

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



III. Photochemistry

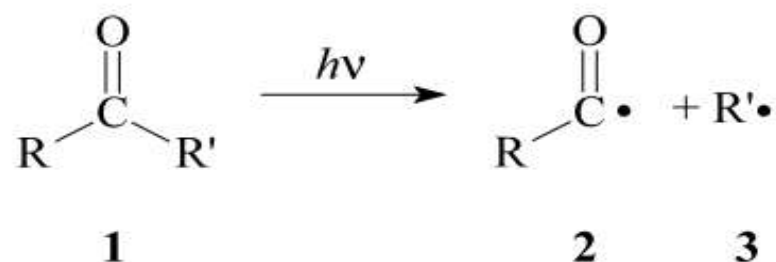
17. Norrish Type I Reaction : Mechanism and Examples



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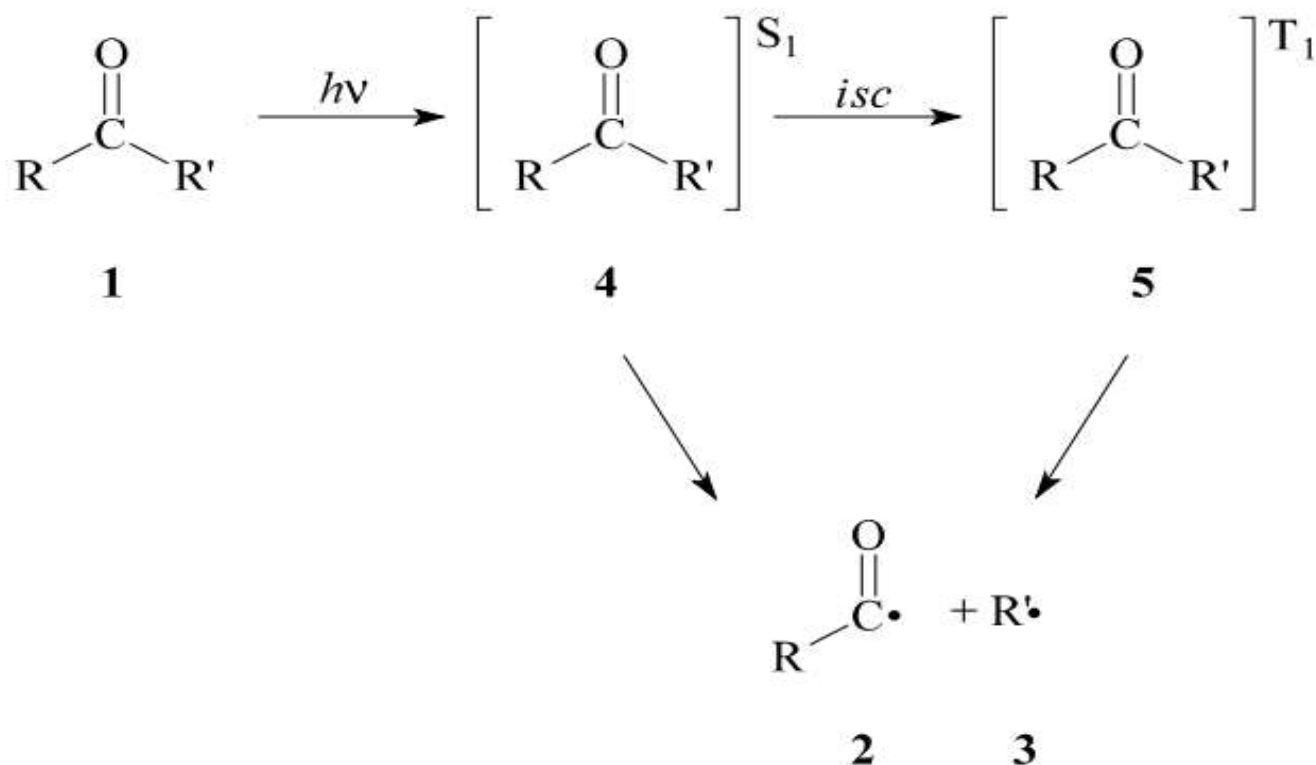
Norrish Type I Reaction

Photochemical cleavage of aldehydes and ketones



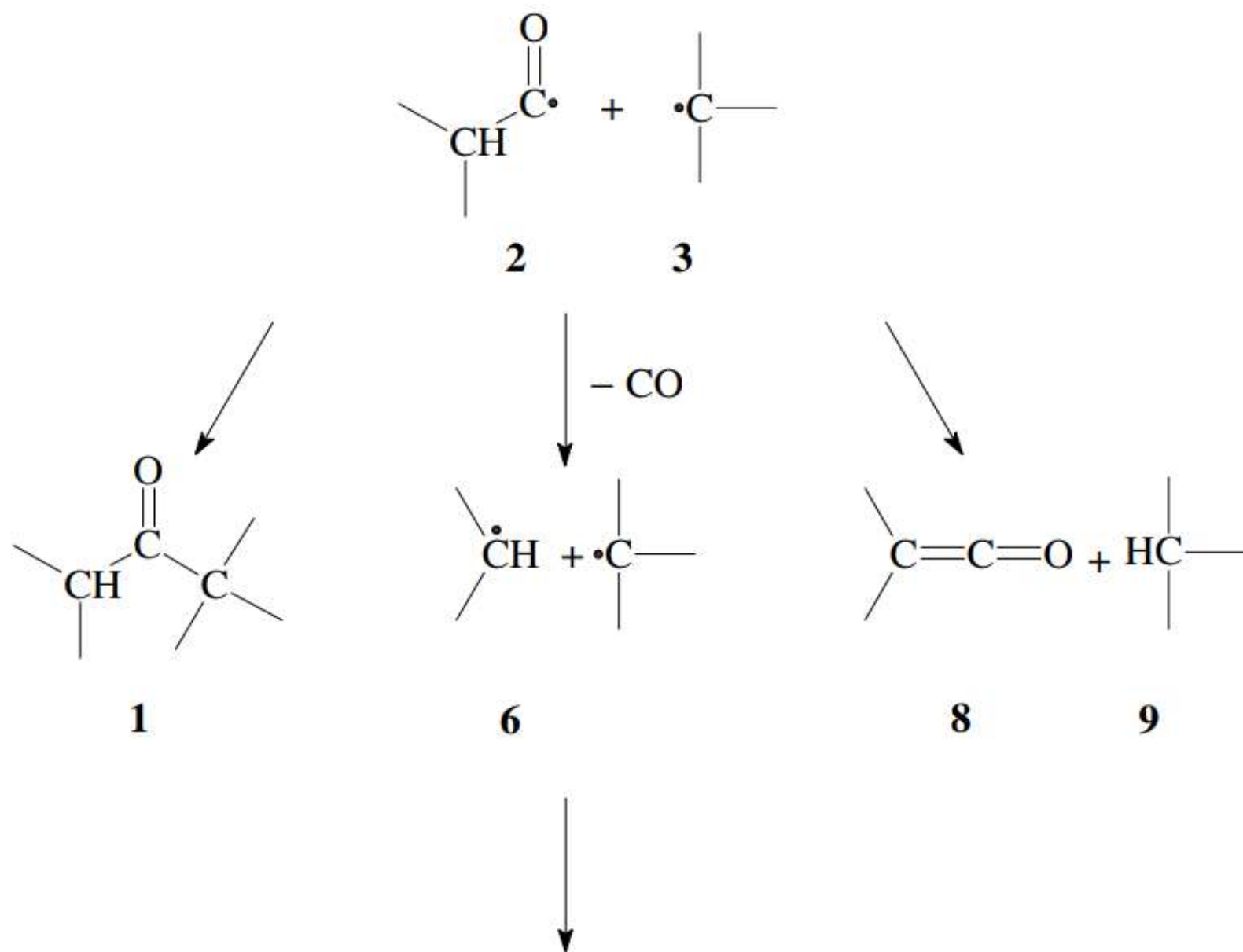
Carbonyl compounds can undergo various photochemical reactions; among the most important are two types of reactions that are named after *Norrish*.¹ The term *Norrish type I fragmentation*¹⁻⁴ refers to a photochemical reaction of a carbonyl compound **1** where a bond between carbonyl group and an α -carbon is cleaved homolytically. The resulting radical species **2** and **3** can further react by decarbonylation, disproportionation or recombination, to yield a variety of products.

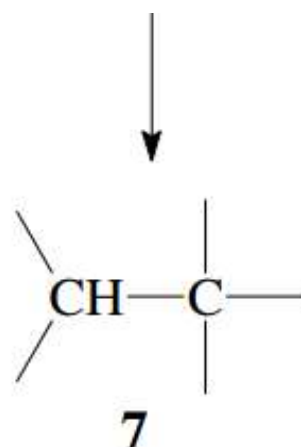
By absorption of a photon of light, a ketone or aldehyde molecule **1** can be converted into a photoactivated species; it is promoted to the singlet excited (S_1)-state **4**, from which it can reach the triplet excited (T_1)-state **5** by *intersystem crossing*. The homolytic Norrish type I cleavage may occur from either or both states, and leads to formation of an acyl radical **2** and an allyl radical **3**. Aromatic ketones generally undergo the photolytic cleavage from the triplet excited state, since the intersystem crossing is usually fast in those cases.



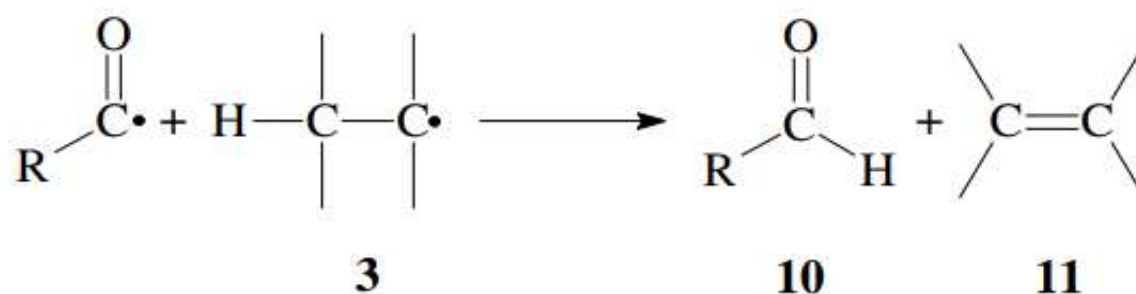
With unsymmetrical ketones two different bonds are available for photolytic cleavage; the actual cleavage pathway depends on the relative stability of the possible radical species $R\cdot$ and $R'\cdot$.

The radical pair **2/3** can undergo various subsequent reactions: the most obvious is the recombination to the starting carbonyl compound **1**. The acyl radical **2** can undergo a fragmentation by loss of CO to the radical **6**, which can further react with radical **3** to yield the hydrocarbon **7** (i.e. $R-R'$). Cleavage of CO from **2** and subsequent combination of **6** and **3** usually is a fast process taking place in a solvent cage, which largely prevents formation of symmetrical hydrocarbons ($R-R$ or $R'-R'$). If the acyl radical **2** bears an α -hydrogen, this hydrogen can be abstracted by radical **3**, resulting in formation of a ketene **8** and hydrocarbon **9**:

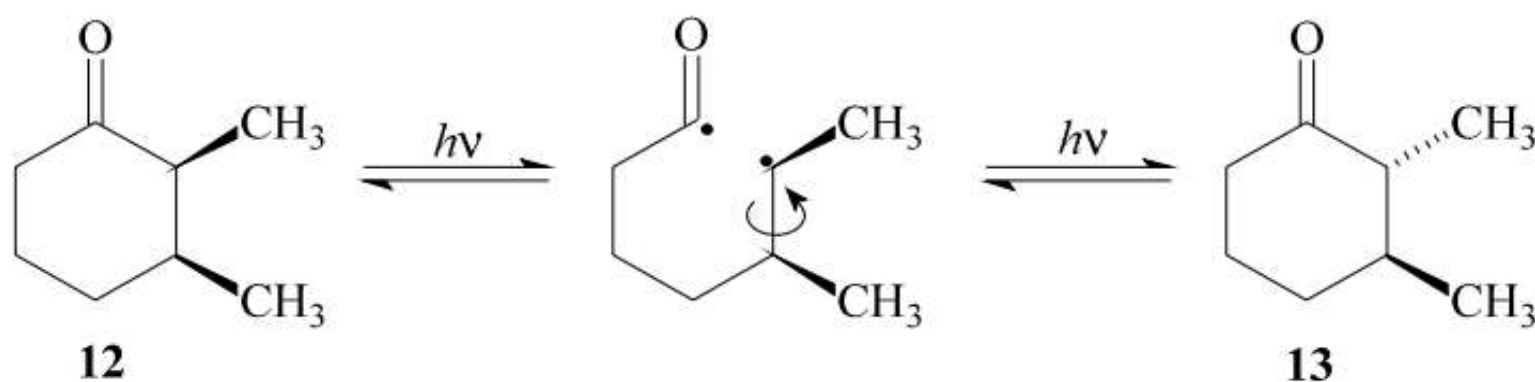




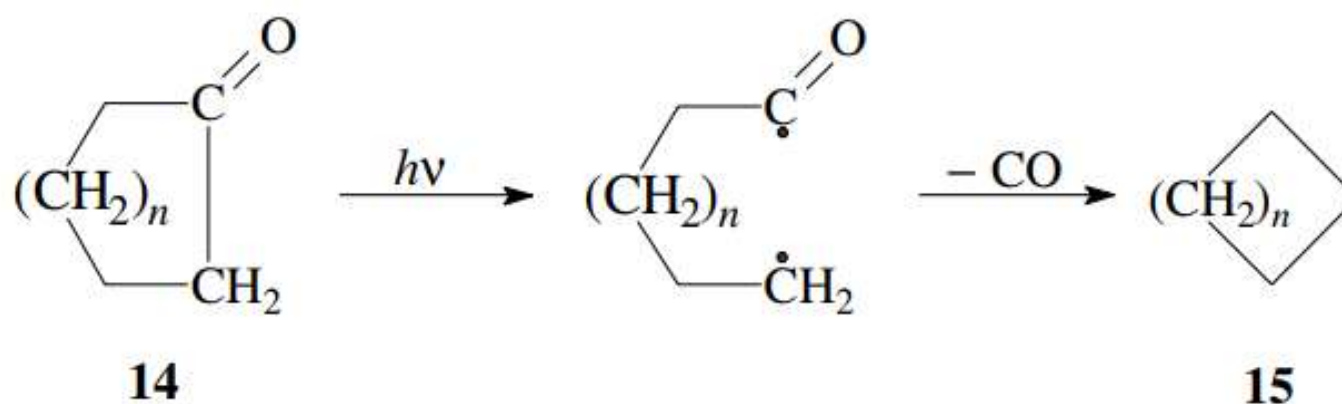
The acyl radical **2** can abstract a β -hydrogen from the radical **3**, to give an aldehyde **10** and an alkene **11**:



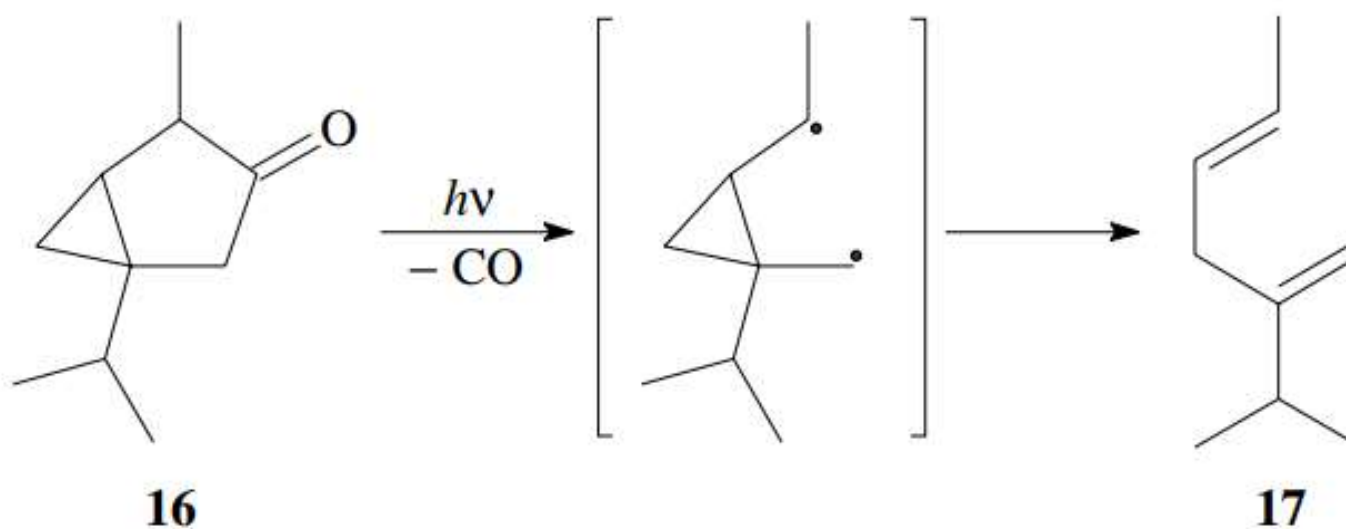
Since the quantum yield of the Norrish type I reaction is generally low, it has been assumed that the initial homolytic cleavage is a reversible process. Evidence came from an investigation by *Barltrop et al.*⁵ which has shown that *erythro*-2,3-dimethylcyclohexanone **12** isomerizes to *threo*-2,3-dimethylcyclohexanone **13** upon irradiation:



The photolytic cleavage of cyclic ketones **14** leads to formation of a diradical species, that can undergo analogously the various reactions outlined above. The decarbonylation followed by intramolecular recombination yields a ring-contracted cycloalkane **15**:



With strained cycloketones the type I-cleavage gives better yields, and can be used as a preparative method. For example photolysis of the bicyclic ketone **16** gives diene **17** in good yield:⁶



In general however the various possible reaction pathways give rise to formation of a mixture of products. The type I-cleavage reaction is only of limited synthetic importance, but rather an interfering side-reaction—e.g. with an attempted *Paterno–Büchi reaction*, or when an aldehyde or ketone is used as sensitizer in a $[2 + 2]$ -cycloaddition reaction.

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. J. S. Swenton, *J. Chem. Educ.* **1969**, 46, 217–226.
4. J. M. Coxon, B. Halton, *Organic Photochemistry*, Cambridge University Press, London, **1974**, p. 58–78.
5. J. A. Barltrop, J. D. Coyle, *J. Chem. Soc. Chem. Commun.* **1969**, 1081–1082.
6. J. Kopecky, *Organic Photochemistry*, VCH, Weinheim, **1991**, p. 119–122.

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