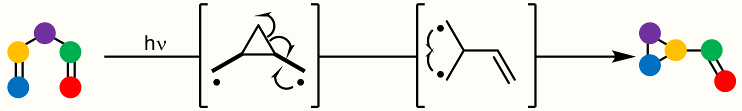
Di-π-methane Rearrangement

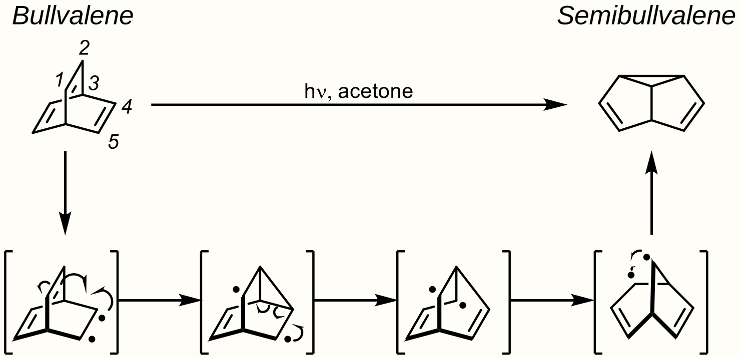
General Scheme:



Zimmerman, H. *J. Am. Chem. Soc.* **1969**, 91, 7, 1718–1727. https://doi.org/10.1021/ja01035a021

The reaction can be summarized as the photolysis of molecules containing two π moieties bound to a single sp^3-hybridized carbon atom. The reaction results in a π-substituted cyclopropane via a formal migration of one π-moiety to the saturated carbon center.

Historical Development:

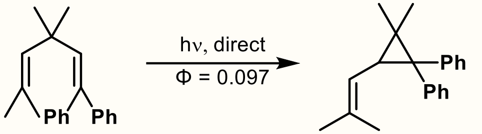


Zimmerman, H. *J. Am. Chem. Soc.* **1966**, 88, 1, 183–184. https://doi.org/10.1021/ja00953a045
Zimmerman, H. *J. Am. Chem. Soc.* **1967**, 89, 15, 3932–3933. https://doi.org/10.1021/ja00991a064

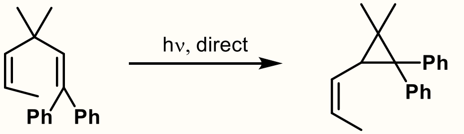
Mechanistically, the reaction was probed through the analysis of the hydrogen disposition in the product formed with a D-labeled bullvalene precursor.
From this mechanism looking at the excited and ground states, the stabilization of the singlet or triplet excited states of the nonconjugated diene results when the orbitals of the C-2 and C-4 occurs. However, later studies would reveal that triplet sensitizers were unable to drive this reaction. Thus, it was determined only the singlet excited state manifold would efficiently drive this reaction forward. The excitation state of these reactions, however, is very substrate dependent.

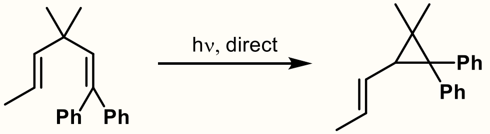
Zimmerman, H. *J. Am. Chem. Soc.* **1969**, 91, 7, 1718–1727. https://doi.org/10.1021/ja01035a021

Regioselectivity and Specificity Probes:



The most stabilized radicals will undergo the final cyclopropanation, resulting in a single regioisomer.





The cis-isomer and trans isomers yielded exclusively their corresponding cis and trans counterparts.

Zimmerman, H. *Chem. Rev.* **1973**, 73, 5, 531–551. https://doi.org/10.1021/cr60285a005

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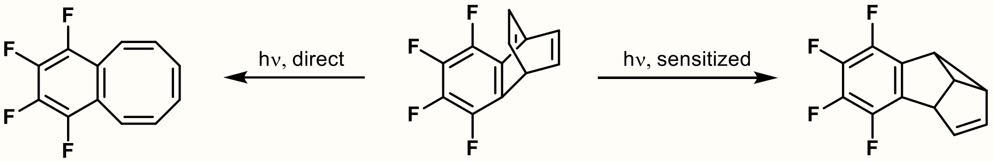
An Example of Irradiation Conditions Changing Products:



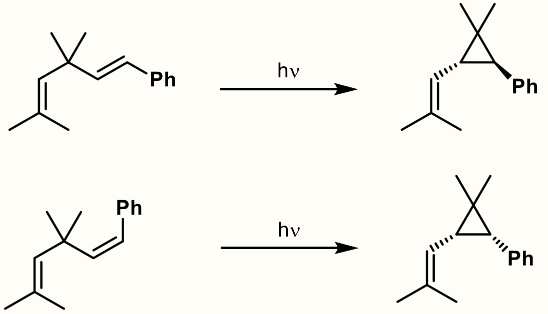
Depending on the methods of initiation, different products will form. The di-π-methane rearrangement above occurs under sensitized conditions only.

Zimmerman, H. *Chem. Rev.* **1973**, 73, 5, 531–551. https://doi.org/10.1021/cr60285a005

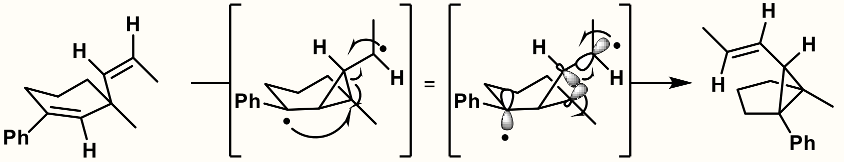
General Reaction Efficiency:

Di-π-methane structural feature	***Singlet excited state***	***Triplet excited state***
Presence of nonconstrained or free π moiety (Acyclic and Monocyclic)	Efficient	Inefficient
Absence of nonconstrained or free π moiety (Bicyclic)	Inefficient	Efficient

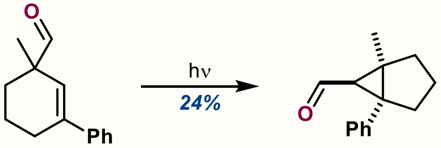
General Stereochemical Outcomes:



In general, diastereoselectivity will be substrate-determined. However, in general, cis π-moieties lead to cis-substituted cyclopropanes, while trans result in trans.



Ko, J. *J. Am. Chem.* **1973**, 95, 26, 8670-8678. https://doi.org/10.1021/ja00807a028



Endo or exo products are generally not predictive but tend to be quite selective per substrate.

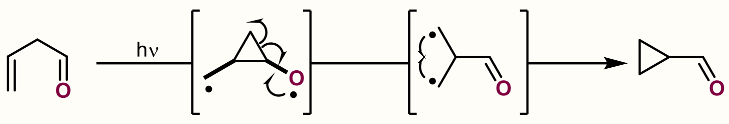
Singlet states proceed via a concerted anti-disrotatory mechanism while the triple state exhibits a two-step process which results in a formal anti-disrotatory mechanism.

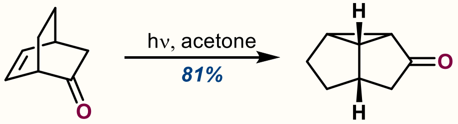
Zimmerman, H. *Chem. Rev.* **1973**, 73, 5, 531–551. https://doi.org/10.1021/cr60285a005

Schaffner, K. *Helv. Chim. Acta* **1980**, 63, 2434–2439. DOI: 10.1002/hlca.19800630836

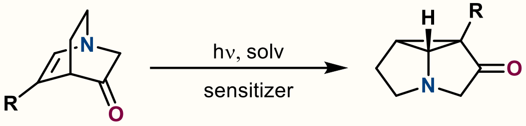
Di-π-methane Rearrangement

Oxa-di-π-methane:



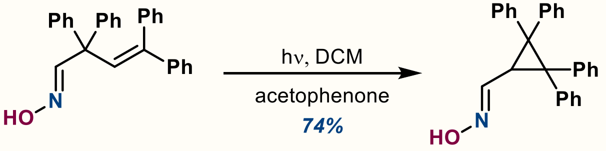


Schaffner, K. *Helvetica Chimica Acta.* **1980**, 63, 8. 258. https://doi.org/10.1002/hlca.19800630836



Link, J. *Org. Lett.* **2003**, 5, 21, 3811–3813. https://doi.org/10.1021/ol035202p

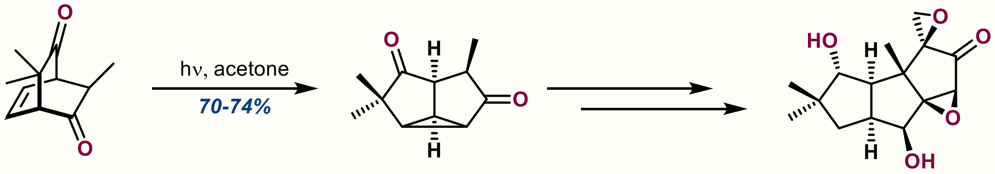
Aza-di-π-methane:



Langa, F. *J. Chem. Soc.* **1989**, 903-906. DOI: 10.1039/P29890000903

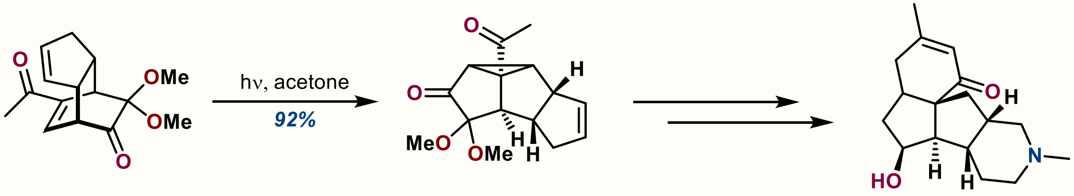
Examples in Total Synthesis:

The Total Synthesis of (-)-Coriolin (Schaffner, 1986):



Schaffner, K. *J. Am. Chem. Soc.* **1986**, 108, 14, 4149–4154. https://doi.org/10.1021/ja00274a050

The Total Synthesis of Magellanine (Liao, 2002):



Liao, C. *Angew.* **2002**, 41, 21, 4090–4093. https://doi.org/10.1002/1521-3773(20021104)41:21<4090::AID-ANIE4090>3.0.CO;2-%23