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LETTERS

Triplet Carbenes and Cyclooctatetraene. 1,4-Addition Is More Common Than We Thought[1]

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Abstract: Almost thirty years after the first (and only) description of 1,4-addition of a carbene to cyclooctatetraene, we report that direct photolysis of ethyl diazomalonate in cyclooctatetraene leads to 13% of the product of 1,4-addition. When the decomposition of the diazo compound is photosensitized by benzophenone, 1,4-addition becomes virtually the sole reaction pathway. © 1999 Elsevier Science Ltd. All rights reserved.

The addition of carbenes to alkenes to give cyclopropanes is the most widely known reaction of divalent carbon, and is often a reasonable synthetic route.[2] It would surely be useful if this reaction could be extended to provide cyclopentenes through 1,4-addition to dienes. This old idea has not been realized, as simple dienes stubbornly fail to undergo the 1,4-addition reaction. One reason appears to be the unfavorable interaction between the filled HOMO of the carbene and $\Psi 2$, the filled HOMO of the diene.[3] In addition, most dienes strongly prefer the s-trans conformation, in which 1,4-addition is not possible.

When the diene is held in the s-cis conformation, a few 1,4-additions have been successfully achieved. Thus, Bickelhaupt and his coworkers have found that 1,4-addition of dibromocarbene to 1,2-dimethylenecyclopentene is competitive with the more facile 1,2-addition,[4] and Burger showed that an intramolecular 1,4-addition was the mechanism of benzvalene formation from 5-cyclopentadienylcarbene.[5]

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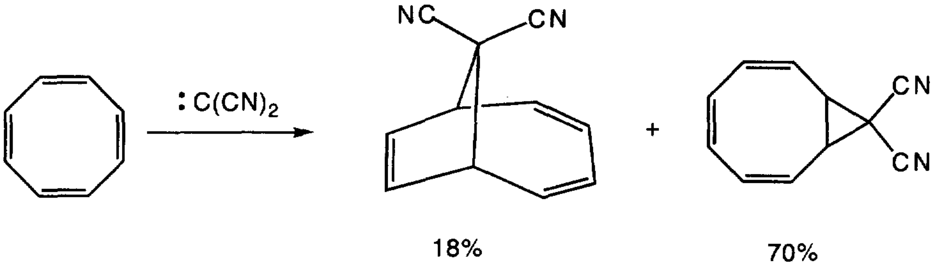
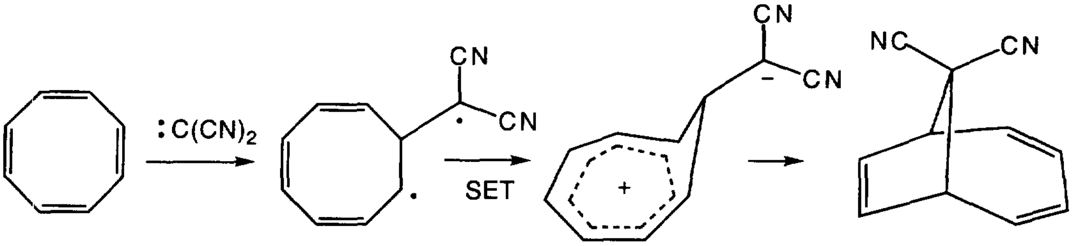
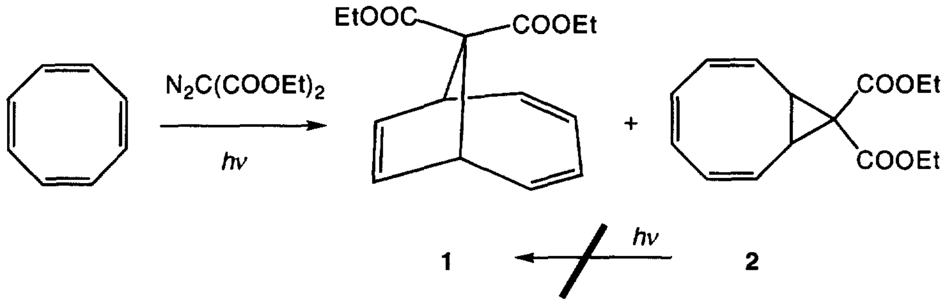
One other spectacular 1,4-addition is known. Cyclooctatetraene (COT) reacted with dicyanocarbene[6] (and cyanonitrene[7]) to give about 18% of the 1,4-adduct, in addition to the more conventional 1,2-adduct.[8] For many years this stood as an isolated example, but as we shall show in this Letter, 1,4-addition to COT is more common than we thought.



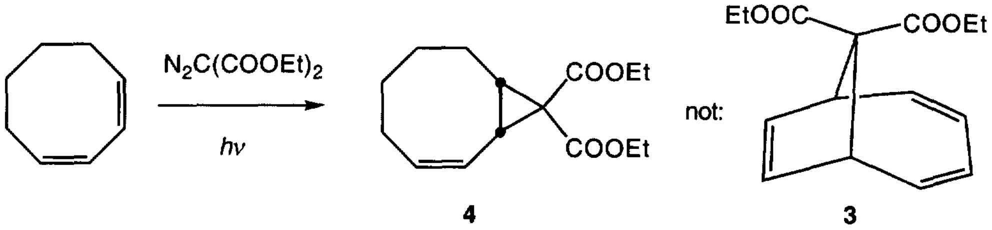
The reaction of COT with dicyanocarbene was thought to give 1,4-addition through the triplet state of the carbene. We initially attempted to add diphenylcarbene and fluorenylidene to COT, but were able to find only the cyclopropanes, products of conventional 1,2-addition.[9] Indeed, this led one of us (MEH) to propose that 1,4-addition required *both* COT and the dicyanocarbene. The essential idea was that the cyano groups were necessary to stabilize a dipolar intermediate formed by electron transfer in the initially produced diradical. COT was necessary to provide entry to the homotropilium ion.[10]



If MEH's idea is correct, other triplets should also lead to 1,4-addition to COT. And so it is. Photolysis of a degassed solution of ethyl diazomalonate in COT led to 13 % **1** and 87 % **2**. Compounds **1** and **2** were identified through HRMS and a comparison of their ^1H NMR spectra with those of the related dicyano compounds, to which they are strikingly similar.[6,7,11] Reactions of dicarboalkoxycarbenes are known to involve some triplet,[9] and a first hypothesis was that the small amount of **1** derived from the triplet carbene, with the bulk of the reaction coming from 1,2-addition of the singlet. In accord with this notion, the addition of benzophenone as photosensitizer led to increased amounts of **1**, with **1** becoming virtually the sole product when 50 mol percent of benzophenone was added. Could **1** come from photolysis of **2**, and the apparent 1,4-addition be an illusion? No, because a control experiment shows that neither direct nor photosensitized photolysis of **2** led to **1**.



Several questions remain. Is 1,4-addition of dicarboethoxycarbene general to cisoid dienes? No, again. For example, there is no evidence for formation of **3** in the reaction of this carbene with 1,3-cyclooctadiene (COD). Instead, the product is resolutely **4** in both the direct and photosensitzed reactions. A new product is formed in the sensitized reaction, but it is not **3**, and forms the subject of the following Letter.



Why does COD fail to give 1,4-addition? It may be that MEH's mechanism is correct, and the product of addition to COD has no access to special stabilization of the positive end of the dipole after electron transfer. Why do diphenylcarbene and fluorenylidene fail to undergo 1,4-addition?[9] It seems to us that they are poor choices, as neither provides much triplet. In particular, despite its reputation as the archetypal triplet, in fact, diphenycarbene cyclopropanates simple alkenes exclusively through its singlet state.[12]

Preliminary data show that other carbenes with accessible triplet states also add in 1,4-fashion to COT, providing a possible route to functionalized bicyclo[4.2.1]nonyl systems.[13]

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1. This paper is dedicated to the memory of Michael Ezell Hendrick (1946-1995). The work was supported by the National Science Foundation through Grant CHE-9702823.

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