ORGANIC LETTERS

2006
Vol. 8, No. 21
4807−4809

Fragmentation of 2,2,2-Triphenylethoxychlorocarbene: Evidence for Ultrafast Fragmentation–Rearrangement in Excited Diazirines

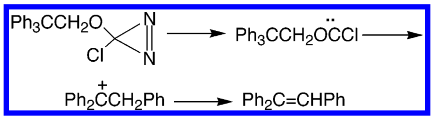
Xiaolin Fu,[†] Robert A. Moss,*[,†] Piotr Piotrowiak,*[,‡] Mykhaylo Myahkostupov,[‡] and Ian R. Gould*[,§]

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, Department of Chemistry, Rutgers, The State University of New Jersey, Newark, New Jersey 07102, and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

moss@rutchem.rutgers.edu

Received July 27, 2006

ABSTRACT



Photolysis of 3-(2,2,2-triphenylethoxy)-3-chlorodiazirine gives 2,2,2-triphenylethoxychlorocarbene which fragments with 1,2-phenyl migration and loss of CO and Cl⁻ to yield the 1,1,2-triphenylethyl cation and thence 1,1,2-triphenylethene by proton loss. However, ps and fs laser flash photolysis provides evidence that up to 25% of the alkene product stems from carbocation that arises directly from excited diazirine rather than from the carbene.

When alkylchlorocarbenes are generated photochemically from alkylchlorodiazirines, rearrangements occurring in conjunction with the loss of nitrogen from the diazirines' excited states parallel rearrangements of the daughter carbenes, so that the rearranged products stem from two sources.[1] Here, we present ultrafast kinetic evidence implying that similar complications attend the generation and fragmentation of 2,2,2-triphenylethoxychlorocarbene from a diazirine precursor. This is the first indication that excited alkoxyhalodiazirines can undergo rearrangement in concert with the loss of N_2 and CO.

Triphenylethanol[2] was converted[3] to isouronium salt **1**,[4] and thence, by oxidation with NaOCl,[5] to 3-(2,2,2-triphenylethoxy)-3-chlorodiazirine **2**.[4] Photolysis of **2** at 350 nm in $CDCl_3$ gave dichloride **3** and triphenylethene **4** in yields of 9% and 91%, respectively. Dichloride **3** is an HCl trapping product of triphenylethoxychlorocarbene **5**. In the presence of pyridine, which scavenges HCl, the dichloride was suppressed, and alkene **4** formed in >95% yield. The latter was identified by ^1H and ^{13}C NMR comparisons to an authentic (commercial) sample, and verified by GC spiking experiments. NMR gave no evidence for the presence of either (unrearranged) 1,1,1-triphenyl-2-chloroethane[6] or (re-

---

[†] Rutgers University, New Brunswick.

[‡] Rutgers University, Newark.

[§] Arizona State University.

(1) (a) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055 and references therein. (b) Review: Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1998;Vol. 2, pp 133f. (c) Review: Merrer, D. C.; Moss, R. A. *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. 3, pp 53f.

(2) Davis, F. A.; Reddy, R. E.; Szewczyk, J. M.; Reddy, G. V.; Portonovo, P. S.; Zhang, H.; Fanelli, D.; Reddy, R. T.; Zhou, P.; Carroll, P. J. *J. Org. Chem.* **1997**, *62*, 2555.

(3) Moss, R. A.; Kaczmarczyk, G. M.; Johnson, L. A. *Synth. Commun.* **2000**, *30*, 3233.

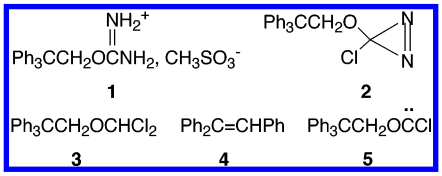
(4) See the Supporting Information for experimental details.

(5) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

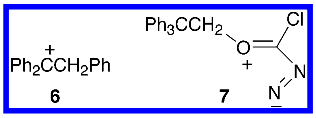
(6) Eisch, J. J.; Kovacs, C. A.; Chobe, P. *J. Org. Chem.* **1989**, *54*, 1275.

10.1021/ol061863l CCC: $33.50

arranged) 1,1,2-triphenyl-1-chloroethane.[7] Attempts to prepare[7] the latter chloride from 1,1,2-triphenylethanol[8] and $SOCl_2$ gave only triphenylethene.

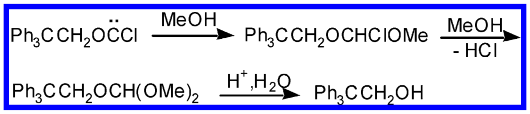


The triphenylethene formed upon photolysis of diazirine **2** in $CDCl_3$ mostly arises by proton loss from triphenylethyl cation **6**, which derives from the fragmentation of carbene **5** coupled with 1,2-phenyl migration. This process parallels the formation of the *t*-amyl cation by the fragmentation of neopentyloxychlorocarbene, coupled with 1,2-methyl migration.[9] However, we now find that the origin of cation **6** is more complicated.



Absolute rate constants for the fragmentations of alkoxyhalocarbenes are generally ~10^5–10^6 s^{-1} [9,10] and can be determined by ns laser flash photolysis (LFP) using the pyridine ylide method.[11] However, no pyridine ylide formed from carbene **5** when diazirine **2** was decomposed by ns LFP at 351 nm in pentane containing 4 M pyridine, in 1,2-dichloroethane (DCE) containing 0.8–4.0 M pyridine, or in methanol with 0.8–4.0 M pyridine. Either the fragmentation of carbene **5** is $\gg 10^6$ s^{-1} and/or the rate of ylide formation is reduced relative to fragmentation, perhaps because of steric hindrance originating at the 3 β-phenyl groups of **5**. Can the carbene be efficiently trapped?

Photolysis of diazirine **2** in neat methanol gives 15–25% of triphenylethene **4** and 75–85% of 2,2,2-triphenylethanol. (Both products are stable to photolysis in methanol at 350 nm.) The triphenylethanol stems from methanolic trapping of the carbene.[12,13] Although methanol efficiently captures carbene **5**, even neat methanol cannot prevent the formation of a significant quantity of rearranged alkene **4**. Moreover,



a correlation of the triphenylethanol/triphenylethene product ratio vs the concentration of methanol in $CDCl_3$ is *curved* (Figure 1); above ~0.4 M MeOH, the product ratio levels off at ~7.5:1. This behavior, which parallels that of alkylchlorocarbenes photogenerated from diazirines,[1] implies that there are 2 sources of alkene **4**, only one of which (carbene **5**) can be intercepted by methanol.

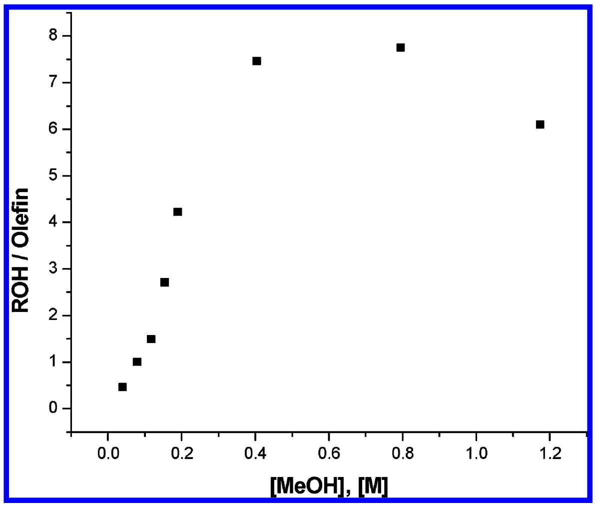


Figure 1. Product ratios of $Ph_3CCH_2OH/Ph_2C{=}CHPh$ vs [MeOH] for the photolysis of diazirine **2** in $MeOH/CDCl_3$. The product ratios were determined by calibrated capillary GC.

We considered the possibility that the 15–25% of triphenylethene that persists even when carbene **4** is generated in neat methanol arose directly by a phenyl shift rearrangement–fragmentation of excited diazirine **2** to cation **6**, followed by proton loss. The cation is known to absorb at 430 nm (in sulfuric acid),[14] but ns LFP of **2** in DCE, MeCN, or MeOH gave no UV evidence for **6**. However, ps LFP of **2** in MeOH at 355 nm[15] revealed a transient at 440 nm that was quenched upon addition of pyridine, and which we assign to cation **6**; cf. Figure 2. Decay of the cation was observed with a lifetime of ~85 ps in methanol, representing proton loss with the formation of triphenylethene. Cation **6** was not formed upon ps LFP of triphenylethene in MeOH, although the alkene's excited state (420 and 670 nm) and radical cation (490 nm) did appear.

On the ultrafast time scale, fs LFP revealed an even shorter-lived transient, formed instantaneously upon n to π^* excitation of the diazirine at 350 nm. The transient exhibited an absorption maximum at 450 nm and decayed with complex, multiexponential kinetics. Within the initial 5 ps time window, the decay was biphasic: a fast component of 110 fs (56% of the total decay) and a slower component of 1.28 fs (27% of the decay); cf. Figure 3.

We tentatively assign this very short-lived 450 nm transient to zwitterionic species **7**, formed by C–N bond cleavage

---

[7] Klages, A.; Heilmann, S. *Chem. Ber.* **1904**, *37*, 1447.

[8] Carter, P. R.; Hey, D. H. *J. Am. Chem. Soc.* **1948**, 150.

[9] Moss, R. A.; Ge, C.-S.; Maksimovic, L. *J. Am. Chem. Soc.* **1996**, *118*, 9792.

[10] Moss, R. A. *Acc. Chem. Res.* **1999**, *32*, 969.

[11] Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

[12] Smith, N. P.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1298.

[13] Moss, R. A.; Zheng, F.; Fedé, J.-M.; Ma, Y. Sauers, R. R.; Toscano, J. P.; Showalter, B. M. *J. Am. Chem. Soc.* **2002**, *124*, 5258.

[14] Toone, T. W.; Lee-Ruff, E.; Khazanie, P. G.; Hopkinson, A. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 607.

[15] See the Supporting Information for details of the ps LFP instrumentation.

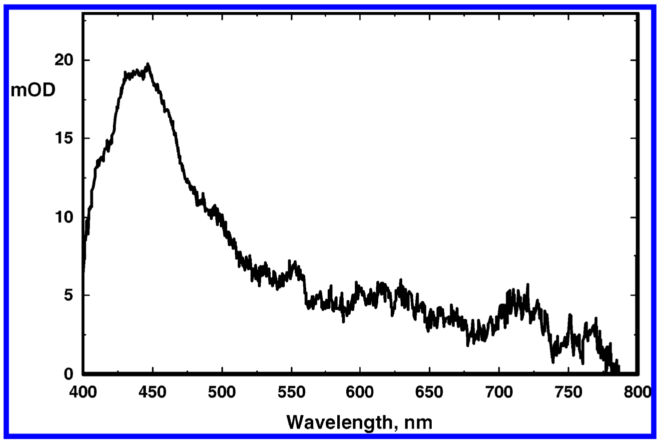


Figure 2. Transient absorption spectrum observed 60 ps after excitation of diazirine **2** in MeOH at 25 °C at low laser power, showing absorption due to cation **6** at 440 nm and negligible absorption at 490 nm due to the radical cation of alkene **4**.[16]

from the "vertical" Franck−Condon S_1 state of **2**.[17] The ultrafast formation of **7** (<50 fs) is aided by release of strain in the diazirine ring and by the likely charge-transfer character of the S_1 state, buttressed by the electronegative substituents on the carbon atom. Evolution to a singlet biradical or zwitterion is a reasonable fate for the S_1 state of a diazirine.[17c] There are two major decay channels available to **7**: loss of N_2 to form carbene **5** or formation of cation **6** by 1,2-phenyl shift coupled with the loss of the $O{=}CClN{=}N^-$ anion, which itself fragments to CO, N_2, and Cl^-.[18] The zwitterion can exist in a range of rotomeric forms which could partition differently between these decay channels. The 450 nm signal reports the overall decay of **7** and does not distinguish individual rotamers. However, we suggest that the 110 fs component is the signature of "hot" zwitterions which undergo chemistry before being fully vibrationally cooled and solvated, while the slower 1.28 ps component originates from fully thermalized and solvated **7**. It is likely that the hot and thermalized zwitterions yield different ratios of the carbene and carbocation.

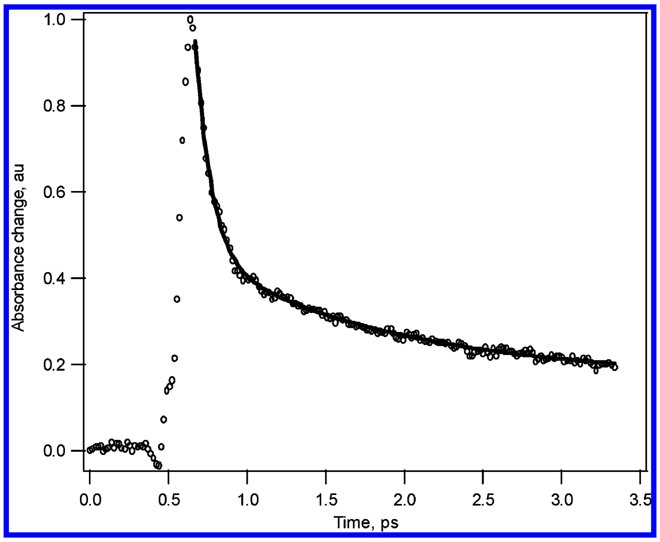
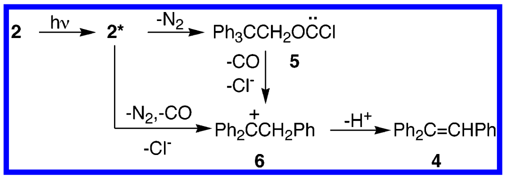


Figure 3. Ultrafast decay of the excited state of diazirine **2** in MeOH, $\tau_1 = 110$ fs, $A_1 = 0.56$; $\tau_2 = 1.28$ ps, $A_2 = 0.27$; $A_\infty = 0.17$. The sample was excited at 350 nm (2.5 μJ, 30 fs fwhm) and probed at 450 nm (1.0 μJ, 45 fs fwhm).

The ultrafast LFP results thus support the contention that up to 25% of the triphenylethene formed upon photolysis of **2** stems from cation **6** that arises directly from the excited diazirine rather than from carbene **5**,[19] cf. Scheme 1. Here, excited **2*** (or **7**) can lose N_2, affording carbene **5** and thence cation **6** by carbene fragmentation concerted with phenyl migration and the loss of CO and Cl^-. Competitively, **2*** (**7**) can give cation **6** *directly* by phenyl migration cojoint with the loss of N_2, CO, and Cl^-. Subsequent loss of a proton from **6** to yield **4** is rapid (<100 ps), so that cation **6**, visible at 440 nm when generated from **2*** on the ps time scale, is not detected by ns LFP when it arises from carbene **5**. This is the first implication of an excited diazirine carbene-mimetic pathway in the photolytic fragmentation of an alkoxychlorodiazirine. It seems quite possible that analogous phenomena may be involved in the photolysis of other alkoxychlorodiazirines.

Scheme 1



Acknowledgment. The authors at all three institutions are grateful to the National Science Foundation for financial support.

Supporting Information Available: Preparations of **1** and **2** and descriptions of the ps LFP facilities. This material is available free of charge via the Internet at http://pubs.acs.org.

OL061863L

---

[16] The diazirine contains small amounts of alkene **4** as an impurity. LFP also gives the singlet excited state and the radical cation of **4**. The former has a lifetime of ~10 ps; the latter is formed in a 2-photon process and can be minimized at low laser power.

[17] On the photophysics of diazirines, see: (a) Arenas, J. F.; Lopez-Tocon, I.; Otero, J. C.; Soto, J. *J. Am. Chem. Soc.* **2002**, *124*, 1728. (b) Muller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275. (c) Platz, M. S. In ref 1b. (d) See also: Diau, E. W.-G.; Abou-Zied, O. K.; Scala, A. A.; Zewail, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 3245.

[18] Zwitterion **7** could also "relax" to the diazo isomer of diazirine **2**. However, we see no evidence for diazoalkane formation by ns LFP−UV. Although a diazoalkane with two lone-pair substituents would be quite unstable, it should survive on the μs−ns time scale.

[19] It is highly unlikely that carbene **5** fragments to cation **6** at ~10^{12} s^{-1}, i.e., 5−6 orders of magnitude faster than the fragmentations of other ROCCl.