Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Course Code: CHC110

Course Title: Organic Chemistry (Section A)

Unit: Photochemistry

Module Name: Norrish Type I and Type II cleavage reactions of ketones, Paterno-Büchi and Barton reaction

Name of the Presenter: Dr. Mira V. Parmekar

Notes

Carbonyl compounds can undergo various photochemical reactions. Among these two types are named after Norrish, viz:

- **Norrish type I fragmentation**
- **Norrish type II fragmentation**

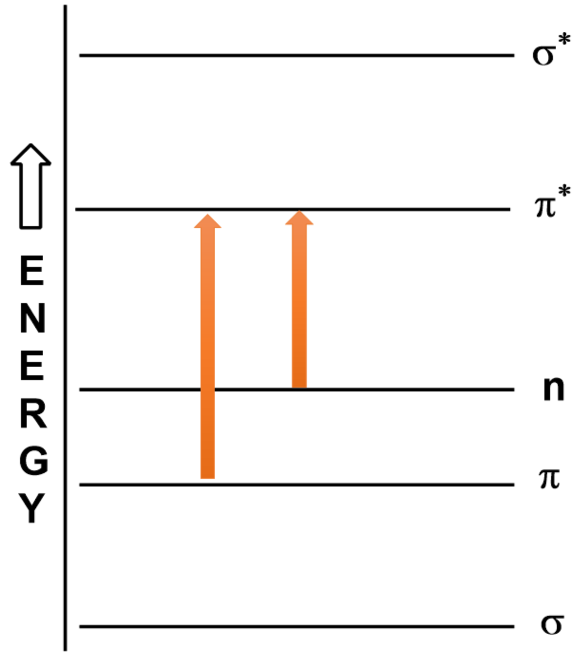
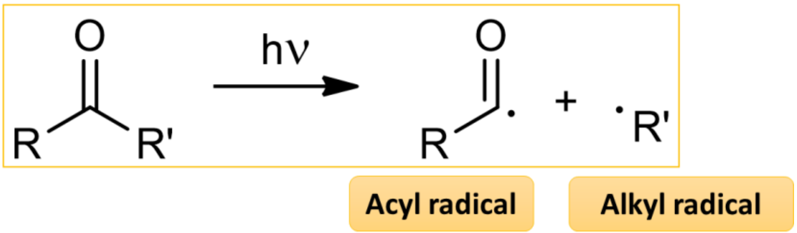


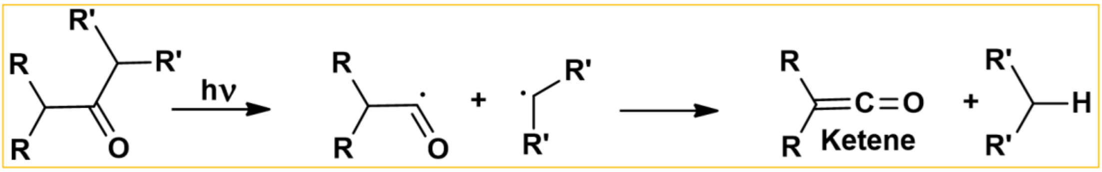
Figure 1 Allowed transitions in carbonyl molecules on irradiation with UV-Visible light

The Norrish type I fragmentation refers to a photochemical reaction of a carbonyl compound where a bond between carbonyl group and the α-carbon is cleaved homolytically. By absorption of a light photon, a ketone/aldehyde molecule is converted into a photoactive species and promoted to a singlet excited (S1) or triplet excited (T1) state by ISC. The homolytic Norrish type I cleavage can occur from either side leading to the formation of an acyl and an alkyl radical.

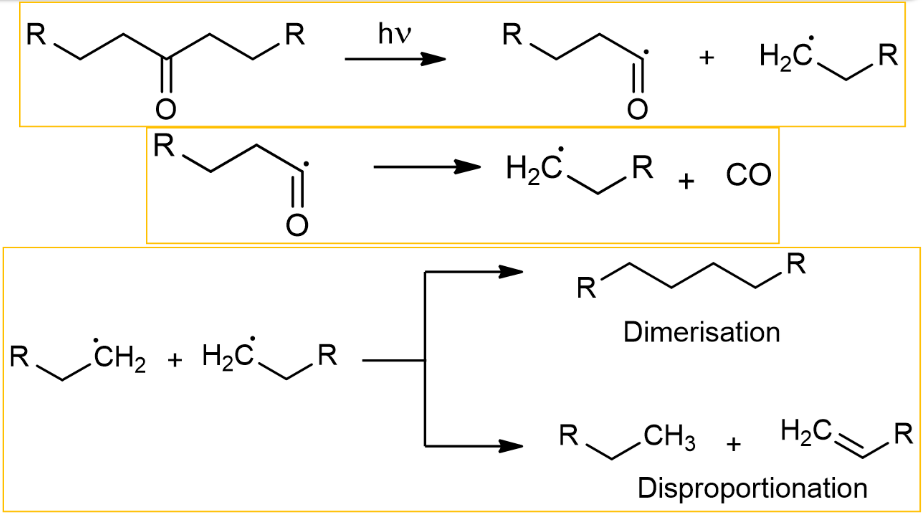


Once Norrish type I of a carbonyl compound occurs, where a bond between carbonyl group and the α-carbon is homolytically broken, the resulting radical species then further can react to give various products either by one of the processes mentioned below.

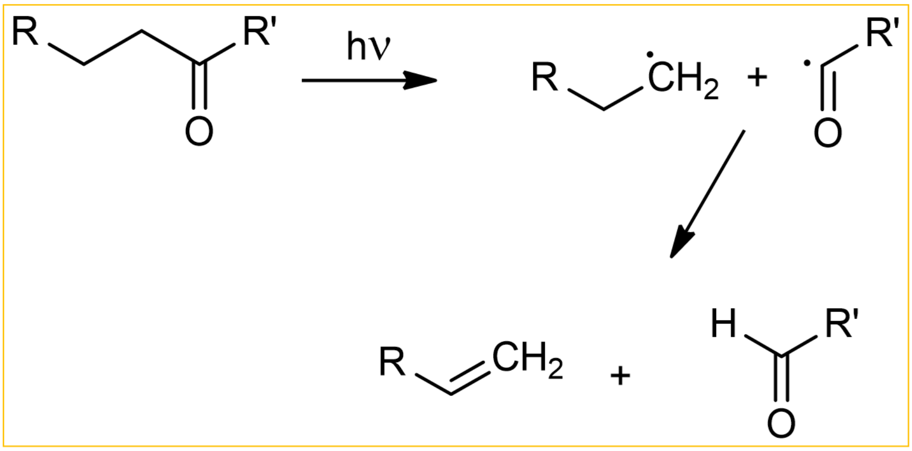
1. Disproportionation to give a ketene



2. Decarbonylation followed by dimerization and/or disproportionation

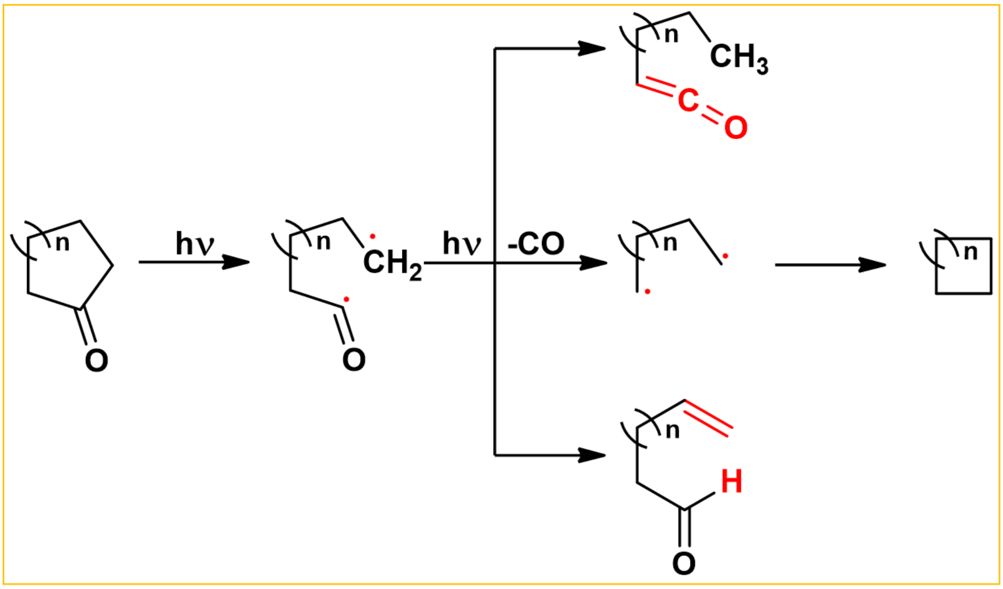


3. Intramolecular hydrogen abstraction by acyl radical

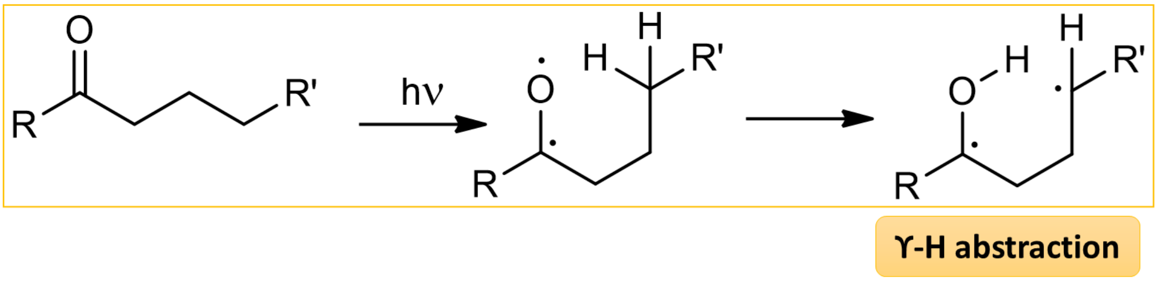


The Norrish type II fragmentation

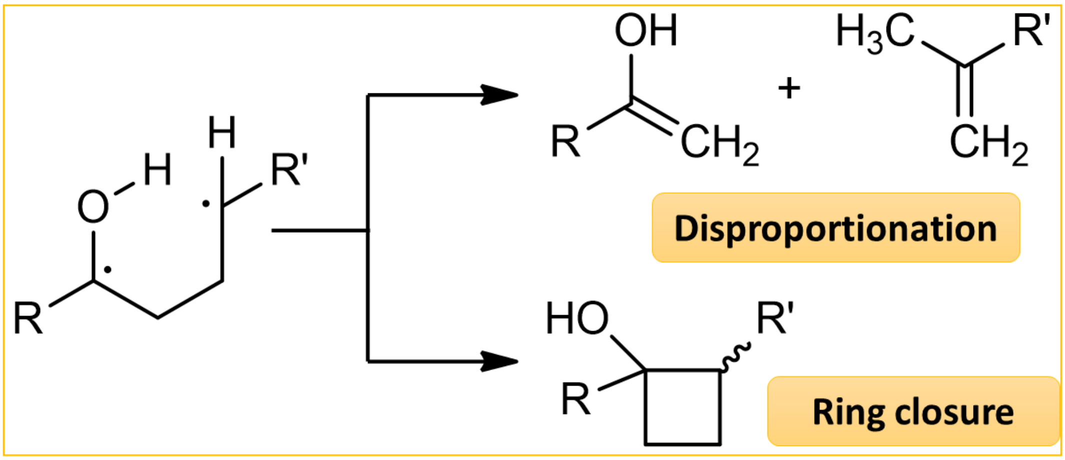
Norrish Type I fragmentation- Example



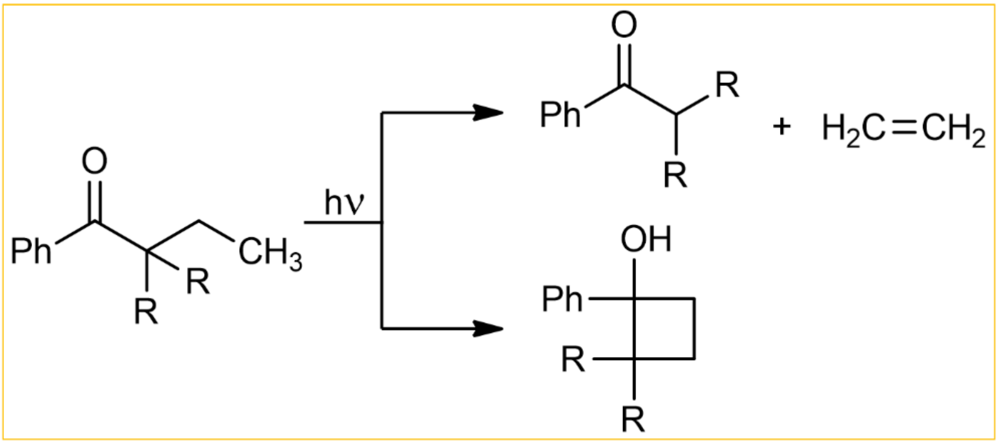
The Norrish type II fragmentation An aldehyde or ketone bearing ϒ-hydrogen atom upon irradiation undergoes an intramolecular hydrogen shift by a process termed as Norrish type II fragmentation reaction. The photoactivated aldehyde or ketone can undergo ϒ-hydrogen abstraction from either S_1 or T_1 state. The reaction proceeds via a cyclic 6-membered transitional state. The



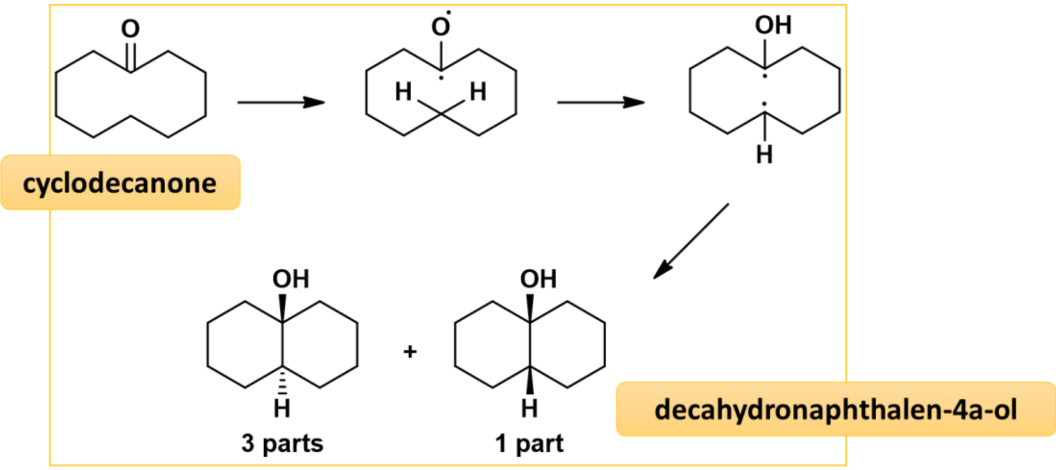
resultant 1,4-diradical species can further undergo either ring closure or fragmentation into an enol and alkene. Mechanism above



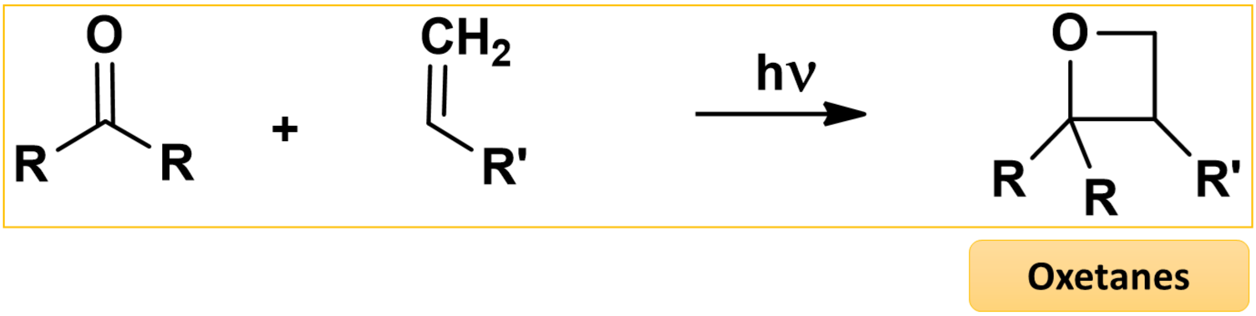
Norrish Type II fragmentation - Example



Norrish Type II Cleavage - Example

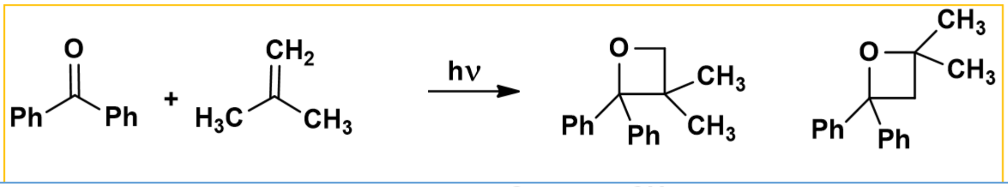


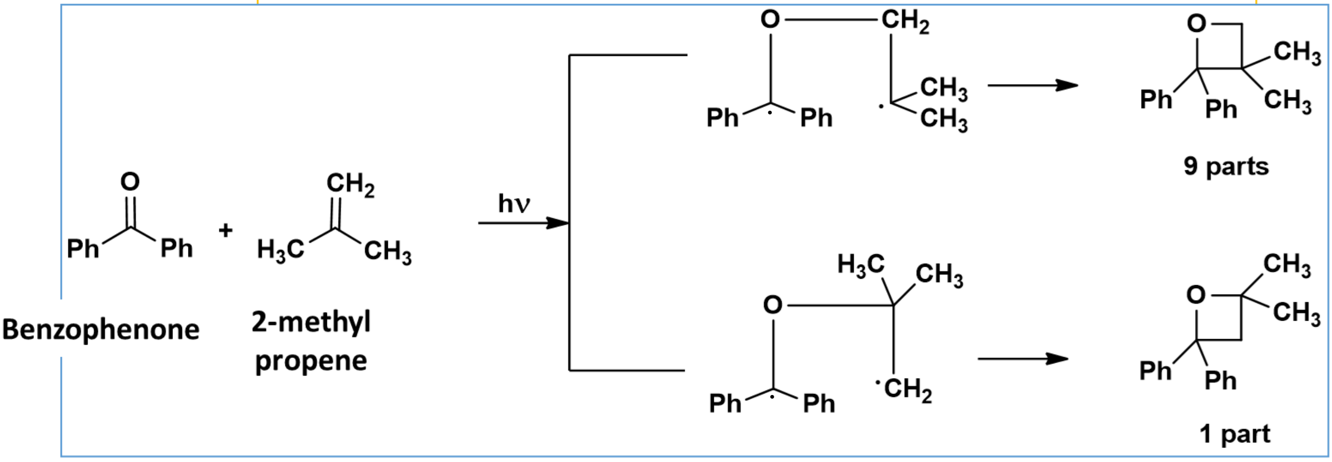
Paterno-Büchi Reaction



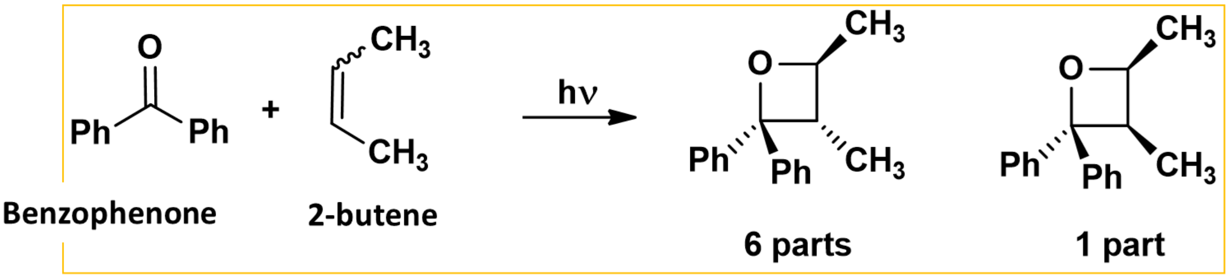
The photochemical cycloaddition of a carbonyl to an alkene to give oxetane is called Paterno-Büchi reaction. It belongs to [2+2]-cycloaddition class of photochemical reactions, generally activating n-∏* transition of carbonyls. The excited carbonyl species react with a GS alkene to give an exciplex which in turn gives a diradical ultimately forming an Oxetane. The excited carbonyl species react with a GS alkene to give an *exciplex* which in turn gives a diradical ultimately forming an Oxetane.

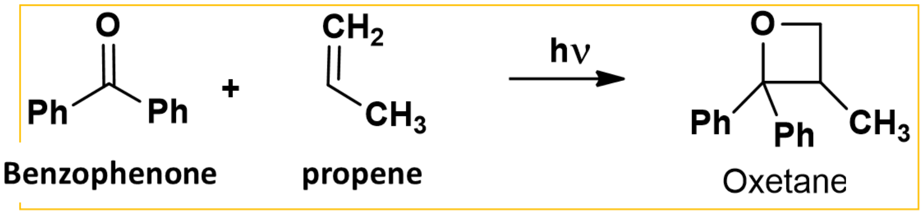
Paterno-Büchi Reaction - Mechanism





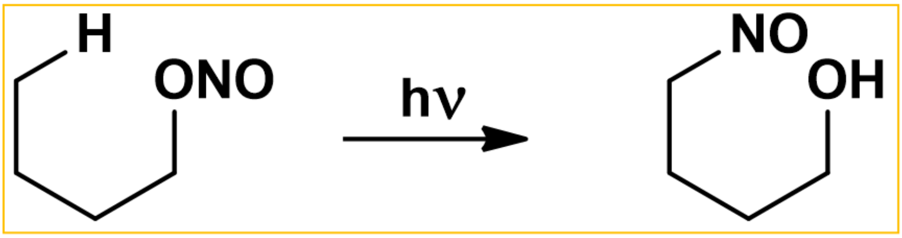
Paterno-Büchi Reaction - Examples





Barton Reaction

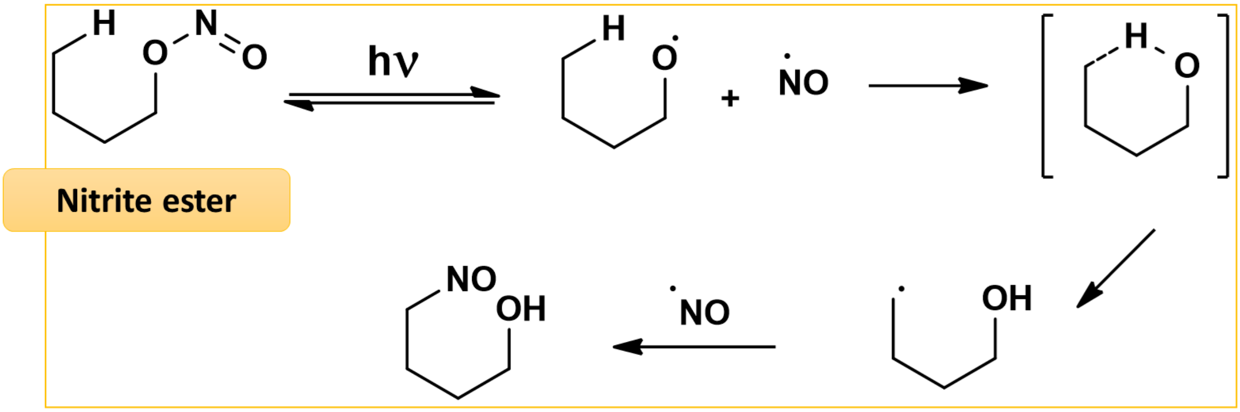
Nitrous acid esters are converted to 4-nitroso alcohols by irradiation with ultraviolet light, this conversion is termed as the Barton reaction. Upon irradiation the nitrous acid ester (nitrite) decomposes to give an alkoxy radical and nitrous oxide (NO). The former further reacts via cyclic 6-membered intermediate through an intramolecular hydrogen abstraction to yield carbon radical species which reacts with the earlier formed NO to finally give 4-nitroso alcohols.



Nitrite

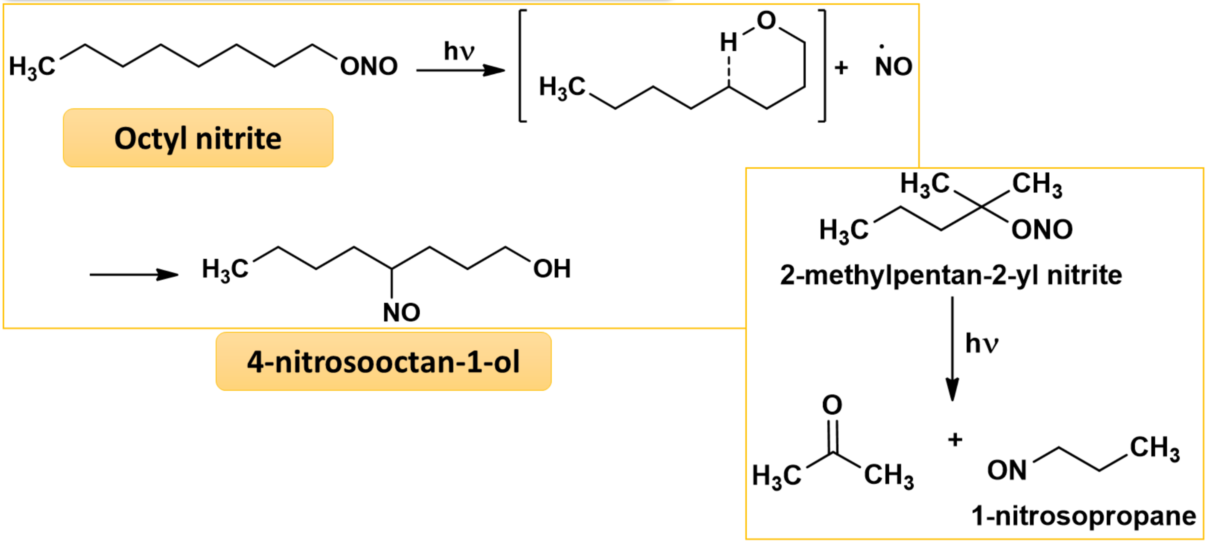
Nitroso alcohol

Barton Reaction - Mechanism



Nitroso alcohol

Barton Reaction - Examples



Octyl nitrite

4-nitrosooctan-1-ol

2-methylpentan-2-yl nitrite

1-nitrosopropane