

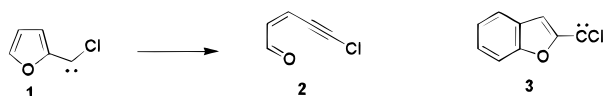
Photochemistry of 2-Benzofurylchlorocarbene: Characterization of a 2,3-Didehydro-2H-pyran

Tania Khasanova and Robert S. Sheridan*

Department of Chemistry, University of Nevada
Reno, Nevada 89557

Received June 23, 2000

In contrast to the extensively studied archetype, phenylchlorocarbene,¹ scant information is available on heteroaryl singlet carbenes. Besides interesting electronic perturbations introduced by heteroaromatic substituents, novel rearrangements become possible. Recently, we described characterization of 2-furylchlorocarbene (**1**), and its stereoselective photochemical ring-opening to enynal **2**.^{2,3} Reasoning that benzannelation of this system might impede fragmentation and potentially open new reaction pathways, we have since probed the chemistry of 2-benzofurylchlorocarbene (**3**). We now report a strikingly rich cascade of reactive intermediates uncovered by this point of entry, including the first observation of a 3,4-didehydropyran.



Irradiation (436 nm, ~10 h) of 2-benzofurylchlorodiazirine^{4,5} (**4**) isolated in an N₂ matrix (~1:800) at 10 K slowly produced carbene **3**. DFT⁶ calculated vibrational spectra (B3LYP/6-31G**) of a *syn/anti*-mixture of **3** gave an excellent fit to the experimental IR. Furthermore, when **3** was generated similarly in a 0.4% HCl-doped N₂ matrix, then warmed to 35 K, the carbene IR bands disappeared and absorptions of dichloride **5** grew. In parallel with other arylchlorocarbenes,^{1,2} **3** displayed a very strong 350 nm UV band.³

The 2-benzofurylcarbene **3** was quite photolabile. Irradiation of the matrix containing **3** (or starting diazirine) for only 5 m at 366 nm completely destroyed the carbene IR, and replaced it with a new spectrum with strongest bands at 1089 and 801 cm⁻¹ (Figure 1). At the same time, the carbene UV disappeared, and a strong band at 305 nm together with a moderately strong, and broad absorption centered at 545 nm grew in. Conversely, irradiation of this new photoproduct at 546 nm for ~12 h slowly converted it back to carbene **3** in the IR and UV (Figure 1).

(1) Pliego, J. R., Jr.; De Almeida, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 7481 and references therein.

(2) (a) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233. (b) For recent calculations on this system, see Sun, Y.; Wong, M. W. *J. Org. Chem.* **1999**, *64*, 9170.

(3) For related work on the parent system, see Albers, R.; Sander, W. *Liebigs Ann.* **1997**, 897.

(4) Diazirine **4** was generated by standard Graham oxidation of the known amidine. Synthetic details are given in the Supporting Information. (a) Amidine: Shridhar, D. R.; Reddy Sastry C V.; Kulbhushan, L. *J. Ind. Chem.* **1979**, *18B*, 254. (b) Diazirine: Graham, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(5) For a description of the matrix isolation instrumentation and techniques, see: Rempala, P.; Sheridan, R. S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2257.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

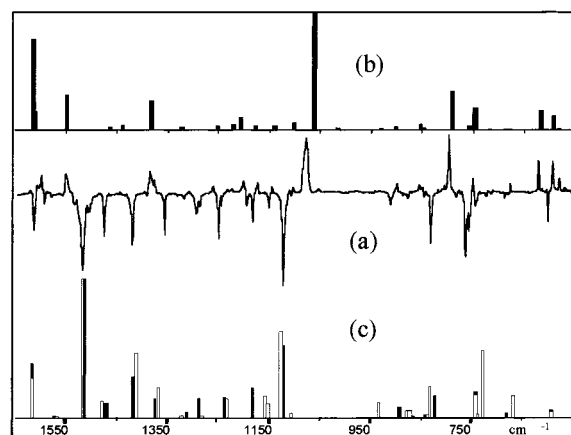
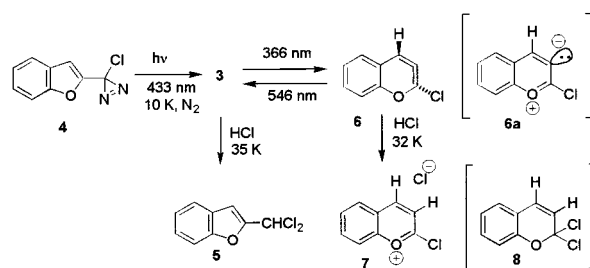


Figure 1. (a) Difference IR spectrum showing conversion of allene **6** (“up bands”) to carbene **3** (“down bands”) on 546 nm irradiation for 135 m. (b) B3LYP/6-31G** calculated IR for allene **6**. (c) B3LYP/6-31G** calculated IR for *syn*-carbene **3a** (solid) and *anti*-carbene **3b** (open). Calculated frequencies are scaled by 0.96.

Calculational modeling and trapping indicate convincingly that this photoproduct of **3** is the novel didehydrobenzopyran **6**. The B3LYP/6-31G** (Figure 1) or MP2/6-31G* calculated IR for **6** nicely fits the experimental spectrum. Warming an HCl-doped (0.4%) N₂ matrix of **6** to 32 K rapidly converted the allene to a new product, with a strongest IR band at 1510 cm⁻¹. The well-known benzopyrylium cations characteristically exhibit strong IR absorptions in this region.⁷ Indeed, the experimental IR of the trapping product matched B3LYP predictions for pyrylium salt **7**.⁶ Calculated spectra of alternative potential products, such as **8**, were completely unsatisfactory. Addition of DCl to **6** in the same manner gave deuterated product with appropriately shifted IR bands that matched DFT predictions.⁶ These results are summarized in Scheme 1.

Scheme 1

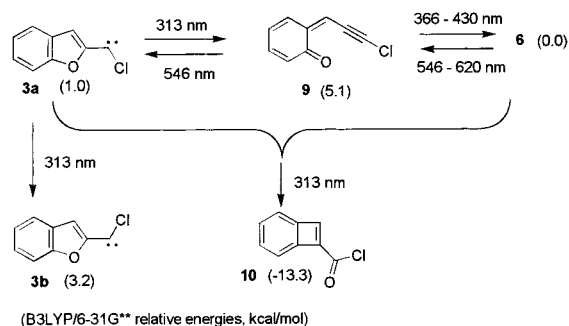


As we have shown with other furylcarbenes,^{2,8} *syn* and *anti* conformers of **3** could be discerned. The IR spectrum of **3** generated from irradiation of allene **6** was subtly different than that produced on initial irradiation of diazirine. In particular, a doublet of moderate intensity bands at 844 and 838 cm⁻¹ was observed from photolysis of **4**, but only the 838 cm⁻¹ peak was produced from allene **6**. The strong UV band of **3** was also blue-shifted to 345 nm when generated from **6**. Conversely, brief (5 m) irradiation of carbene **3** at 313 nm caused the disappearance of the 838 cm⁻¹ band, concurrent growth of the 844 cm⁻¹ absorption, and a shift of the carbene UV to 360 nm. B3LYP calculations predict very similar IR spectra for *syn*-**3a** and *anti*-**3b**, but slightly lower frequency for the ~840 cm⁻¹ band in *syn*-

(7) Brogden, P. J.; Gabbut, C. D.; Hepworth, J. D. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon Press: New York, 1984; Vol. 3, p 573.

(8) Khasanova, T.; Sheridan, R. S. *Org. Lett.* **1999**, *1*, 1091.

Scheme 2



3a.⁶ CIS/6-31G** calculations⁶ predict weak $\sigma-\pi^*$ transitions at 485 and 520 nm, and intense $\pi\pi^*$ absorptions at 261 and 271 nm, for the *syn*-**3a** and *anti*-**3b** carbenes, respectively. We could not distinguish the very weak visible carbene absorptions from the background of the other intermediates. Nevertheless, the IR and UV spectra together suggest that *syn*-**3a** is generated from rearrangement of allene **6**, and 313 nm irradiation converts **3a** to **3b**.

Short exposure of carbene **3** to 313 nm light generated another species in the IR, offering a key to the mechanism interconverting carbene and allene. Bands appearing at 2190 and 1656 cm^{-1} signaled formation of quinone methide **9**. Again, B3LYP calculated IR spectra for **9** matched experiment.⁶ This mixture of **3** and **9** was rapidly (15 m) converted to allene **6** on irradiation at 404 nm. Alternatively, when matrices containing **6** were irradiated for short periods (~ 5 m) at 620, 578, or 546 nm, the resulting IR spectrum of carbene **3** was accompanied by small amounts of **9**, which eventually disappeared on further irradiation as allene was depleted. These observations are most consistent with intermediacy of quinone methide **9** providing a pathway for carbene/allene isomerization. We were not able to assign specific electronic absorptions to **9**. But, its photochemical reactivity suggests absorptions covering much of the UV and visible regions, extending beyond 600 nm, in line with other conjugatively substituted quinone methides.⁹

Prolonged irradiation (20 h) at 313 nm ultimately converted matrices containing carbene **3**, quinone methide **9**, and/or allene **6** to yet another photoproduct, characterized by a strong 1746 cm^{-1} IR band. The UV/vis spectrum of the matrix showed strong 240 nm absorption, a broad maximum centered at 440 nm, and tailing out to ca. 500 nm. These spectral signatures suggest that this final photoproduct is the benzocyclobutadienyl acyl chloride **10**.¹⁰ This tentative assignment was supported by good congruence between the experimental and B3LYP calculated IR spectra.⁶ Scheme 2 outlines these phototransformations.

Theory⁶ (B3LYP/6-31G**) suggests that the various $\text{C}_9\text{H}_5\text{OCl}$ intermediates lie fairly close in energy (Scheme 2), with benzocyclobutadiene **10** lowest. Didehydropyran **6** is predicted to be somewhat twisted, with the substituents at each end of the "allene" subunit displaced $\sim 10-20^\circ$ from the plane defined by the three central carbons.⁶ The central allenic carbon is bent severely to an angle of 118° in the minimized structure. The theoretical IR spectrum indicates that the ca. 1600 cm^{-1} band in **6** (partially obscured by overlap with H_2O absorption) corresponds to the

asymmetric $\text{C}=\text{C}=\text{C}$ stretch. Planar structure, **6a**, is calculated to lie only 2.5 kcal/mol higher in energy than **6**; one imaginary frequency in the DFT calculations is consistent with its role as a transition state for enantiomerization of **6**. CIS/6-31+G** calculations for **6** predict a moderate absorption at 411 nm, corresponding primarily to excitation from the HOMO, which is dominated by an approximately in-plane "lone-pair" on the allenic C, to the LUMO which is mainly π^* in character. Although the calculated value is somewhat shorter in wavelength than the observed 545 nm λ_{max} in **6**, this transition is quite sensitive to the geometry of the didehydropyran. For example, CIS calculations for the zwitterionic planar structure **6a** predict 528 nm for the analogous transition. The CIS calculations also predict a strong $\pi\pi^*$ transition for the twisted allene **6** at 278 nm, consistent with experiment.

Although we believe that this is the first direct observation of an allenic-didehydropyran, the parent didehydrobenzopyran has recently been generated and trapped in solution by Christl and Drinkuth.¹¹ Their product analyses indicated significant zwitterionic reactivity consistent with our observation of protonation of **6** at cryogenic temperatures. Shevlin and co-workers¹² have suggested, based on calculational results, that the related nitrogen analogues to **6**, generated from carbon atom addition to pyrroles, have planar dehydropyridinium ylid structures.^{13,14}

In summary, benzofurylcarbene **3** provides entry to a readily interconverting system of reactive intermediates, where product selection is highly sensitive to irradiation wavelength. Thus, photolysis of **3** at its strong UV maximum at 366 nm induces ring opening to quinone methide **9**. The key intermediate **9**, in turn, photochemically cyclizes to allene **6**, which absorbs weakly if at all at this wavelength. Conversely, excitation of didehydropyran **6** in the visible drives the system, via ring-opening followed by alternate cyclization, to carbene **3**. Similar photochemical ring closures of enynes to give trappable furylcarbenes have been reported.¹⁵ Finally, we speculate that a 1,3-aryl shift from allene **6** to the photostable benzocyclobutadiene **10** completes the process.¹⁶

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supporting Information Available: Experimental details for the synthesis of diazirine **4**, geometries, and tabulated experimental/calculated IR spectra for **3a**, **6**, **9**, and **10** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA002281G

(11) Christl, M.; Drinkuth, S. *Eur. J. Org. Chem.* **1998**, 237, 7.

(12) (a) Emanuel, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991. (b) Pan, W.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 5091.

(13) Solution cyclization of a possible *o*-quinoiminomethide to nitrogen analogues of **3** and **6** has recently been proposed: Frey, L. F.; Tillyer, R. D.; Ouellet, S. G.; Reamer, R. A.; Grabowski, E. J. J.; Reider, P. R. *J. Am. Chem. Soc.* **2000**, *122*, 1215.

(14) Possible electronic states of strained allenes are discussed in Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(15) (a) Nakatani, K.; Maekawa, S.; Tanabe, K.; Saito, I. *J. Am. Chem. Soc.* **1995**, *117*, 10635. (b) Nakatani, K.; Tanabe, K.; Saito, I. *Tetrahedron Lett.* **1997**, *38*, 1207. (c) Natatani, K.; Adachi, K.; Tanabe, K.; Saito, I. *J. Am. Chem. Soc.* **1999**, *121*, 8221.

(16) A stable diphosphorous six-membered allene has recently been reported: Hofmann, M. A.; Bergstrasser, U.; Reiss, G. J.; Nyulaszi, L.; Regitz, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1261.

(9) Diao, L.; Yang, C.; Wan, P. *J. Am. Chem. Soc.* **1995**, *117*, 5369.

(10) Toda, F.; Garrat, P. *Chem. Rev.* **1992**, *92*, 1685.