

**M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry**



III. Photochemistry

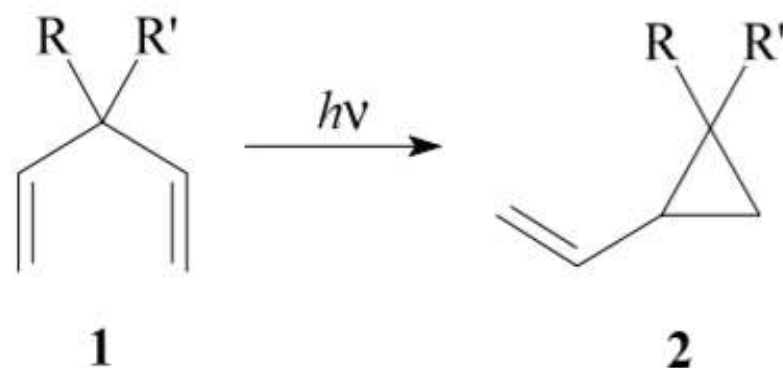
23. Di- π -Methane Rearrangement : Mechanism and Examples



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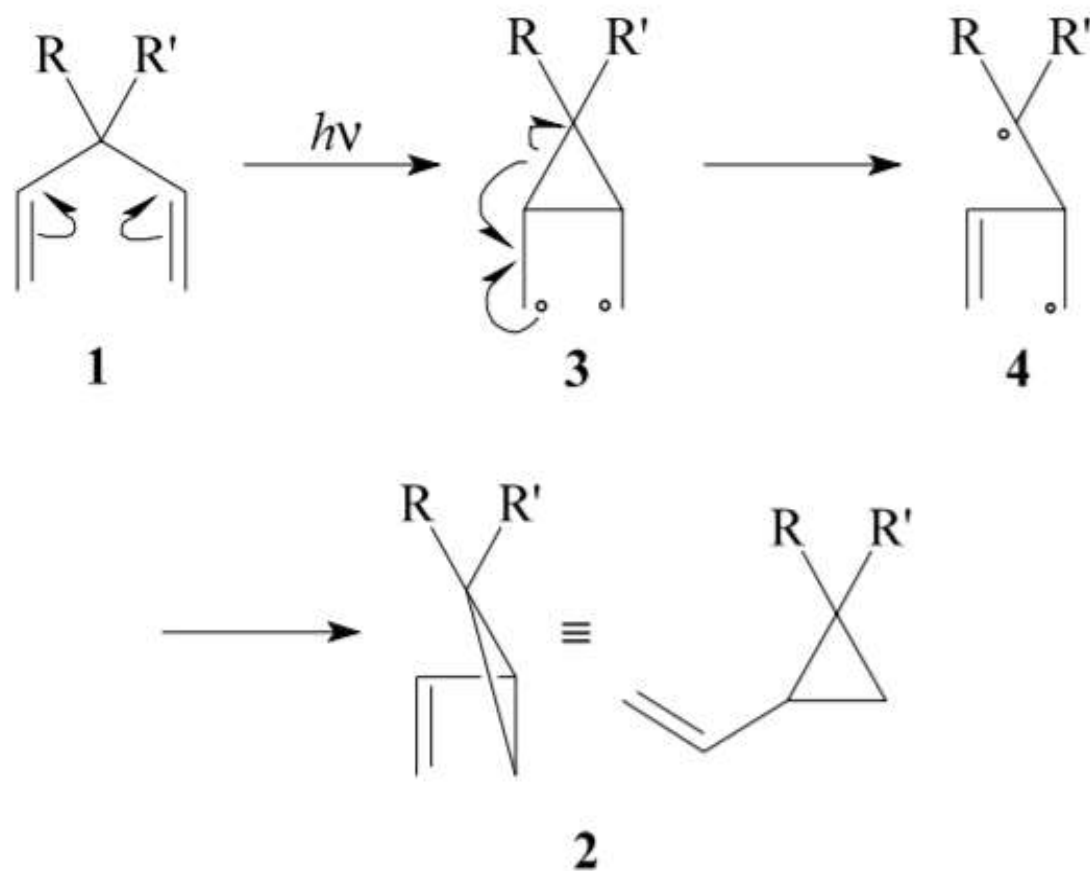
Di- π -Methane Rearrangement

Photochemical rearrangement of 1,4-dienes to vinylcyclopropanes

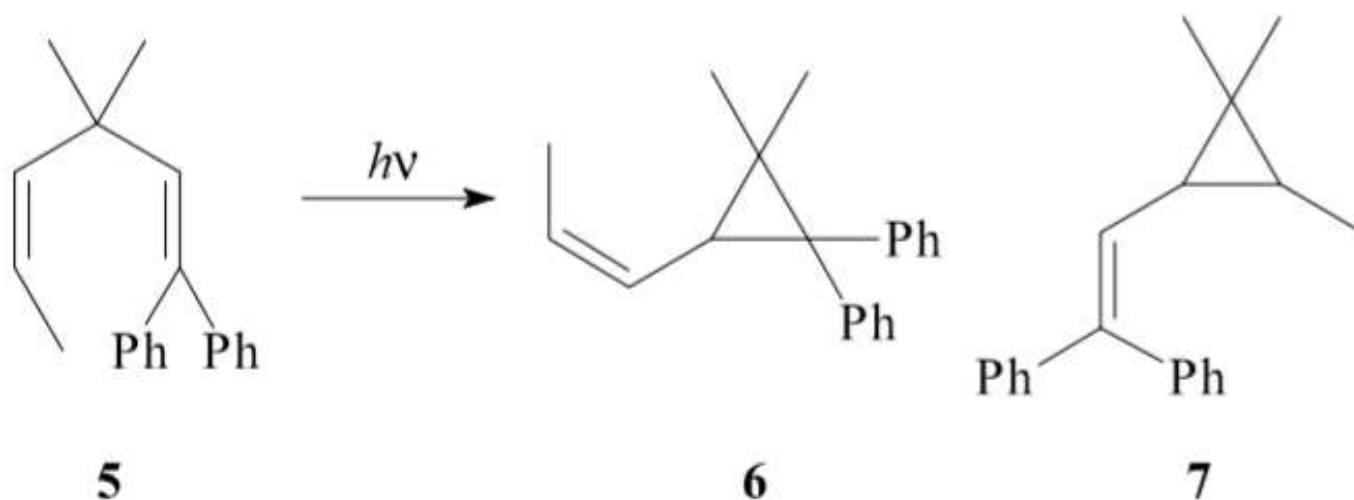


The photochemical isomerization of 1,4-dienes **1**, bearing substituents at C-3, leads to vinyl-cyclopropanes **2**, and is called the *di- π -methane rearrangement*.^{1,2,3} This reaction produces possible substrates for the *vinylcyclopropane rearrangement*.

A mechanism has been formulated² that would involve formation of diradical species **3** and **4**, which however might not be real intermediates. At least one substituent at C-3 is required in order to stabilize the radical **4**, and thereby facilitate the cleavage of the C-2/C-3 bond:

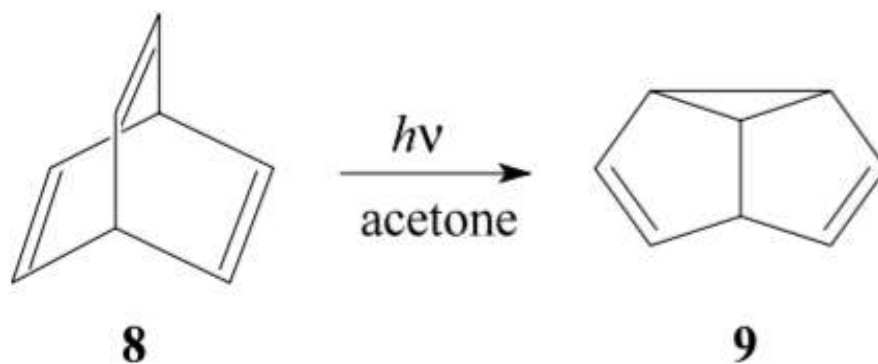


The rearrangement proceeds from the S_1 -state of the 1,4-diene **1**. The T_1 -state would allow for different reactions like double bond isomerization. Rigid systems like cyclic dienes, where E/Z -isomerization of a double bond is hindered for steric reasons, can react through the T_1 -state. When the rearrangement proceeds from the S_1 -state, it proves to be stereospecific at C-1 and C-5; no E/Z -isomerization is observed. *Z*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene **5** rearranges to the *Z*-configured vinylcyclopropane **6**.⁴ In this case the reaction also is regiospecific. Only the vinylcyclopropane **6** is formed, but not the alternative product **7**.⁴

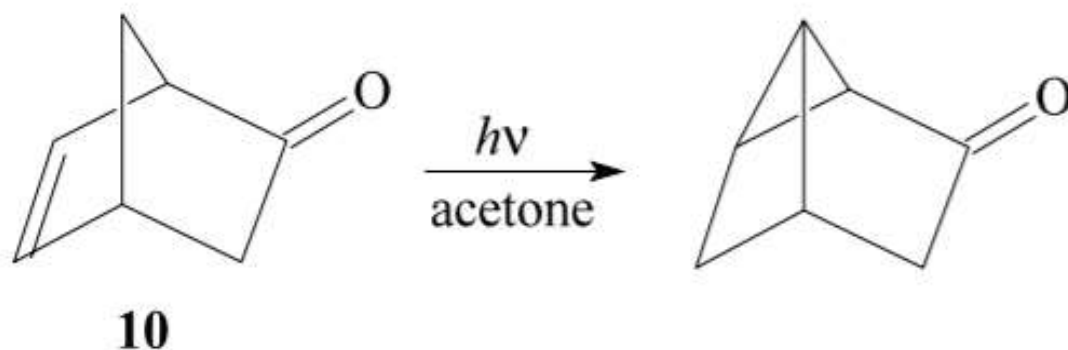


However, from substrates where the substituents at C-1 and C-5 are not that different in structure, a mixture of regioisomers may be obtained.

The di- π -methane rearrangement is a fairly recent reaction. One of the first examples has been reported in 1966 by Zimmerman and Grunewald¹ with the isomerization of barrelene **8** to semibullvalene **9**. This rearrangement reaction occurs in the presence of acetone as photosensitizer, and proceeds from the T_1 -state.⁵



A related reaction is the *oxa-di- π -methane rearrangement*,^{2,6} where one of the C=C double bonds is replaced by a C=O double bond. The substrates are thus β,γ -unsaturated ketones. The rearrangement proceeds from the triplet state. This *oxa*-variant gives access to highly strained molecules containing small rings, as has been demonstrated by irradiation of norborn-5-ene-2-one **10**:



Yields of the di- π -methane rearrangement reaction strongly depend on substrate structure, and are ranging from poor to nearly quantitative. Acetone and acetophenone have been used as photosensitizers.^{4,5}

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