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# Piperidine trapping of conformationally restricted cyclopropylcarbenes

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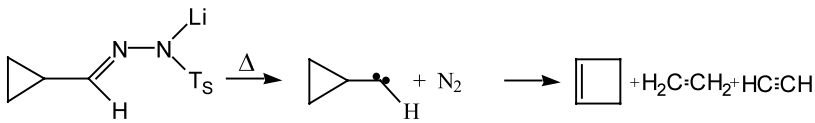
**Abstract**—Conformationally restricted cyclopropylcarbenes were formed by photolysis (300+436 nm) of the corresponding oxadiazolines, and trapped with piperidine. 

In 1960 Friedman and Shechter reported that pyrolysis of cyclopropane tosylhydrazone salt **1**, led to the formation of nitrogen, cyclobutene, ethylene and acetylene as major products, presumably via the intermediacy of cyclopropylcarbene **2**.[1] The rearrangements and fragmentations of cyclopropylcarbenes have fascinated chemists ever since.



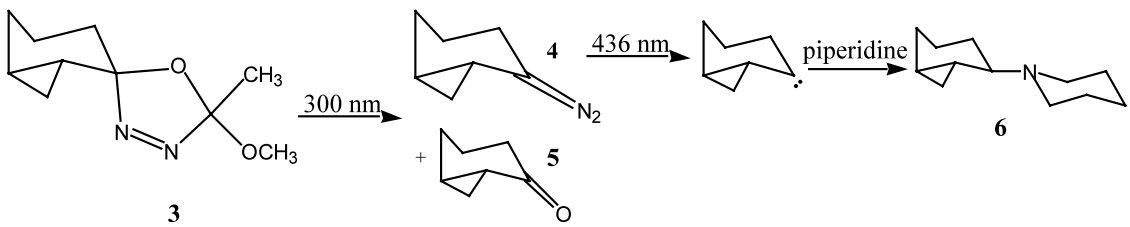

**1** **2**

McKee and Shevlin's calculations indicate that cyclopropylcarbene exists in two conformations, *syn* and *anti*, separated by a barrier that is large compared to the barriers of their distinctive unimolecular processes.[2] Interaction of the empty *p*-orbital of the carbene with a Walsh orbital of the cyclopropane ring is responsible for the substantial barrier to *syn–anti* interconversion.

Laser-flash photolysis (LFP) studies of cyclopropylcarbene and its derivitives are consistent with the presence of only a single pyridine trappable intermediate.[3] Such a simple kinetic picture can arise in at least three ways. First, if *syn–anti* interconversion of the carbene is fast relative to the trapping reaction then simple kinetics will be observed. This, however, would be in serious conflict with theory.[2] Secondly, the two conformers may interconvert slowly but fortuitously disappear at comparable rates, or thirdly only a single isomer (e.g. **2**-*syn*) reacts with pyridine, solvent, or another external trap. If this latter viewpoint is correct, then **2**-*anti* cannot be intercepted because the carbene center is sterically blockaded by the cyclopropyl ring and preferentially undergoes rearrangement ($k_R \gg k_{anti}$[Trap], Scheme 1). Herein, we report experiments which favor the second interpretation.

To test these mechanistic possibilities two conformationally locked cyclopropylcarbenes were studied. Photolysis (300+436 nm)[4] of oxadiazoline **3**[5] in cyclohexane (10°C) produces ketone **5**[6] (8%) and a product $C_7H_{10}$[8] (13%). In the presence of piperidine adduct **6** is produced as a mixture of diastereomers.[9]

The yield of **6** increases smoothly with increasing piperidine concentration, but the concentration of amine




**3** **6**

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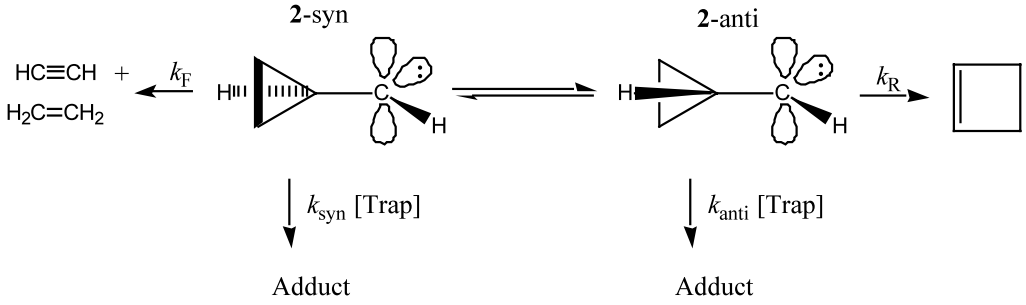



**Scheme 1.**

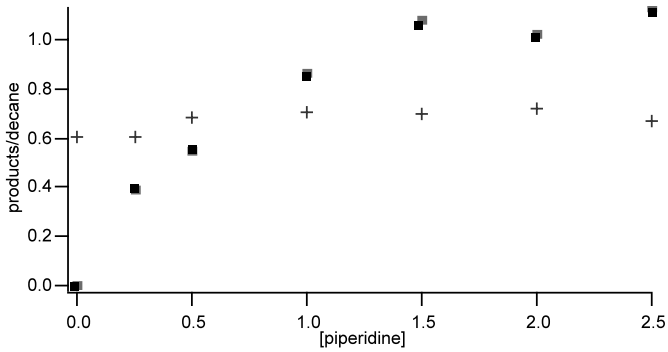



**Figure 1.** Plots of (adduct **6**)/decane (■) and rearrangement product $C_7H_{10}$/decane (+) as a function of piperidine concentration produced upon photolysis of **3**.

trap has no effect on the yield of the $C_7H_{10}$ product (Fig. 1). Under these conditions the 'apparent' product of a formal carbene rearrangement ($C_7H_{10}$) from a conformationally restricted cyclopropylcarbene precursor is not formed from the carbene. We have observed this pattern of results before with a conformationally mobile cyclopropylcarbene precursor and concluded that its rearrangement proceeds in an excited state of the diazirine precursor.[3a] This seems likely with oxadiazoline precursor **3**, as well.

Photolysis of **7**[10] in cyclohexane (10°C) produces ketone **8**[11] (21%) and three products of composition $C_8H_{12}$ (74%).[8]

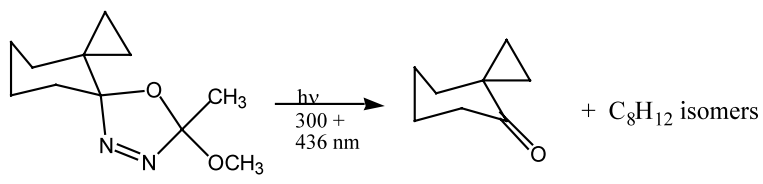
Photolysis of **7** under the same conditions in the presence of piperidine produces adduct **9**.[12]

Carbene **11**, which is *anti*, neither rearranges too rapidly, nor is too sterically blockaded, to react with piperidine. The absolute yields of adducts **6** (22%) and **9** (5%) are low but comparable. Plots of 1/**6** and 1/**9** versus 1/[piperidine] are linear (Figs. 2 and 3). The ratio of the intercept/slope of these plots is $k_{pip}\tau_c$ where $k_{pip}$ is the absolute rate constant of carbene reaction with piperidine and $\tau_c$ is the carbene lifetime in cyclohexane in the absence of piperidine. If we assume that $k_{pip}$ is $1\times10^9$ $M^{-1}$ $s^{-1}$ for each carbene we estimate that the lifetimes of the carbenes of this work are comparable (1–2 ns), and similar to that of other cyclohexylidenes.[7]

In conclusion we have generated cyclopropylcarbenes locked into either *syn* and *anti* conformations. Each carbene is trappable with piperidine and each carbene has a lifetimes of 1–2 ns in cyclohexane (10°C). This work supports our contention[3] that in solution (0–25°C) cyclobutenes are formed by excited-state rearrangements of nitrogenous precursors which bypass carbene intermediates.[3a]

## Acknowledgements

Support of this work by the NSF (CHE-9613861) is gratefully acknowledged.

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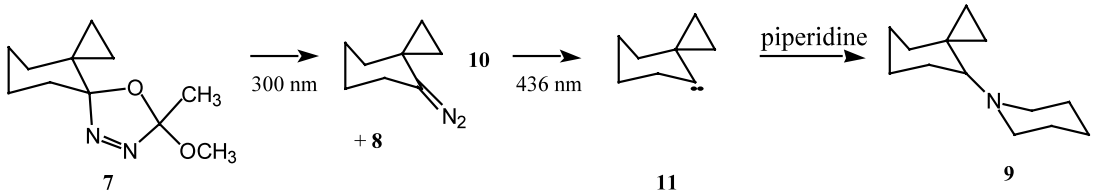


7 + 8 11 9

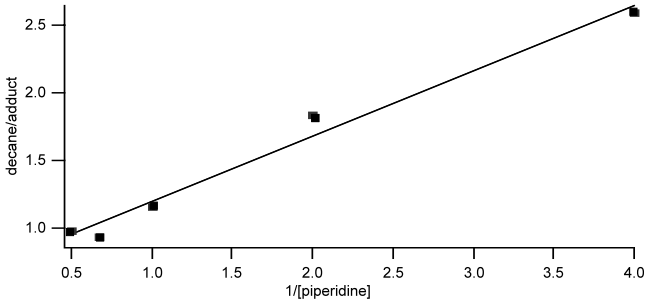


**Figure 2.** A plot of decane/(adduct **6**) versus 1/[piperidine] with fused precursor **3** utilizing dual irradiation with both 436 and 300 nm light.

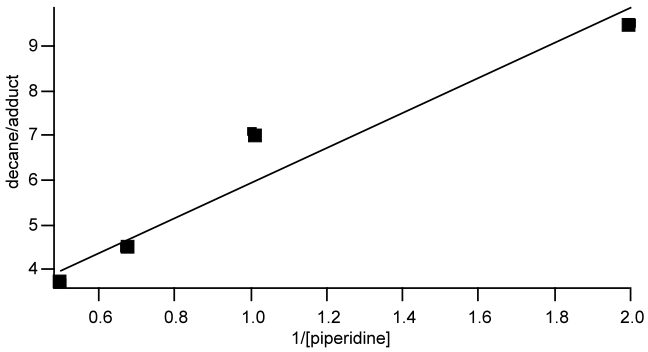


**Figure 3.** A plot of decane/(adduct **9**) versus 1/[piperidine] with spiro precursor **7** utilizing dual irradiation with both 436 and 300 nm light.

## References


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4. 300 nm light converts an oxadiazoline (e.g. **3**) to a diazo compound (e.g. **4**). 436 nm light excites the diazo compound and promotes nitrogen extrusion and carbene formation. The yellow color of the intermediate diazo compound is produced and then fades during the photolysis.
5. Oxadiazoline **3** was prepared in two steps from ketone **5**[6] using the method of Pezacki:[7] UV–vis: oxadiazoline band at 316 nm; $^1$H NMR: $\delta$ 0.7 (q), 0.77 (m), 1.1–1.8 (m), 1.4–1.6 (m), 2.0 (d), 2.1 (d), 3.3 (m), 3.6 (m) ppm; $^{13}$C NMR: $\delta$ 168.2, 129.6, 126.1, 66.2, 58.7, 23.4, 19.3, 16.4, 10.6, 9.6 (four diastereomers) ppm; MS (EI): 196 (0.02), 110 (21), 93 (21), 79 (84), 43 (100); HRMS calcd for $C_{10}H_{16}N_2O_2$: 196.1211; found: 196.1229.
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8. The identities of these hydrocarbon products will be reported later.
9. Adduct **6** was prepared from **5** by the method of Barney, C. L.; Huber, W. E.; McCarthy, J. *Tetrahedron Lett.* **1990**, *39*, 5547; $^1$H NMR: $\delta$ 0.4 (q), 0.7 (q), 0.79 (m), 1.02 (m), 1.09 (m), 1.4 (m), 1.7 (m), 2.87 (s), 7.2 (s) ppm; $^{13}$C NMR: $\delta$ 64.9, 50.7, 24.4, 23.3, 22.8, 22.5, 17.6, 13.1, 12.2, 11.4, 10.5, 9.2 ppm; MS (EI): 179 (18), 150 (46), 136 (22), 124 (100), 110 (54), 95 (42), 95 (42), 84 (60), 67 (28), 55 (27), 41 (44); HRMS calcd for $C_{12}H_{21}N$: 719.1674; found: 79.1670.
10. UV–vis: oxadiazoline band at 321 nm; $^1$H NMR: $\delta$ 0.01–0.1 (m), 1.2 (m), 1.22 (m), 1.25 (m), 1.5 (s), 1.55 (m), 2.1 (t), 3.03 (s), 3.07 (s) ppm; $^{13}$C NMR: $\delta$ 132.3, 124.4, 51.3, 35.4, 34.5, 25.5, 24.8, 23.6, 23.2, 9.9, 9.3 ppm; MS (EI): 211 (2), 93 (72), 72 (100), 55 (11), 43 (64); HRMS calcd for $C_{11}H_{18}N_2O$: 210.1368; found: 211.1454 ($M^+$ was not detected).
11. Ryu, L.; Murai, S.; Sonoda, N. *Tetrahedon Lett.* **1977**, *18*, 4661.
12. $^1$H NMR: $\delta$ 0.01–0.3 (m), 0.36–1.0 (m), 1.1–2.02 (m), 2.24 (s), 2.26 (s), .8 (s), 3.3 (s) ppm; $^{13}$C NMR: $\delta$ 68.2, 52.2, 31.5, 28.6, 26.6, 25.9, 25.1, 24.8, 22.8, 21.3, 20.7, 15.8, 10.1 ppm; MS (EI): 193 (14), 150 (21), 124 (100), 111 (34), 98 (17), 84 (27), 67 (18), 55 (12), 41 (20); NRMS calcd for $C_{13}H_{23}N$: 193.1825.