

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



III. Photochemistry

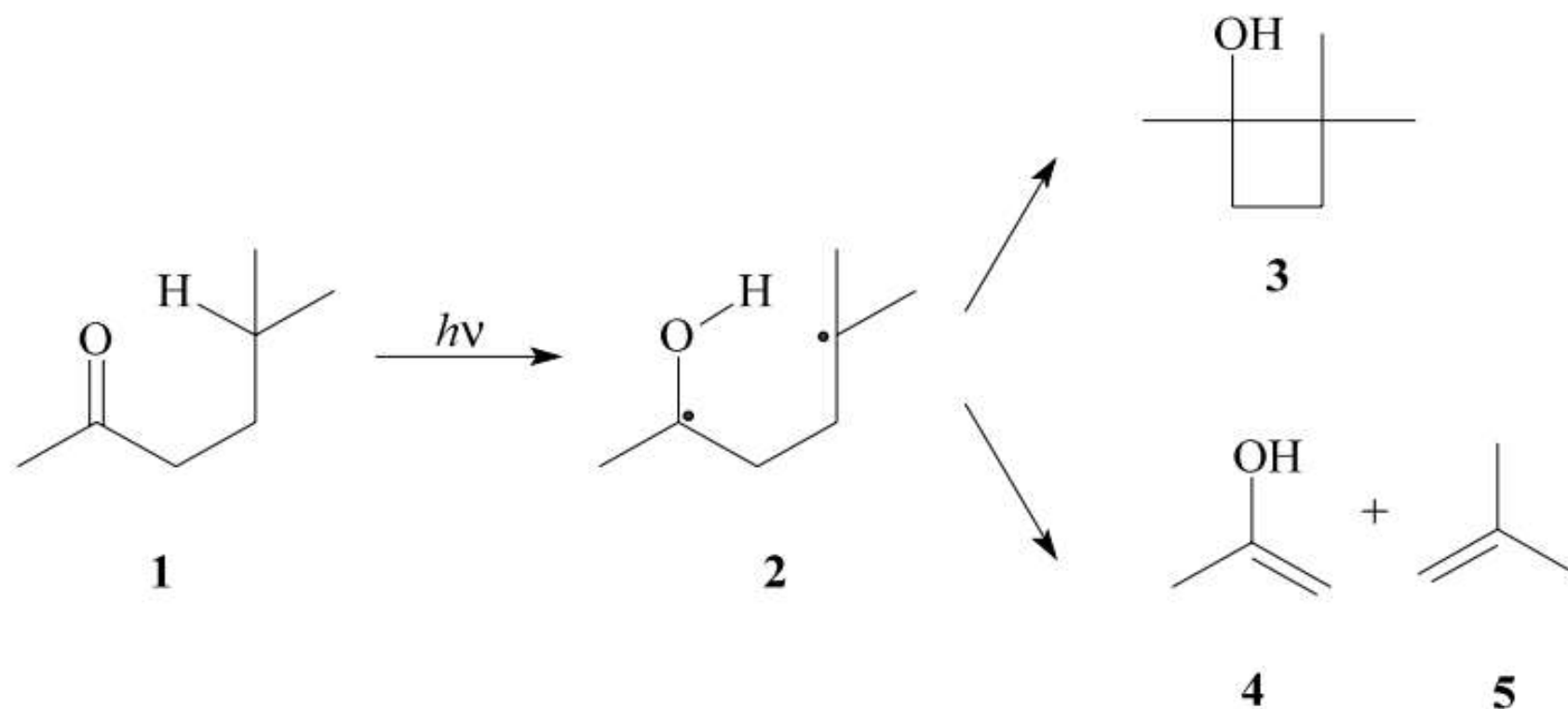
18. Norrish Type II Reaction : Mechanism and Examples



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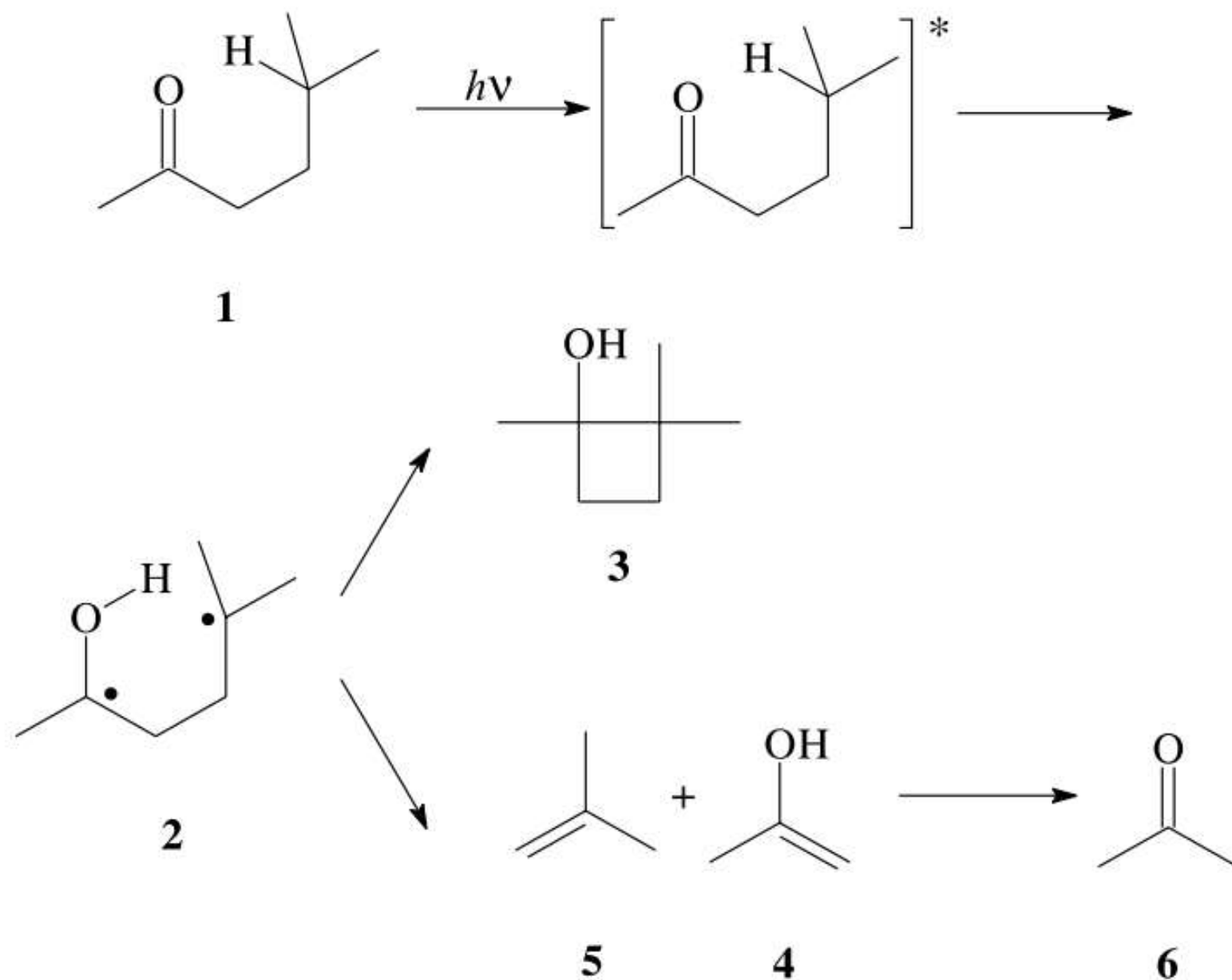
Norrish Type II Reaction

Photochemical reaction of aldehydes or ketones bearing γ -hydrogens

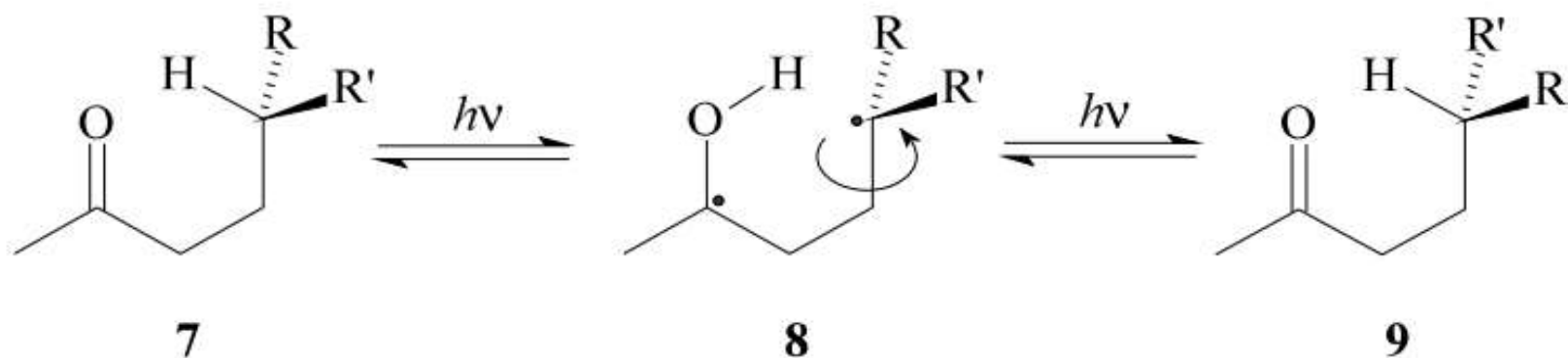


An aldehyde or ketone **1** bearing a γ -hydrogen atom can upon irradiation undergo an intramolecular hydrogen shift by the so-called *Norrish type II reaction*.¹⁻⁴ The resulting diradical species **2** can undergo a subsequent ring closure reaction to yield a cyclobutanol **3**, or suffer fragmentation to yield an enol **4** and an alkene **5**.

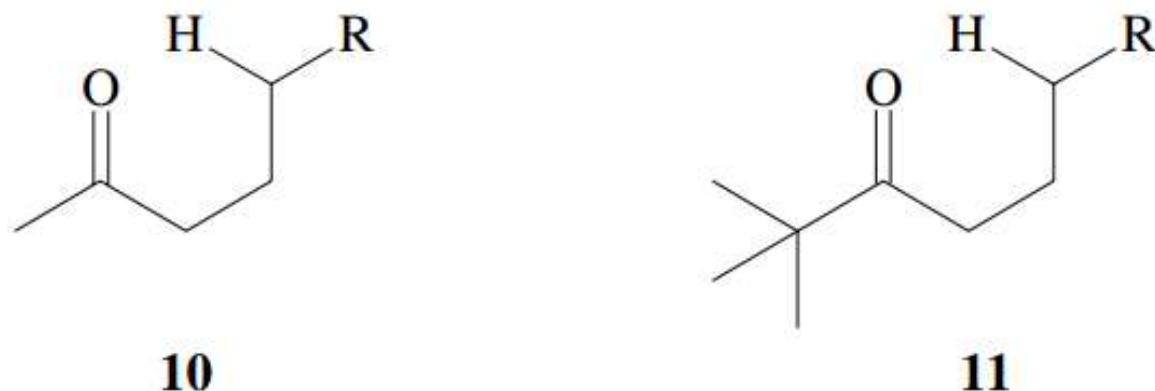
Photoactivated aldehyde or ketone molecules with γ -hydrogens can undergo the intramolecular hydrogen abstraction from the singlet excited (S_1)-state as well as the triplet excited (T_1)-state. This reaction proceeds via a cyclic six-membered transition state. The resulting 1,4-diradical species **2** can further react either by ring closure to give a cyclobutanol **3** or by carbon-carbon bond cleavage to give an enol **4** and an alkene **5**; enol **4** will subsequently tautomerize to carbonyl compound **6**:



The fragmentation/cyclization ratio is determined by the relative orientation of the respective molecular orbitals, and thus by the conformation of diradical species **2**.⁵ The quantum yield with respect to formation of the above products is generally low; the photochemically initiated 1,5-hydrogen shift from the γ -carbon to the carbonyl oxygen is a reversible process, and may as well proceed back to the starting material. This has been shown to be the case with optically active ketones **7**, containing a chiral γ -carbon center; an optically active ketone **7** racemizes upon irradiation to a mixture of **7** and **9**:



As a side reaction, the *Norrish type I reaction* is often observed. The stability of the radical species formed by α -cleavage determines the Norrish type I/Norrish type II ratio. For example aliphatic methyl ketones **10** react by a Norrish type II-mechanism, while aliphatic *tert*-butyl ketones **11** react preferentially by a Norrish type I-mechanism.



There are only a few examples for a preparative use of this reaction;⁵ of more importance have so far been mechanistic aspects.⁶

1. R. G. W. Norrish, *Trans. Faraday Soc.* **1937**, 33, 1521–1528.
2. J. N. Pitts, Jr., J. K. S. Wan in *The Chemistry of the Carbonyl Group* (Ed.: S. Patai), Wiley, New York, **1966**, p. 823–916.
3. P. J. Wagner, *Acc. Chem. Res.* **1971**, 4, 168–177.
4. J. M. Coxon, B. Halton, *Organic Photochemistry*, Cambridge University Press, London, **1974**, p. 58–78.
5. J. Kopecky, *Organic Photochemistry*, VCH, Weinheim, **1991**, p. 123–125.
6. S. D. Feyter, E. W.-G. Diau, A. H. Zewail, *Angew. Chem.* **2000**, 112, 266–269; *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 260.

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