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Laser Flash and Dual Wavelength Photolysis of 3,4-Diaza-2,2-dimethoxy-1-oxa[4.5]spirooct-3-ene. Migration of Hydrogen and Carbon in Cyclobutylidene and in the Excited State of Its Precursor

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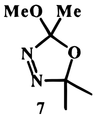
The most common photochemical sources of carbenes are diazirines and diazo compounds[5] but such nitrogenous precursors can form the same products from either the carbenes or the excited states of the precursors, albeit in different ratios.[6] Consequently, the observed product ratios are not necessarily indicative of carbene chemistry.[6] Dialkyldiazo compounds themselves can be generated by direct[7] (300 nm) or sensitized[8] photolysis of oxadiazolines. At 25 °C, the diazoalkanes are thermally and photochemically (300 nm) fairly stable, affording azines slowly together with only traces of coproducts associated with intramolecular rearrangement of corresponding dialkylcarbenes.

We are pleased to report that laser flash photolysis (LFP, 308 nm) of 3,4-diaza-2-methoxy-2-methyl-1-oxa[4.5]spirooct-3-ene (**1a**) in the presence of pyridine gave the pyridinium ylide of carbene **4** (λ_{max}= 350−360 nm), permitting estimates of the lifetime of **4**. Moreover, while 300 nm steady state (SS) irradiation (Rayonet) of **1b**[9] gave primarily diazocyclobutane (**2**),[10] a little of the corresponding azine, and traces of alkenes,[11] two-color photolysis (SS, 250 and 300 nm) of **1b** gave a mixture of cyclobutene (CB) and methylenecyclopropane (MC).[12] In the presence of tetramethylethylene (TME), carbene **4** was trapped as cycloadduct **5**.[13] Together, the LFP and SS results permitted estimates of rate constants for the 1,2-rearrangements of **4** and the determination of the product ratio (CB/MC) from carbene and excited state sources.

LFP (308 nm) of either **1a** or **1b** in the presence of pyridine gives an intense spectrum of the pyridinium ylide of **4**. The similarity of transient spectra and lifetime from an oxadiazoline and a diazirine was established by LFP of **7** (308 nm) and **8** (351 nm).[14−17] Presumably a two-photon or a multiphoton process is responsible for the generation of **4** from **1a** in the laser beam. Analysis of the data[14,19] from different pyridine concentrations gave the lifetimes (τ) of **4** in $CF_2ClCFCl_2$, cyclohexane, or cyclohexane-d_{12}, as 4−20 ns (±20%) and, in acetonitrile, 0.4−2 ns (±20%), assuming[18] that $k_{pyr} = 1-5 \times 10^9$ M^{-1} s^{-1}. Stern−Volmer (LFP) experiments[14] reveal that carbene **4** reacts with TME and pyridine with the same rate constant within experimental error. As τ is identical in C_6H_{12} and C_6D_{12}, we conclude that the lifetime of **4** in alkane solvent is controlled by intramolecular processes and that the sum of the rate constants for 1,2-H and 1,2-C migrations, $k_H + k_C = 0.5 - 2.5 \times 10^8$ s^{-1} at ambient temperature.



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[9] Oxadiazolines **1a** and **1b** show the same photochemistry except that **1a** gives methyl acetate and **1b** gives dimethyl carbonate. The advantage in using **1b** is that the ^{1}H-NMR spectrum is not complicated by diastereotopicity of the cyclobutyl hydrogens.

[10] (a) Brinker, U. H.; Boxberger, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 974. (b) Applequist D. E.; McGreer D. E. *J. Am. Chem. Soc.* **1960**, *82*, 1965.

[11] Photolysis with 300 nm light alone (Pyrex, Rayonet) gave solutions of diazocyclobutane that were persistent for many hours, slowly affording primarily cyclobutanone azine and only traces (GC) of alkenes. Similar irradiation of 2-methoxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline gave, even after prolonged exposure, only trace amounts of propene from facile 1,2-H migration in dimethylcarbene. In an apparent conflict with the LFP, 308 nm light converts oxadiazoline to carbene whereas in SS experiments 300 and 250 nm light are required simultaneously in order to produce carbene efficiently. The LFP method, however, is much more sensitive than chemical analysis, and it can involve multiphoton processes which are not possible in SS photolysis.

[12] Photolyses were for 2−3 h in degassed and sealed quartz NMR tubes in a Rayonet chamber holding 14 × 250 nm lamps and 2 × 300 nm lamps. A mixture of CB and MC (2−5% yield, relative to internal standard, remainder mostly diazocyclobutane) was isolated by preparative GC and identified by ^{1}H-NMR and GC-MS. ^{1}H-NMR (C_6D_6, 200 MHz) showed δ 5.46 (quintet, J = 2.1 Hz, 2H) and 0.88 (t, J = 2.1 Hz, 4H) from MC and δ 5.91 and 2.44 (singlets; unresolved coupling) from CB. GC-MS (oven 30 °C) showed a broad peak at *ca.* 2 min retention time (before solvent) with M = 54 (C_4H_6) and a base peak of mass 39 (M − 15).

[13] Adduct **5** was isolated by preparative GC. ^{1}H-NMR (microprobe, C_6D_6, 500 MHz) δ: 1.87 (m, 6H), 0.88 (s, 12H). Single peak in the GC-MS trace (oven 30 °C) at retention time *ca.* 12 min, mass 138 (M, $C_{10}H_{18}$) and base peak 123 (M − 15).

[14] Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mullins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinet.* **1994**, *19*, 93.

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[16] Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press, Greenwich, CT, 1994; Vol. 1, p 89.

[17] Although methoxymethylcarbene might also be generated from **1a**, it is known to react slowly with pyridine (k_{pyr} = 6.6 × 10^5 M^{-1} s^{-1}) to form an ylide with λ_{max} = 380 nm.[18]

[18] Ge, C. S.; Jane, E. G.; Jefferson, E. A.; Liu, W.: Moss, R. A.; Włostowska, J.; Xue, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1479.

[19] (a) Frey, H. M. *Adv. Photochem.* **1964**, *4*, 225. (b) Frey, H. M. *J. Am. Chem. Soc.* **1962**, *84*, 2293.

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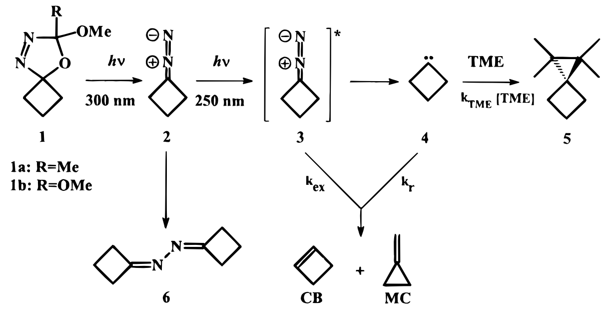
Scheme 1



Simultaneous steady state photolysis of **1b**, with 250 and 300 nm wavelengths at ambient temperature, gave CB and MC which is consistent with the original report[20] of thermal decomposition of the sodium salt of cyclobutanone tosylhydrazone and with the results of dehalogenation of *gem*-dihalocyclobutanes.[21] Two-color photolysis of **1b** in neat TME gave 4,4,5,5-tetramethyl[2.3]spirohexane (**5**)[13] (Scheme 1). Diazocyclobutane is known to undergo [3 + 2] cycloaddition reactions with alkenes to give pyrazolines[10a] which can subsequently lose N_2 thermally[10b] or photochemically.[10a] Therefore precursor **1b** was photolyzed in neat TME with 300 nm light alone to determine whether **5** was the indirect result of [3 + 2] cycloaddition of **2** to TME or the direct result of carbene trapping. The resulting mixtures, analyzed by ^{1}H-NMR and GC-MS, revealed that **5** was not formed with 300 nm light alone, excluding diazo compound **2** as the source of adduct **5**.

Photolyses of **1b** (250 and 300 nm) in cyclohexane solutions with different concentrations of TME[22] showed that yields of CB and MC decreased as a function of increasing [TME] and then leveled off, indicating that part of the rearrangement reactions cannot be quenched by a carbene trap. Yields of **5** showed a similar saturation, at a maximum near 21% relative to CB and MC, with increasing [TME]. On the basis of the observed ratio of MC/CB (5.5:1) in cyclohexane, upper limits at ~25 °C would be $k_H = 4 \times 10^7$ s^{-1} and $k_C = 2 \times 10^8$ s^{-1}. Corresponding lower limits would be $k_H = 8 \times 10^6$ s^{-1} and $k_C = 4 \times 10^7$ s^{-1}. However, the ratio of 1,2-H and 1,2-C migrations was also observed to change as a function of [TME]. The data suggest that *ca.* 21% of the observed products are the result of the intramolecular rearrangement of **4** and that the remainder results from migrations in the excited state (**3**) of diazo precursor **2**.[23] Since TME at ≥3 M captured all of **4**, the limiting ratio CB/MC reflects the partitioning of **3** between 1,2-C and 1,2-H migration. At [TME] = 0, when the ratio reflects a composite of excited state and carbene rearrangements, the value was *ca.* 5.5 in cyclohexane, while at high [TME] it was 3.6. In order to change the ratio from 3.6 (excited state alone) to 5.5 (composite) with a 21% contribution from **4**, it is clear that most or all of **4** must rearrange to MC.[24] Given that the lifetime (τ) of **4** was measured as 4−20 ns in cyclohexane-d_{12} (above), based[18] on $k_{pyr} = 1{-}5 \times 10^9$ M^{-1} s^{-1} , upper and lower limits of the absolute rate constant for 1,2-C migration would then be 2.5×10^8 s^{-1} and 5.0×10^7 s^{-1}, at ~25 °C, respectively.

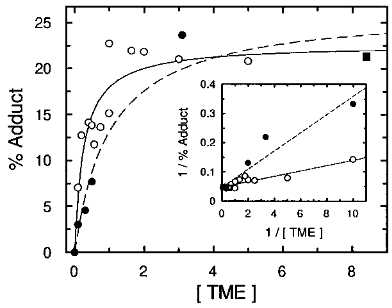


Figure 1. Percent yield of **5** vs TME concentration in cyclohexane-d_{12} (○), in acetonitrile-d_3 (●), and in neat TME (■). Curve fitting of the data in cyclohexane solutions is shown by the solid line and in acetonitrile solutions by the dashed line. The plot shows a leveling off at ~21% indicating that an unquenchable reaction is occurring. The inset shows double reciprocal plots for quenching of **4** by TME in cyclohexane-d_{12} (○) and in acetonitrile-d_3 (●).[14,19] The slope/intercept ratio gives $k_q\tau$ in each solvent.

Two-color photolyses of **1b** in acetonitrile gave changes in MC/CB ratios, as a function of [TME], analogous to those obtained in cyclohexane solvent. Thus, for **4**, solvent effects on 1,2-H and 1,2-C migrations are similar. Yields of **5** as a function of [TME] increased more rapidly in cyclohexane compared with acetonitrile solutions (Figure 1). Double reciprocal plots[14,19,25] (Figure 1, inset) gave the ratio intercept/slope which is equal to $k_{TME}\tau$ for quenching. For cyclohexane, the ratio was 5.2 M^{-1} meaning that $k_{TME} = 0.26{-}1.3 \times 10^9$ M^{-1} s^{-1} at ~25 °C ($\tau = 4{-}20$ ns). For acetonitrile, the ratio was 1.3 M^{-1} indicating that **4** has a much shorter lifetime in that solvent (0.3−1 ns). Both results are consistent with the data obtained by quenching with pyridine (above). More facile 1,2-H and 1,2-C migrations in a polar solvent indicates that corresponding transition states from **4** are polar. 1,2-Hydrogen migration in carbenes appears to be accelerated in other cases by polar solvents.[26] 1,2-Carbon migration is special for **4**, which rearranges through a dipolar, nonclassical transition structure according to Schoeller[27] and Sulzbach et al.[28]

We are currently investigating other carbenes and other alkene traps in order to determine product distributions and pathways to product formation.

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Supporting Information Available: Figures showing transient absorption vs wavelength, [Py] vs A_y, and 1/[Py] vs 1/A_y and table giving yields and ratios of products of quenching of **4** by TME (3 pages). See any current masthead page for ordering and Internet access instructions.

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(22) A merry-go-round Rayonet apparatus ensured that all solutions were photolyzed under identical conditions. Yields at low conversion were obtained by 500 MHz ^{1}H NMR spectroscopy with suppression of the TME singlet as well as digital filtering of that singlet outside the spectral window. Integrations of unobscured signals were compared with that of internal standard hexamethyldisilane.

(23) Another interpretation would ascribe these results to the formation of a carbene−olefin complex which can rearrange to CB and MC or collapse to form adduct. See: Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454. Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 3829 and references therein.

(24) While the data require that the 21% contribution from **4** be in the form of MC, it is not possible to exclude CB formation entirely, because of experimental errors. If excited state chemistry is not involved but **4** forms a complex with TME,[23] then the ratio MC:CB without added TME represents the product distribution from the free carbene. In either case, the data suggest that 1,2-C migration is highly favored.

(25) Curvature in the plots of quenching data in both solvents, as a result of more than one adduct forming intermediate, could introduce additional errors in $k_q\tau$.

(26) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

(27) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811.

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