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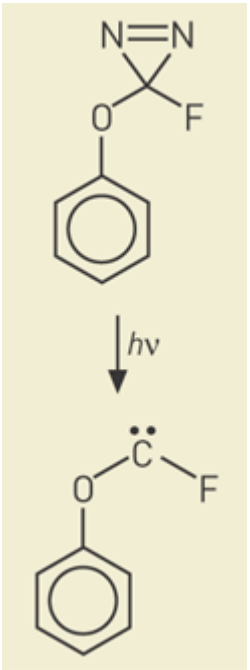
Capsuled Carbene

Transient intermediate is stabilized inside a cage at room temperature

RON DAGANI

For the first time, a transient singlet carbene has been trapped--and stabilized--for days inside the cavity of a cage molecule at ambient temperature, according to chemists at Rutgers University.



LONG LIFE When fluorophenoxycarbene is generated from a diazirine inside a hemicarcerand, it can persist for days.

For decades, chemists have stabilized and studied transient carbenes by creating them in frozen matrices at very low temperatures. This approach, however, limits the types of studies that can be carried out on these fleeting intermediates. Researchers also have learned how to make carbenes that are intrinsically so stable that they can be isolated and stored in a bottle. But how do you extrinsically stabilize at ordinary temperatures a carbene that normally dimerizes or reacts with nearby molecules within milliseconds?

Robert A. Moss, Ralf Warmuth, Ronald R. Sauers, and coworkers Xuejun Liu and Gaosheng Chu accomplished this by confining the carbene inside a cage structure known as a hemicarcerand [*Angew. Chem. Int. Ed.*, published online Feb. 21, http://www3.interscience.wiley.com/cgi-bin/abstract/109930253]. They first encased 3-fluoro-3-phenoxydiazirine inside the cage and then photolyzed it to generate fluorophenoxycarbene. This particular carbene was chosen, in part, because it's unlikely to react with the cage.

Fluorophenoxycarbene does, however, react in an acid-catalyzed process with water molecules that diffuse into the hemicarcerand. But when the researchers made sure that pyridine was present in the reaction mixture to soak up any stray protons, the carbene persisted in its cage for days without any reaction.

Among the advantages of this approach, Moss points out, is that they were able to record the carbene's nuclear magnetic resonance spectra and deduce that it prefers the more compact--but less stable--cis conformation inside the cage. This approach also allows them to study how the carbene reacts with small probe species that slip into the cage--something not possible in cryogenic matrices.

Chemistry professor Matthew S. Platz of Ohio State University calls the Rutgers paper "a landmark result" and says it "will excite the organic chemistry community."

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