

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



**III. Photochemistry**

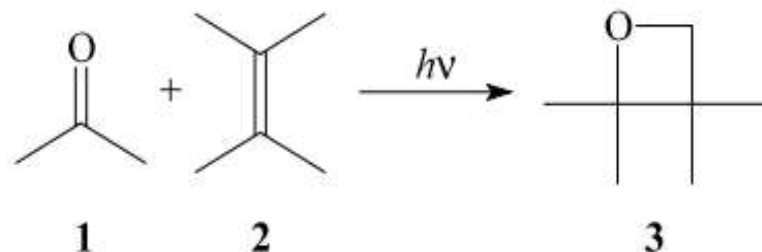
**19. Paterno-Büchi Reaction : Mechanism and Examples**



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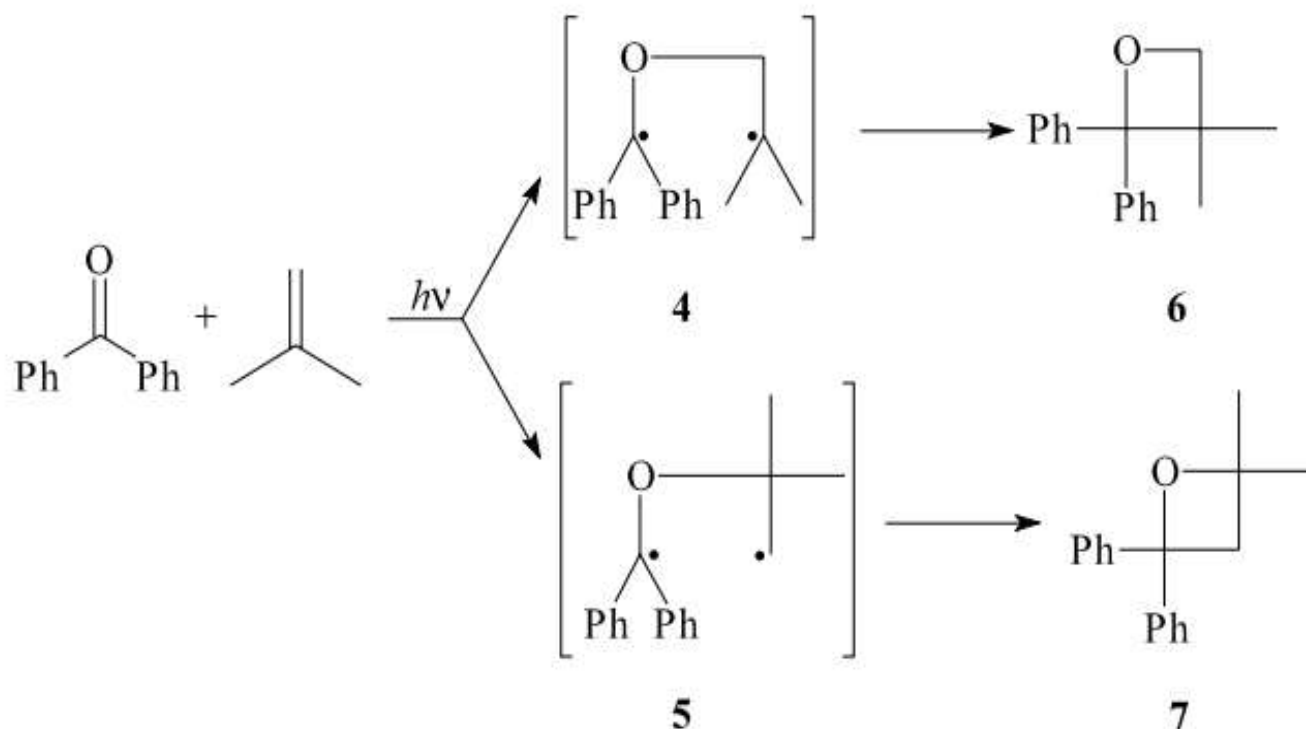
## *Paterno–Büchi Reaction*

Cycloaddition of a carbonyl compound to an alkene



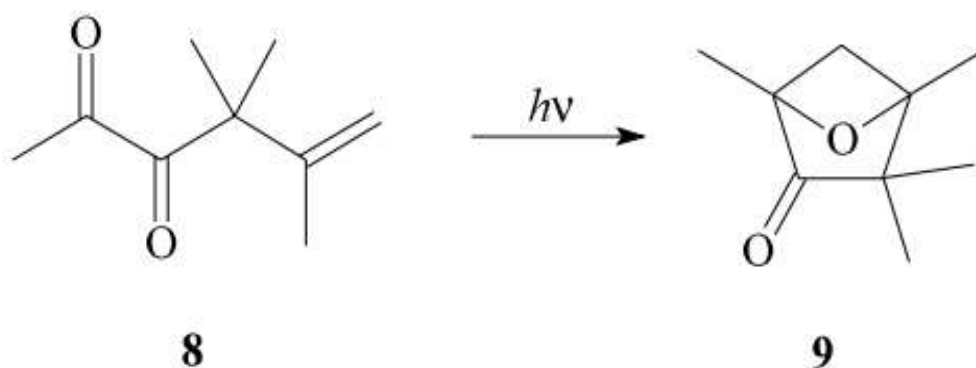
The photochemical cycloaddition of a carbonyl compound **1** to an alkene **2** to yield an oxetane **3**, is called the *Paterno–Büchi reaction*.<sup>1,2</sup> This reaction belongs to the more general class of photochemical [2 + 2]-cycloadditions, and is just as these, according to the Woodward–Hofmann rules,<sup>3</sup> photochemically a symmetry-allowed process, and thermally a symmetry-forbidden process.

The irradiation is usually carried out with light of the near UV region, in order to activate only the  $n \rightarrow \pi^*$  transition of the carbonyl function,<sup>4</sup> thus generating excited carbonyl species. Depending on the substrate, it can be a singlet or triplet excited state. With aromatic carbonyl compounds, the reactive species are usually in a  $T_1$ -state, while with aliphatic carbonyl compounds the reactive species are in a  $S_1$ -state. An excited carbonyl species reacts with a ground state alkene molecule to form an *exciplex*, from which in turn diradical species can be formed—e.g. **4** and **5** in the following example:



Diradical species **4** is more stable than diradical **5**, and the oxetane **6** is thus formed preferentially; oxetane **7** is obtained as minor product only. Evidence for diradical intermediates came from trapping experiments,<sup>5</sup> as well as spectroscopic investigations.<sup>6</sup>

In addition to the intermolecular Paterno–Büchi reaction, the intramolecular variant has also been studied;<sup>2</sup> the latter allows for the construction of bicyclic structures in one step. For example the diketone **8** reacts quantitatively to the bicyclic ketone **9**:



Although the Paterno–Büchi reaction is of high synthetic potential, its use in organic synthesis is still not far developed.<sup>2</sup> In recent years some promising applications in the synthesis of natural products have been reported.<sup>8</sup> The scarce application in synthesis may be due to the non-selective formation of isomeric products that can be difficult to separate—e.g. **6** and **7**—as well as to the formation of products by competitive side-reactions such as *Norrish type-I-* and *type-II fragmentations*.

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