Molecule of the Month

Cyclobutadiene in a Molecular Prison!

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A novel way to isolate the highly reactive cyclobutadiene molecule is by trapping it inside a much larger molecule.

Cyclobutadiene (**1**) has been one of the most popular molecules for experimentalists and theoreticians. This molecule is unstable as it is *antiaromatic* (4π electrons in a cyclic array). Even though some highly substituted cyclobutadienes, for example, compound 2 and the $Fe(CO)_3$ complex of cyclobutadiene (**3**) are known, all attempts to isolate 1 under normal laboratory conditions have failed, since it reacts with itself, or with other molecules rapidly.

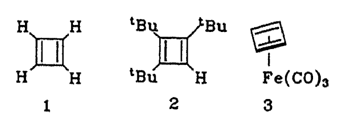
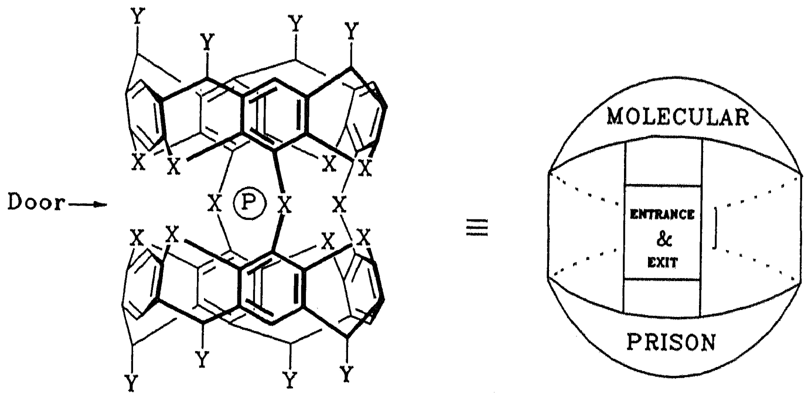


***Figure 1** Cyclobutadiene (1), compound 2 and $Fe(CO)_3$ complex of cyclobutadiene (3).*

The most logical way to reduce the reactivity of a molecule of 1 would be to put a *single* molecule of **1** in an unreactive "cage". Chemistry Nobel winner Donald J. Cram (1987) has shown that it is indeed possible (*Angew. Chem. Int. Ed. Engl.*, **30**, 1028. 1991)! Cram and co-workers synthesized a variety of spheroidal molecular prisons (*carcerands*) by linking two 'hemispheres' with three or four connecting units (see *Figure 2* below for carcerand **4**). The molecular prison with three linkages is more like a prison with a



4: $X = -OCH_2O-$; $Y = (CH_2)_2Ph$

***Figure 2** Molecule P imprisoned inside 4.*

small door as shown. A molecule (whose size is similar to the space available inside the carcerand) can be made to go inside through the door under certain conditions. Once it is inside, you really have a single molecule floating around in the empty space (a fourth phase of matter?) created *within* a much larger molecule. One can then easily carry out unimolecular reactions on the molecule.

In order to 'imprison' cyclobutadiene, Cram and co-workers put a molecule of 5 inside carcerand (**4**). Photolysis of the complex of **4**:**5** first produces a new complex, **4**:**6**, which then loses CO_2 (too small to be trapped, it comes out rapidly through the door) and produces **4**:**1**, which is our cyclobutadiene trapped inside **4**! Spectroscopic studies on the complex **4**:**1** leaves no doubt that it is indeed **4** with cyclobutadiene inside. Prolonged photolysis of **4**:**1** was shown to produce acetylene. On the other hand, heating complex **4**:**1** with THF (tetrahydrofuran) resulted in an exchange of **1** with THF, and as soon as **1** came out of the prison, it dimerized to form **7**, which eventually produced cyclooctatetraene (**8**), as it does in a thermal reaction.

This example, therefore, gives us hope that many compounds which are thermodynamically unstable, can be isolated by making them kinetically inert by preventing their access to their decomposition pathways.

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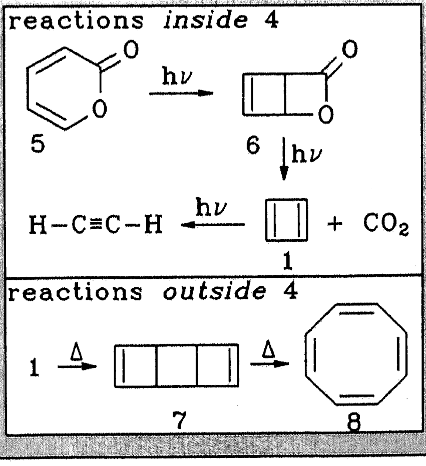

Figure 3 Reactions inside and outside carcerand (4).

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