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Stereochemical Effects in Carbene Photochemistry: 2-Furylchlorocarbene

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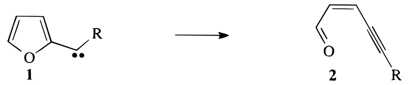
Although 2-furylcarbenes (**1**) might be envisioned to have considerable synthetic potential, these intermediates are notoriously difficult to trap.[1] Attempts to generate carbenes such as **1** in solution primarily lead to the ring-opened products **2**. This novel rearrangement, termed a coarctate reaction by Herges,[2] dominates even 1,2-CH shift in alkyl derivatives of **1** and prohibits trapping of the carbenes with alkenes.[1] Sander and co-workers[3] have reported recently that the parent 2-furylcarbene (**1,** R = H) likewise cannot be observed in low-temperature matrixes. We now report that chlorine substitution stabilizes this carbene significantly, enabling direct characterization of 2-furylchlorocarbene (**4**) at low temperatures, as well as trapping with olefins in solution.[4] Interestingly, two conformations of **4** are observed, which exhibit significant differences in their photochemical reactivity.



Previously unknown 2-furylchlorodiazirine (**3**) was synthesized from the corresponding amidine[5] via conventional Graham procedures.[6] The detonation-sensitive diazirine **3** was found to be bright-yellow, reflecting nπ^* absorption (λ_{max} 408, 385, 364 nm) red-shifted significantly compared to that of phenylchlorodiazirine (λ_{max} 389, 369, 350 nm).[7] Irradiation (404 nm) of **3** isolated in a N_2 matrix (ca. 700:1) at 8 K for 20 min gave 2-furylchlorocarbene (**4**), characterized by comparison of IR spectra with data from ab initio calculations (vide infra) together with subsequent chemistry.[8] The IR spectrum[9] of **4** was dominated by a strong band at 1404 cm^{-1}, and the carbene exhibited a weak, very broad visible absorption from 400 to 800 nm (λ_{max} 600 nm) accompanied by a very strong UV band at 330 nm. Broad-band irradiation of **4** (λ > 400 nm) for 2 h destroyed the IR and UV/vis spectra of **4**, with attendant growth of characteristic IR bands[9] of aldehyde acetylene **5** at 2219 and 1690 cm^{-1}.

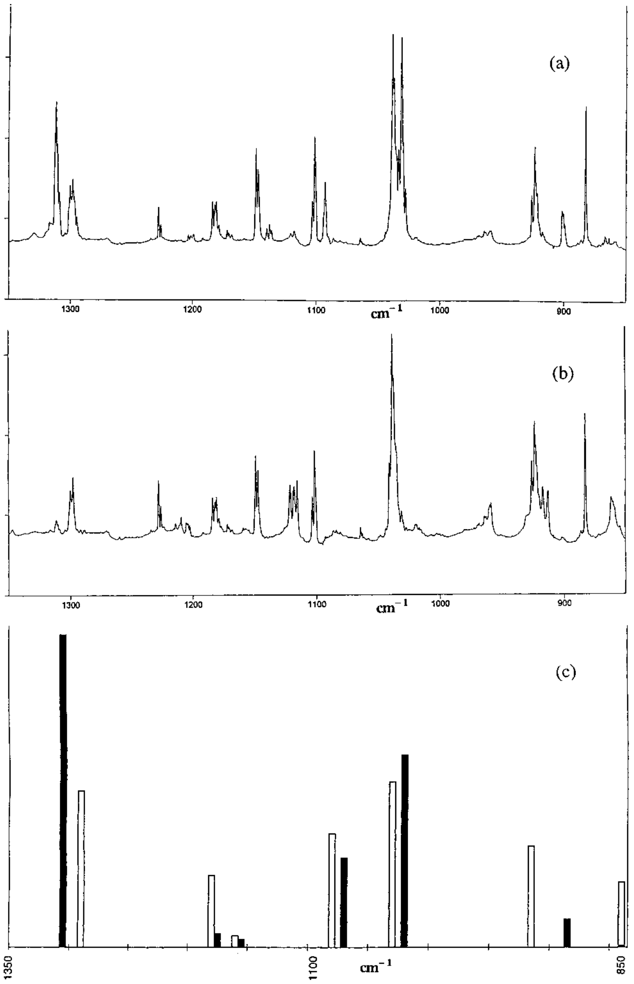
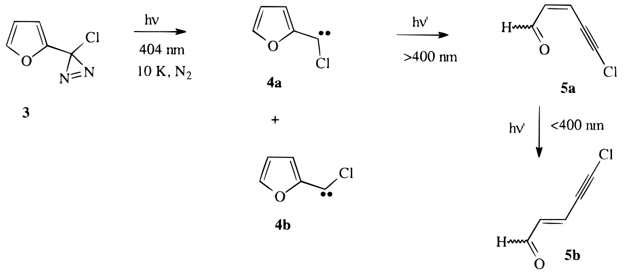


Figure 1. (a) IR spectrum of N_2 matrix isolated carbene mixture **4a** and **4b** after irradiation of diazirine **3** at 404 nm for 10 m (recorded in absorbance mode) (b) IR spectrum of same matrix at 620 nm for 165 m. (c) MP2/6-31G* calculated IR spectra for **4a** (solid) and **4b** (open) (frequencies scaled by 0.95 factor).



It could be anticipated that the carbene would be formed in two distinct planar conformations, **4a** and **4b**. Indeed, careful scrutiny of the IR spectra of **4** revealed two sets of bands exhibiting differential photoreactivity. Careful irradiation of matrixes containing the carbene (e.g., 620 nm, 45 m) selectively destroyed one set of bands, with concomitant formation of product **5** (Figure 1). The other group of IR bands corresponding to **4** were only converted to **5** on a much longer time scale (>4× slower under the same conditions). Similar photoselectivity was observed at other irradiation wavelengths (e.g., 420 or 320 nm).

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[1] (a) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1971**, *93*, 5940. (b) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927. (c) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7934.

[2] Herges, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 255.

[3] (a) Albers, R.; Sander, W. *Liebigs Ann.* **1997**, 897. For related recent papers, see: (b) Sander, W.; Albers, R.; Komnick, P.; Wandel, H. *Liebigs Ann. Chem.* **1997**, 901. (c) Albers, R.; Sander, W. *J. Org. Chem.* **1997**, *62*, 761.

[4] The stabilization of "elusive carbenes" by halogen substitution is well precedented. See, for example: Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788.

[5] Decroix, B.; Dubus, P. *C. R. Seances Acad. Sci., Ser. C* **1974**, *279*, 343.

[6] Graham, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 4396. Diazirine **3** was purified by trap-to-trap vacuum distillation: IR (N_2, 10 K, major bands, rel intensity) 1571 (47), 1563 (42), 959 (100), 859 (48), 750 (55), 747 (59) cm^{-1}; ^{1}H NMR (C_6D_6) 6.60 (m), 5.95 (d), 5.75 (dd) ppm.

[7] Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

[8] For a description of the matrix isolation instrumentation and experimental techniques, see: (a) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. (b) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

[9] IR spectra for **4** and **5** are listed numerically in the Supporting Information. A small amount of the corresponding diazo isomer of **3** was also observed at ca. 2140 cm^{-1} during irradiations.

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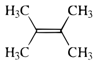
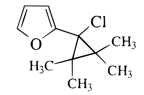
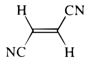
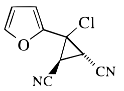
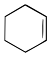
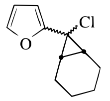
Formation of multiple conformational/geometric isomers of enynal **5** was also evident in the evolution of the IR spectra throughout the irradiations. In the long-wavelength photodecomposition of carbene **4** (λ > 400 nm), multiple sets of IR bands for **5** were observed; these bands converged on one set of absorptions with extended irradiation at shorter wavelengths (λ < 400 nm).

To identify the differently reactive conformations of the furylcarbene, MP2 and B3LYP/6-31G* calculations were performed on **4a** and **4b** and on various geometric/conformational isomers of aldehyde alkyne **5**.[10] Vibrational spectra predicted by both methods fit experimental values well and clearly identify **4a** as the more photochemically reactive conformer (Figure 1). Interestingly, the syn isomer **4a** was calculated to lie slightly lower in energy (1.3 kcal/mol by DFT, corrected for zero-point energies) than the anti isomer **4b**. However, transition state calculations at this level predict that **4a** should have a significantly lower energy barrier (13 vs 20 kcal/mol, respectively) toward ring opening. Although Herges[2] has analyzed the π molecular orbital topology of this "coarctate" rearrangement, with the conclusion that the reaction of **1** to **2** is thermally allowed, differential reactivity of conformational isomers was not examined. It is tempting to speculate that an anti-periplanar arrangement between the carbene lone pair and the breaking C−O bond in **4a** facilitates cleavage relative to conformer **4b**.[11] Although excited-state reactivity need not parallel the ground state, it is interesting that syn **4a** is the isomer showing greater photochemical lability. It is suggestive that the excited state of **4a** benefits from similar stereoelectronics to the ground state of the carbene or that photochemical ring opening occurs via a vibrationally hot ground state of **4**

CIS/6-31G*//MP2/6-31G* calculations[10] predict $\sigma\pi$ transitions for **4a** at 471 nm (f = 0.0093) and for **4b** at 489 nm (f = 0.0087), both in reasonable agreement with experiment. The UV/vis spectrum, and the excellent match between experimental and calculated IR spectra, suggest that the carbene is a ground-state singlet as expected. Finally, comparison of DFT calculated IR spectra of the ring-opened photoproduct **5** with the matrix results indicates that (Z)-enynal **5a** is initially formed at long wavelengths, and photochemically isomerizes to the (E)-isomer **5b** at shorter wavelengths.[10] The experimental spectra were fit best with calculated spectra for *s-cis/s-trans* conformational mixtures of both **5a** and **5b**. Sander and co-workers[3a] have observed similar product isomerization in attempted observations of the parent carbene **1**.

Table 1. Solution Trapping of 2-Furylchlorocarbene (**4**)[12]

Olefin	Adduct	Yield (recrystallized, based on amidine)
	 **6a**	57 %
	 **6b**	30 %
	 **6c**	40 % (ca. 1:3 endo - exo)

Halogen substitution also rendered carbene **4** trappable in solution. Room-temperature solution thermolysis of diazirine **3** in the presence of a variety of olefins gave reasonable yields of the corresponding cyclopropanes **6a**−**c** (Table 1).[12,13] These preliminary data suggest that **4** exhibits fairly broad reactivity and may have some synthetic utility. More complete studies with other olefins and halogen carbene substituents are underway.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for generous support of this work. We also thank Pawel Rempala for calculational assistance.

Supporting Information Available: Calculated geometries and IR spectra for **4a**, **4b**, *s-trans* **5a**, *s-cis* **5a**, *s-trans* **5b**, *s-cis* **5b**, and transition states for ring-opening of **4a**, and **4b**, together with tabulated experimental IR data on **4** and **5** (11 pages). See any current masthead page for ordering and Internet access instructions.

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[10] *Gaussian 94, Revision D.4*; 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, Inc.: Pittsburgh, PA, 1995. Although both MP2 and B3LYP calculations fit the experimental IR spectra of **4a** and **4b** quite well, the former gave a slightly better match of the relative intensities (Figure 1). For calculated geometric parameters and vibrational spectra, see the Supporting Information.

[11] In **4a**, we would expect better overlap between the carbene lone pair and the fragmenting C−O σ* orbital, compared to that in **4b**. B3LYP/6-31G** calculations on the parent carbenes (**1**, R = H) similarly predict barriers for ring-opening of 1.2 (syn conformer) and 4.7 (anti conformer) kcal/mol. These results support our stereoelectronic interpretation and highlight the stabilizing influence of Cl in **4**. For similar analyses of stereoelectronic control in bond fragmentations, see: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983.

[12] Diazirine **3** was vacuum transferred to a 77 K trap from a solution of 200 mg of the corresponding amidine hydrochloride, NaOCl, and NaCl in DMSO as per standard Graham conditions.[6] A 10-fold excess of alkene in pentane or dichloromethane was added, and the solution was held at room temperature for 24 h. Removal of solvent in vacuo gave crude product, which was carefully purified by recrystallization. Yields are not optimized. The adducts between **4** and the olefins shown in Table 1 were characterized by ^{1}H NMR, ^{13}C NMR, GCMS, and HRMS (for tetramethylethylene and fumaronitrile adducts). Photolyses of diazirine gave qualitatively similar results.

[13] In the absence of trapping agents, photolysis or thermolysis product mixtures from **3** were complicated and difficult to characterize, apparently from ready polymerization of **5**.