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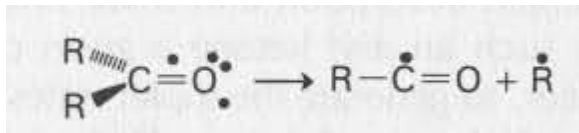
*Photochemistry of Carbonyl Compounds*

- Earliest systematic studies of both mechanistic and synthetic photochemistry was done on carbonyls.
- Carbonyl compounds absorb readily accessible wavelengths of ultraviolet light e.g. some aromatic ketone reacts in sunlight and their products can be easily isolated and analysed
- Substrates of most organic photochemical reactions are ketones than any other organic compounds
- Aliphatic ketone:
  - Absorbs weakly ( $\epsilon = 20 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) at around 280nm as a result of  $n-\pi^*$  transition which is forbidden on both the grounds-symmetry and overlaps
  - Intersystem crossing of  $n-\pi^*$  is efficient from singlet excited state to triplet state because energy and electron distribution of  $n-\pi^*$  triplet states are not very different from corresponding singlet state
  - Both states in fact react in the same manner though with different rate constants.
  - Reactions observed on direct irradiation of saturated ketones may be singlet derived, triplet derived or a mixture of both.
- For conjugated, unsaturated ketones ( $\alpha,\beta$ -enones or aryl ketones),  $n-\pi^*$  and  $\pi-\pi^*$  singlet states are closer in energy and the lowest energy excited state especially in the triplet manifold may be  $\pi-\pi^*$ . This is because photochemical reactions normally occur through the lowest states and radical like properties of  $n-\pi^*$  are not shared by  $\pi-\pi^*$  states. Products or efficiency of reaction can be effected by substituent that influence the relative energy levels and even on the nature of solvent for borderline cases.
- Intersystem crossing of aryl ketones is very efficient. So, most of the reactions are resulted due to triplet state processes. Together with long wave length absorption and small energy difference between singlet and triplet excited state, they are used as triplet sensitizers
- Aldehyde have similar triplet excited state properties and photochemistry but carboxylic acid and its most derivatives are different
- The major classes of reactions of carbonyls are:
  - (a) Norrish type I
  - (b) Norrish type II
  - (c) Photoaddition and photoreduction
  - (d) Paternobuchi reaction
- ***Norrish type I reaction:***

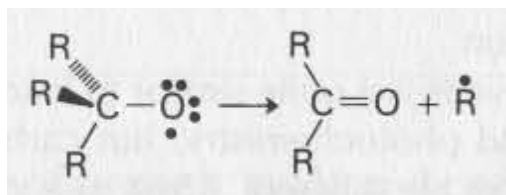
→  $\alpha$  cleavage

→ most readily in vapour phase

→ in initial primary process, a diradical is formed e.g. a  $n-\pi^*$  excited aliphatic carbonyl.

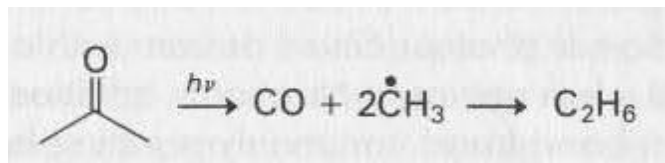


→ the ready cleavage ( $n-\pi^*$ ) excited state at alpha bond to generate acyl radical and alkyl radical parallel with cleavage of alkoxy radical which has an unpaired electron in a non bonding orbital of oxygen which breaks down to ketone and alkyl radical.

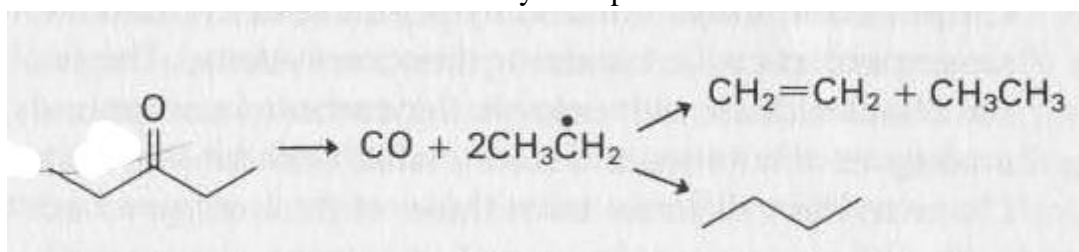


→ for acyclic saturated ketones, the outcome of alpha cleavage is generally loss of carbon monoxide, by the cleavage of acyl radical, so that either the alkyl may undergo combination to form alkane or disproportionation.

Photolysis of acetone



Photolysis of pentan-3-one

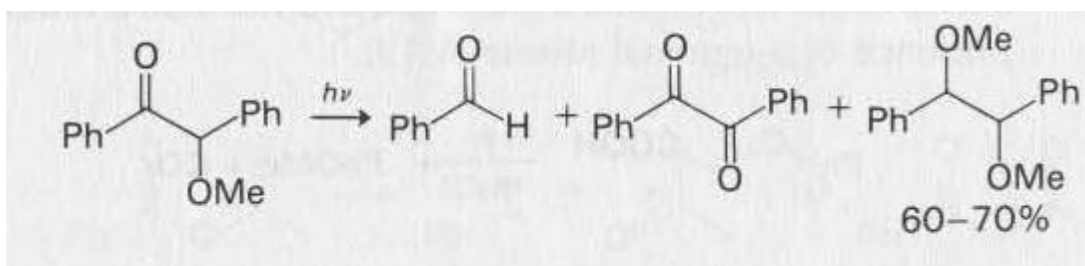
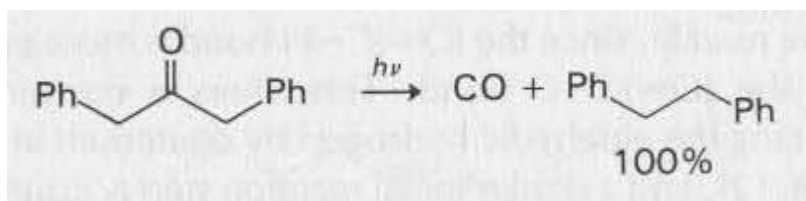
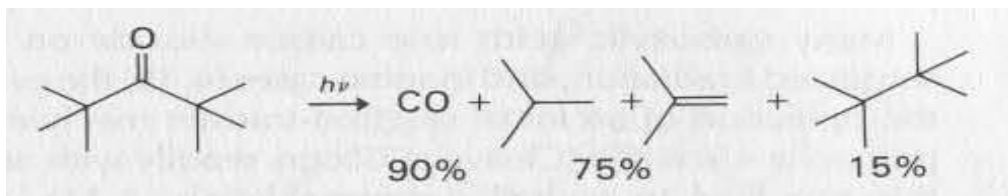


→ There is a fine balance of energy in cleavage step of these ketones. At lower temperature less vibrational energy or in liquid phase more vibrational deactivation takes place and decarbonylation reduced. That's why acetone is used as solvent for photochemical reaction at room temperature.

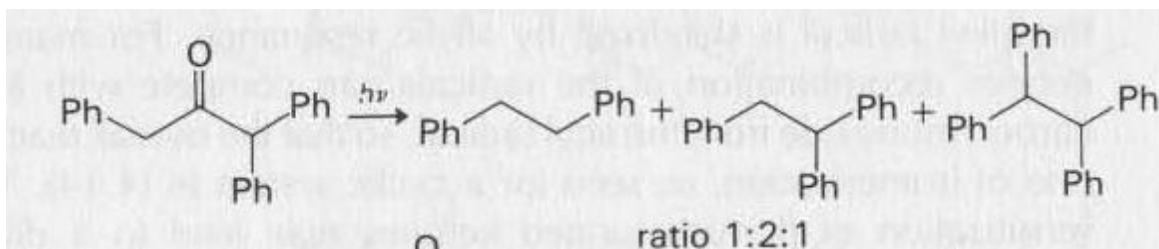
→  $\alpha$  cleavage for ketones in solutions at room temperature can be promoted if structural factor can cause the bond a little bit weaker than normal.

→ for example tertiary alkyl ketones undergo cleavage readily

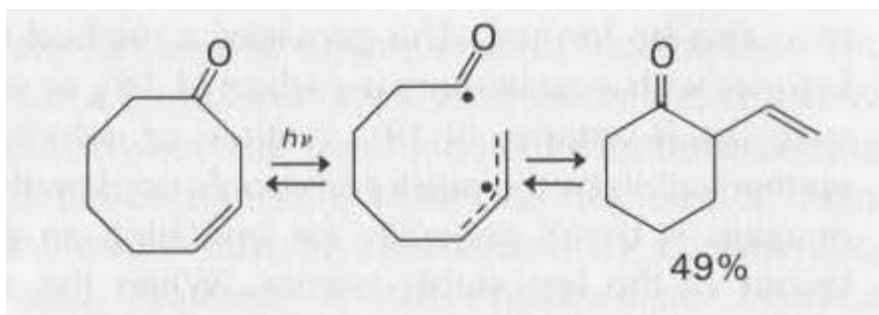
→ since excited energy states of diaryl ketones and simple alkyl aryl ketone do not undergo fragmentation on irradiation in solution even at high temperature. This photostability factor makes benzophenone or acetophenone a good triplet sensitizer.



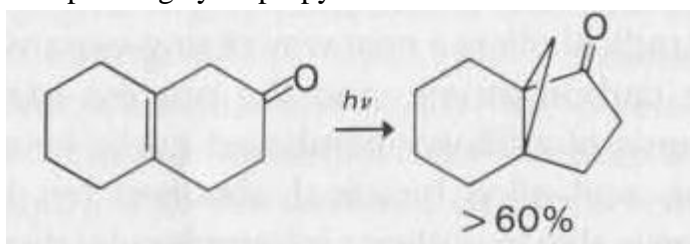
→ the use of an unsymmetrical ketone also shows that discrete radicals are produced in the cleavage reaction, since the formation of hydrocarbons suggests random combination of radicals



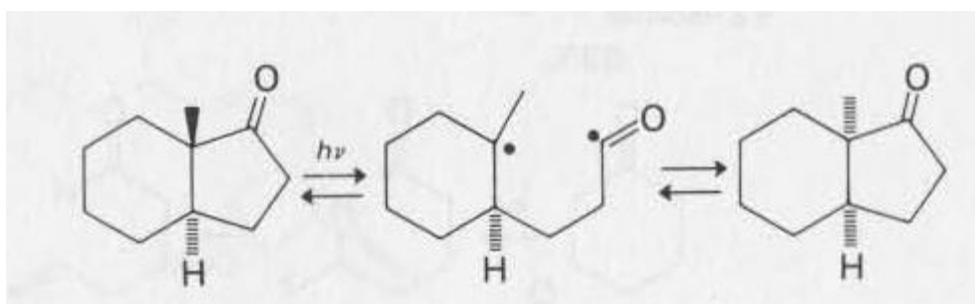
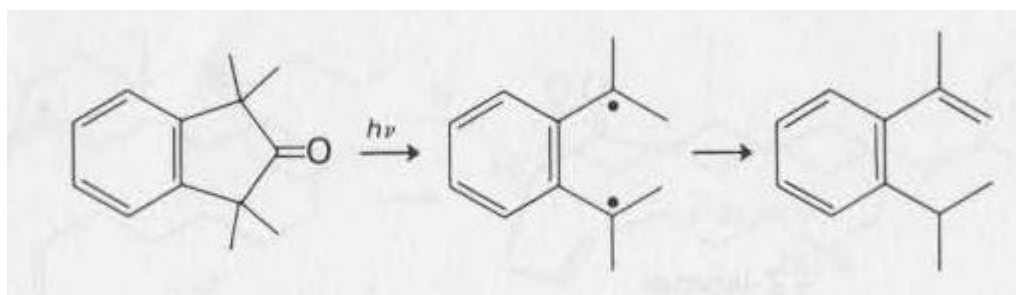
→  $\beta$ - $\gamma$  unsaturated ketones promotes  $\alpha$  cleavage because alkyl radicals get stabilised by allylic resonance. The recombination can compete with decarbonylation and forms isomer

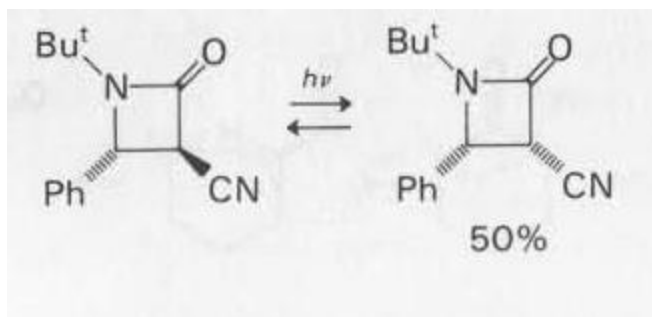


→ triplet sensitization of  $\beta$ - $\gamma$  unsaturated ketones may give different products by incorporating cyclopropylketone.

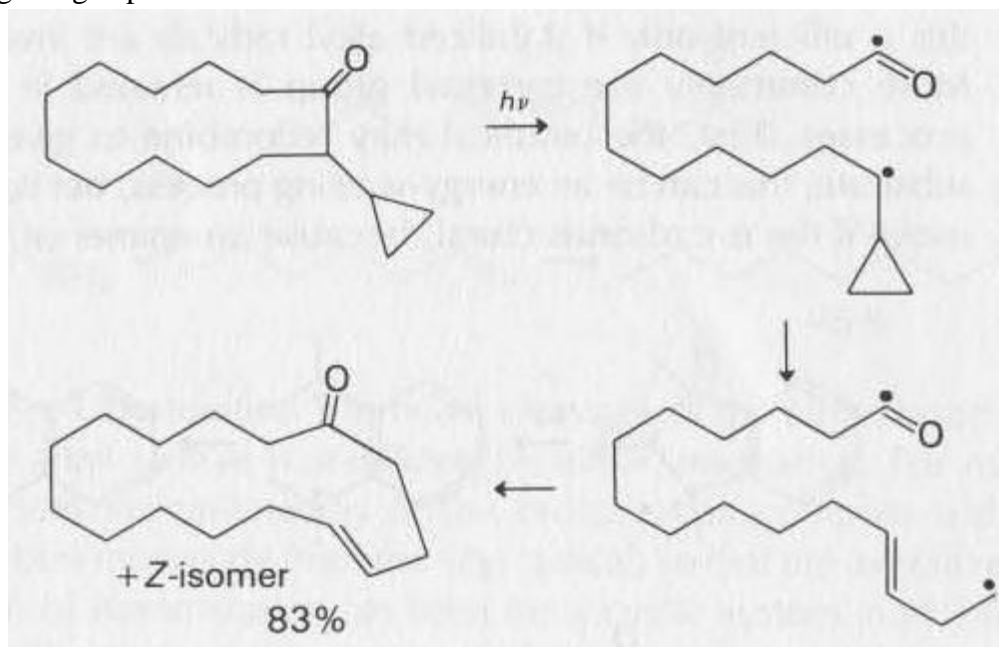


- With saturated and unconjugated cyclic ketones,  $\alpha$  cleavage takes place in solution on irradiation usually in triplet state process. The acyl alkyl biradical can undergo different reactions. Loss of carbonyl takes place if stable alkyl radicals are produced. More commonly carbonyl group is retained. In one out of four processes. First the biradical may combine once again but this is an energy wasting step. But it is useful for chiral carbons as it produced epimer. E.g sensitive  $\beta$  lactams

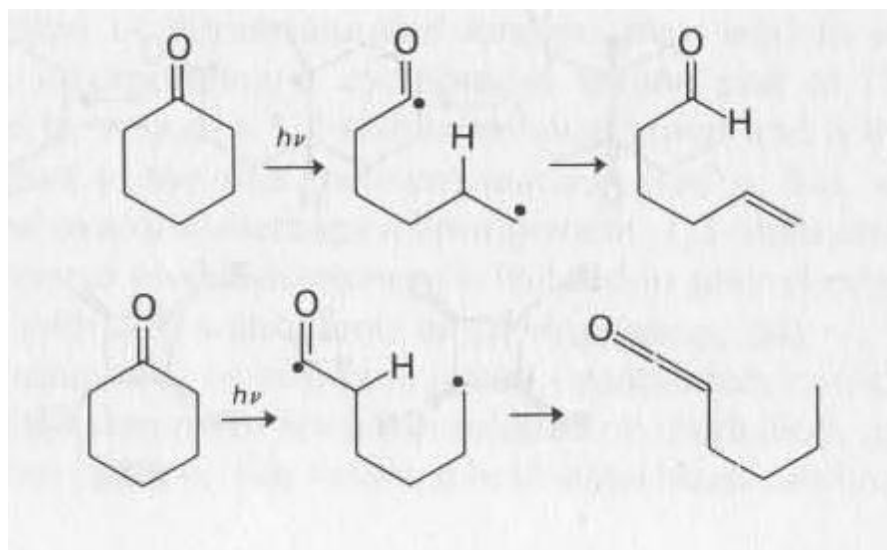




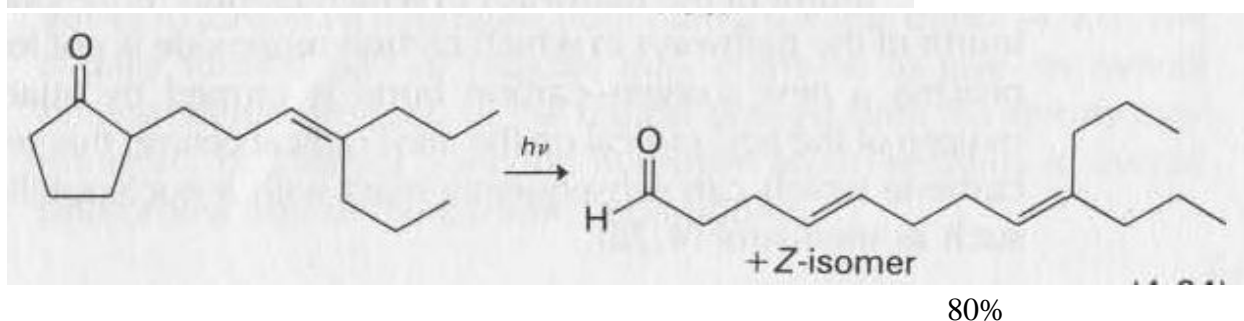
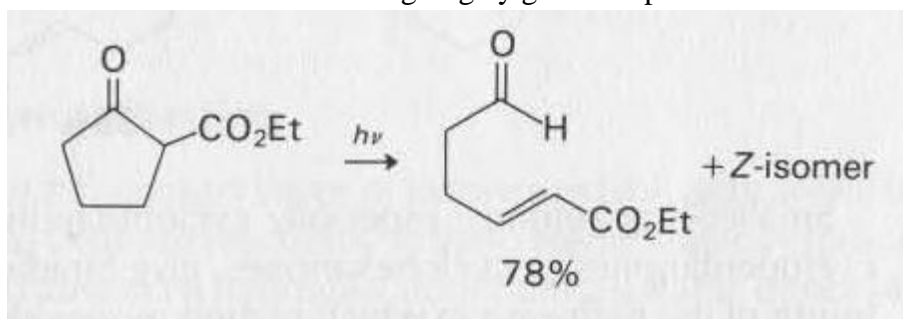
- When a cyclic ketone carries a cyclopropyl ring, the diradical obtained on irradiation undergo ring expansion to three carbons.



- For cyclic ketones, the biradical obtained after  $\alpha$  - cleavage undergo intramolecular rearrangement in two ways. Firstly, hydrogen radical get transferred from adjacent carbon to alkyl radical to carbonyl radical to form aldehyde with one double bond & alternately, hydrogen get transferred from carbon adjacent to acyl radical carbon to alkyl radical to form ketene.

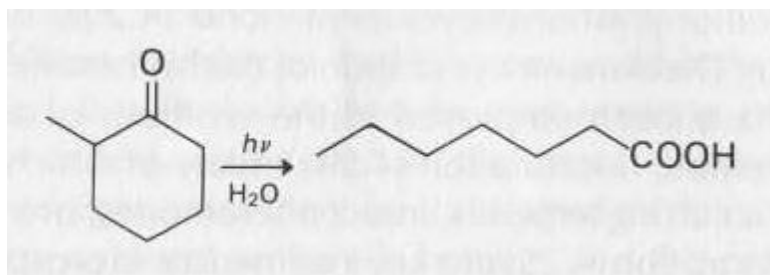


Many ketenes are labile and the use of nucleophilic solvent or addend, such as water, alcohol or amines to get entrapped and form carboxylic acid, ester or amides respectively. The competition between the two modes depends on – ring size and position of substituent. Five membered ring largely gives the product unsaturated aldehyde.

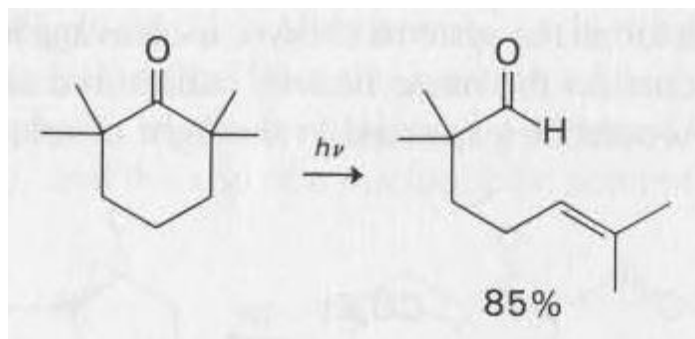


**Note :** for all the systems  $\alpha$  cleavage in ketone take place from the side which is highly substituted.

- Ketene formation is most important with six membered ketone  
2- alkyl hexanone give straight chain carboxylic acid by formation of ketene on irradiation in the presence of water



If ketene formation is prevented due to structural factor, it will form unsaturated aldehyde.



Smaller cyclic ketone, e.g cyclobutanone the biradical is formed and no loss of carbon monoxide takes place. The oxygen of carbonyl group attacks alkyl radical to form ring and carbene which undergo reaction with nucleophilic solvents such as methanol.

