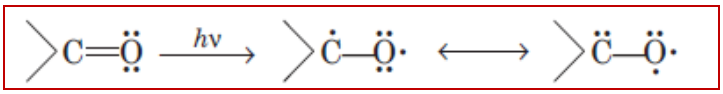
Photochemistry of carbonyl compounds

The photochemical reactions of carbonyl group is initiated by $n \rightarrow \pi^*$ transition. Promotion of an electron will lead to either a singlet state or a triplet state. Photochemical reactions given by carbonyl group takes place either by singlet state or by triplet state or by both states.



Carbonyl compounds give four type of reactions. These reactions include:

(*i*) α - Cleavage

(*ii*) β - Cleavage

(*iii*) Intramolecular and intermolecular hydrogen abstraction by carbonyl oxygen.

(*iv*) Addition of carbonyl oxygen atom to a carbon-carbon multiple bond.

α – CLEAVAGE or NORRISH TYPE I PROCESS

Norrish type I process is given by three type of ketones:

(*i*) Saturated acyclic ketones.

(*ii*) Saturated cyclic ketones.

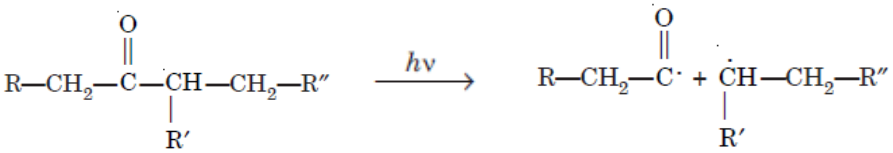
(*iii*) β, γ -Unsaturated ketones./ β,γ – unsaturated ketones/ Oxa DPM rearrangement

Norrish Type I Process Given By Acyclic Saturated Ketones

Saturated carbonyl compounds undergo photoinduced decarbonylation in the gas phase. This process was first observed by R.G.W. Norrish and is known as Norrish Type I or α-cleavage process. Norrish Type I process is commonly encountered in the gas phase.

Primary Processes

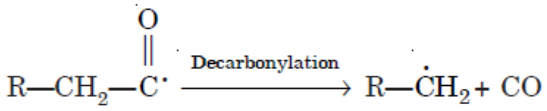
Norrish Type I process is characterised by initial cleavage of the carbonyl carbon and *alpha* carbon bond to give an **acyl** and an **alkyl** radicals. This process is known as primary photochemical process.

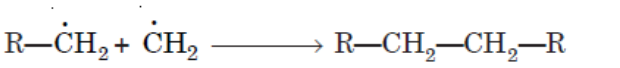


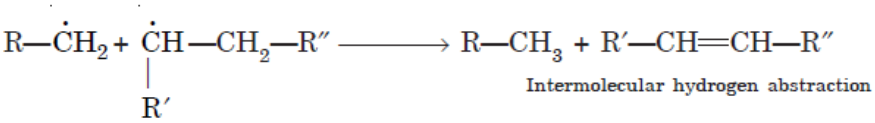
The initially formed acyl radical is stabilised by one of the secondary processes. Similarly the alkyl radical can be stabilised by recombination or disproportionation.

Secondary Processes

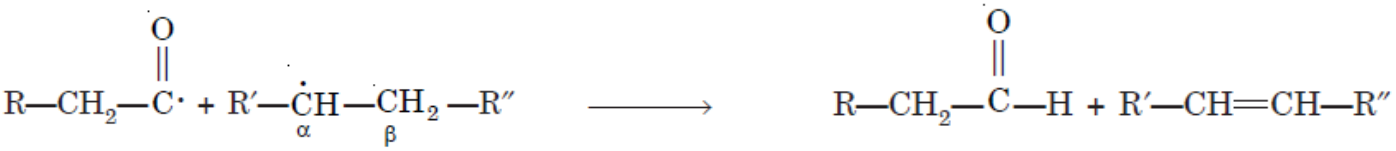
(*a*) Decarbonylation of acyl radical to give carbon monoxide and an alkyl radical. This alkyl radical can recombine to give an alkane or can undergo intermolecular hydrogen abstraction to form an alkane and an alkene





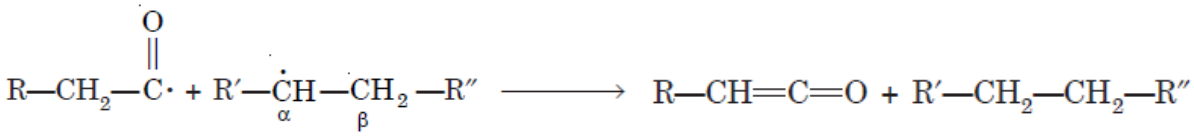


(*b*) Intermolecular hydrogen abstraction by the acyl radical from the alkyl radical to give an aldehyde and an alkene

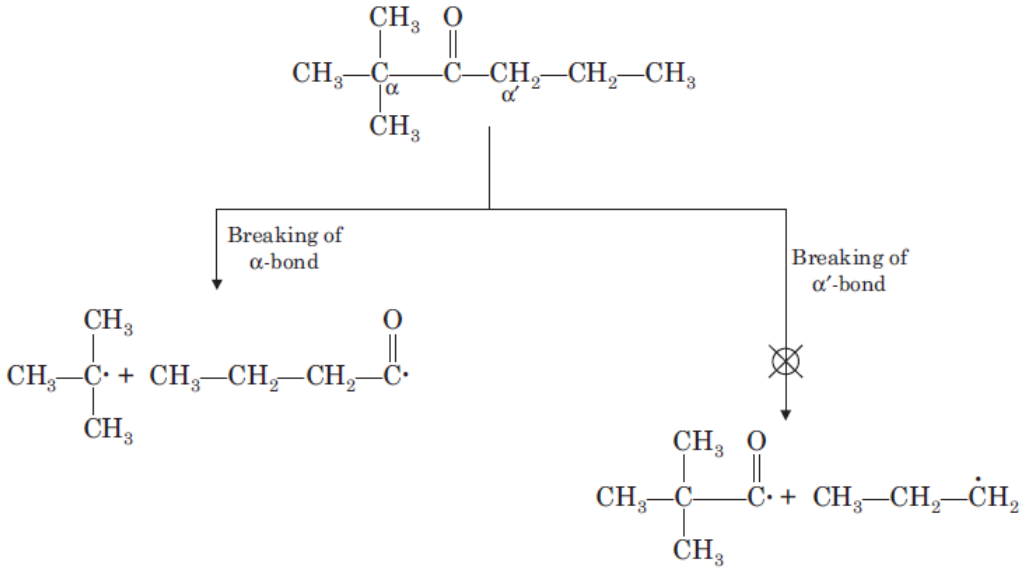


This process can only be possible if alkyl radical has atleast one β-hydrogen.

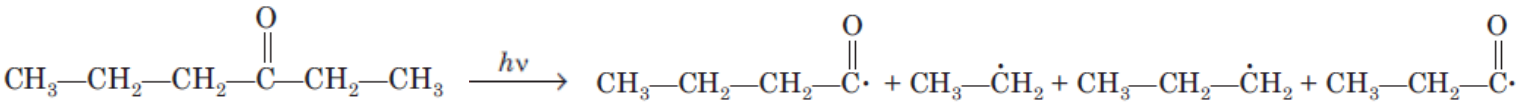
(*c*) Intermolecular hydrogen abstraction by the alkyl radical from the α-carbon of the acyl radical to form a ketene and an alkane



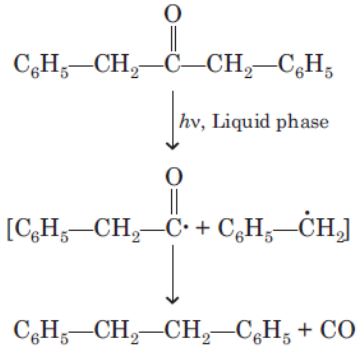
In Norrish Type I reactions there is a preference for the formation of most stable alkyl radical in case of unsymmetrical ketones (Rexn next page)



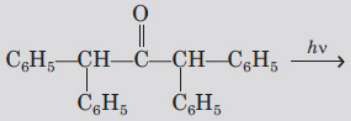
In the above case, only α - bond undergoes cleavage. If both alkyl substituents are same then there is little selectivity of bond cleavage.



Norrish Type I process is efficient in liquid phase only if a stable radical is formed. The stable radical includes allylic, benzylic, *tert* alkyl and acyl radicals.

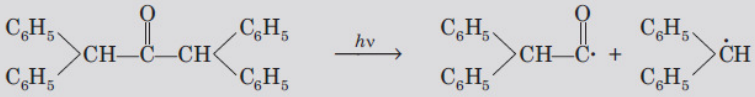


Problem 1: *Complete the following Norrish Type I reaction:*



Solution: Compound is saturated acyclic ketone. It will give Norrish Type I process in gases as well as in solution phase.

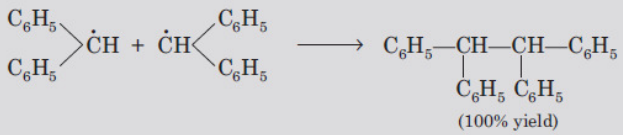
Primary process:



Secondary process:

(*i*) Decarbonylation

(*ii*) Recombination



(100% yield)

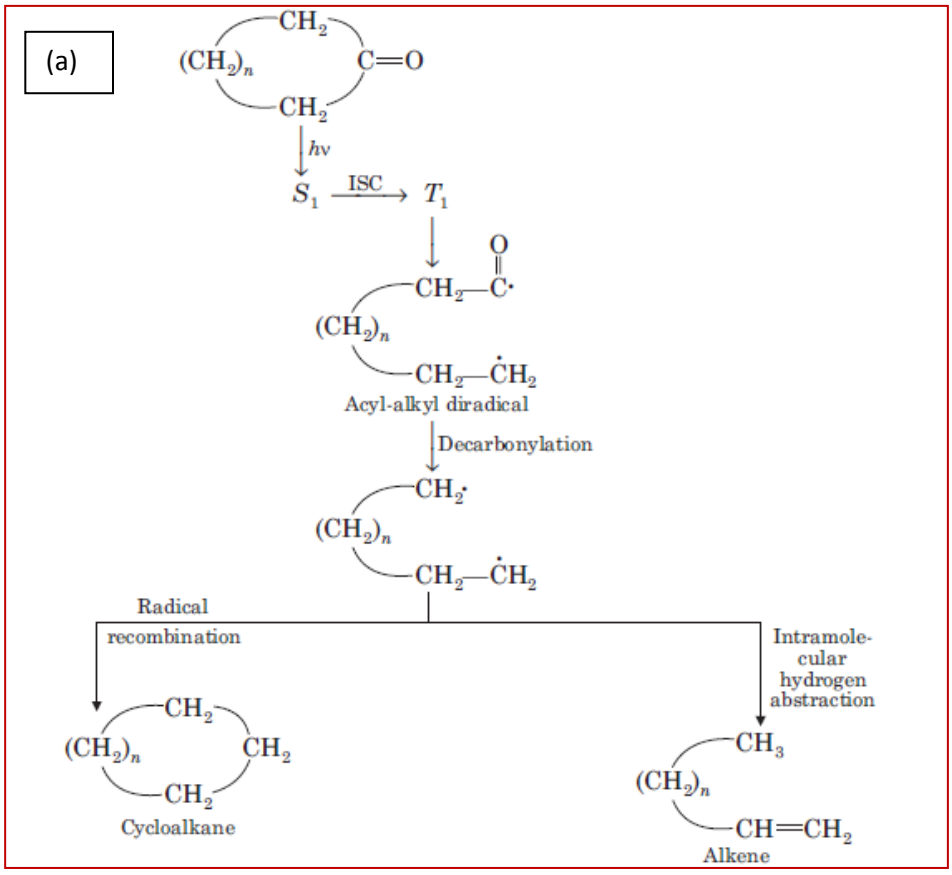
Norrish Type I Reaction of Saturated Cyclic Ketones

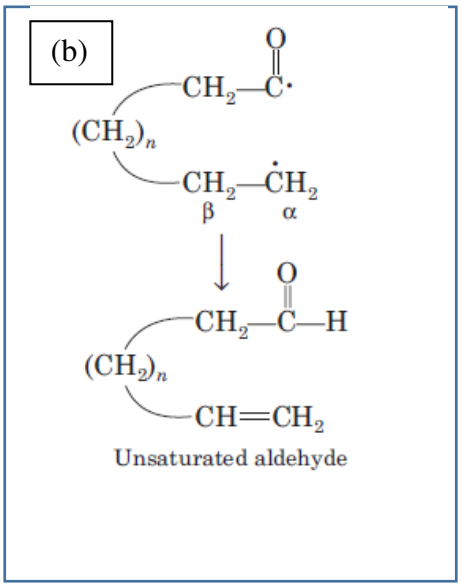
Norrish Type I process involves the initial cleavage of a carbonyl carbon-*alpha* carbon bond. Subsequent

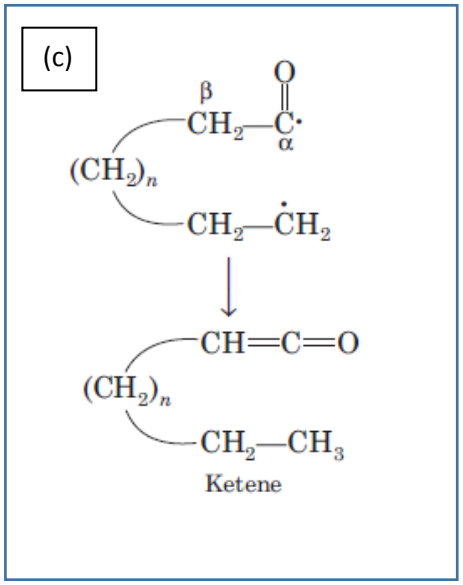
(*a*) Decarbonylation of acyl-alkyl diradical to give carbon monoxide and a dialkyl radical. The dialkyl radical can recombine to give a cycloalkane or it undergoes intramolecular hydrogen abstraction to form an alkene.

(*b*) Intramolecular hydrogen abstraction by the acyl radical from the β-carbon of the alkyl radical to give an unsaturated aldehyde

(*c*) Intramolecular β-hydrogen abstraction from the acyl radical by the alkyl radical to produce a ketene

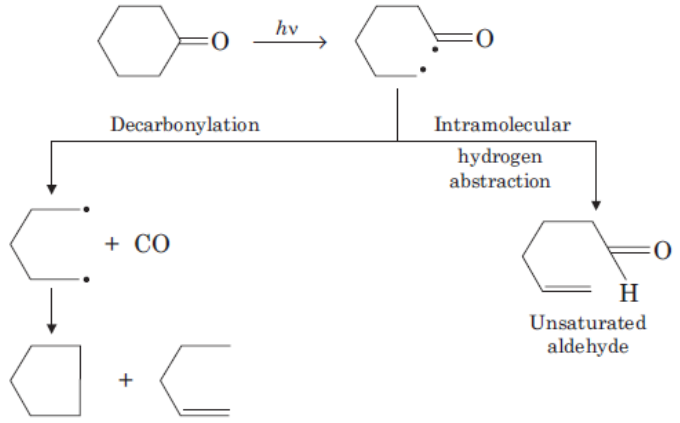




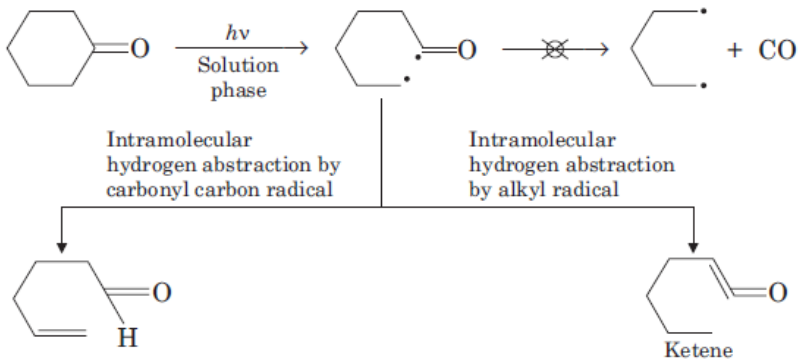


The biradical of cyclic ketones can undergo one of the two hydrogen transfer processes [(*b*) and (*c*)] *via* a cyclic transition state in which a hydrogen atom is transferred to one radical centre from the atom adjacent to other radical centre.

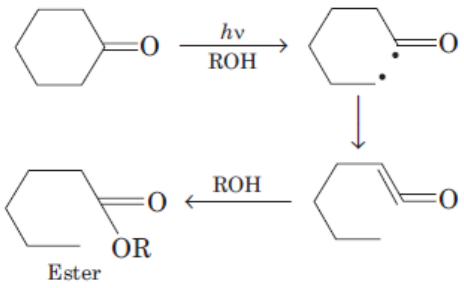
Photolysis of cyclic ketones in gases phase gives decarbonylation as well as intramolecular hydrogen abstraction. Intramolecular hydrogen abstraction mainly leads the formation of unsaturated aldehyde.



In solution phase biradical pair is not usually stabilised by decarbonylation. In this case, biradical is mainly stabilised by intramolecular hydrogen atom transfer. This intramolecular hydrogen atom transfer leads to the formation of either unsaturated aldehyde or a ketene or both.

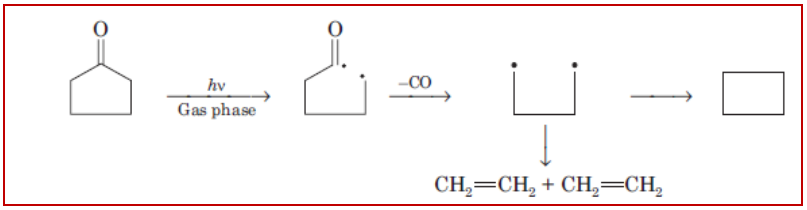


When photolysis is carried out in the presence of polar protic solvent than the main species is ketene. This ketene than undergoes solvent addition to give carboxylic acid (with water) or its derivative (ester with alcohol) as the only product.



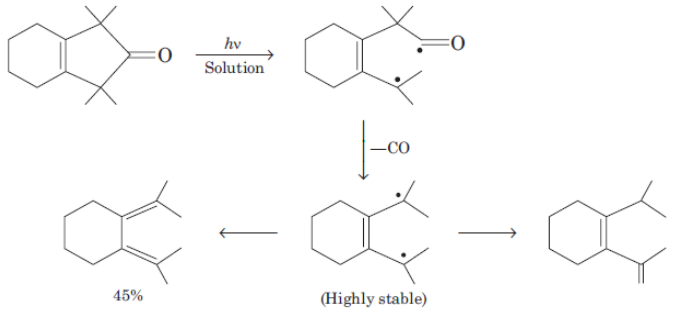
Norrish Type I Process Given by Cyclopentanones

Cyclopentanone also decarbonylates on irradiation in the gas phase. In this case also a two step process is involved, affording a biradical which decarbonylates to another biradical, which either fragment to ethylene or undergoes bond formation to cyclobutane. Fission to ethylene is much more efficient in comparison to cyclobutane formation.

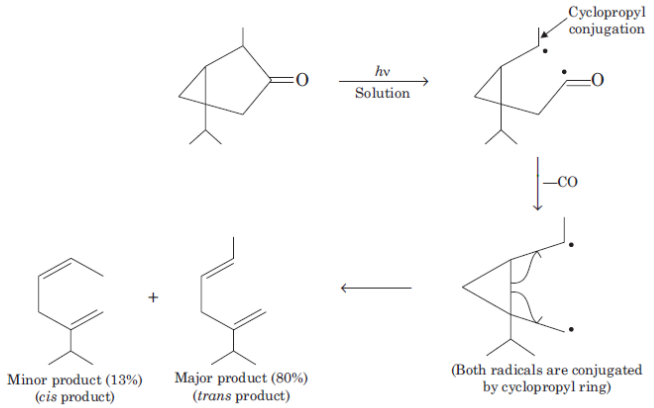


In solution the loss of carbon monoxide from a cyclopentanone is a major path only when the radical centres formed are stabilised by alkyl substitution, double bond or cyclopropyl ring.

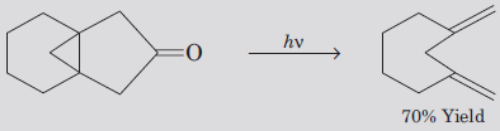
(a)



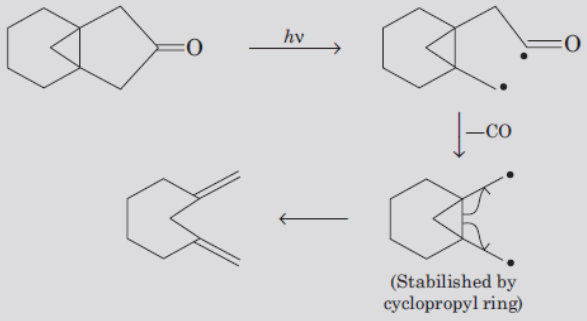
(b)



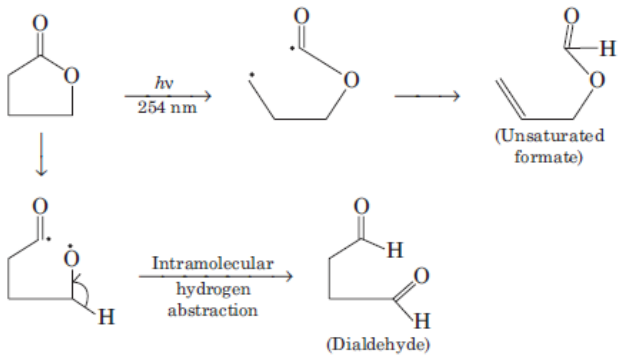
Problem 5: *Give mechanism of the following transformation:*



Solution:



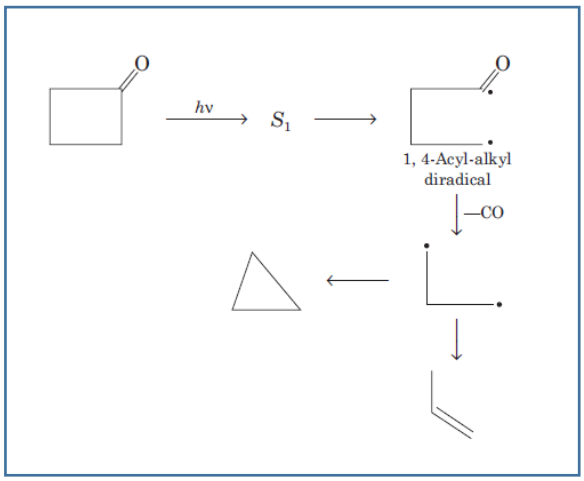
α-Cleavage is not given only by cyclic ketones. Other cyclic compounds such as lactones, lactams and cyclic anhydrides undergo α-cleavage to give a biradical species on photolysis in gas or solution phase.



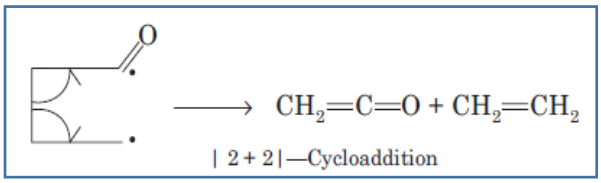
α – Cleavage Given by Cyclobutanones:

There are three following different pathways for stabilisation of the diradical:

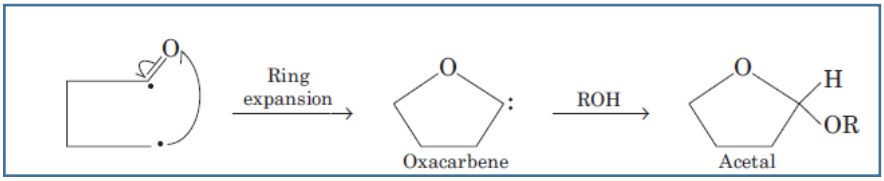
(i) Loss of carbon monoxide and formation of 1, 3-diradical that undergoes either recombination to cyclopropane or an hydrogen abstraction to form propene.



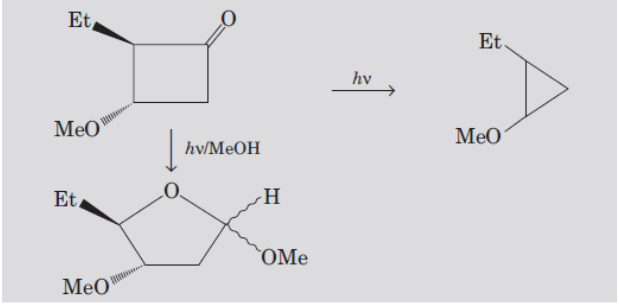
(*ii*) By a subsequent β-cleavage and formation of ethylene and ketene.



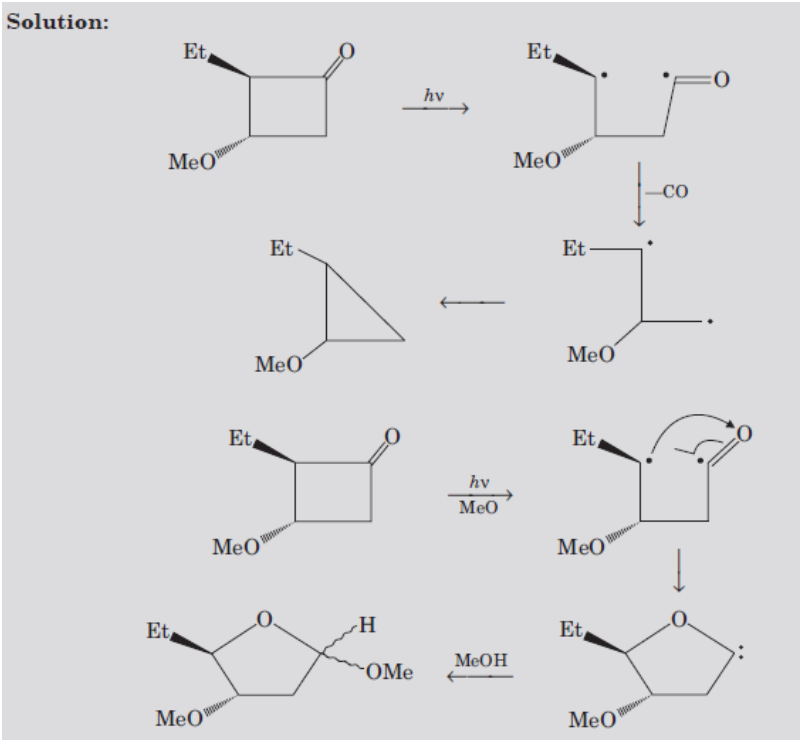
(iii) 1, 4-Acyl-alkyl biradical can undergo ring expansion by rebonding to oxygen to give **oxacarbene.** This carbene can be trapped by polar protic nucleophile solvents. The over all reaction is a ring expansion.



Give mechanism of the given reaction:



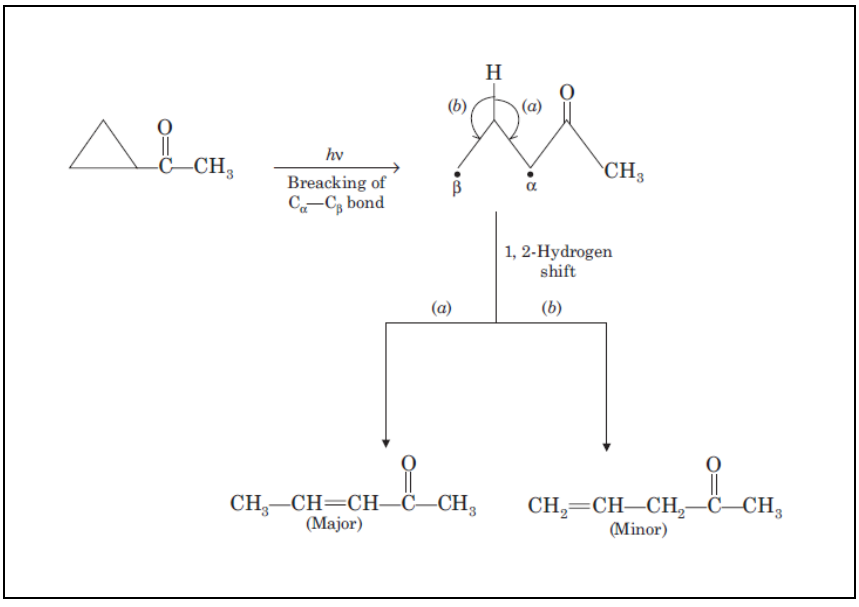
Solution:



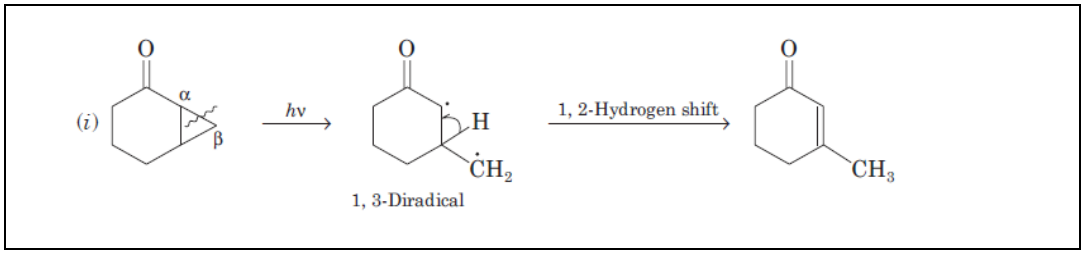
β – CLEAVAGE REACTION

Some compounds have relatively weak Cα—Cβ bonds which can undergo cleavage as a result of electronic excitation of the carbonyl group. The mechanism of the reaction has been shown to involve the formation of a biradical intermediate.

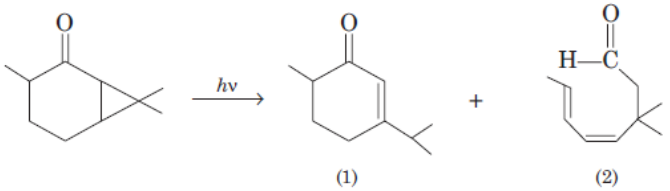
(a) Photolysis of acetylcyclopropane leads to Cleavage of cyclopropane ring, and this is followed by a hydrogen shift.



(b) Bicyclo [4, 1, 0] heptane-2-ones undergo cleavage of one of the cyclopropyl C—C bonds.

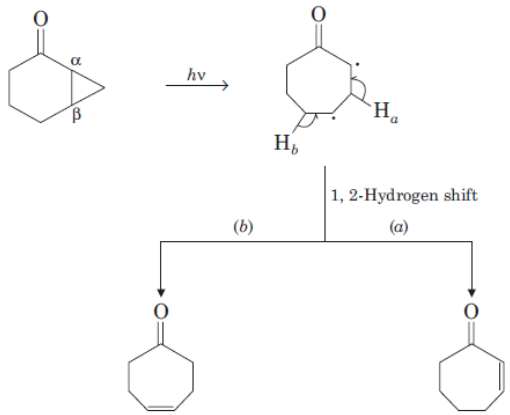


(c)

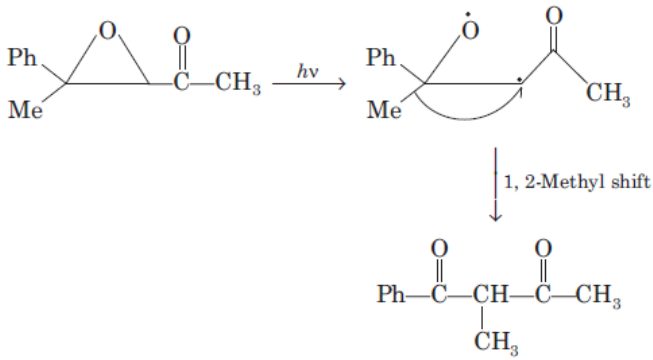


β-cleavage α - cleavage

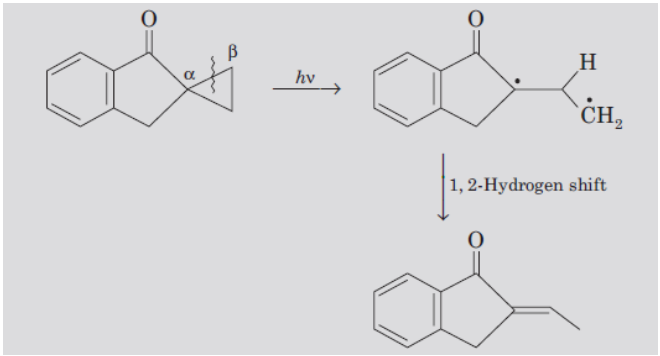
(d)



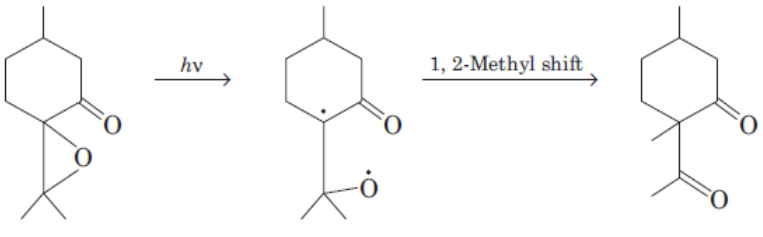
(e)



(g)

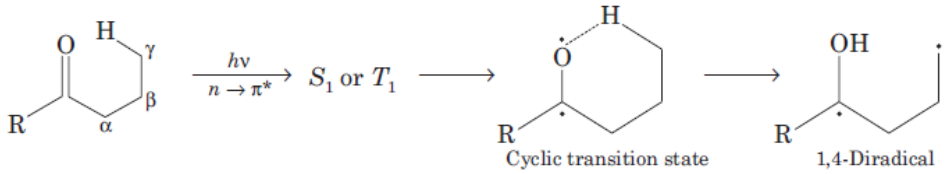


(f)



INTRAMOLECULAR HYDROGEN ABSTRACTION (γ – HYDROGEN ABSTRACTION)

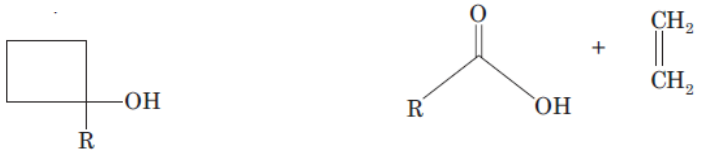
1, 3 (n, π*) excited carbonyl compounds having an accessible hydrogen atom in the γ-position undergo a characteristic 1, 5-hydrogen atom transfer by an intramolecular cyclic process with the formation of ketyl like 1, 4-diradical.



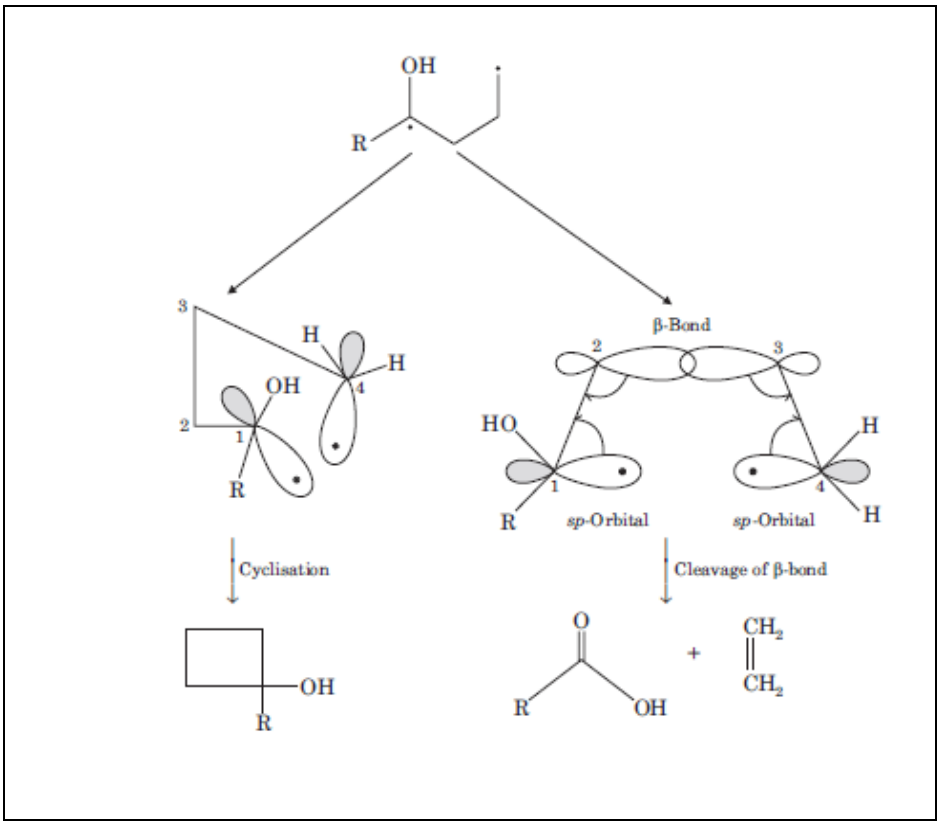
Depending on the conformation of the initially formed 1, 4-diradical, two different pathways to stabilisation are possible:

(*i*) If only the *sp*-orbitals of the radical centres can overlap, a cyclobutanol is the product.

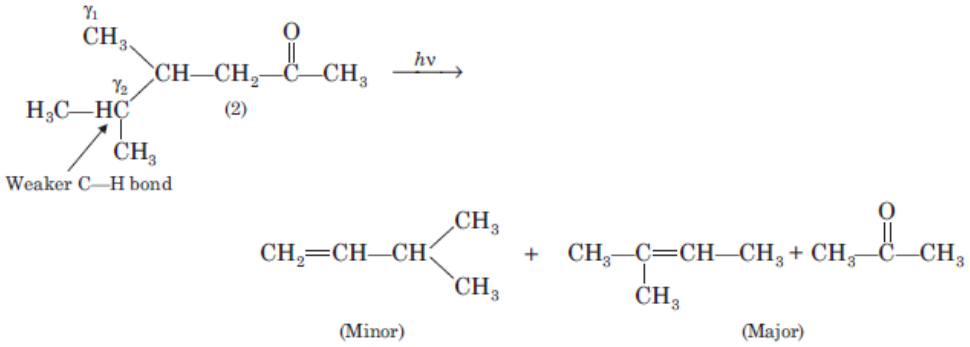
(*ii*) If the *sp*-orbitals of the radical centres are parallel to the β-bond, they participate in the formation of two double bonds (one in the enol and one in the alkene), a result of the cleavage of the β-bonds.



Cyclobutanol enol and alkene

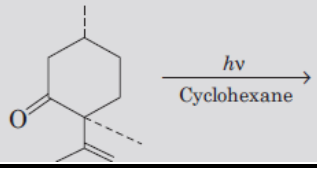


When a molecule has two γ-carbons both having hydrogens, transfer of hydrogen in the Norrish Type II process is marked by a preference of cleavage of the weaker carbon-hydrogen bond as in case of ketone

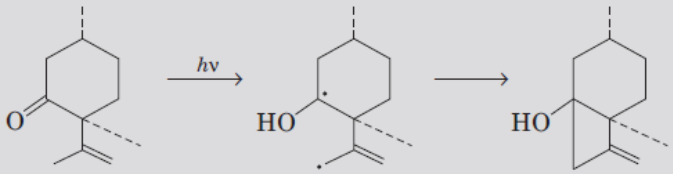


Examples:

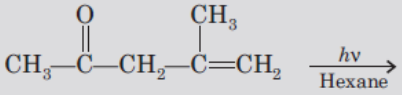
Complete the following:



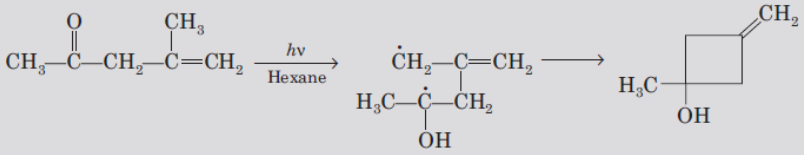
Solution: Compound has hydrogen on γ-carbon which is an allylic carbon. Hence 1, 4-diradical has allylic character. This will lead the cyclisation.



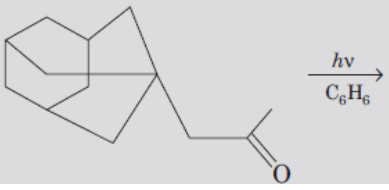
Complete the following reaction:



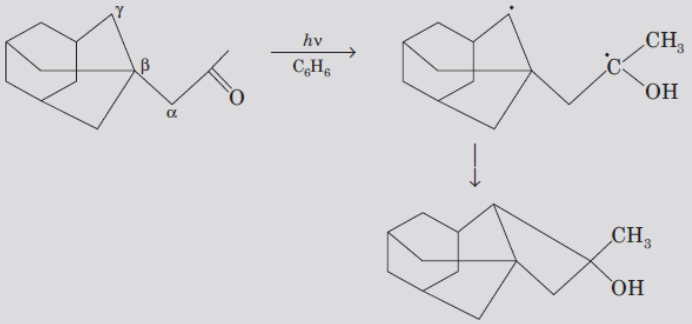
Solution: γ-Carbon is allylic carbon, hence 1, 4-diradical will be allylic free radical. Thus cyclisation will be main reaction.



Complete the following reaction:

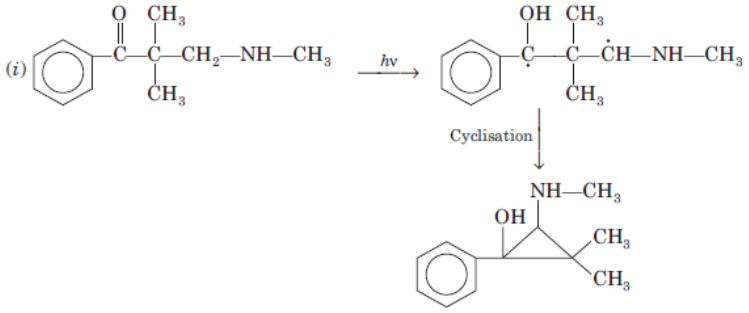


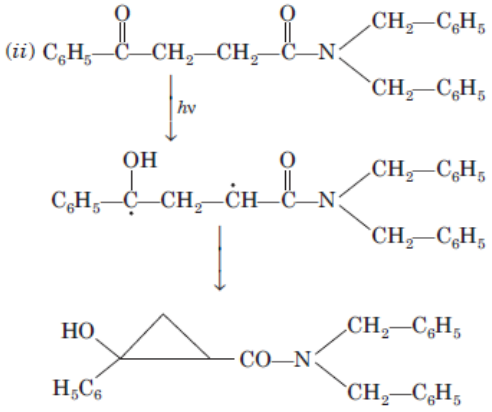
Solution: Compound has rigid geometry and has hydrogen on γ-carbon, hence reaction should be cyclobutanol formation.



β-Hydrogen abstraction

β-Hydrogen abstraction can only be possible if substrate has no γ-hydrogen and the biradical is stabilised by the presence of hetero atoms.

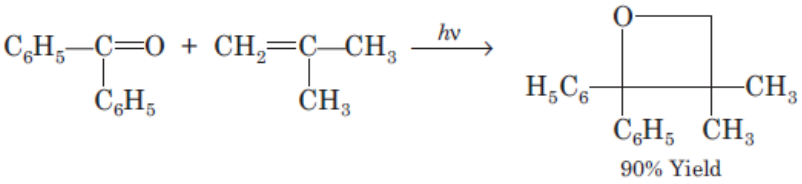




Photocycloaddition reaction (Paterno-Büchi reaction)

Formation of oxetanes from addition of carbonyl compounds to alkenes in presence of photolight is known as the Paterno-Büchi reaction.

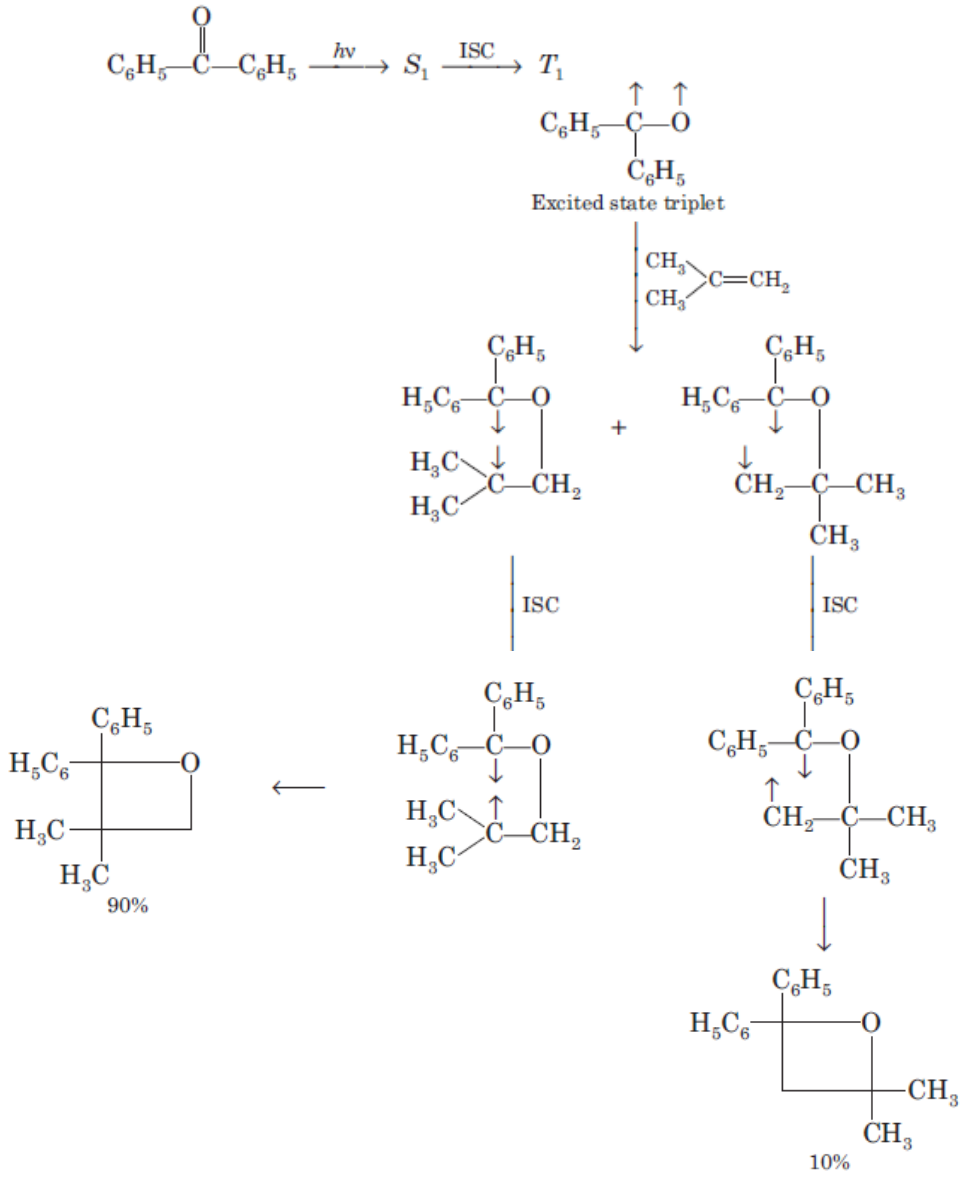
Example: Benzophenone with isobutene gives a high yield of an oxetane.



Paterno-Büchi reaction can be studied under two categories and the categories depend on the nature of alkenes.

1. Addition to Electron Rich Alkenes:

Reaction pathway varies according to the type of carbonyl compound and alkenes involved. Addition of simple aliphatic or aromatic ketones to electron rich alkenes involves attack on ground state alkene by the $n \rightarrow \pi^*$ triplet state of the carbonyl compound in a non-concerted manner, giving rise to all possible isomers of the oxitane. The reaction is non-concerted because the reactive excited state is a triplet state. The initial adduct of this reaction is a triplet 1, 4-diradical, which must undergo spin inversion before product formation is complete. Stereospecificity is lost if the intermediate 1, 4-diradical undergoes bond rotation faster than ring closure



Two important rules for the successful synthesis of oxitanes have been put forward.

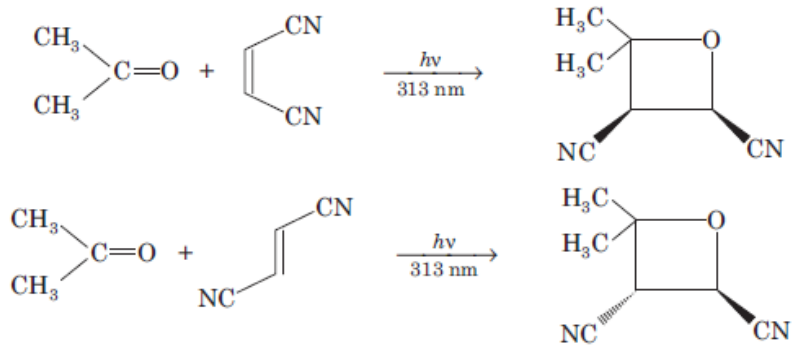
These rules are as follows:

(*i*) Only carbonyl compounds with a low-lying $n \rightarrow \pi^*$ state will form oxitanes.

(*ii*) The energy of the carbonyl excited state must be less than that of the alkene to prevent energy transfer from the carbonyl excited state to the alkene.

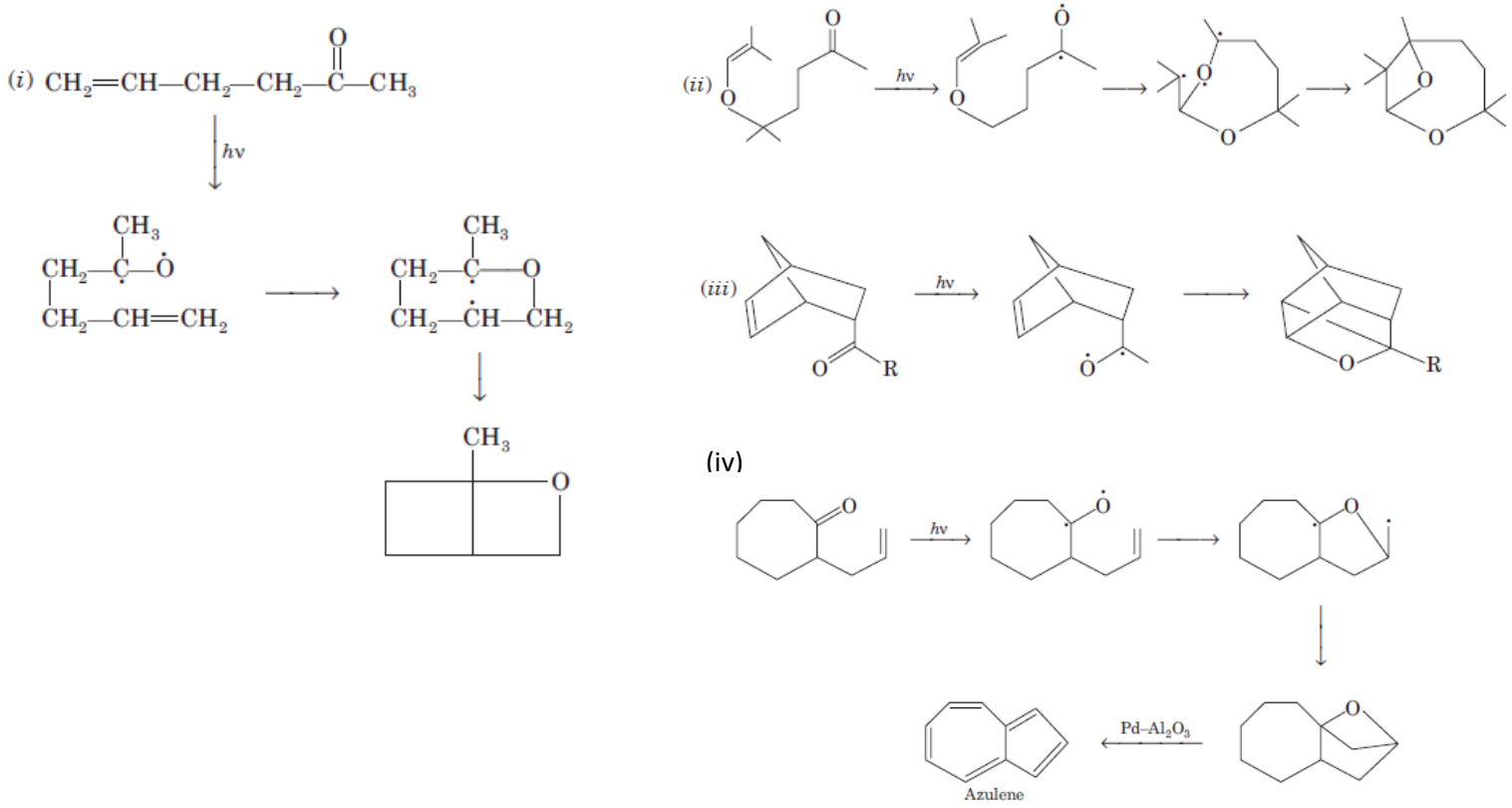
2. Addition to Electron Deficient Alkenes:

Photocycloaddition of aliphatic ketones to electron-deficient alkenes, particularly dicyanoethene, involves addition of singlet state ($n \rightarrow \pi^*$) excited ketone to ground state alkene. The reaction is stereospecific and the stereochemistry of the alkene is retained in the product oxitane.



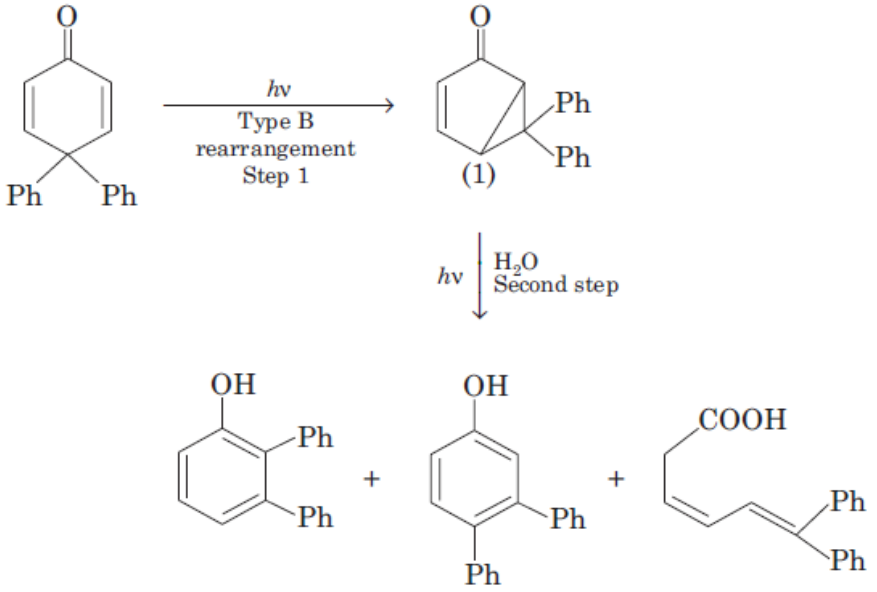
Intramolecular Paterno-Büchi reaction

Intramolecular Paterno-Büchi reaction is mainly given by γ–δ-enones. This reaction is highly efficient and versatile method for the synthesis of variety of compounds that are difficult or impossible to prepare by other methods.

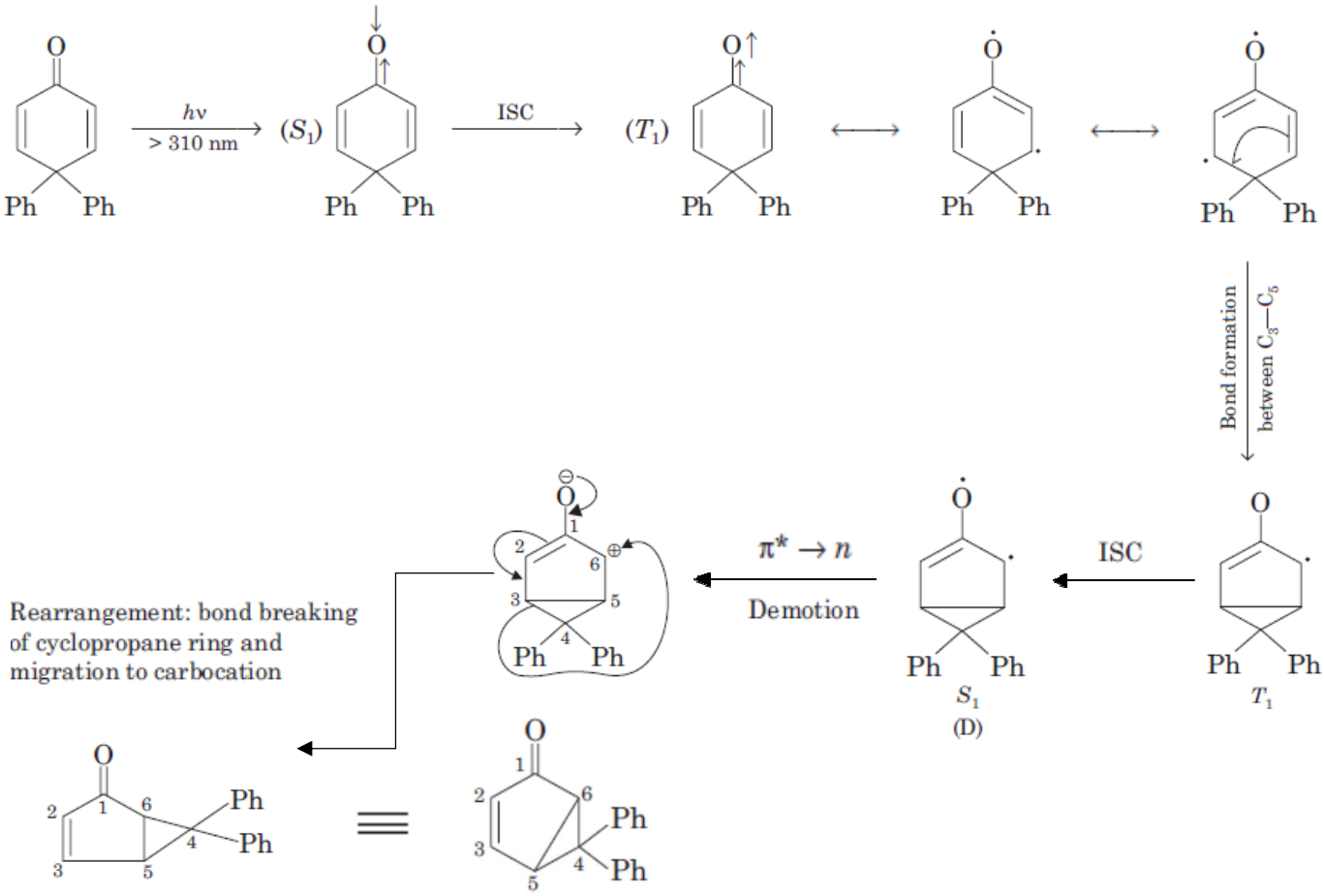


Rearrangement of Dienones:

One of the most important dienones is the cross-conjugated dienones for photochemicalrearrangements. 4, 4-Disubstituted cross-conjugated dienone. Inthe Type B rearrangement of cross-conjugated 4, 4-disubstituted-2, 5-cyclohexadienones, the first photochemical step occurs with a high quantum yield (φ = 0.85). The efficiency of the second step is substantially lower (φ = 0.013).

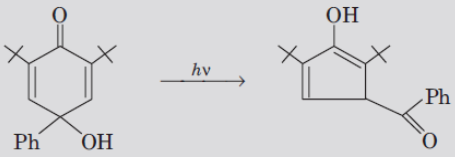


Mechanism:

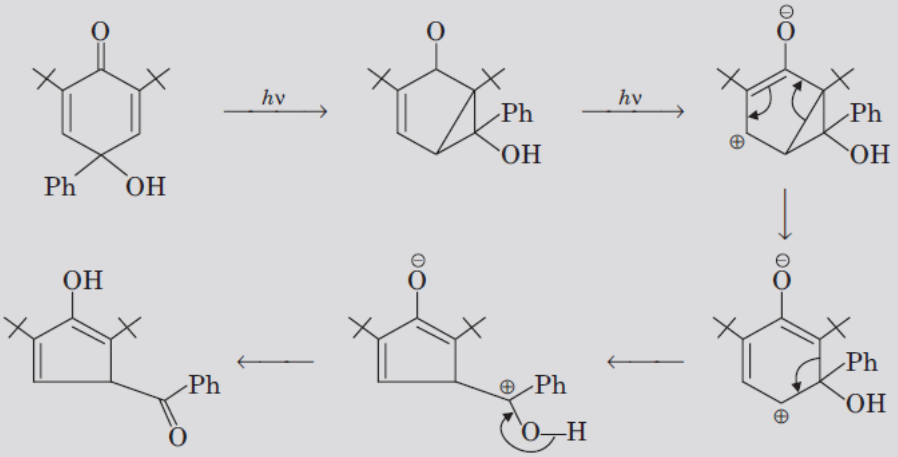


Product of the rearrangement still have enone system capable of undergoing excitation. Hence many other products were obtained.

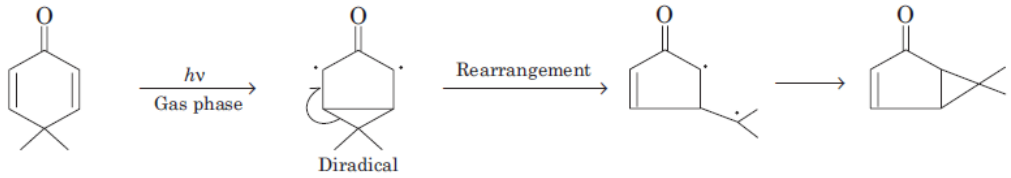
Give mechanism of the given reaction:



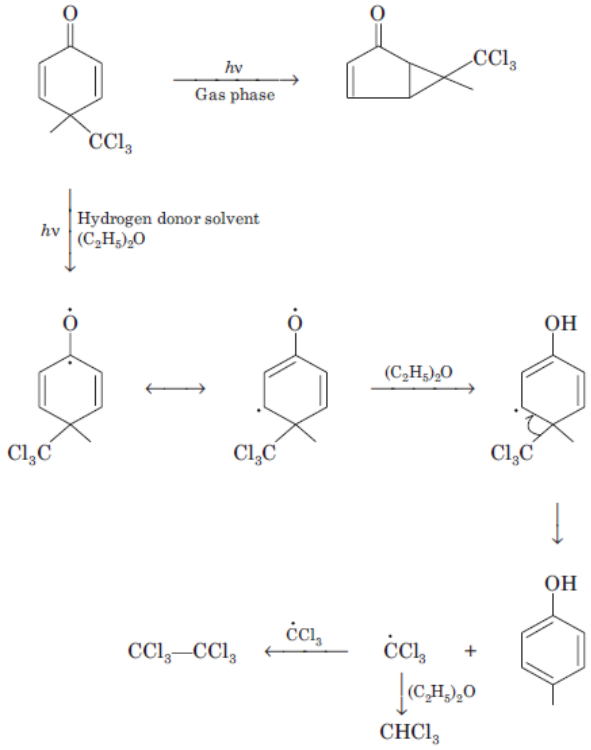
Solution:



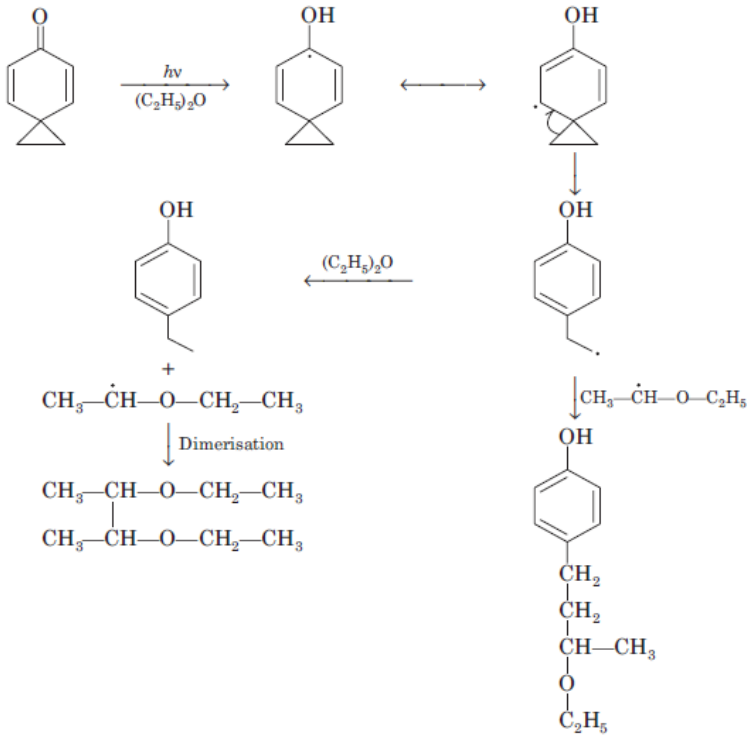
Rearrangement of 4, 4-disubstituted-2, 5-cyclohexadienones undergo rearrangement *via* formation of Zwitterion reaction intermediate in the solution. The rearrangement of these substrates in the gas phase occur *via* formation of biradical intermediates. The rearrangement in gas phase closely resembles the di-π-methane rearrangement.



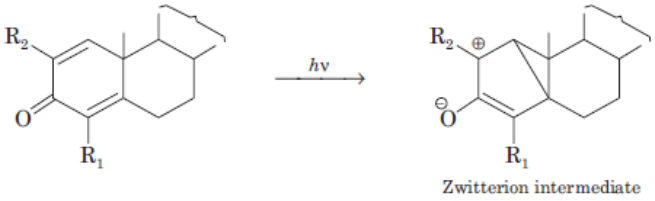
A cyclohexan-2, 5-dienone with a good leaving group on C-4 undergoes a different reaction in solvents with a readily abstracted hydrogen atom. Intermolecular hydrogen abstraction followed by the elimination of the group from C 4 leads a phenolic product.



Radical intermediates are also involved in the photochemical reaction of the spirocyclopropyldienon which is a good source of hydrogen atom.



Natural products particularly terpenoids and steroids having cross-conjugated ketone system undergo dienone rearrangement *via* formation of Zwitterion intermediate.



Zwitterion intermediate

In the presence of dioxane Zwitterion converts into lumiketone.

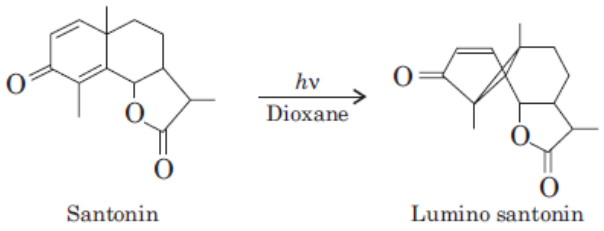
Lumiketone

Photochemistry in Natural Products

Natural products such as santonin and cross conjugated ketone system such as Terpenoids and steroids are best exmples for enone rearrangement.

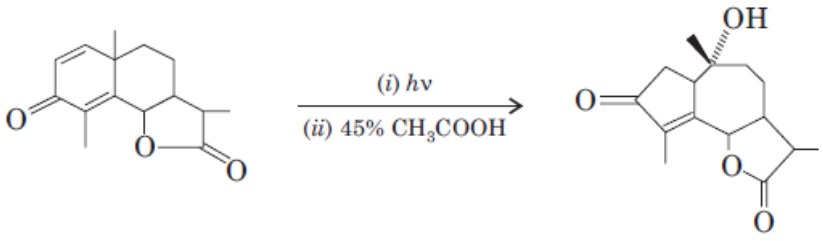
(i) Photoisomerisation of Santonin in Neutral Medium

Santonin in the presence of dioxane gives Luminosantonin



Santonin Lumino santonin

(ii) Photoisomerisation of Santonin in Acidic Medium



Hydroazulenone

(iii) Steroid also gives the above result in the presence of acidic medium