 2) <sup>a</sup>	$k_q\tau$ ( $\tau$ , $\mu$ s) (Stern-Volmer meth, carbene 2 and excited state 1*) <sup>b</sup>	"apparent" $k$ , M <sup>-1</sup> s <sup>-1</sup> (Stern-Volmer meth, carbene 2) <sup>h</sup>	concn range of quencher, M
thiophene		$1.75 \pm 0.6 \times 10^6$	—	—	0.12–0.312
diazirine 1		$2.87 \pm 0.41 \times 10^7$	—	—	$(7.23 \times 10^{-4})$ – $(1.27 \times 10^{-2})$
pyridine	$2.32 \times 10^{-4}$	$1.54 \pm 0.23 \times 10^6$	4.25 <sup>c</sup> (2.30)	$1.85 \pm 0.84 \times 10^6$	0–0.371
<i>n</i> -butyl vinyl ether	$3.23 \times 10^{-4}$	$3.80 \pm 0.27 \times 10^5$	0.54 <sup>c</sup> (1.14)	$4.73 \pm 0.27 \times 10^5$	0–1.55
diethyl fumarate	$2.99 \times 10^{-4}$	$1.53 \pm 0.24 \times 10^6$	11.18 <sup>d</sup> (1.91)	$5.85 \pm 0.34 \times 10^6$	0–0.214
triethylsilane	$3.16 \times 10^{-4}$	$3.31 \pm 0.42 \times 10^5$	1.73 <sup>d</sup> (2.65)	$6.52 \pm 0.66 \times 10^6$	0–1.41
diphenylsilane	$2.99 \times 10^{-4}$	$1.02 \pm 0.10 \times 10^6$	14.81 <sup>d</sup> (1.98)	$7.49 \pm 0.65 \times 10^6$	0–0.14
phenylsilane	$2.99 \times 10^{-4}$	$2.03 \pm 0.30 \times 10^6$	25.17 <sup>d</sup> (1.95)	$1.3 \pm 0.1 \times 10^7$	0–0.162
<i>p</i> -nitrophenol <sup>f</sup>	$1.04 \times 10^{-2}$	$3.41 \pm 0.76 \times 10^9$	—	—	$(1.37 \times 10^{-4})$ – $(2.4 \times 10^{-3})$
acetic acid	$1.85 \times 10^{-4}$	$5.55 \pm 0.48 \times 10^9$	6934 <sup>e</sup> (2.03)	$3.41 \pm 0.25 \times 10^9$	0–0.0042
acetic acid- <i>d</i>	$1.50 \times 10^{-4}$	$4.81 \pm 0.65 \times 10^9$	5400 <sup>e</sup> (3.40)	$1.59 \pm 0.12 \times 10^9$	0–0.012
methanol	$2.42 \times 10^{-4}$	<i>g</i>	85 <sup>e</sup> (2.10)	—	0–0.05
methanol- <i>d</i> <sub>4</sub>	$1.86 \times 10^{-4}$	<i>g</i>	33 <sup>e</sup> (1.97)	—	0–0.11
2-propanol	$1.83 \times 10^{-4}$	<i>g</i>	27 <sup>e</sup> (2.35)	—	0–0.20
<i>tert</i> -butyl alcohol	$1.39 \times 10^{-4}$	<i>g</i>	13 <sup>e</sup> (2.50)	—	0–0.36

<sup>a</sup> Absolute rate constants of reaction of adamantanylidene 2 obtained by measuring the effect of quencher on the rate constant of formation of thiophene ylide 3a. <sup>b</sup> Apparent  $k_q\tau$  values obtained from the effect of the quencher on the yield of thiophene ylide 3; the variation in  $\tau$  is due to variation in [1]. <sup>c</sup> Quencher intercepts mainly carbene 2. <sup>d</sup> Quencher intercepts both carbene 2 and transient precursor. <sup>e</sup> Quencher intercepts only the transient precursor of the carbene. <sup>f</sup> Absolute rate constant of 2 with *p*-nitrophenol obtained by monitoring the growth rate of *p*-nitrophenolate ion. <sup>g</sup> Too slow to measure. <sup>h</sup> These numbers were calculated for the sake of comparison only using  $\tau$  values of carbene 2. The apparent rate constants are meaningful for adamantanylidene only for pyridine, acetic acid, acetic acid-*d*, and *n*-butyl vinyl ether.

of 4 has been observed by Moss<sup>4a</sup> and found to be persistent at –78 °C. It is economical to hypothesize that the transient precursor to carbene 2 may also isomerize to diazo compound 4 as shown in Scheme I, but our data do not require this to be the case. We suspect that much chemistry that could be reasonably attributed to carbene 2 may actually derive from reactions of the transient precursor to carbene 2 and to the ground state of 4. In fact the immediate photochemical production of 2 may well be a minor process as the analogous yield of ylide 3b is 3 times lower than the yield of ylide derived from the reaction of another dialkylcarbene, homocubanylidene,<sup>5f</sup> with pyridine, as determined by LFP.<sup>12</sup> Photoisomerization of 1 may well be the major process as photolysis of 1 at 96 K in 3-methylpentane produces an intense IR band at 2042 cm<sup>-1</sup> which is most reasonably attributed to 4.

Our inability to measure the rate constant of reaction of 2 with methanol does not mean that the carbene does not react with this alcohol. It means only that the concentrations of methanol needed to intercept 2 are sufficient to intercept the transient carbene precursor (1\*, 2\*, or 4\*) and thereby prevent the formation of the carbene. The rate constant of reaction of acetic acid with 2 is very large. Thus the measurement of the absolute rate constant of reaction of 2 with acetic acid required the presence of only a small quantity of quencher. The acetic acid was sufficiently dilute that the transient carbene precursor was not intercepted and the kinetics of 2 could be discerned by the effect of quencher on both the rate of formation and the yield of ylide 3a.

The recent report of Kirmse<sup>13</sup> and co-workers on the protonation of diphenylcarbene prompted us to attempt a similar reaction with adamantanylidene. LFP of 1 in the presence of highly dilute *p*-nitrophenol in acetonitrile produces the *p*-nitrophenoxide ion. A plot of the absolute rate constant of phenolate ion formation versus *p*-nitrophenol concentration is linear, and the slope of this plot is equal to the rate constant of reaction of 2 with *p*-nitrophenol (Table I).<sup>9</sup> The inverse of the intercept of this plot ( $\tau = 965$  ns) is comparable to that observed in the thiophene quenching plot, which suggests that it is carbene 2 rather than 1\*, 2\*, or 4\* that is reacting with dilute *p*-nitrophenol to form ion pair 6. It is clear that the reaction of 2 with hydroxylic substrates proceeds by proton transfer, which explains why the more acidic quenchers (acetic acid, *p*-nitrophenol) are so much more effective at interception of adamantanylidene than simple alcohols.

It is interesting to note that adamantanylidene 2 reacts much more slowly with typical scavengers such as methanol and pyridine than does the only other dialkylcarbene, homocubanylidene,<sup>5f</sup> studied as yet by LFP techniques. The study of pyridine and *p*-nitrophenol trapping of other dialkylcarbenes is in progress to discover the origin of this effect.

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**Supplementary Material Available:** Transient spectra of ylides 3a and 3b and of *p*-nitrophenolate ion and a plot of the observed rate constant of formation of *p*-nitrophenolate ion as a function of *p*-nitrophenol concentration (4 pages). Ordering information is given on any current masthead page.

## CO Is neither an Intermediate nor a Catalyst in MTG Chemistry on Zeolite HZSM-5

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Two conflicting roles for CO in the conversion of methanol to gasoline on zeolite HZSM-5 (MTG process<sup>1</sup>) have recently been proposed. In their studies of the reaction of methanol on HZSM-5, Anderson and Klinowski,<sup>2</sup> observing the presence of CO prior to hydrocarbon formation and its absence afterward, concluded that CO is an intermediate in the reaction. This was rationalized by proposing that CO and methanol undergo Fisher-Tropsch style chemistry on Fe<sup>3+</sup> impurities to form ethanol, which then eliminates ethylene. In another recent paper, Jackson and Bertsch<sup>3</sup>

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(12) This assumes that the extinction coefficients of 3b and the homocubanylidene-pyridine ylide are comparable.

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