Time-Resolved IR Studies of 4-Diazo-3-isochromanone: Direct Kinetic Evidence for a Non-Carbene Route to Ketene

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The Wolff rearrangement of diazocarbonyl compounds to ketenes, a reaction discovered at the beginning of the 20th century,[1] is still receiving attention even as a new century begins.[2] In the mid-1960s Kaplan and Meloy demonstrated that acyclic diazocarbonyl compounds exist as equilibrium mixtures of syn and anti forms (Scheme 1) and suggested that the relative contribution of these conformations could have a significant impact on the mechanism of photoinduced ketene formation.[3] Subsequent work has confirmed the important role that conformation plays in this rearrangement process.[4,5] The mechanistic picture that has emerged from these investigations is that concerted rearrangement to ketene from a singlet excited state is facile from the syn conformation, but carbene production occurs from the anti form.[6] (As will be shown below, carbene formation can also occur from the syn form.) The evidence for involvement of precursor excited states in such rearrangement chemistry has been based mainly on product studies. For example, even in the presence of a large excess of a carbene trap such as alcohol, ketene rearrangement products are still observed for diazocarbonyls with significant population of the syn conformer.[7]

Recently we reported a nanosecond time-resolved infrared (TRIR) investigation of naphthyldiazoester **1**.[8] In this case, we found that the rate of ketene growth is equivalent to the rate of carbene decay, demonstrating that ketene **3** arises entirely from carbene **2** (Scheme 2). This result is in excellent agreement with the alcohol trapping experiments of Platz and co-workers, who isolated essentially only carbene-derived adducts,[9] and the calculations of Bally, McMahon, and co-workers.[10] Those calculations indicate that naphthyldiazoester **1** is planar and exists almost entirely (99%) in conformations in which the diazo and carbonyl groups are anti. Thus, the preferred conformation of **1** leads to efficient carbene production upon photolysis with very little if any direct rearrangement to ketene **3**.

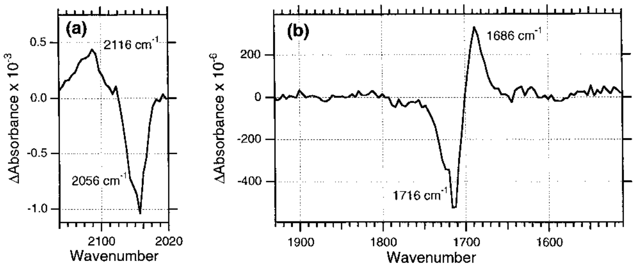
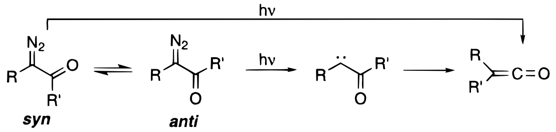
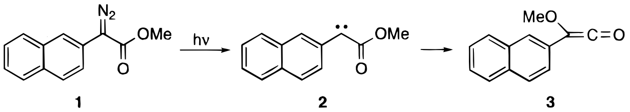


Figure 1. TRIR difference spectra observed over the first 500 ns following 266 nm laser photolysis (90 ns, 0.4 mJ) of ^{15}N-labeled **4** (2 mM) in argon-saturated Freon-113 for the spectral regions (a) 2150−2020 and (b) 1930−1510 cm^{-1}.

Scheme 1



Scheme 2



The lack of excited-state involvement for **1** is in contrast to behavior in systems that have substantial equilibrium concentrations of the syn conformer. To examine the effect that conformation has on ketene growth kinetics, we are pleased to report herein a TRIR investigation of 4-diazo-3-isochromanone (**4**), a cyclic analogue (phenyl version) of **1** that is locked in the syn conformation.

Typical TRIR data[11] observed following 266 nm laser excitation of ^{15}N-labeled **4** in argon-saturated Freon-113 (1,1,2-trichlorotrifluoroethane) are shown in Figure 1 for the spectral regions 2150−2020 and 1930−1510 cm^{-1}. Data are obtained in the form of difference spectra. As will be discussed below, we attribute the positive bands at 1686 and 2116 cm^{-1} to triplet carbene **5** and ketene **6**, respectively; the negative bands at 2056 and 1716 cm^{-1} are due to depletion of ^{15}N-labeled **4**. The use of ^{15}N-labeled **4** was required to shift a strong negative depletion signal in the unlabeled compound away from the positive ketene IR band of interest.[12]

As shown in Figure 2, the 1686 cm^{-1} carbene band decays with a lifetime of 526 ± 50 ns in argon-saturated Freon-113 ([**4**] = 2 mM). The 2116 cm^{-1} ketene band, however, in dramatic contrast to the data observed with acyclic diazocarbonyl **1**,[8] is produced faster than the current time resolution (50 ns) of our spectrometer. We, therefore, hypothesize that ketene **6** is formed not from carbene **5**, but entirely from the singlet excited state of **4** (Scheme 3). In agreement with this hypothesis, oxygen and methanol quench carbene **5**, but they leave the initial intensity of the ketene IR band unaffected.[13] These results are consistent with

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(1) (a) Wolff, L. *Justus Liebigs Ann. Chem.* **1902**, *325*, 129. (b) Wolff, L. *Justus Liebigs Ann. Chem.* **1912**, *394*, 23.

(2) For a recent review see: Toscano, J. P. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1998; Vol 2, p 215.

(3) (a) Kaplan, F.; Meloy, G. K. *Tetrahedron Lett.* **1964**, 2427. (b) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950.

(4) For examples see: (a) Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759. (b) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Org. Chem.* **1980**, *45*, 5278. (c) Toscano, J. P.; Platz, M. S.; Nikolaev, V. *J. Am. Chem. Soc.* **1995**, *117*, 4712.

(5) There is ample evidence in the literature that excited states of diazo compounds and diazirines often display carbene-like reactivity. For a review see: Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, p 133 and references therein.

(6) Alternative explanations have also been proposed: (a) Torres, M.; Ribo, J.; Clement, A.; Strausz, O. P. *Can. J. Chem.* **1982**, *61*, 996. (b) Marfisi, C.; Verlaque, P.; Davidovics, G.; Pourcin, J.; Pizzala, L.; Aycard, J.-P.; Bodot, H. *J. Org. Chem.* **1983**, *48*, 533.

(7) (a) Rando, R. R. *J. Am. Chem. Soc.* **1970**, *92*, 6706. (b) Rando, R. R. *J. Am. Chem. Soc.* **1972**, *94*, 1629. (c) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

(8) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 2875.

(9) Wang, J.-L.; Lithovorik, I.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 2883.

(10) Zhu, Z.; Bally, T.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

(11) TRIR experiments were performed following the method of Hamaguchi and co-workers ((a) Iwata, K.; Hamaguchi, H. *Appl. Spectrosc.* **1990**, *44*, 1431. (b) Yuzawa, T.; Kato, C.; George, M. W.; Hamaguchi, H. *Appl. Spectrosc.* **1994**, *48*, 684) as described previously.[8]

(12) ^{15}N-labeled **4** was synthesized by diazo transfer from ^{15}N-labeled *p*-toluenesulfonyl azide (made from the reaction of *p*-toluenesulfonyl hydrazide with ^{15}N-labeled sodium nitrite) to 3-isochromanone. Spectroscopic details concerning **4** and ^{15}N-labeled **4** are included as Supporting Information.

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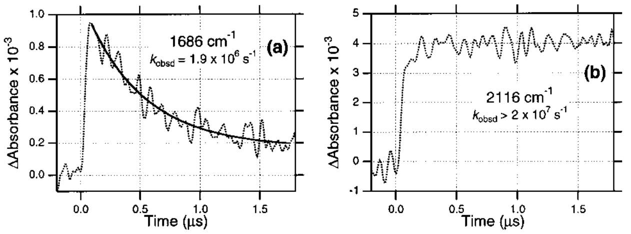
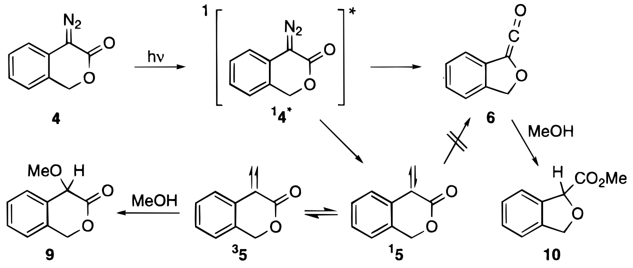
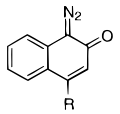


Figure 2. Kinetic traces observed at (a) 1686 and (b) 2116 cm^{-1} following 266 nm laser photolysis (5 ns, 1.5 mJ) of ^{15}N-labeled **4** (2 mM) in argon-saturated Freon-113. The dotted curves are experimental data; the solid curve is the calculated best fit to a single-exponential function.

Scheme 3



previously reported photochemical studies of **4**[14] and the related diazonaphthoquinones **7**[15] and **8**.[16]



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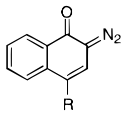

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R = H, SO_3^-

The lifetime of carbene **5** is reduced to less than 50 ns in oxygen-saturated Freon-113. Methanol quenching was analyzed according to the pseudo-first-order equation, $k_{obsd} = k_0 + k_{MeOH}$[methanol], where k_{MeOH} is the second-order rate constant for the reaction of methanol with carbene **5** and k_0 is the rate of carbene decay in the absence of methanol and at a fixed concentration of diazoester **4**. Values of k_{obsd} were linearly dependent on methanol concentration for the range examined (0−62 mM). This analysis provides $k_{MeOH} = (4.0 \pm 0.4) \times 10^7$ M^{-1} s^{-1} in Freon-113, consistent with previous studies of triplet carbene reactions with methanol.[17]

Further support for our IR band assignments comes from B3LYP/6-31G* calculations,[18] which have been shown to provide accurate carbene energies, structures, and vibrational frequencies. Calculated IR frequencies (scaled by 0.96)[20] diagnostic of diazoester **4**, triplet carbene **5**, and ketene **6** agree well with TRIR-observed values.[20] Geometries of the lowest singlet and triplet states of carbene **5** reveal that, as expected,[21] the carboalkoxy group in ^{1}**5** adopts a conformation significantly out of the phenyl carbene plane, whereas these groups are nearly coplanar in ^{3}**5**. The triplet state is calculated to be 7.06 kcal/mol lower in energy than the singlet in the gas phase;[22] ketene **6** lies 30.75 kcal/mol below ^{3}**5**. This calculated singlet−triplet gap is larger than the corresponding one calculated for acyclic carbene **2** (4.52 kcal/mol) presumably because of the constraints of the ring system in carbene **5**. We calculate that ^{1}**5** is separated from ketene **6** by a barrier of 5.20 kcal/mol in good agreement with the previously CCSD(T)/6-311G(df,p) calculated barrier between singlet formylmethylene and ketene (5.88 kcal/mol).[23]

Additional evidence for a photochemically produced noncarbene precursor to ketene **6** is provided by product analysis. Photolysis of **4** in neat methanol leads to both carbene-derived (i.e., **9** in 75% absolute yield) and ketene-derived adducts (i.e., **10** in 18% absolute yield), but thermolysis of **4** in neat methanol (sealed tube at 170 °C) provides only **9** (91% absolute yield).[24] The ratio of **9** to **10** in the photolysis experiment suggests that the diazaoester excited state ^{1}**4*** partitions between carbene production and ketene formation in an approximately 4 to 1 ratio confirming that syn diazoesters can form carbene intermediates as has been previously observed.[16,25]

The kinetic data of Figure 2 indicate that carbene **5**, under the conditions of our TRIR experiments, does not form ketene **6**, in contrast with the observed reactivity of acyclic carbene **2**. Platz and co-workers determined that carbene **2** is separated from ketene **3** by a 3.4 kcal/mol barrier in hexafluorobenzene.[9] It is likely that the higher singlet/triplet gap for carbene **5** relative to that of **2** raises the effective barrier to rearrangement. We find, by monitoring the lifetime of carbene **5** as a function of concentration of diazoester **4**, that **5** is effectively quenched by **4** with $k_{diazo} = (5.0 \pm 0.5) \times 10^8$ M^{-1} s^{-1} in Freon-113. This observation suggests that a major decay route of the carbene under the conditions of our experiment is formation of azine.

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Supporting Information Available: Spectroscopic details for **4** and ^{15}N-labeled **4**, details of product analysis following photolysis and thermolysis of **4** in neat methanol, and results of B3LYP/6-31G* calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Ketene **6** is observably quenched by methanol only at high (>0.5 M) concentrations indicating a relatively slow rate constant for the reaction of ketene with methanol in accord with previous work: (a) Barra, M.; Fisher, T. A.; Cernigliaro, G. J.; Sinta, R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2630. (b) Andraos, J.; Chiang, Y.; Huang, C.-G.; Kresge, A. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605. (c) Lucus, N. C. d.; Andraos, J.; Netto-Ferreira, J. C.; Scaiano, J. C. *Tetrahedron Lett.* **1995**, *36*, 677.

(14) Carbene **5** has been reported to have a lifetime in the microsecond range in nonaqueous solvents: Chiang, Y.; Jefferson, E. A.; Kresge, A. J.; Popik, V. V.; Xie, R.-Q. *J. Phys. Org. Chem.* **1998**, *11*, 610.

(15) The formation of the ketene derived from **7** has been reported to be complete within 10 ns following laser photolysis in aqueous solution.[13b]

(16) Picosecond transient absorption experiments have indicated that the carbene derived from **8** (R = H) has a lifetime of 20 ps in methanol; however, the ketene growth rate could not be determined due to overlap with carbene absorption: Vleggaar, J. J. M.; Huizer, A. H.; Kraakman, P. A.; Nijssen, W. P. M.; Visser, R. J.; Varma, C. A. G. O. *J. Am. Chem. Soc.* **1994**, *116*, 11754. See also ref 13a.

(17) Scaiano, J. C. Representative Kinetic Behavior of Carbenes. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 211.

(18) Calculations were carried out with the Gaussian 94 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Rev. E.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(19) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(20) B3LYP/6-31G* calculated geometries for ^{1}**5**, ^{3}**5**, **6**, and the transition state separating ^{1}**5** and **6** are included as Supporting Information. Also included are calculated energies, Cartesian coordinates, and all vibrational frequencies and intensities for **4**, ^{1}**5**, ^{3}**5**, **6**, and the transition state separating ^{1}**5** and **6**.

(21) (a) Strausz, O. P.; Gosavi, R. K.; Denes, A. S.; Czismadia, I. G. *J. Am. Chem. Soc.* **1976**, *98*, 4784. (b) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333. (c) Kim, K. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 5390. (d) Tanaka, K.; Yoshimine, M. *J. Am. Chem. Soc.* **1980**, *102*, 7655. (e) Gosavi, R.; Torres, M.; Strausz, O. P. *Can. J. Chem.* **1991**, *69*, 1630. (f) Xie, Y.; Schaefer, H. F. *Mol. Phys.* **1996**, *87*, 389.

(22) The singlet−triplet energy gap is likely lower in solution.[8]

(23) Scott, A. P.; Nobes, R. H.; Schaefer, H. F., III; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 10159.

(24) Product identities and yields were determined by NMR spectroscopic analysis both before and after hydrolysis of **9** and **10**. Details are given as Supporting Information. Yields are accurate to ±5%.

(25) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.