J|A|C|S
COMMUNICATIONS

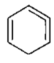
Characterization of a Didehydrobenzoxazine Intermediate in a Novel Carbene-to-Carbene Transformation

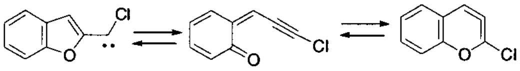
Asya Nikitina and Robert S. Sheridan*

Department of Chemistry, Mail Stop 216, University of Nevada, Reno, Nevada 89557

Received March 24, 2002

Cyclohexa-1,2,4-triene (**1**), or "isobenzene", has long fascinated experimentalists and theoreticians.[1] Despite considerable strain (**1** lies ca. 75 kcal/mol above benzene[1a]), **1** and its derivatives have been postulated as intermediates in thermal electrocyclic ring-closure of hexa-1,3-dien-5-ynes,[1,2] in Diels−Alder reactions of alkynes with vinyl acetylenes,[3] and in a variety of related synthetically useful transformations in heterocyclic[4] and polycyclic[5] systems. Our group has recently reported an unusual entry to such a species, which could be characterized spectroscopically.[6] Specifically, we discovered a facile photochemical interconversion between the benzofurylcarbene **2** and the highly strained didehydrobenzopyran **4**, mediated by the intercession of ring-opened quinomethide **3**.

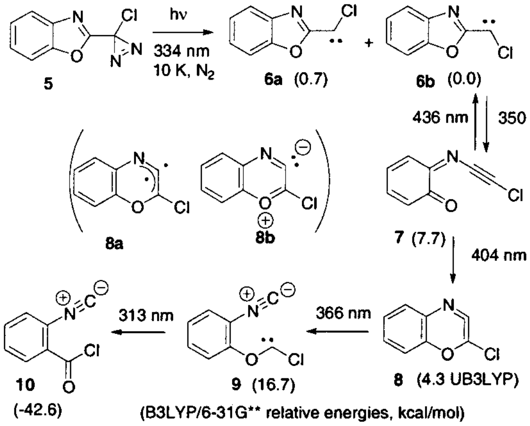

1


2 **3** **4**

We were attracted by the possibility that the corresponding benzoxazolylcarbene system might afford the corresponding strained ketenimine. We found, however, that the presence of nitrogen not only changed the photochemistry of this system significantly, but also opened an unexpected new fragmentation channel, yielding yet another carbene. We now report our observations on this unusual system.

Our experimental observations are summarized in Scheme 1. Photolysis of matrix-isolated diazirine **5**[7] (ca. 1:800, N_2, 10 K) at 366 nm, at the center of its $n\pi^*$ absorption, produced a complex IR spectrum that evolved over time and clearly reflected the presence of several sequential products.[8] On the other hand, 334 nm irradiations gave the expected carbene **6** relatively cleanly (but, together with **7**, vide infra). The experimental IR spectra fit predictions by B3LYP/6-31G** calculations[9] nicely for a mixture of *anti*-**6a** and *syn*-**6b** conformations of the carbene. A very strong UV band for the carbene at ca. 360 nm appeared simultaneously.

Scheme 1



Even on brief 334 nm irradiations of diazirine **5**, the carbene was accompanied by quinoimine **7**, signified by strong 2125 and 1660 cm^{-1} IR bands. The similarity between the experimental spectrum and that predicted by DFT calculations[9] confirmed this assignment. Continued irradiation at 334 nm, or more effectively at 350 nm, converted the initially formed **6** to **7** completely. Quinoimine **7** also absorbed strongly in the UV at ca. $\lambda_{\max}$ 375 nm, overlapping absorption of **6**, but could be distinguished from the carbene by its long tail extending well into the visible. Ring-opening of the carbene was reversible; irradiation of **7** at 436 nm (or more slowly at 578 nm) gave back **6**. Carbene **6** and quinoimine **7** could be recycled several times by alternating 350 and 436 nm irradiations. However, subsequent products could be observed to grow through this process, at the expense of **6** and **7** (vide infra).

Irradiation of either **6** or **7** at 404 nm caused slow transformation to a new intermediate, whose IR spectrum was dominated by a strong band at 1121 cm^{-1}. Simultaneously, a broad and weak visible absorption centered at 575 nm appeared. The similarity of the IR and UV/vis spectra to those of **4**,[6] together with the mode of generation, suggested that this new photoproduct was cyclic ketenimine **8**. However, the IR predicted by *restricted* B3LYP/6-31G** calculations for **8** bore only marginal similarity to the experimental spectrum.[9] Theory suggests that cumulenes constrained to small rings may have considerable diradical character,[1] which in this case (i.e. **8a**) might compromise restricted calculations on the ketenimine. Indeed, we found that a broken-spin symmetry *unrestricted* singlet B3LYP calculation[9,10] led to a lower energy optimized structure for **8**. Moreover, the IR spectrum predicted by the unrestricted singlet calculation fit the experiment quite well (Figure 1).

---

* Corresponding author. E-mail: rss@chem.unr.edu.

[1] (a) Engels, B.; Schöneboom, J. C.; Münster, A. F.; Groetsch, S.; Christl, M. *J. Am. Chem. Soc.* **2002**, *124*, 287. (b) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

[2] Prall, M.; Krüger, A.; Schreiner, P. R.; Hopf, H. *Chem. Eur. J.* **2001**, *7*, 4386.

[3] Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218.

[4] (a) Wills, M. S. B.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9378. (b) 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. (c) Kimball, D. B.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 1572.

[5] (a) Scott, L. T.; Chen, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963. (b) Zimmermann, G. *Eur. J. Org. Chem. 2001*, 457.

[6] Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8585.

[7] Graham, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 4396. See the Supporting Information for synthetic details

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

[9] See the Supporting Information for calculational details and additional experimental IR spectra. See refs 2 and 4c for DFT methodology applied to similar intermediates. Restricted DFT methods have been shown to be effective with singlet halo carbenes: Cramer, C. J.; Hillmyer, M. A. *J. Org. Chem.* **1999**, *64*, 4850.

10.1021/ja026300t CCC: $22.00

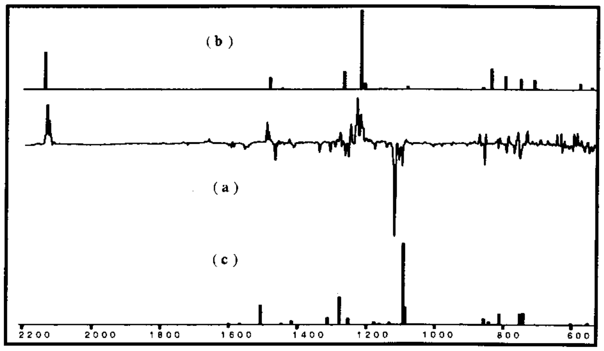


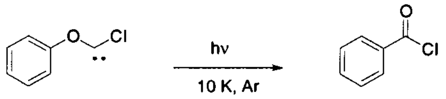
Figure 1. (a) Difference IR spectrum showing conversion of ketenimine **8** ("down bands") to carbene **9** ("up bands") on 366 nm irradiation. (b) B3LYP/6-31G** calculated IR for carbene **9**. (c) UB3LYP/6-31G** calculated IR for ketenimine **8**. Calculated frequencies are scaled by 0.97.

Although in our earlier work[6] **4** could be interconverted readily with the corresponding carbene **2**, photolysis of **8** at 366 nm gave a different product that displayed a puzzling IR with prominent 2135 and ca. 1232 cm^{-1} bands (Figure 1). This same product could be generated alternatively from matrices containing **6**, **7**, and/or **8** with >400 nm broadband irradiation. After considering and calculationally modeling several possible products, we discovered that the new bands arose from an unexpected fragmentation of **8**; the calculated IR of ring-opened phenoxycarbene **9** matched the experimental spectrum very well (Figure 1). Corroborating this assignment, irradiation of **9** at 313 nm gave the expected rearrangement product, acid chloride **10**, signified by a strong band at 1798 cm^{-1} (confirmed by modeling the IR spectrum with DFT calculations).

We found previously that in the benzofuryl system, quinomethide **3** was particularly photolabile, and could only be formed in minor amounts on irradiation of either **2** or **4**.[6] In contrast, the corresponding quinoimine **7** could be produced cleanly. The dominant product in the facile **6**/**7** equilibrium depended on the wavelength of irradiation. Irradiation on the short-wavelength side of the overlapping strong ca. 360 nm absorptions favored ring-opened **7**. Conversely, **7** absorbs more strongly at 436 nm, and thus rearranged selectively to carbene **6** at this wavelength. Interestingly, comparison with calculated spectra indicated that initial cyclization of **7** produced mainly *syn*-**6b**, as might be expected stereoelectronically.[11] Longer exposure to 436 nm light slowly converted **6b** to the anti isomer **6a**.

The alternate closure of **7** to ketenimine **8** was much less efficient, but minor amounts of **8** and **9** were also formed during the photochemical interconversions of carbene **6** and quinoimine **7**. Irradiation at 404 nm, however, where both **6** and **7** absorb strongly, drove the system slowly to **8**. The electronic spectrum of **8**, with weak broad absorption centered at 575 nm and strong absorption at 360 nm, was similar to that observed for the corresponding didehydropyran **4** (545 and 305 nm, respectively).[6] The amount of **8** could be maximized with 404 nm light, at a wavelength between these maxima. However, irradiation of **8** at 366 nm caused rapid ring opening, primarily to carbene/isonitrile **9**, but also return to **7** to a minor extent.

The IR and UV spectra of carbene **9** are similar to those of phenoxychlorocarbene (**11**), whose low-temperature generation and characterization we reported a number of years ago.[12,13] Carbene **11** showed similar strong absorption in the ca. 1250 cm^{-1} region, which calculations attribute to stretching of the C−O partial double bond in the carbenes. Moreover, both **9** and **11** rearrange to the corresponding acid chlorides on photolysis.



11

Theory indicates that cumulenes constrained to small rings can acquire diradical (**8a**) or zwitterionic (**8b**) character as the systems become increasingly deformed.[1] Recent high-level calculations by Engels et al.[1a] and McKee et al.[14] support the intuitive concept that the amounts of zwitterionic and open-shell contributions to the electronic structure of strained allenes are also sensitive to adjacent hetereoatoms, as well as aromatic stabilization. MR-CI calculations indicate that the didehydrobenzopyran **4** (without chloro substitution) should have a twisted allenic ground state, with zwitterionic and singlet diradical planar excited states 5.4 and 9.6 kcal/mol higher in energy, respectively.[1a] Consistent with these theoretical predictions, our previous work demonstrated that the spectra of didehydrobenzopyran **4** could be modeled satisfactorily with restricted DFT calculations;[6] all attempts to locate a lower energy singlet diradical electronic state at the UB3LYP level failed. In contrast, broken spin symmetry UB3LYP singlet calculations gave an optimized structure for **8** that was 1.2 kcal/mol lower than that predicted by restricted DFT, suggesting some diradical character (i.e. **8a**) in the ketenimine.[10] Both methods, however, gave rather similar geometries, somewhat twisted about the cumulenic bonds, and not unlike that calculated for allene **4**. The calculations indicate that the C=C=N asymmetric stretch in **8** corresponds to the IR band observed at 1558 cm^{-1}, shifted considerably from that of unstrained ketenimines normally found at ca. 2000 cm^{-1}.[15]

In summary, we have uncovered a novel transformation of a benzoxazolyl carbene to a phenoxycarbene, by way of a highly strained cyclic ketenimine **8**. Ring opening of **8** to **9**, formally a double-bond cleavage to two carbenes, appears unlikely at first glance. However, the pseudopericyclic[16] nature of the fragmentation is more apparent, perhaps, when contributions from **8b** to the electronic structure are considered. The need for unrestricted calculations[10] to model the IR spectrum of **8** may suggest the first direct spectroscopic support for diradical character in such geometrically constrained cumulenes. Higher level theory[1a] will be necessary to confirm this point, however.

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

Supporting Information Available: Synthetic details for diazirine **5**, calculation results for **6**−**10**, and experimental/calculated IR for interconversions of **6**−**10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026300T

---

(10) The similar energies predicted for **8** and **8a** indicate that DFT cannot resolve the exact nature of the observed intermediate (or even whether both **8** and a planar **8a** are present). The broken spin symmetry UB3LYP calculations on **8** actually result in a mixed singlet−triplet diradicaloid state, with $S^2 = 0.58$. For a discussion of this methodology, see for example: (a) Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1. (b) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2001**, *66*, 5338.

(11) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233.

(12) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844.

(13) The splitting in the ca. 1230 cm^{-1} band of **9** may indicate the presence of several conformations. However, the conformation shown in scheme **9** was the only realistic energy minimum found calculationally (see the Supporting Information), and fits the IR well overall.

(14) McKee, M. L.; Shevlin, P. B.; Zottola, M. *J. Am. Chem. Soc.* **2001**, *123*, 9418.

(15) Patai, S. *The Chemistry of Ketenes, Allenes, and Related Compounds, Part 2*; John Wiley & Sons: New York, 1980.

(16) Birney, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 10917.