C-301 U II Photochemistry -06

Photochemical oxidations and reductions

Photochemical oxidations:

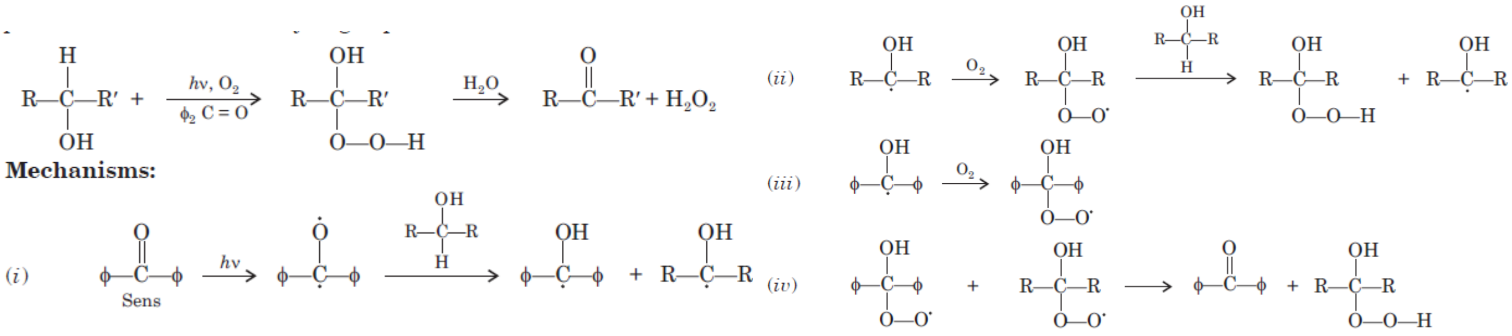
Incorporation of oxygen in the presence of UV light is known as photochemical oxidation.

There are two mechanisms by which oxygen is incorporated in photochemical oxidation reactions.

1. The first is the ***Backstrom mechanism*** which is also known as photosensitisation oxidation mechanism. Its main characteristic is abstraction of hydrogen by the sensitiser (Sens) in its excited triplet state followed by addition of oxygen to the newly created radical. This type of photooxygenation is known as type I photooxygenation.

$$\text{Sens} + h\nu \longrightarrow \overset{\uparrow\uparrow}{\text{Sens}}$$
$$\overset{\uparrow\uparrow}{\text{Sens}} + \text{A}-\text{H} \longrightarrow \text{Sens}-\dot{\text{H}} + \dot{\text{A}}$$
$$\dot{\text{A}} + O_2 \longrightarrow \text{A}-\text{O}-\dot{\text{O}}$$
$$\text{A}-\text{O}-\dot{\text{O}} + \text{AH} \longrightarrow \text{A}-\text{O}-\text{O}-\text{H} + \dot{\text{A}}$$
$$\text{A}-\text{O}-\dot{\text{O}} + \text{Sens}-\dot{\text{H}} \longrightarrow \text{A}-\text{O}-\text{O}-\text{H} + \text{Sens}$$

Example: Oxidation of secondary alcohols to hydroxy hydroperoxides which in aqueous medium decomposes to form ketones and hydrogen peroxide.



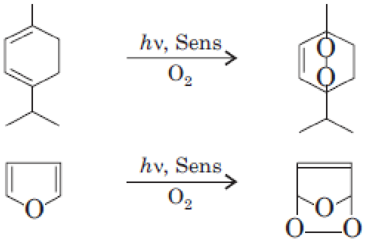
The second mechanism known as *photosensitised oxygen transfer* involves the direct combination of the substrate with oxygen. There are two proposals regarding the state of oxygen involved. This type of photooxygenation is known as type II photooxygenation. Schenck's favours an oxygen-transfer step in which the triplet sensitiser forms an adduct with triplet oxygen.

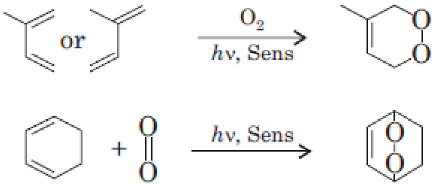
$$\text{Sens}^{\bullet} \xrightarrow{h\nu} {}^3\text{Sens}$$
$${}^3\text{Sens} + O_2 \longrightarrow \dot{\text{Sens}}-\text{O}-\dot{\text{O}}$$
$$\text{A} + \dot{\text{Sens}}-\text{O}-\dot{\text{O}} \longrightarrow \text{AO}_2 + \text{Sens}$$

$$\text{Sens} \xrightarrow{h\nu} {}^3\text{Sens}^*$$
$$O_2\ (\text{Triplet}) + \text{Sens}^*\ (\text{Triplet}) \longrightarrow O_2\ (\text{Singlet}) + \text{Sens}$$
$$\text{A} + O_2\ (\text{Singlet}) \longrightarrow \text{AO}_2$$

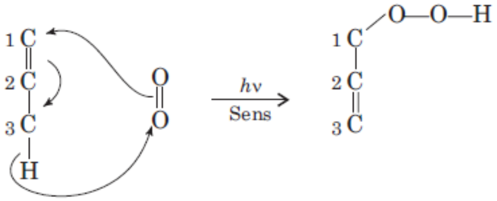
Alkenes, dienes and polyenes are attacked by singlet oxygen. The singlet oxygen may be generated by thermal methods (*e.g.*, by the reaction of hydrogen peroxide with sodium hypochlorite), by excitation of ground state oxygen (triplet oxygen) in a microwave discharge or by the use of visible radiation and photochemical sensitiser such as methylene blue, Rose Bengal, chlorophyll, riboflavin, fluorescein or halo fluorescein.

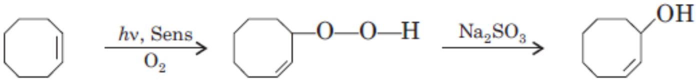
Acyclic or cyclic conjugated dienes gives 1, 4-cycloaddition reaction with singlet oxygen to form six-membered cyclic adduct, *i.e.,* cyclic peroxide.

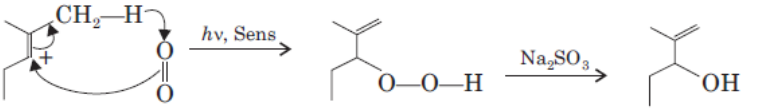


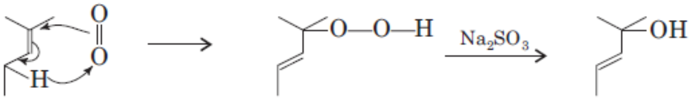


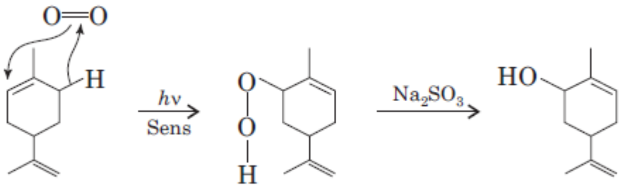
The formation of hydroperoxides in photosensitised oxygen-transfer reactions that follow the Schenck type of mechanism occurs only when hydrogen is present on allylic carbon. The reaction has, moreover, some definite steric and electronic requirements. Oxygen always becomes attached to one of the double bonded carbon, which then shifts into the allylic position. The reaction is like ene reaction.



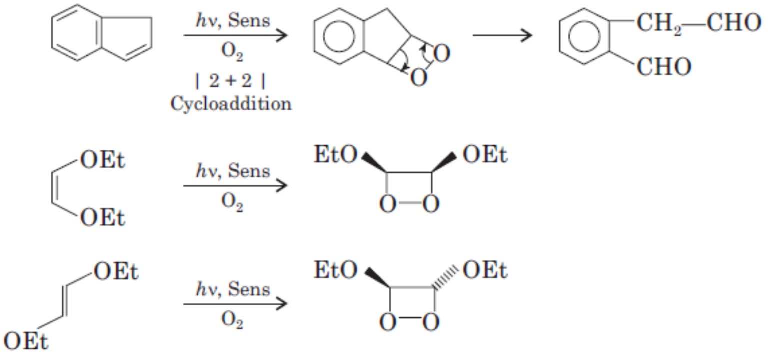




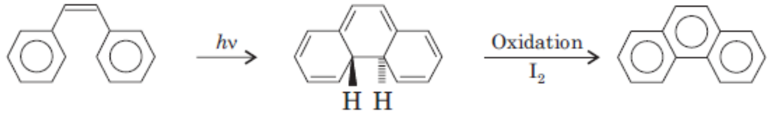




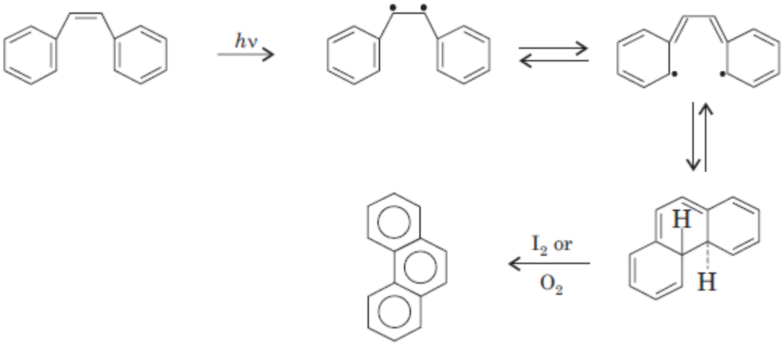
Some substituted alkenes behave differently with singlet oxygen and form a dioxetane in a cycloaddition reaction. Some dioxetanes are stable but others readily decompose to two carbonyl compounds. Electron rich alkenes undergo this reaction and reaction is stereospecific.



The oxidative cyclisation of conjugated trienes to form aromatic system is one of the more extensively studied photochemical oxidations. The conversion of *cis*-stilbene to phenanthrene is a main example of such a ring closure. The reaction takes place in the presence of hydrogen acceptors (O2, I_2, $FeCl_3$).



Mechanism of the reaction is as follows:



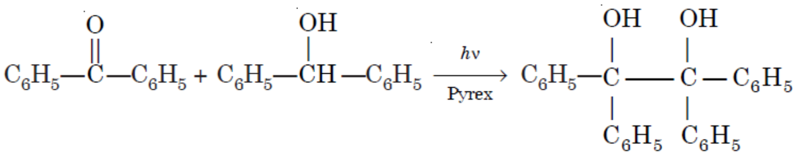
<u>Note:</u> Assignment questions:

1. Write the Molecular orbital diagram for O_2 in ground state, singlet excited state and triplet excited state and comment on their magnetic property.
2. Write the synthesis of Phenol and acetone by Cumene process which is also known as Cumene-Phenol process or Hock Process with suitable mechanism.

Photochemical Reduction:

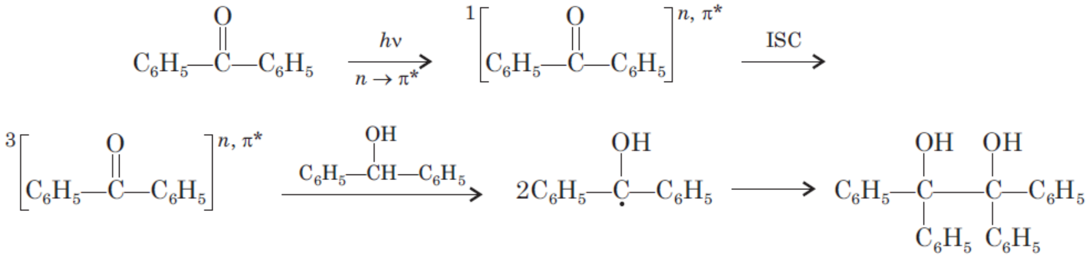
Photo reduction of carbonyl compounds is one of the important photochemical processes.

Ex: Reduction of benzophenone in benzene in a pyrex tube by exposing it to sunlight for few days. The reduction takes place in the presence of benzhydrol.



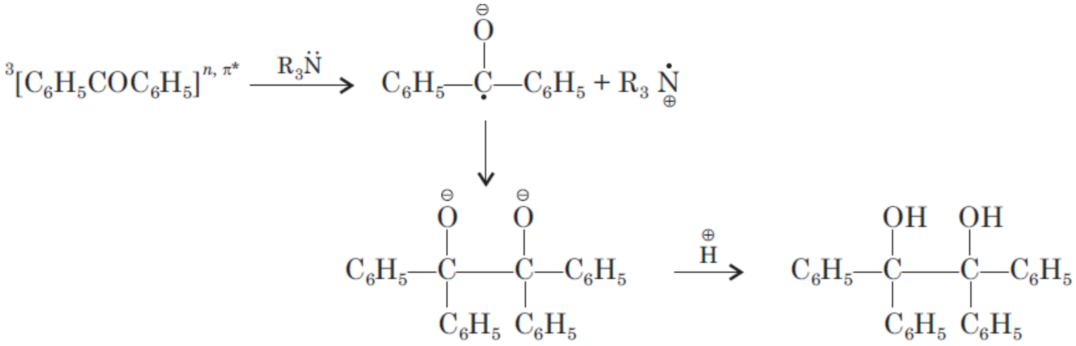
Benzpinacol

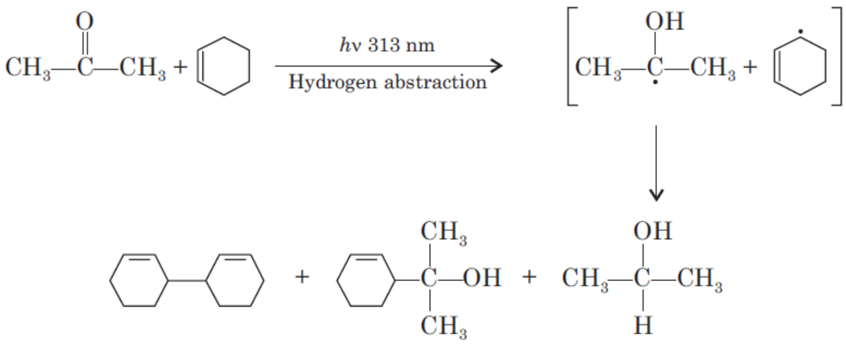
The first step is excitation of the benzophenone to the 1[*n*, π*] state which intersystem crosses to the 3[*n*, π*] state. Hydrogen abstraction from alcohol gives two diphenyl hydroxyl methyl radicals which combine to form benzpinacol.



Ketones undergo photo reduction in the presence of a variety of hydrogen atom donors other than secondary alcohols. Hydrogen atom abstraction is much more efficient for *n*, π* than π, π* for ketones.

Excited ketones can be reduced by tertiary amines. The key reaction in this case is electron transfer from the amine to the ketone producing ketyl radical and the cation radical from the amine.



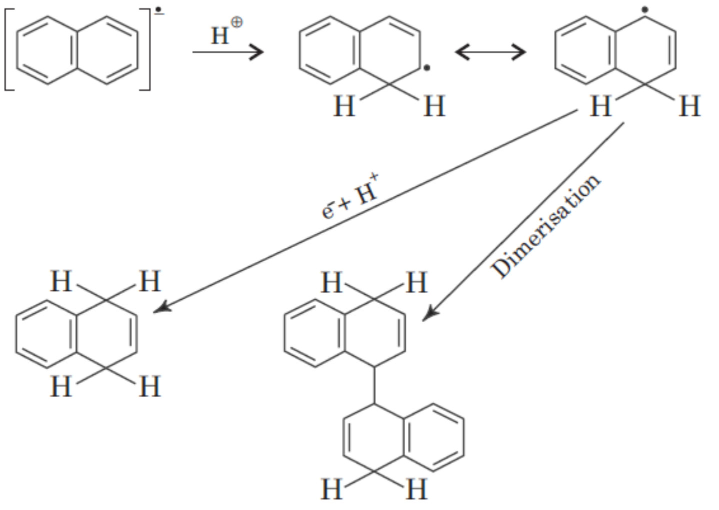


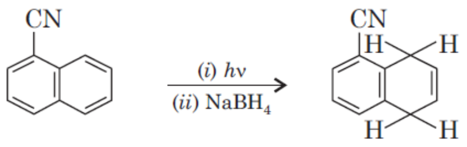
Aromatic hydrocarbons also undergo Photo reduction.

Ex: Benzene, Biphenyl, Naphthalene, Methoxy derivative of naphthalene and Anthracene react with amine to give reduction products and aminated products.

The reaction is initiated by the transfer of an electron from nitrogen lone pair orbital to the half filled highest bonding molecular orbital of the excited aromatic compound.

$$ArH^* + R_3\ddot{N} \longrightarrow [Ar\dot{H}]^{-} + R_3\overset{+}{\underset{\bullet}{N}}$$





Mechanism: