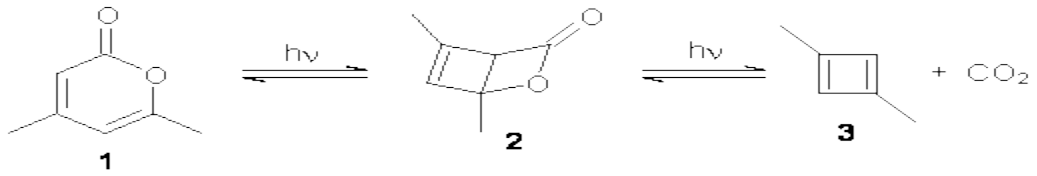
HAS A CYCLOBUTADIENE SPECIES BEEN ISOLATED?

Barboiu made the astonishing claim of the x-ray characterization of 1,3-dimethylcyclobutadiene, brought about by the photolysis of 4,6-dimethyl-α-pyrone encapsulated in a guanidinium-sulfonate-calixarene crystal (Reaction 1).[1] I had not blogged on this paper because Henry Rzepa did a quite thorough analysis of it in this blog post. Now, a couple of rebuttals have appeared and it is time to examine this study.



Alabugin calls in question whether the reaction has in fact proceeded beyond **2**.[2] They note that in the x-ray crystal structure, the distance between a carbon of the purported cyclobutadiene ring and the carbon of CO_2 is only 1.50 and 1.61 Å. Barboiu called this a "strong van der Waals contact", but this is a distance much more attributable to a covalent bond.

In fact, the shorter distance is in fact shorter than some of the other C-C distances in the structure that Barboiu calls covalent! Perhaps more bizarre is that the

putative CO_2 fragment is highly bent: 119.9°, a value inconsistent with CO_2 but perfectly ordinary for an sp^2 carbon. In fact, B3LYP/6-31G** computations suggest that bending CO_2 this much costs about 75 kcal mol^{-1} – and tack on another 7 kcal mol^{-1} to make the two C-O distances unequal (as found in the x-ray structure!). Thus, Alabugin suggests that only**2** has been formed, and notes that the cleavage to **3** would likely require light of much higher energy that that used in the Barboiu experiment.

Scheschkewitz argues that the x-ray data can be better interpreted as suggesting only the Dewar β-lactone **2** is present, though in its two enantiomeric forms.[3] There is no evidence, he suggests of any cyclobutadiene component at all.

It should be noted that Barboiu stands[4] by his original work and original assignment, claiming that these types of x-ray experiments are quite difficult and large error bars in atom positions are inherent to the study.

Henry Rzepa has blogged again on this controversy and has a paper coming out on this soon. I shall update when it appears. Henry notes in one of the comments to his blog that a TD-DFT computations does show that the Dewar β-lactone **2** is transparent from 320-500nm.

Source: http://comporgchem.com/blog/?p=1324