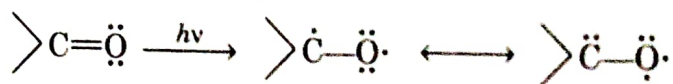


7

CHAPTER

Photochemistry of Carbonyl Compounds

Saturated ketones exhibit four main bands in their ultraviolet absorption spectra. These bands are centered on 280, 195, 170 and 155 nm. The most important band is at 280 nm for the photochemistry of carbonyl group. This band corresponds to the $n \rightarrow \pi^*$ transition. 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.



According to the Kasha's rule, only the lowest excited states will be involved in the primary photochemical or photophysical processes of organic molecules in solution.

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.

In many cases the four processes are competitive and the major process followed is sensitive to structural variations in the ketones and the choice of the solvents.

7.1 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.

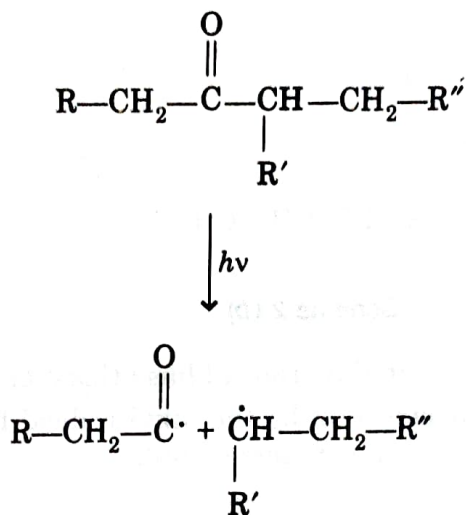
7.1.1 Norrish Type I Process Given by Acyclic Saturated Ketones

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. The solution phase reaction of this type is uncommon.

Primary Processes

Norrish Type I process is characterised by initial cleavage of the carbonyl carbon and α carbon bond to give an acyl and an alkyl radical. This process is known as primary photochemical process (Scheme 1).

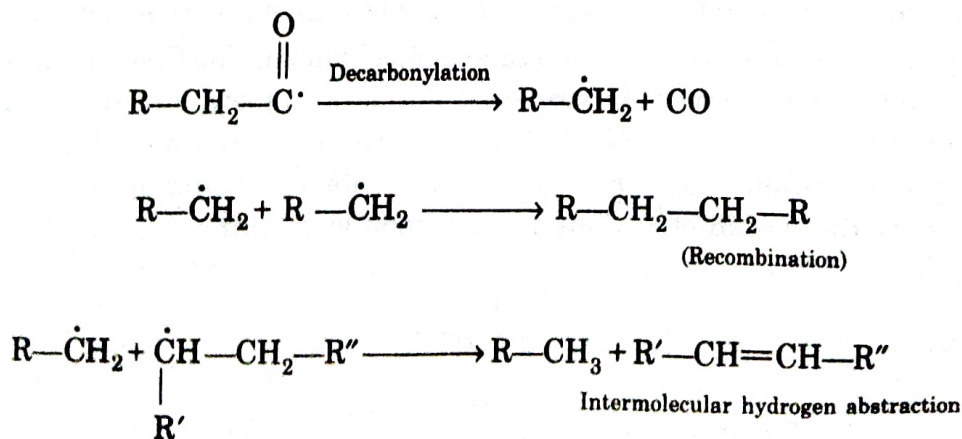


Scheme 1: Primary process

The initially formed acyl radical and alkyl radical is stabilised by one of the secondary processes [(a) – (c)] shown in the Scheme 2. Similarly the alkyl radical can be stabilised by recombination or disproportionation (Scheme 2).

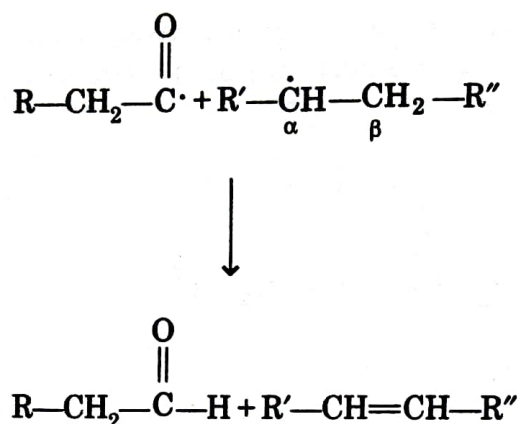
Secondary Processes

(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 [Scheme 2(a)].



Scheme 2 (a)

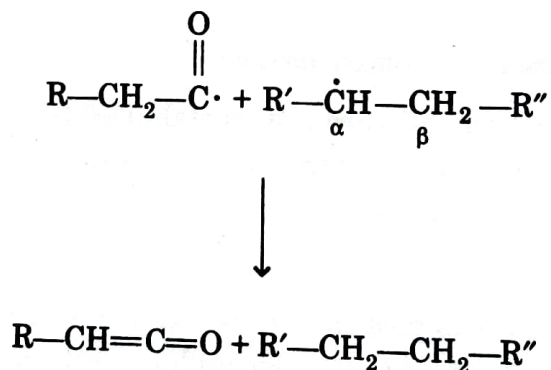
(b) Intermolecular hydrogen abstraction by the acyl radical from the alkyl radical to give an aldehyde and an alkene [Scheme 2(b)].



Scheme 2 (b)

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

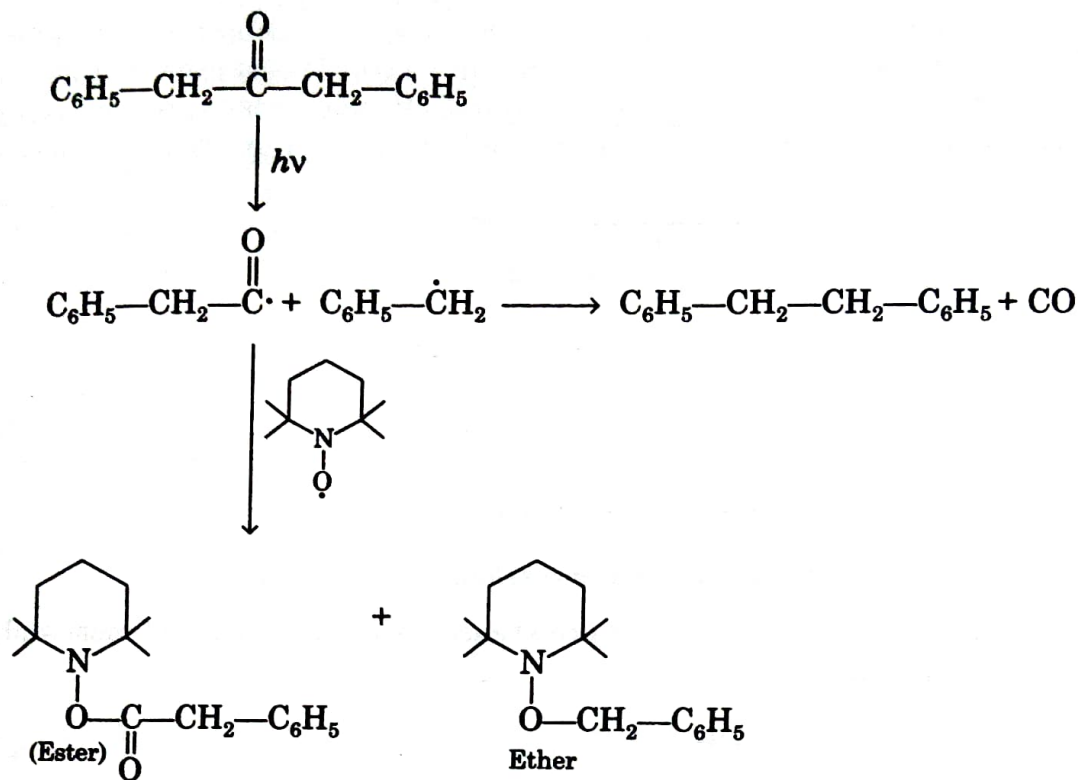
(c) Intermolecular hydrogen abstraction by the alkyl radical from the α -carbon of the acyl radical to form a ketene and an alkane [Scheme 2 (c)].



Scheme 2 (c)

The main secondary reaction of saturated acyclic ketones is decarbonylation.)

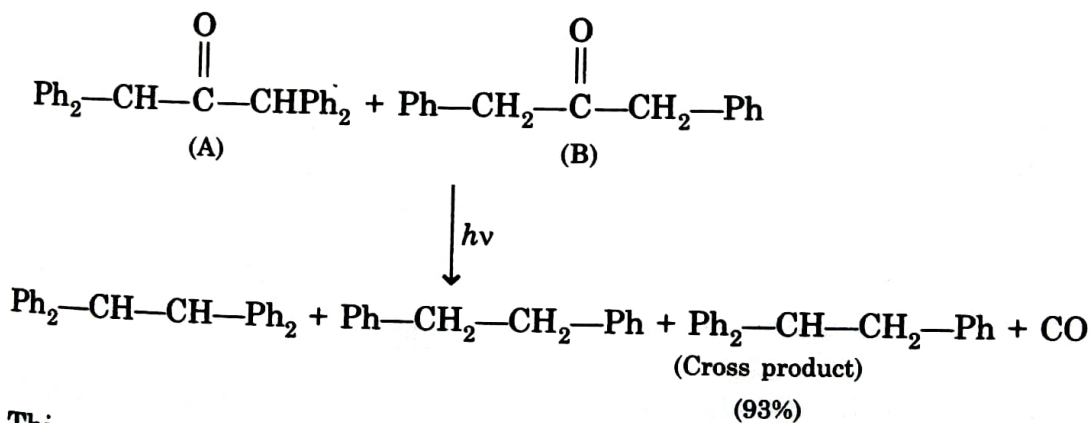
Norrish Type I process is thus a two step radical mechanism. The first step is a primary process and the second step is the secondary process. Formation of acyl and alkyl radicals can be proved by trapping of these radicals by the use of suitable trapping agents. 2, 2, 4, 4-Tetramethylpiperidine-1-oxyl radical was used for the trapping and the radical fragments produced by the fission of 1, 3-diphenylacetone were trapped as an ester and an ether (Scheme 3).



Scheme 3

Formation of ether and ester confirms that there should be the formation of acyl and alkyl radicals.

The formation of radical intermediates is also readily demonstrated by photolysis of a mixture of ketones (A) and (B) which give products from mixed radical combination.



This cross over experiment also confirmed the two steps radical mechanism.

Norrish Type I process occurs from both the excited singlet and the triplet states of $n \rightarrow \pi^*$ transition. Photolysis of di-tert-butylketone results in high yield of carbon monoxide (90%) from both the excited singlet and triplet states. This clearly shows that the Norrish Type I processes occur from both the excited states. The lifetime of the singlet state is $4.5 - 5.6 \times 10^{-9}$ sec as compared with 0.11×10^{-9} sec for the excited triplet state. Since the reaction occurs from both the singlet and triplet excited states, the Type I process must occur about 100 times faster from triplet than from singlet excited state. Studies with triplet quenchers, such as 1, 3-cyclopentadiene, have also shown that Norrish Type I processes occurs from both triplet and singlet excited states.

Norrish Type I cleavage is given mostly by those ketones whose $n \rightarrow \pi^*$ state is the lowest excited states. In most of the cases, the $n \rightarrow \pi^*$ state is the lowest excited state. However, α cleavage in arylalkyl ketones and diaryl ketones is less efficient because $n \rightarrow \pi^*$ excited state is not the lowest excited state. In this case, there is a large barrier on the reaction coordinate (Fig. 7.1).

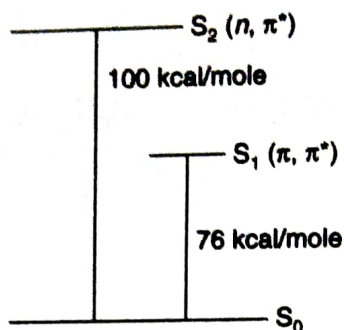
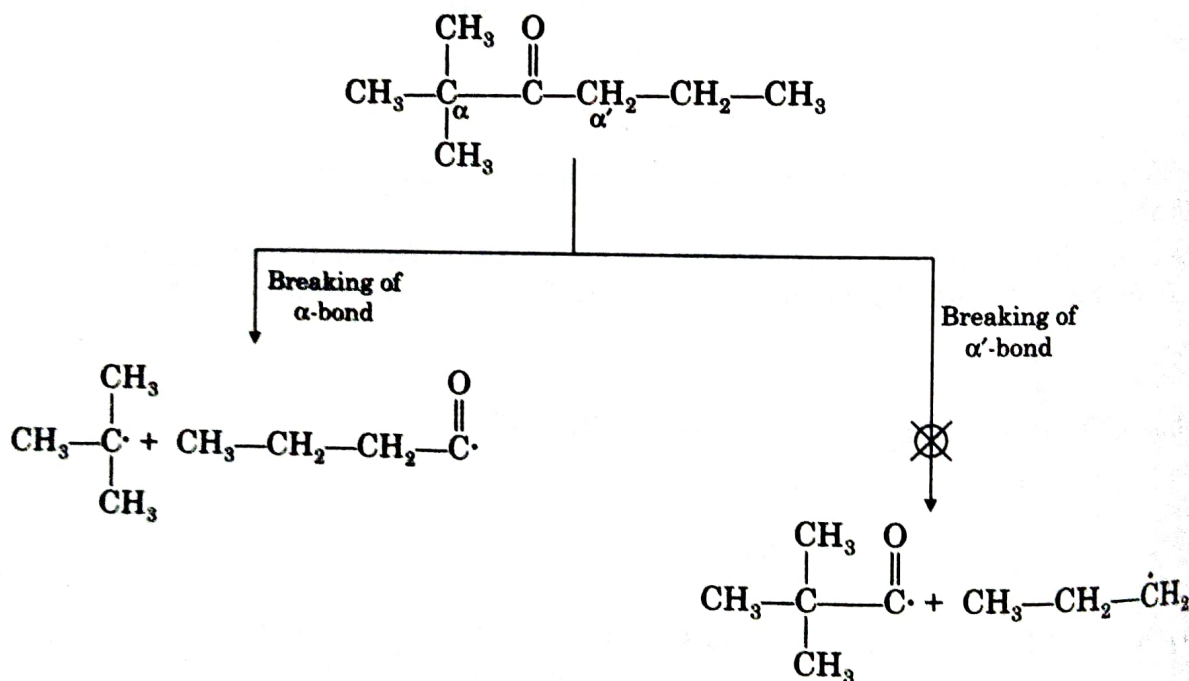
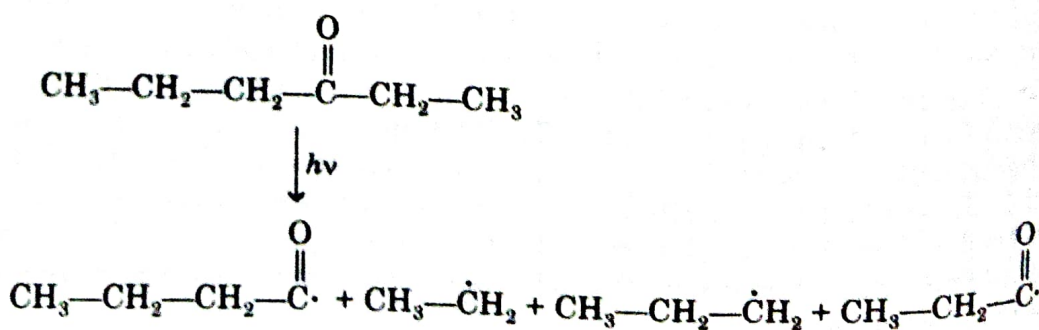


Fig. 7.1 Energy of diphenyl ketone ($C_6H_5COC_6H_5$)

In Norrish Type I reactions there is a preference for the formation of most stable alkyl radical in case of unsymmetrical ketones.

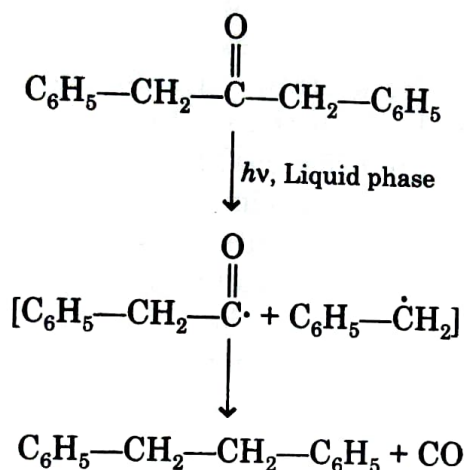


In the above case, only α -bond undergoes cleavage. If both alkyl substituents are same then there is little selectivity of bond cleavage.

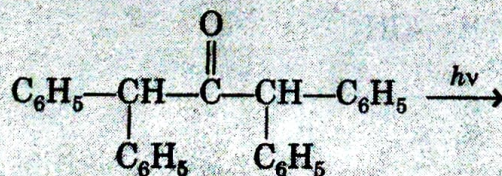


The Norrish Type I process is mostly favoured by photolysis in the vapour phase and is less pronounced for photolysis in the inert solvents. In inert solvent formation of solvent cage takes place. Formation of solvent cage facilitates recombination of the initially generated radical pair. Thus low quantum yield of products is obtained in inert solvents.

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.

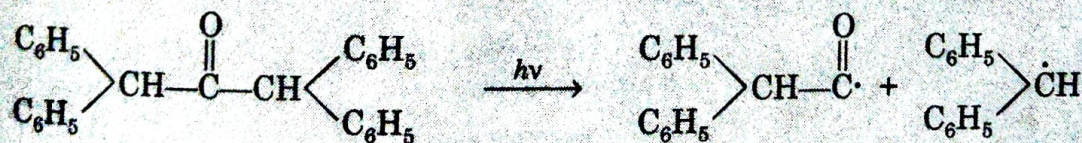


Problem 1: Complete the following Norrish Type I reaction:



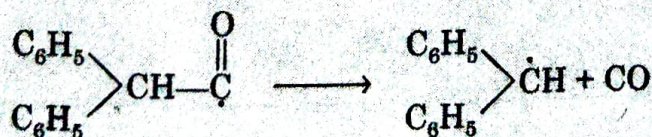
Solution: Compound is saturated acyclic ketone. It will give Norrish Type I process in gases as well as in solution phase.

Primary process:

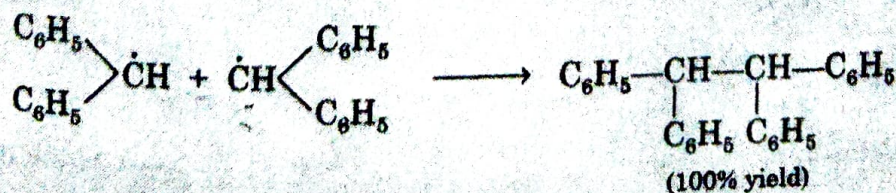


Secondary process:

(i) Decarbonylation



(ii) Recombination



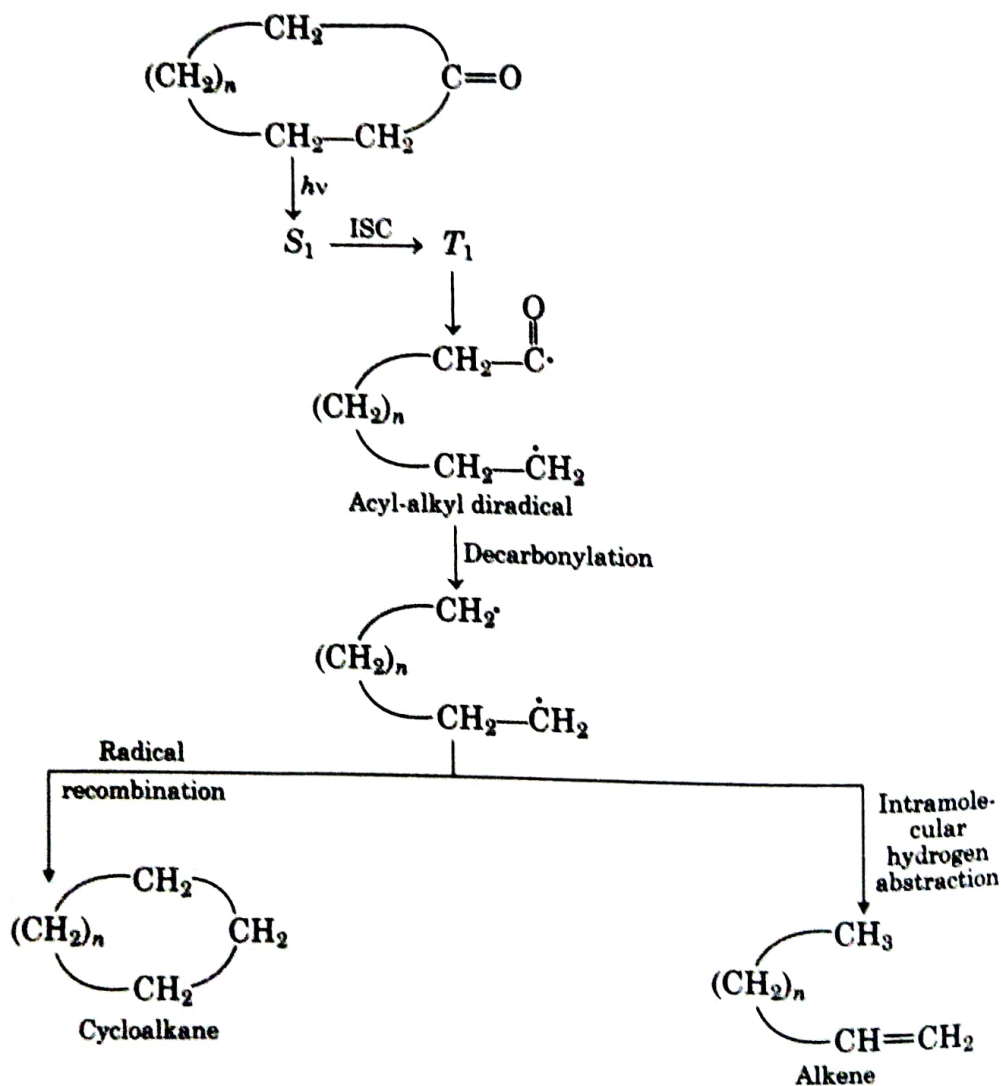
7.1.2 Norrish Type I Reaction of Saturated Cyclic Ketones

Cyclic ketones, in contrast to the acyclic ketones, show a greater tendency to undergo α -cleavage to furnish acyl-alkyl biradicals. (Norrish Type I cleavage of acyclic ketones take place by singlet as well as by triplet excited state. *In cyclic ketones, the reaction takes place exclusively by the triplet state.*) It is possible, however, that inter system crossing in cyclic ketones is so rapid that reaction from the singlet state would not be observed. The triplet state is at least 100 times more reactive than the excited singlet state.

Available information indicates that the excited triplet state for Norrish Type I processes is $n \rightarrow \pi^*$ triplet state. This was demonstrated first for the irradiation of cyclopentanone in both gases and in solution phases. Under both conditions, the product is 4-pentenal. Formation of 4-pentenal takes place at 313 nm and 254 nm. The formation of the aldehyde can be quenched by 1, 3-cyclopentadiene. This quenching experiment confirms the formation of the triplet state.

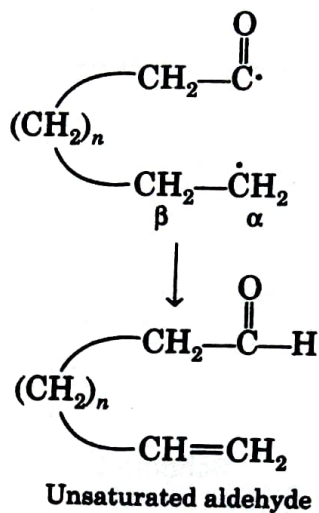
Norrish Type I process involves the initial cleavage of a carbonyl carbon- α carbon bond. Subsequent secondary processes [(a) to (c)] correspond to those observed for acyclic ketones.

(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. [Scheme 4 (a)].



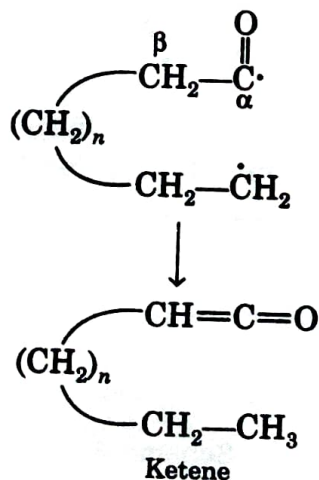
Scheme 4 (a)

(b) Intramolecular hydrogen abstraction by the acyl radical from the β -carbon of the alkyl radical to give an unsaturated aldehyde [Scheme 4 (b)].



Scheme 4 (b)

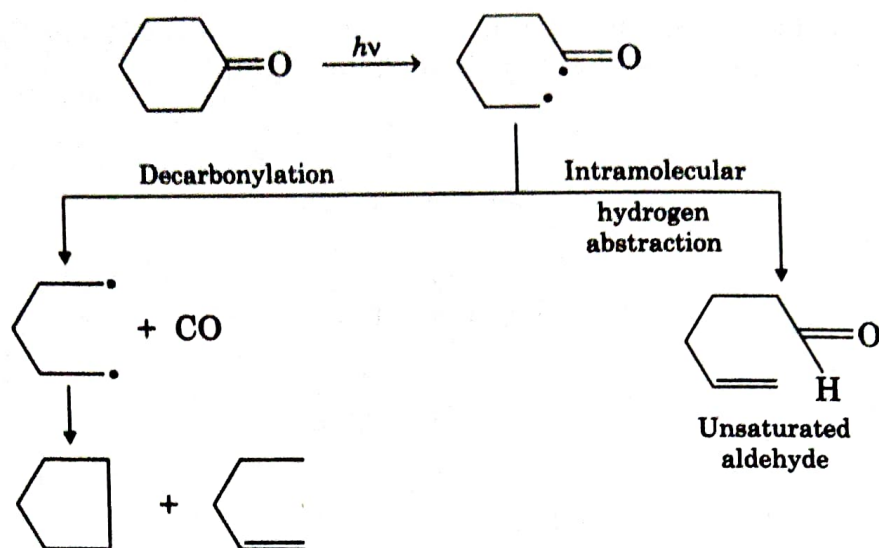
(c) Intramolecular β -hydrogen abstraction from the acyl radical by the alkyl radical to produce a ketene [Scheme 4 (c)].



Scheme 4 (c)

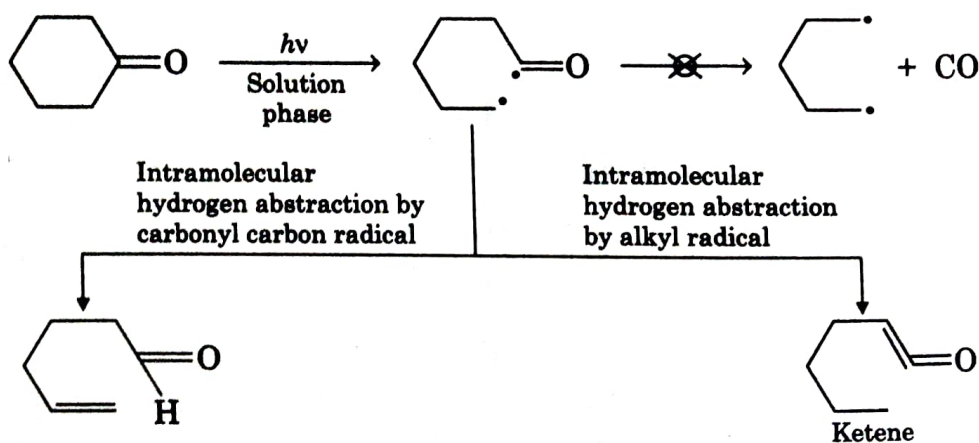
The biradical of cyclic ketones can undergo one of the two hydrogen transfer processes [(b) and (c)] via a cyclic transition state in which a hydrogen atom is transferred to one radical centre from the atom adjacent to other radical centre.

Photolysis of cyclic ketones in gas phase gives decarbonylation as well as intramolecular hydrogen abstraction. Intramolecular hydrogen abstraction mainly leads to the formation of unsaturated aldehyde (Scheme 5).



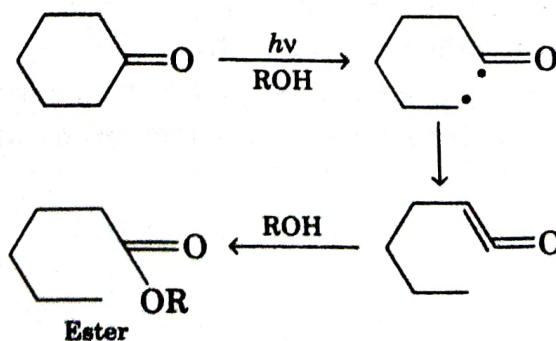
Scheme 5

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 (Scheme 6).



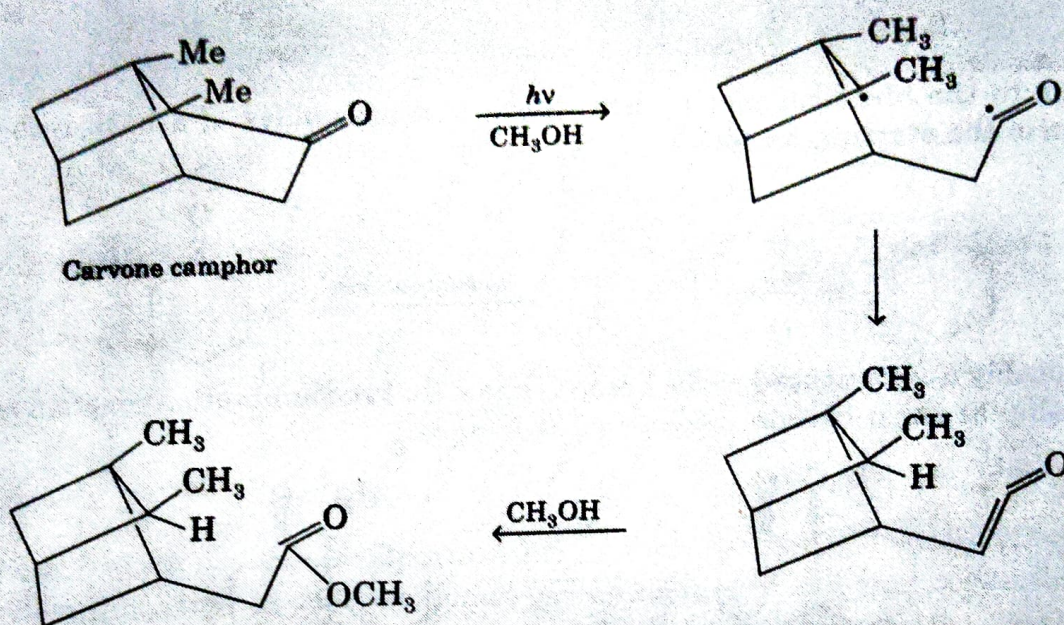
Scheme 6

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



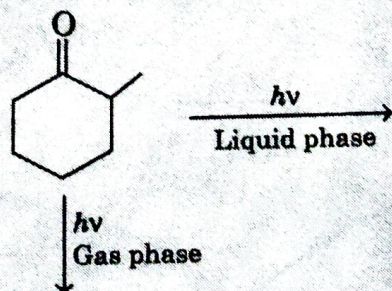
Problem 2: What will the product of the reaction when carvone camphor is irradiated with UV light in the presence of MeOH?

Solution: In the presence of polar protic solvent, cyclic ketone forms only ketene.

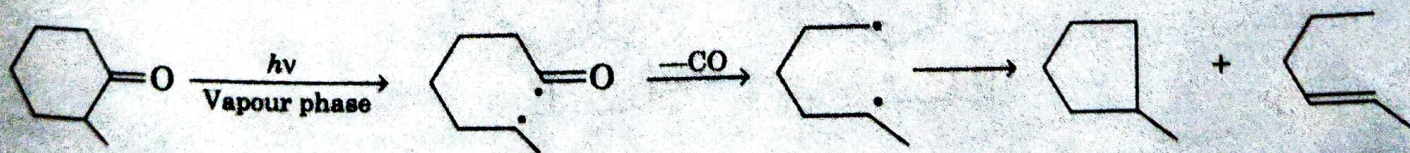


In case of unsymmetrical ketones, the α -bond that produces more stable alkyl radical cleaves preferentially.

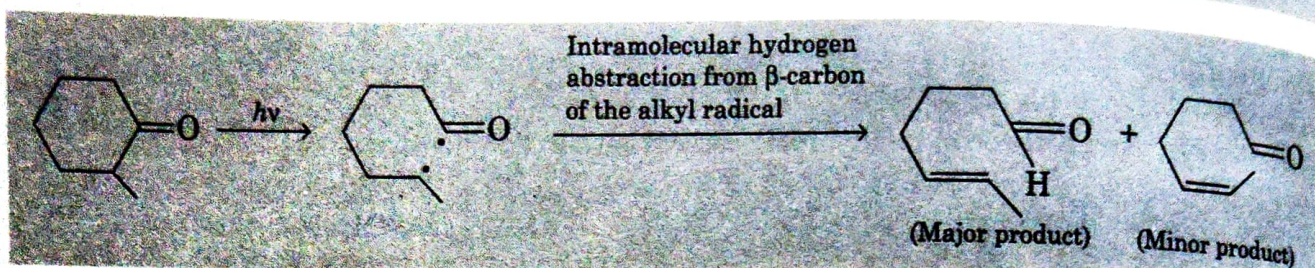
Problem 3: Complete the following reaction:



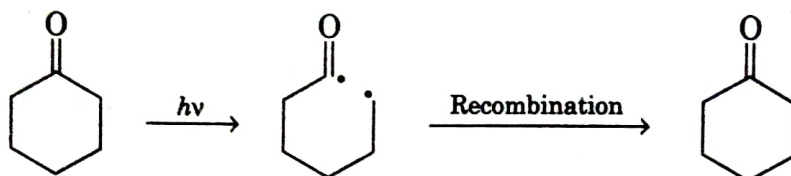
Solution: The α -bond that produces the more stable alkyl radical cleaves preferentially in unsymmetrical ketone. The vapour phase photolysis gives decarbonylation and intramolecular hydrogen abstraction.



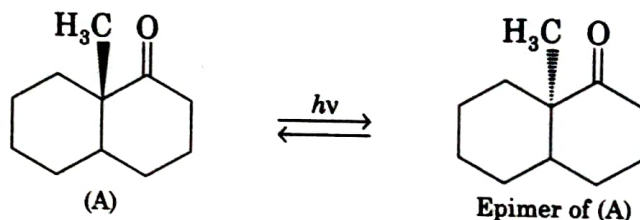
In the liquid phase, the main reaction is intramolecular hydrogen abstraction which leads to the formation of unsaturated aldehydes.



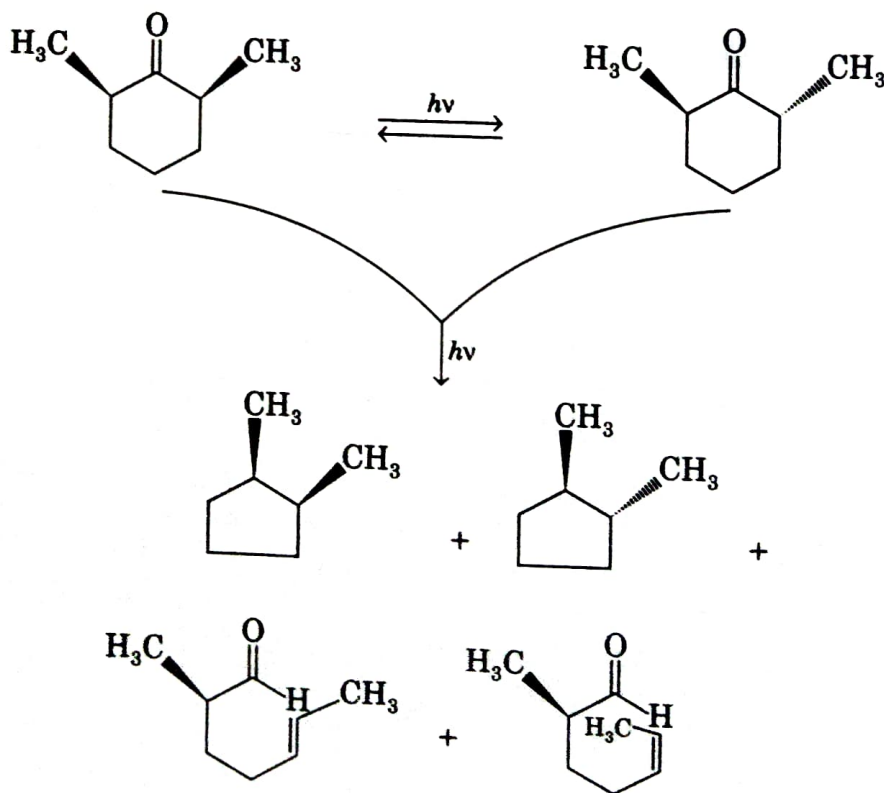
According to the biradical mechanism, there is a possibility of a back recombination reaction to reform the starting material.



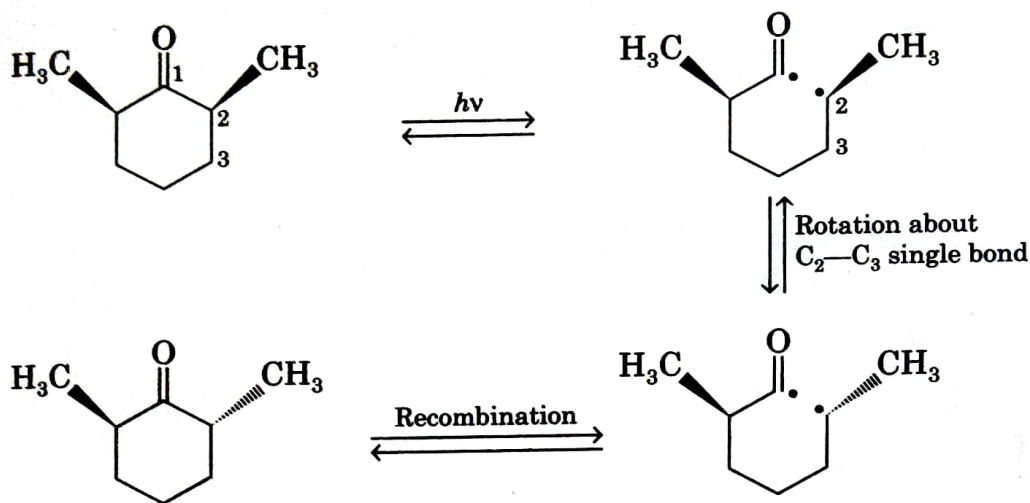
Use of suitably α -substituted cyclic ketones show that recombination reaction resulted in epimerisation at the α -carbon if α -carbon is a chiral.



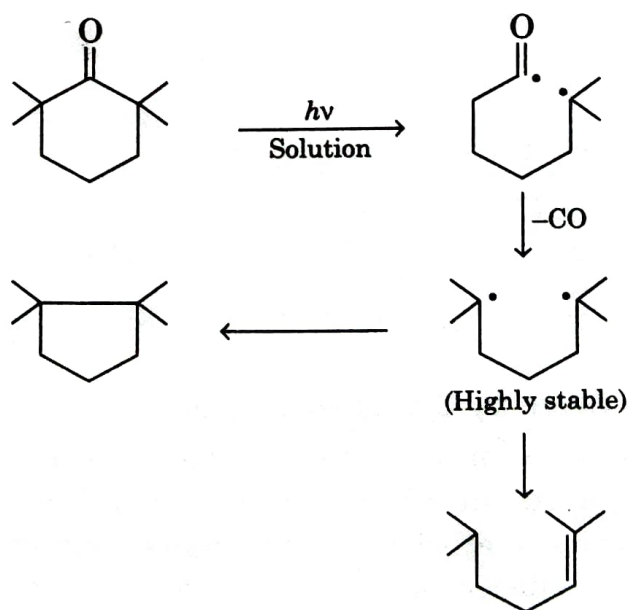
Experimentally it has been found that photolysis product formation *via* route [(a) - (c)] is faster than the photochemical interconversion of the epimers. Since there is the formation of epimeric mixtures, each epimer affords the same mixture of products.



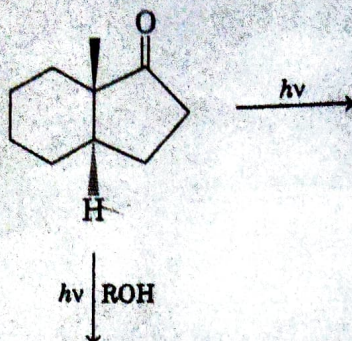
Each epimer affords the same mixture of products. This clearly indicates that the configurational integrity of the α -carbon is lost during the course of the reaction. This loss of integrity is due to the free rotation about C_2-C_3 bond in the diradical.



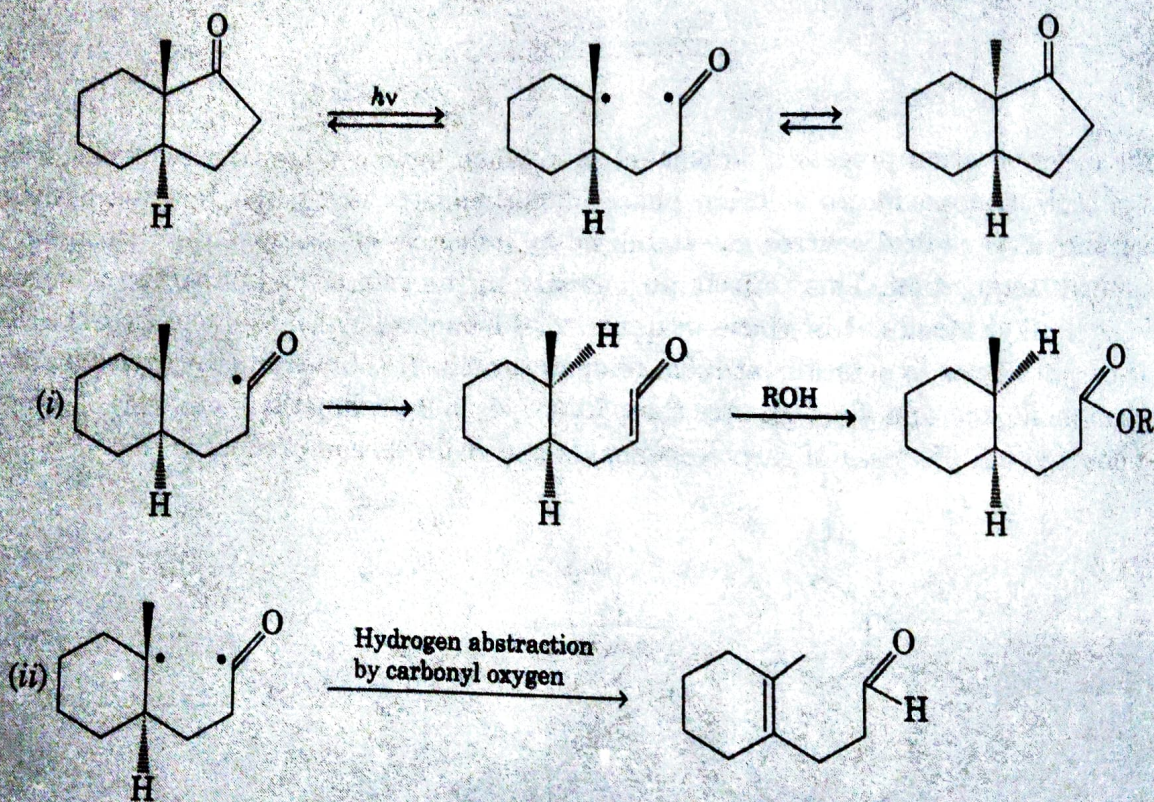
The recombination process is important even when hydrogen transfer reactions occur, but loss of carbon monoxide in solution phase photochemistry is a major reaction pathway only when the alkyl radical centres are stabilised by inductive effect, by β , γ -unsaturation or by cyclopropyl conjugation. This reflects an increase in the rate of loss of carbon monoxide from the acyl-alkyl biradical in these systems. 2, 6-Dimethyl-cyclohexanone gives carbon monoxide on photolysis in solution at room temperature. 2, 2, 6, 6-tetramethylcyclohexanone gives carbon monoxide in a yield greater than 70%, 7, 7, 9, 9-tetramethylbicyclo [4, 3, 0] non-1, 6-en-8-one gives 100% yield of carbon monoxide and hydrocarbon products.



Problem 4: Complete the following reaction:

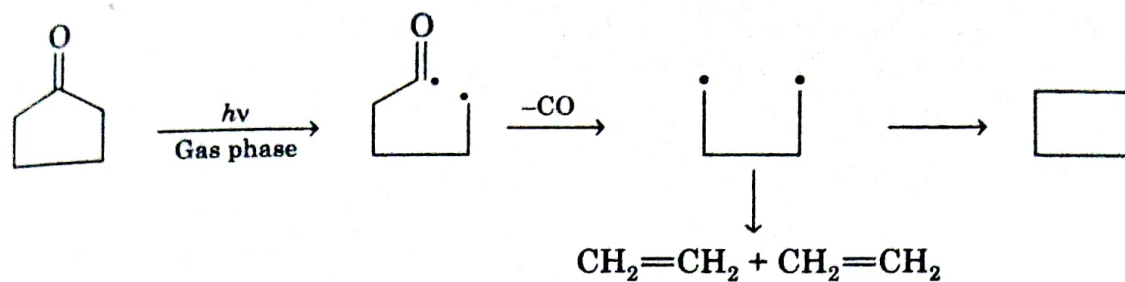


Solution:



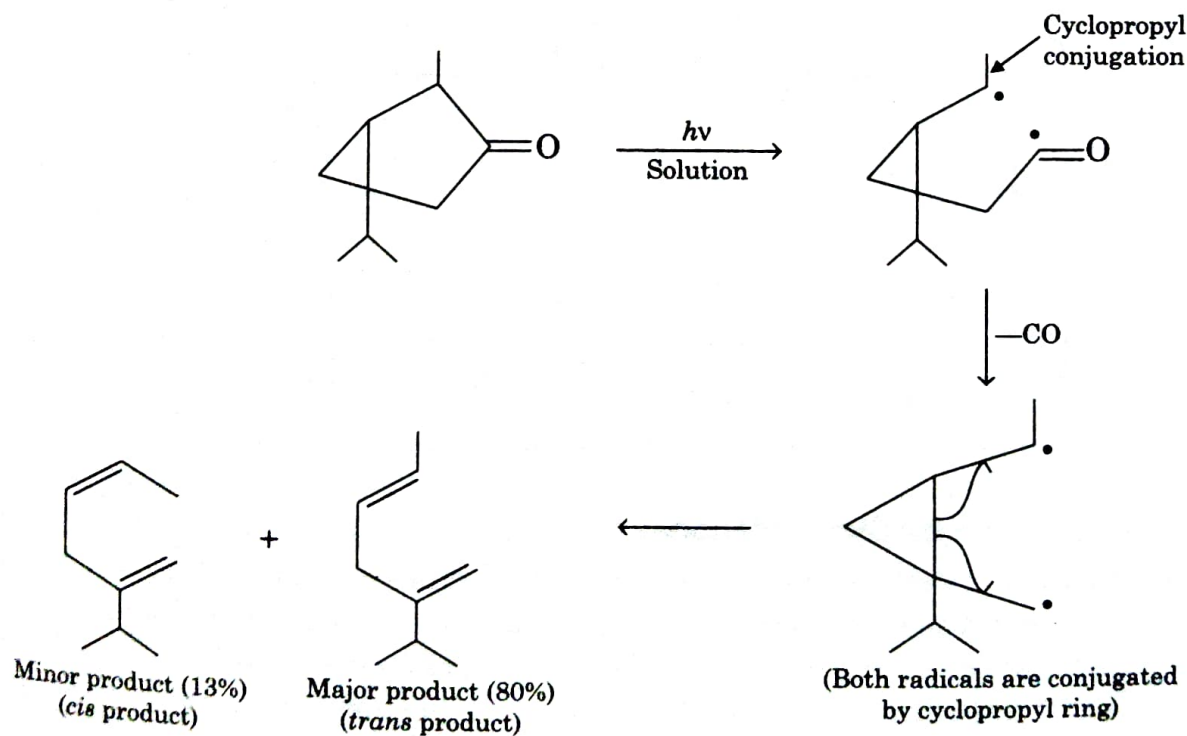
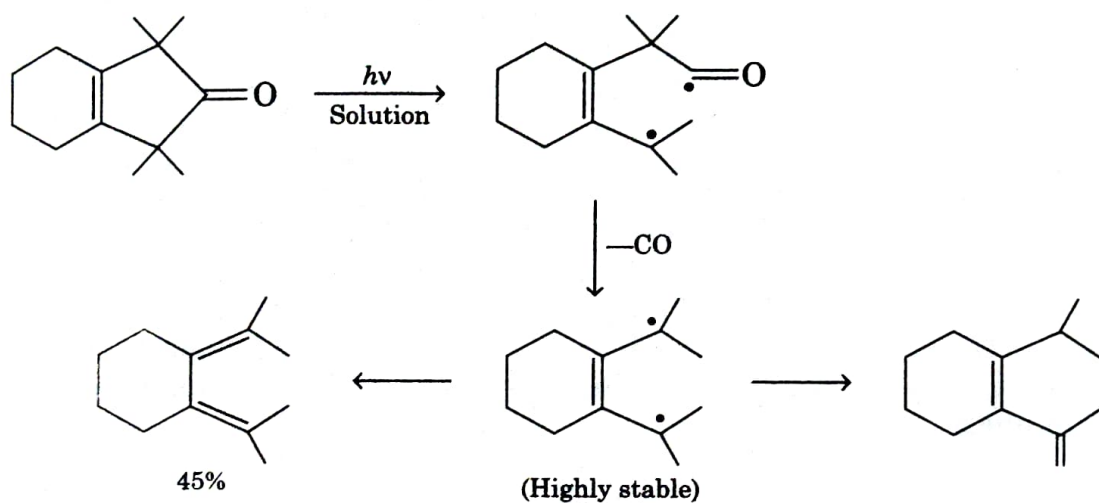
7.1.3 Norrish Type I Process Given by Cyclopentanones

Cyclopentanone also decarbonylates on irradiation in the gas phase at 147 nm. In this case also a two step process is involved, affording a biradical which decarbonylates to another biradical, which either fragments to ethylene or undergoes bond formation to cyclobutane. Fission to ethylene is much more efficient in comparison to cyclobutane formation (Scheme 7).

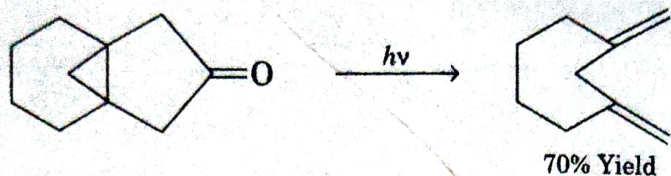


Scheme 7

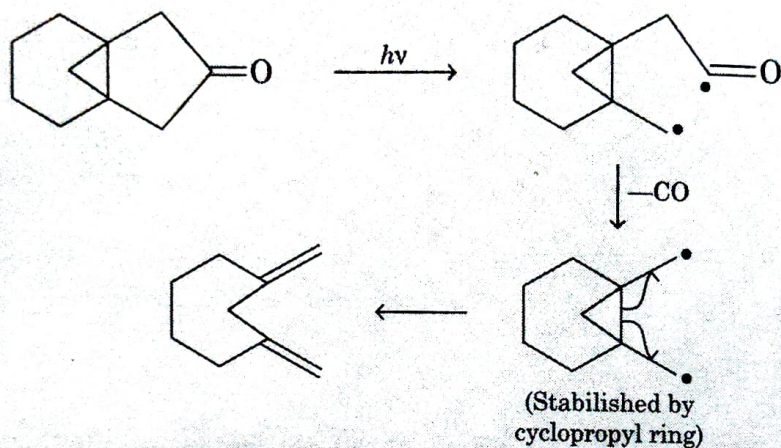
In solution the loss of carbon monoxide from a cyclopentanone is a major path only when the radical centres formed are stabilised by alkyl substitution, double bond or cyclopropyl ring.



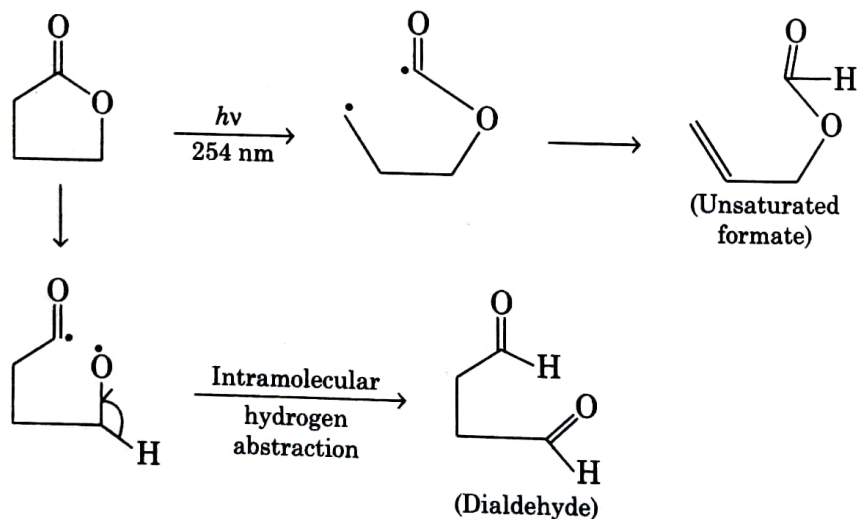
Problem 5: Give the mechanism of the following transformation:



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.

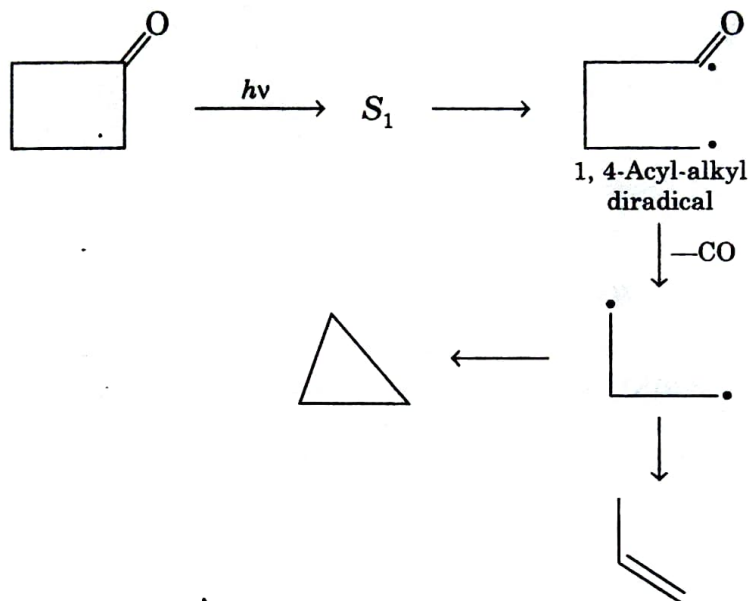


7.1.4 α -Cleavage Given by Cyclobutanones

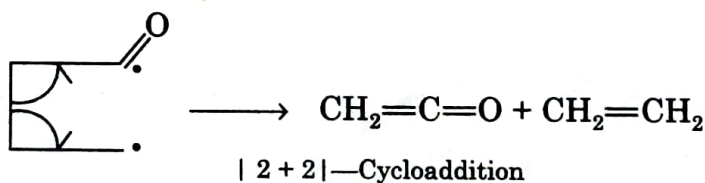
Cyclobutanone also gives α -cleavage reaction. The efficiency of α -cleavage reaction of cyclobutanone is ten times more than the cyclopentanone due to the angle strain. Angle strain and steric strain increase the efficiency of α -cleavage. The photochemistry of α -cleavage of cyclobutanone differs significantly from the photochemistry of α -cleavage of other cyclic ketones.

Unlike other ketones, cleavage occurs from S_1 ($n \rightarrow \pi^*$) and leads to the formation of a 1, 4-acyl-alkyl diradical. There are three following different pathways for stabilisation of the diradical:

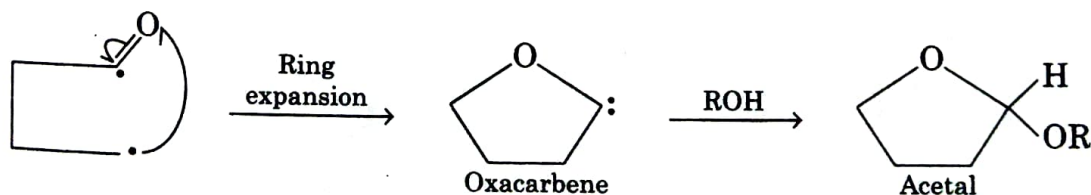
(i) Loss of carbon monoxide and formation of 1, 3-diradical that undergoes either recombination to cyclopropane or an hydrogen abstraction to form propene.



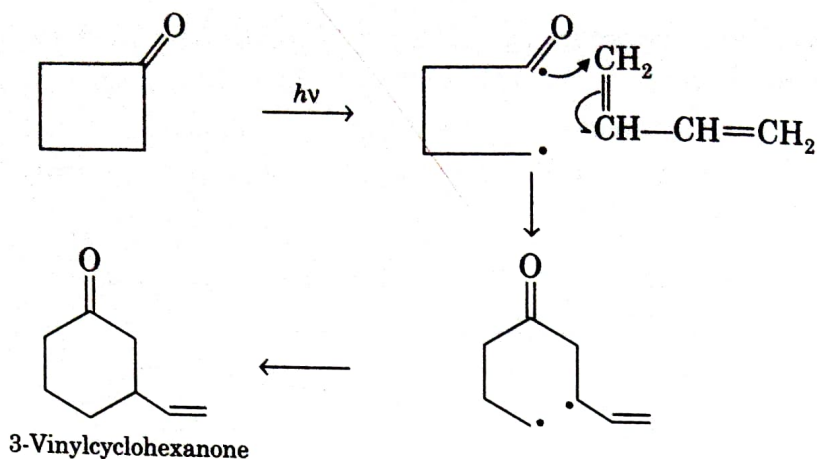
(ii) By a subsequent β -cleavage and formation of ethylene and ketene.



(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.

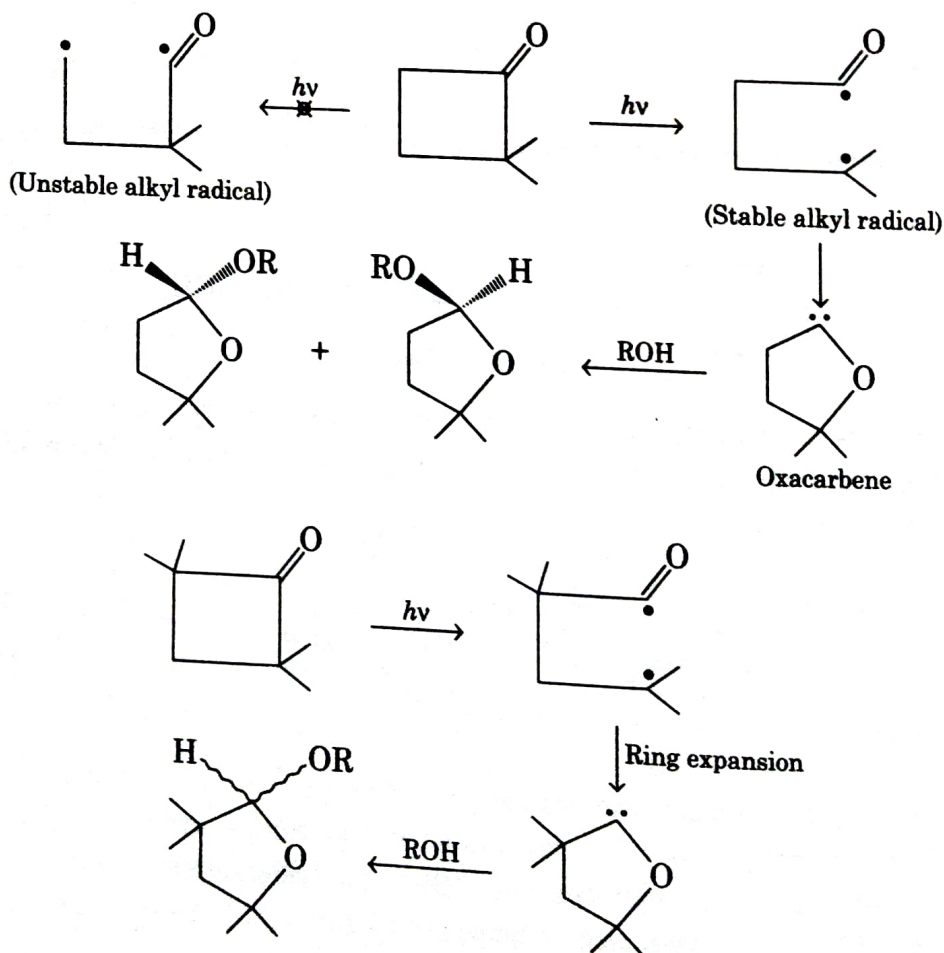


Formation of 1, 4-acyl-alkyl radical can be proved by trapping experiment. 1, 4-acyl-alkyl diradical can be trapped by 1, 3-butadiene at low temperature (-78°C) because low temperature suppress the decarbonylation and | 2 + 2 | —cycloaddition reaction. Photolysis of cyclobutanone at -78°C in the presence of trapping agent, 1, 3-butadiene gives 3-vinylcyclohexanone.

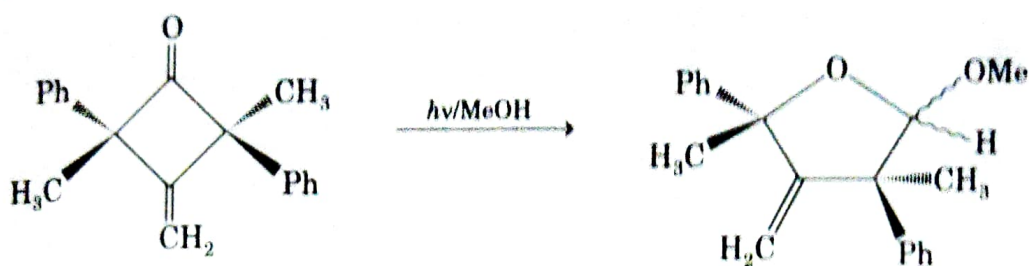


Scheme 8: Trapping of 1,4-acyl-alkyl diradical by 1,3-butadiene

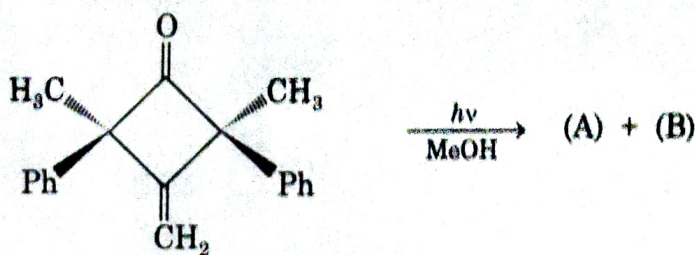
Ring expansion of unsymmetrical cyclobutanones is highly regioselective which indicates the need for a more stable alkyl radical to attack the oxygen atom of the acyl radical. Indeed alkyl substitution does increase the yield of ring expanded products. Both 2,2-dimethyl and 2,2,4,4-tetramethyl-cyclobutanone form ring-expansion products predominantly.



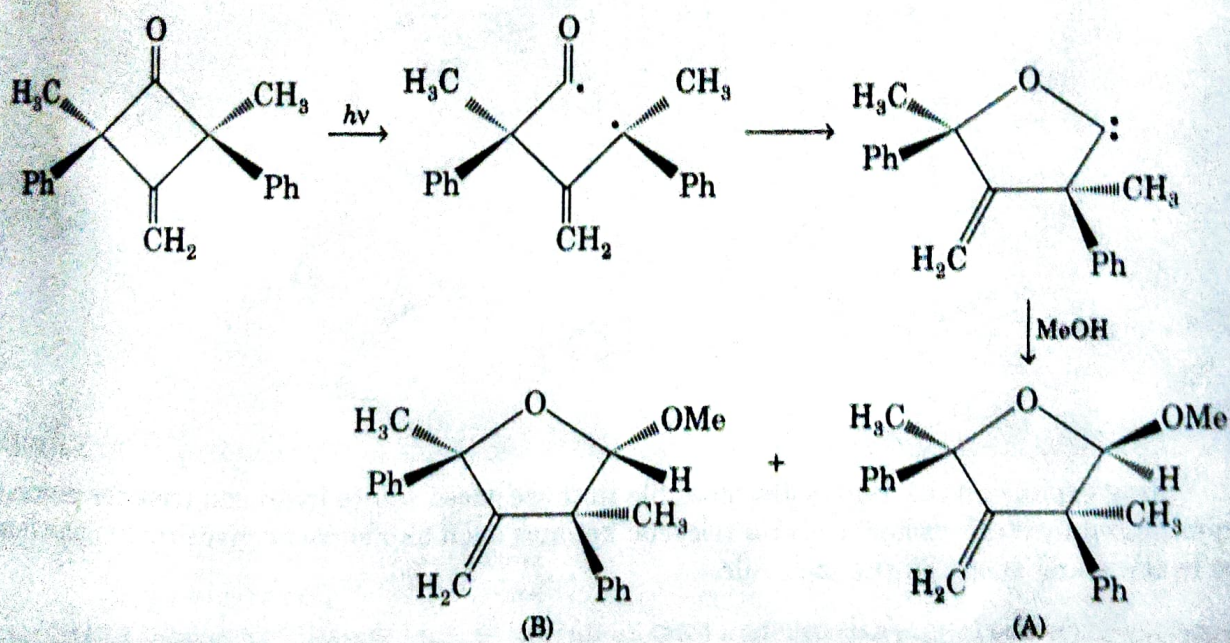
Photolysis of cyclobutanone is also stereospecific reaction. Stereochemistry at C-2 is retained during the rearrangement to the oxocarbene. Ring expansion reaction always exhibit retention of configuration in methanol.



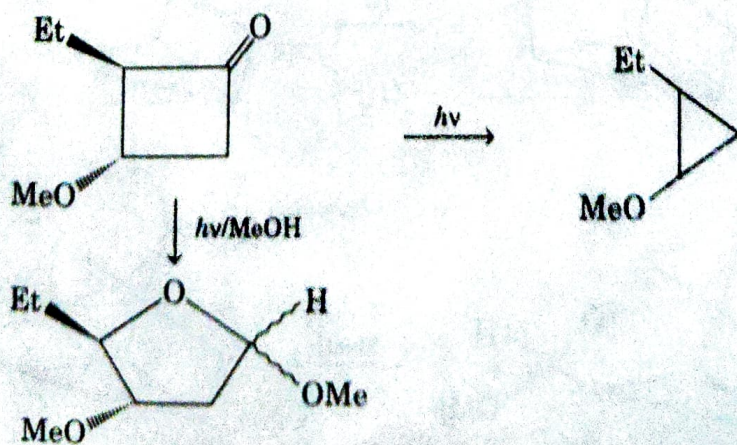
Problem 6: Identify (A) and (B) in this reaction:



Solution:



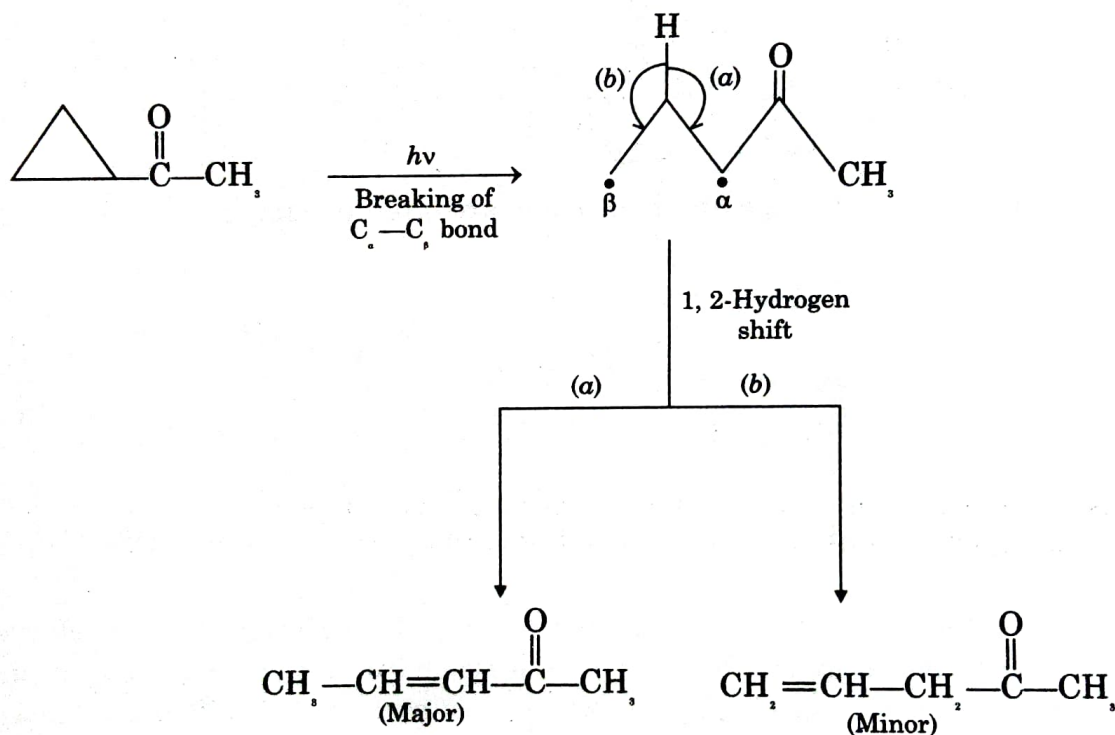
Problem 7: Give mechanism of the given reaction:



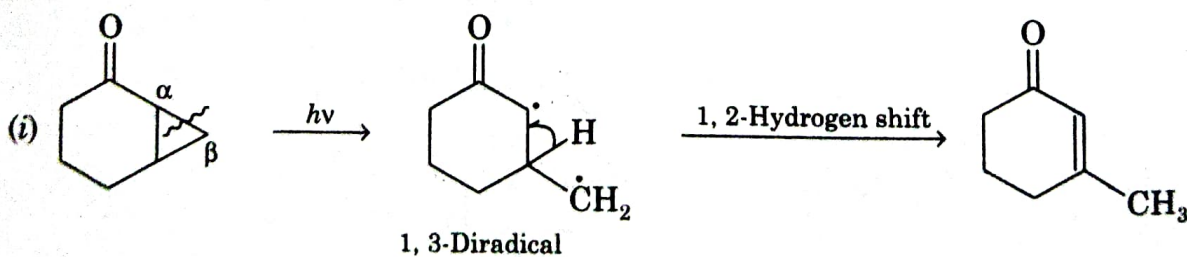
7.2 β -CLEAVAGE REACTION

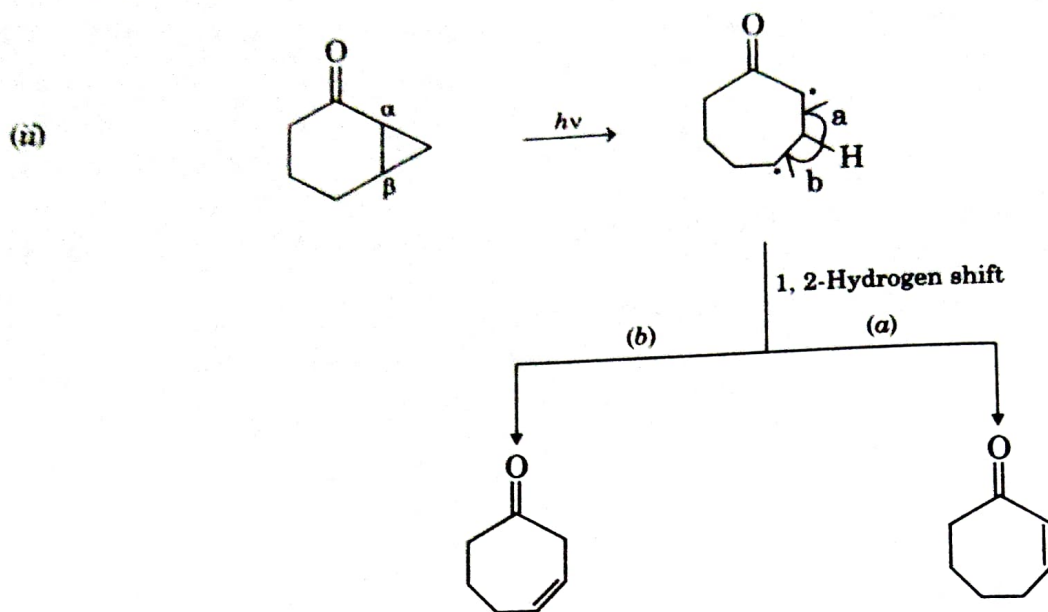
Some class of compounds have relatively weak $C_\alpha-C_\beta$ bonds which can undergo cleavage as a result of electronic excitation of the carbonyl group. Cyclopropyl ketones are one such class, and evidence for interaction between the carbonyl and cyclopropyl groups, which provides a mechanism by which energy may be transferred from the carbonyl group to the bond which is broken, is found in the UV spectrum.

The mechanism of the reaction has been shown to involve the formation of a 1,3-biradical intermediate. Photolysis of acetylcyclopropane leads to the cleavage of the cyclopropane ring, and this is followed by a 1,2-hydrogen shift or alkyl shift.

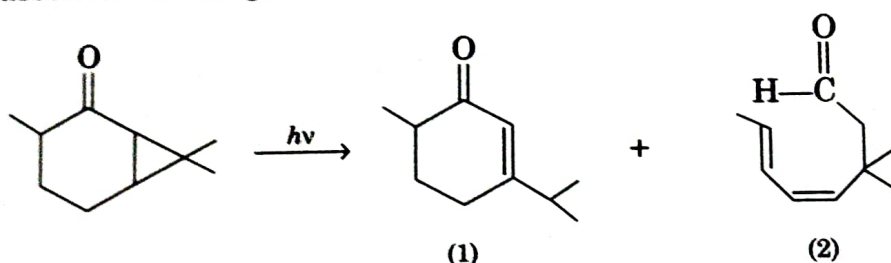


In a similar way, bicyclo [4, 1, 0] heptane-2-ones undergo cleavage of one of the cyclopropyl $C-C$ bonds.



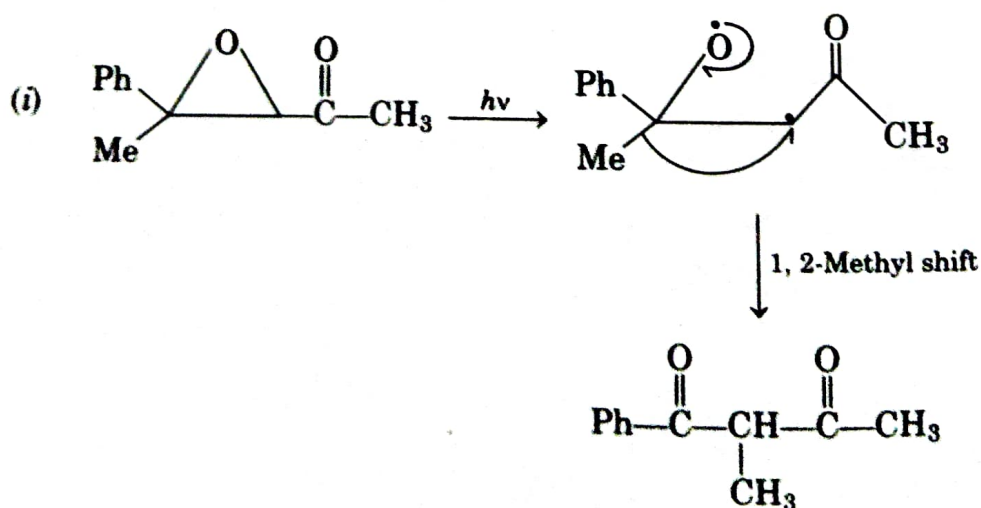


In some cases the α -cleavage and β -cleavage are often in competition as shown below:



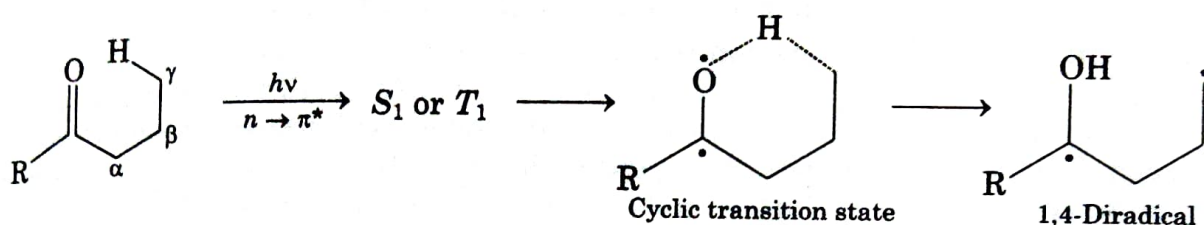
In the above case, product (1) is formed due to the β -cleavage and product (2) is formed due to the α -cleavage.

α , β -Epoxy ketones have also a relatively weak $C_\alpha-C_\beta$ bond which can be cleaved in the excited state. Epoxy ketone reacts by way of β -cleavage and alkyl migration on photolysis. Mechanistically this reaction arises from a singlet $n\pi^*$ state and result is the fission of the $C-O$ bond. The migratory aptitudes shown within such compounds is best explained via the involvement of a biradical species formed by $C-O$ bond fission. Some examples are:



7.3 INTRAMOLECULAR HYDROGEN ABSTRACTION (γ -HYDROGEN ABSTRACTION)

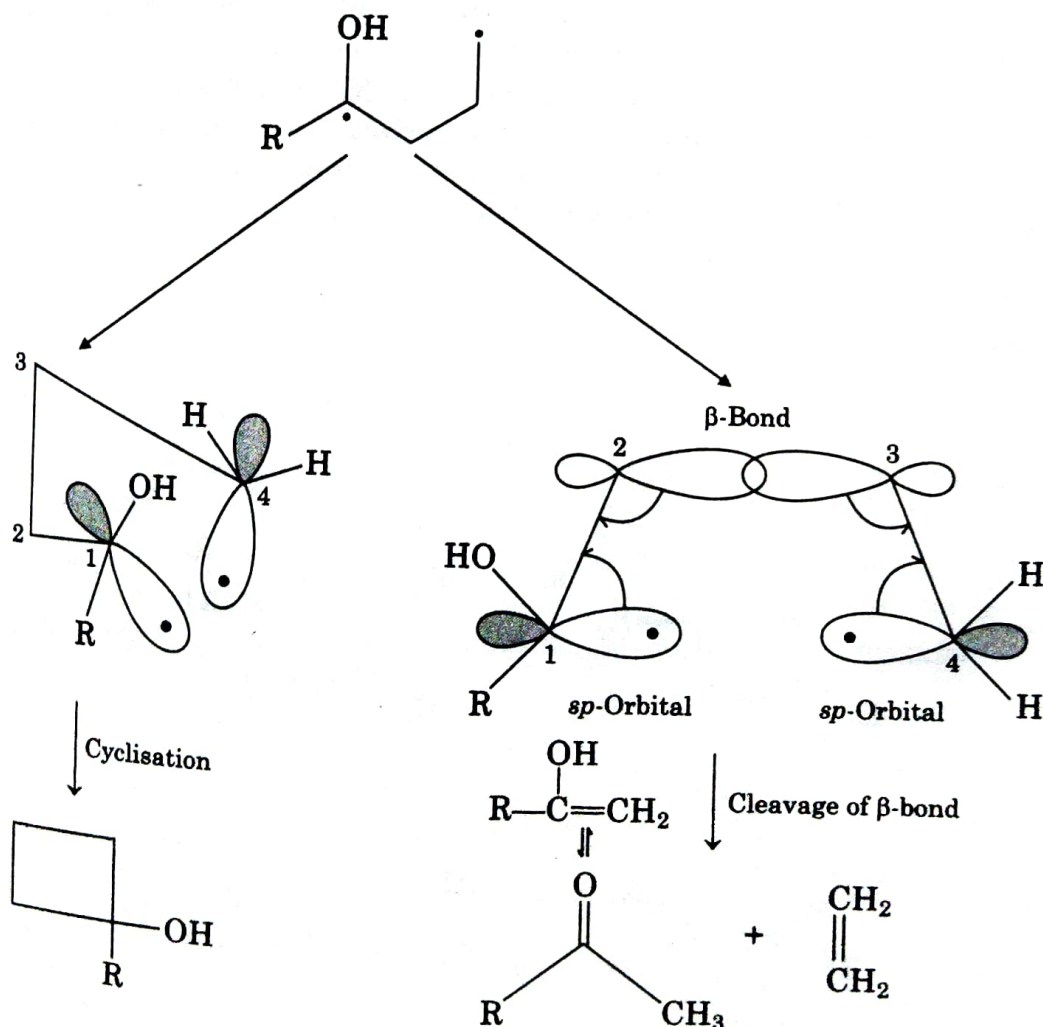
1, 3 (n, π^*) excited carbonyl compounds having an accessible hydrogen atom in the γ -position undergo a characteristic 1, 5-hydrogen atom transfer by an intramolecular cyclic process with the formation of ketyl like 1, 4-diradical.



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.

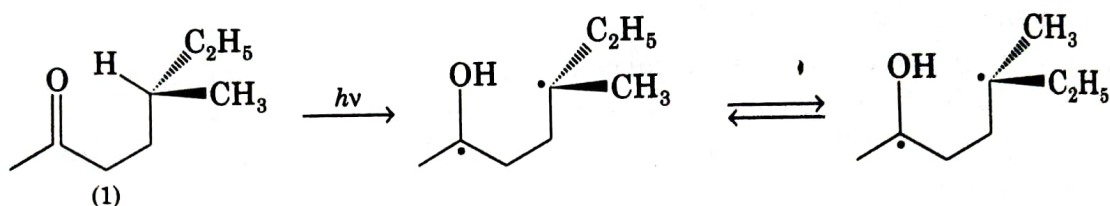
(ii) If the sp -orbitals of the radical centres are parallel to the β -bond, they participate in the formation of two double bonds (one in the enol and one in the alkene), a result of the cleavage of the β -bonds.



The second process of this reaction is known as Norrish Type II process which leads to the formation of alkene and alkenol.

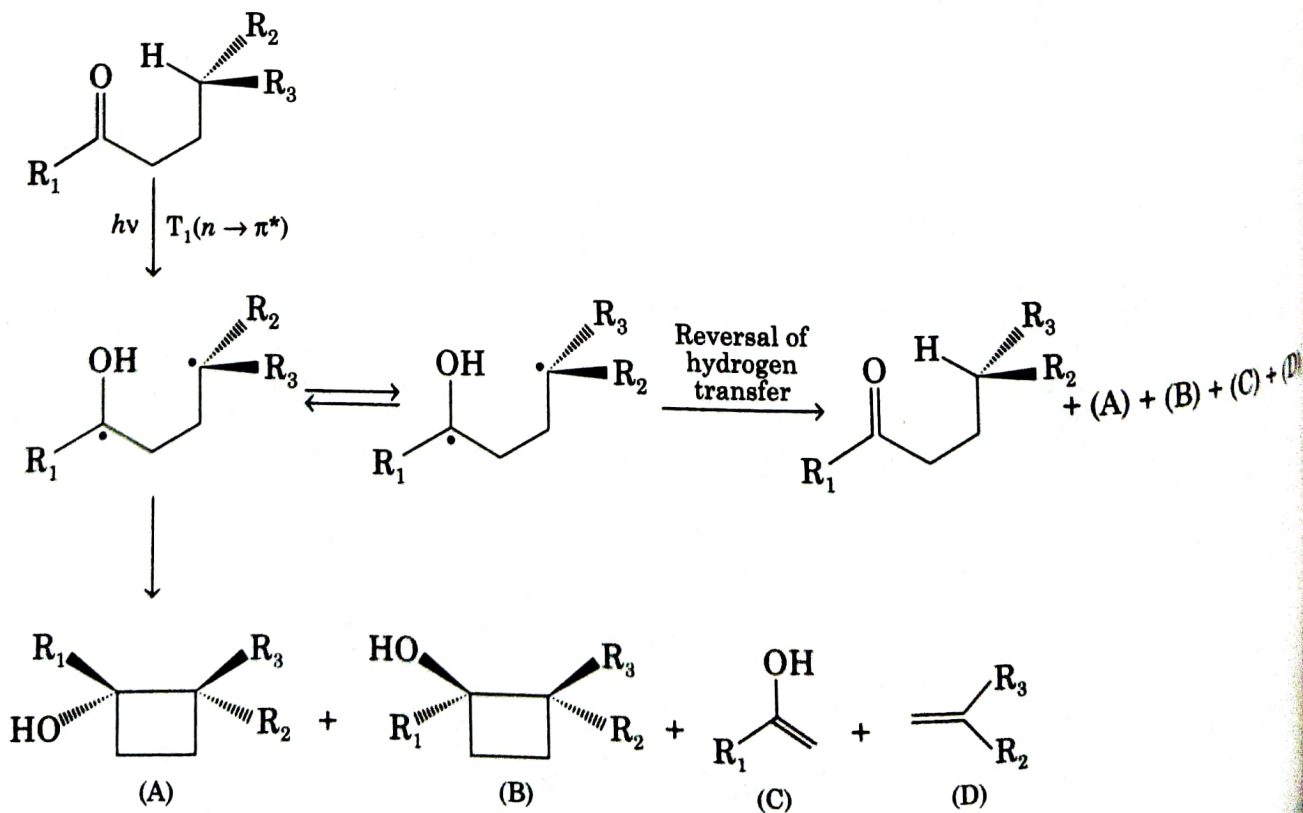
Although the reaction occurs from both the singlet and the triplet states of n, π^* transition, the quantum yield from the singlet state is generally lower than that from the triplet state. In the case of aryl-alkyl ketones, the reaction occurs only with the triplet state because aromatic ketones can undergo rapid intersystem crossing. Solvents also affect the efficiency of the reaction. The singlet state reactions are unaltered in the presence of polar solvents. Polar solvents such as alcohol, on the other hand, enhance the reaction from the triplet state.

The quantum yield of the reaction is poor since radiationless deactivation from the S_1 and T_1 states and reversal of the hydrogen transfer can compete with reactions proceeding to products. The reversal process is confirmed by using the optical active ketone (1) having a chiral γ -carbon. Ketone (1) undergoes racemisation. Racemisation reaction confirmed that the reaction intermediate is 1, 4-diradical. This also confirmed the back transfer of hydrogen atom.

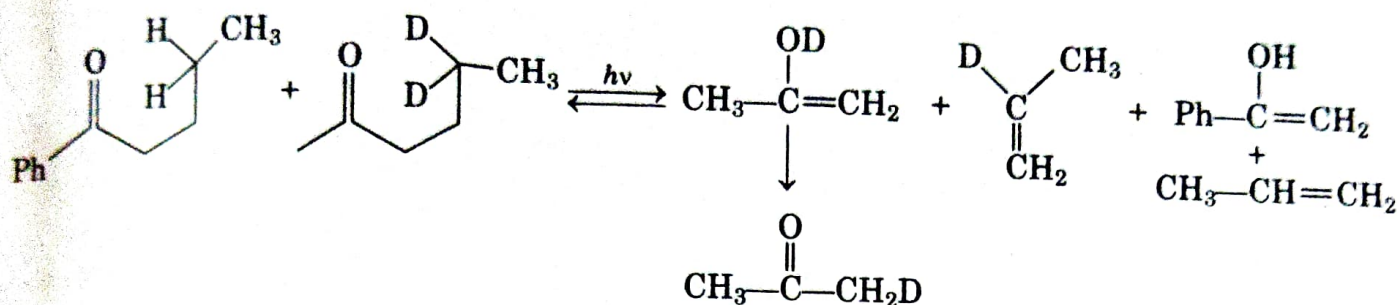


Back transfer of hydrogen atom *i.e.*, photoracemisation can be quenched by the addition of 1, 3-cyclopentadiene. This quenching experiment confirmed the formation of triplet state.

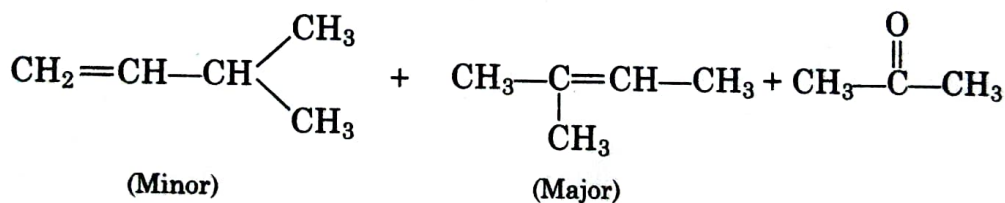
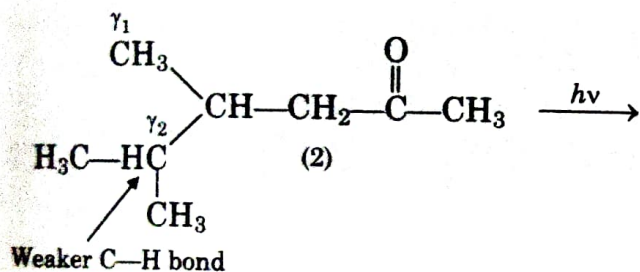
Participation of a 1, 4-diradical intermediate in the Norrish Type II reaction has been confirmed by trapping experiments and spectroscopic techniques. Formation of 1, 4-diradical has also been proven chemically. Photoracemisation of a ketone with a γ -chiral carbon atom and loss of the chirality in the product was observed.



The γ -hydrogen transfer to the oxygen atom has been shown to be intramolecular. The transfer involves a six membered cyclic transition state. 5, 5-Dideuteriohexan-2-one on irradiation gives 2-deuteriopropene and 1-deuteroacetone. Formation of these products confirms that the transfer of hydrogen takes place from γ -carbon and process is intramolecular.



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 (2).



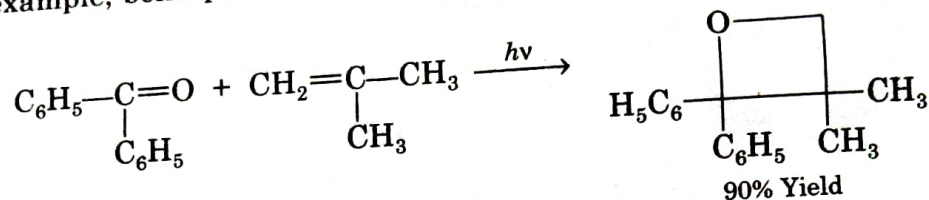
Intramolecular hydrogen abstraction is not possible if γ -carbon has no hydrogen.

For alkylaryl ketones the electron donating groups such as *p*-methyl and *p*-methoxy substituents decreases the rate and quantum yield for Norrish Type II cleavage. Following this trend *p*-hydroxy, *p*-amino and *p*-phenyl substituents inhibit the reaction completely. This is because in such cases energy for $\pi \rightarrow \pi^*$ excitation is less than that for the $n \rightarrow \pi^*$ excitation.

The rate of radical recombination to give cyclobutanols compared with α , β -bond cleavage is often dependent on α -substitution.

7.7 PHOTOCYCLOADDITION REACTION (PATERNO-BÜCHI REACTION)

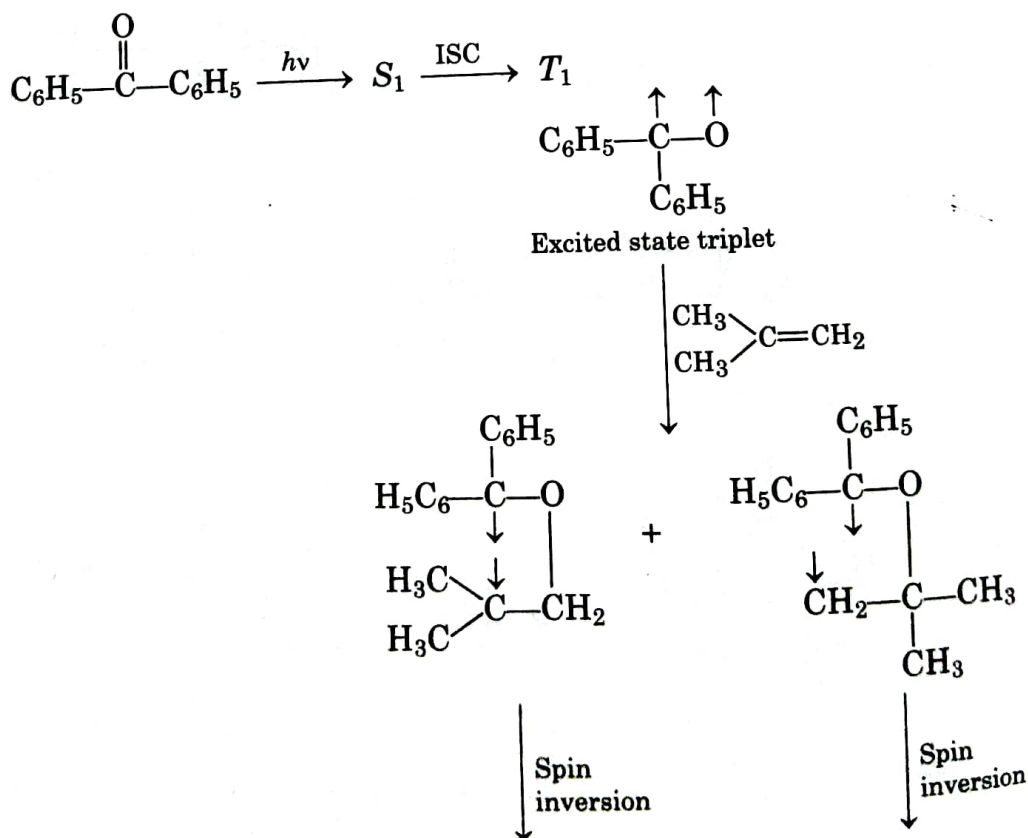
One of the first photocycloaddition reactions to be studied was the formation of oxetanes from addition of carbonyl compounds to alkenes. This reaction is known as the Paterno-Büchi reaction. For example, benzophenone with isobutene gives a high yield of an oxetane.

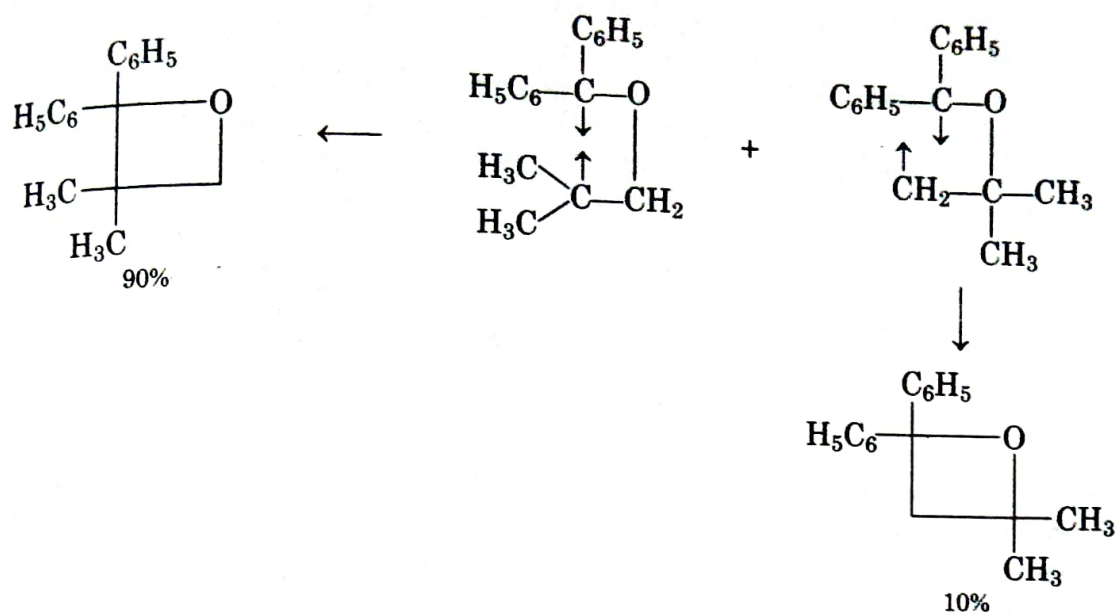


Paterno-Büchi reaction can be studied under two categories and the categories depend on the nature of alkenes.

7.7.1 Addition to Electron-Rich Alkenes

Mechanistic studies have shown that the 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 oxetane. 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 (Scheme 8).





Scheme 9

Although the reaction is not stereospecific, there is a preference for one orientation of addition, which can be rationalised in terms of initial attack on the alkene by the oxygen atom of the excited carbonyl group to give a biradical intermediate. The existence of biradicals has been confirmed by picosecond spectroscopy. The more energetically stable of the two possible biradicals is formed more readily. Thus reaction is regioselective reaction. The consideration of biradical stability is certainly applicable to the prediction of the major product of the cycloaddition (see Scheme 9).

Two important rules for the successful synthesis of oxetanes have been put forward. These rules are as follows:

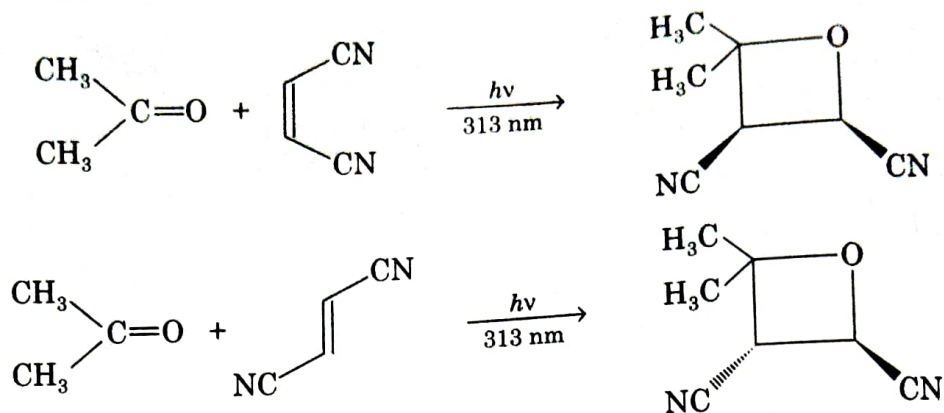
- (i) Only carbonyl compounds with a low-lying $n \rightarrow \pi^*$ state will form oxetanes.
- (ii) The energy of the carbonyl excited state must be less than that of the alkene to prevent energy transfer from the carbonyl excited state to the alkene.

As far as the addition of aromatic carbonyl compounds is concerned only the triplet state is reactive (because inter system crossing is very efficient in case of aromatic ketones) and consequently a triplet biradical intermediate is produced.

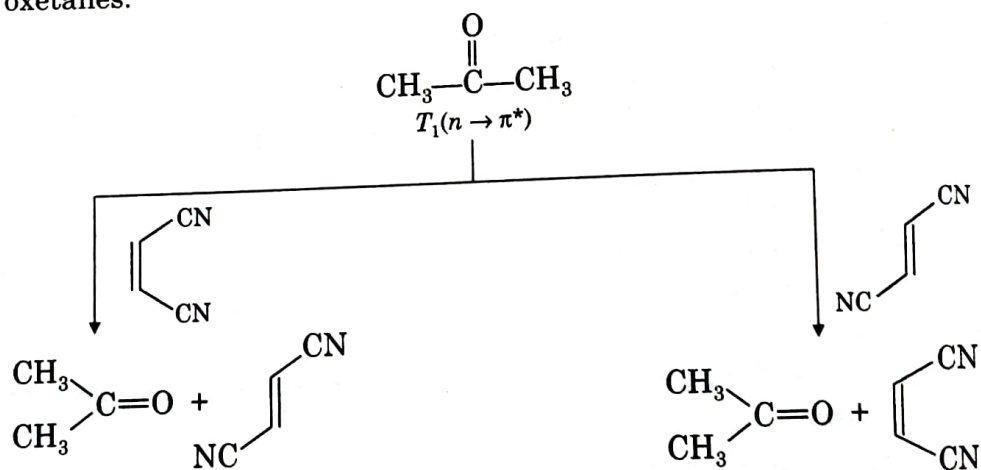
The reaction of alkyl ketones can be complicated by the less efficient inter system crossing thus permitting reaction of both the singlet and the triplet state. Both singlet and triplet state show equal reactivity for the reaction. The singlet state reaction is obtained at high concentration of the alkene. On the other hand, triplet state reaction is obtained at low concentration of the alkene.

7.7.2 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, oxetane.

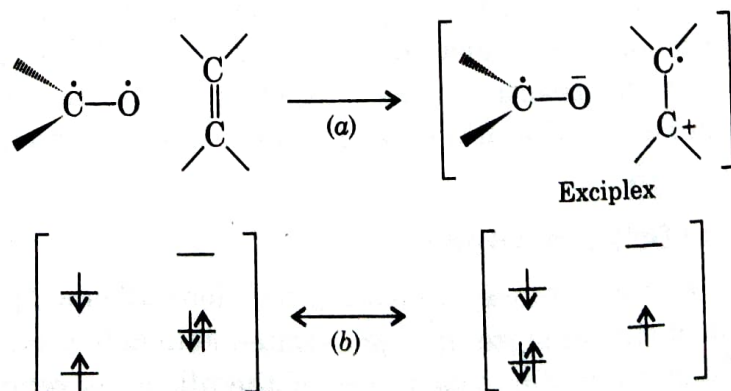


The course of the photocycloaddition of electron-deficient alkenes to ketones follows certain rules. While oxetanes are formed only from $S_1(n, \pi^*)$ state, the $T_1(n, \pi^*)$ state stereospecifically sensitises the *cis-trans* isomerisation of electron-deficient alkenes and does not lead to oxetanes.



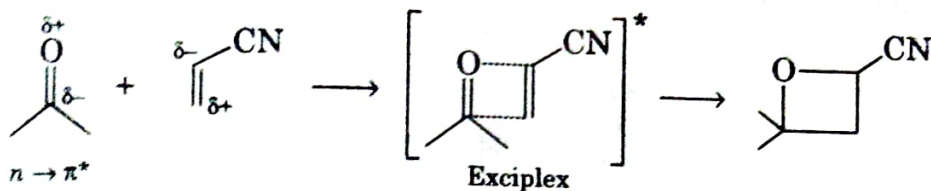
Stereospecificity of the oxetane formation with electron-deficient alkenes can be explained as follows:

It is suggested that in case of electron-deficient alkenes, oxetane formation takes place *via* formation of exciplex. Exciplex formation takes place between the singlet excited state of ketone and ground state of alkene. Exciplex is stabilised by charge transfer as well as energy transfer between the constituent molecules.



- (a) Formation of an exciplex between a carbonyl excited state and an olefin ground state
 (b) Charge transfer interaction in the formation of the carbonyl-olefin exciplex.

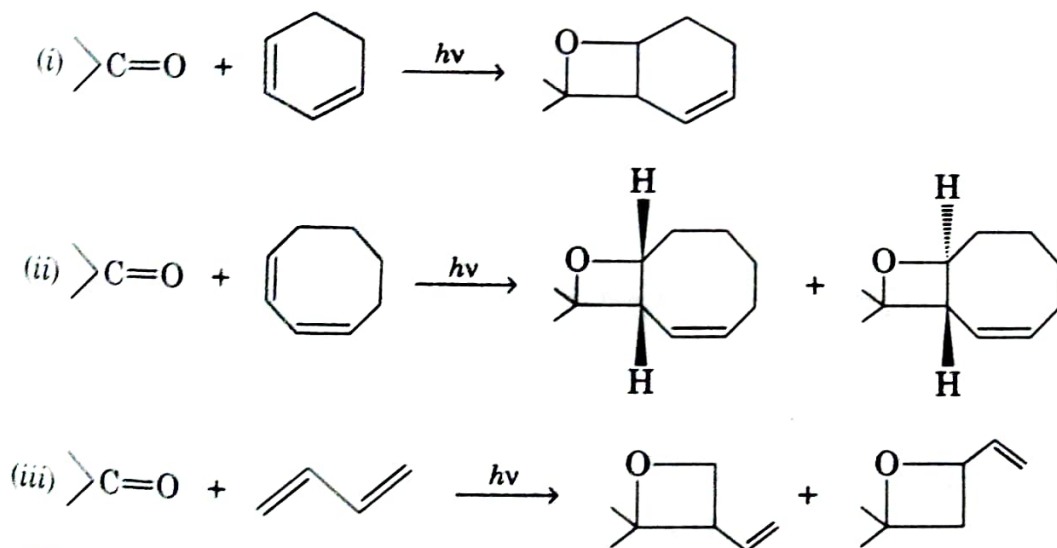
The exciplex (i.e., excited state cyclic complex) has considerable charge-transfer and the stereospecific formation of the products is accounted for if both new bonds are formed simultaneously in the complex, or if the second is formed after the first at a rate faster than the rate of bond rotation. There is again a preference for one orientation of addition, but this is opposite to that expected on the basis of the most stable biradical intermediate. The preference reflects the preferred orientation in the exciplex which is governed by charge densities as illustrated.



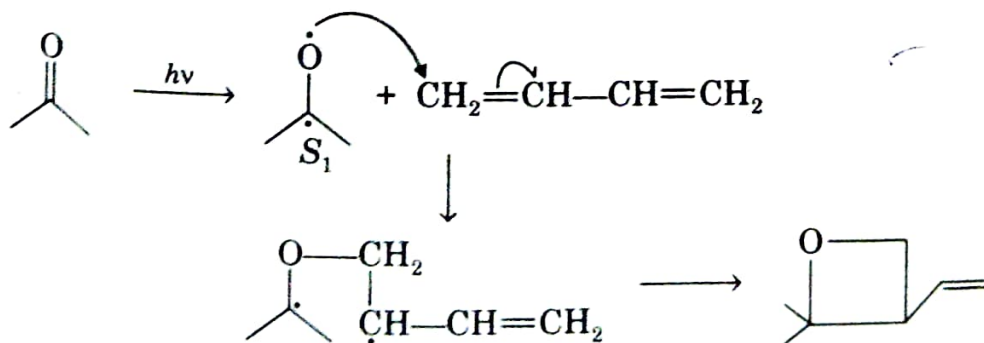
7.7.3 Oxetane Formation with Dienes and Alkynes

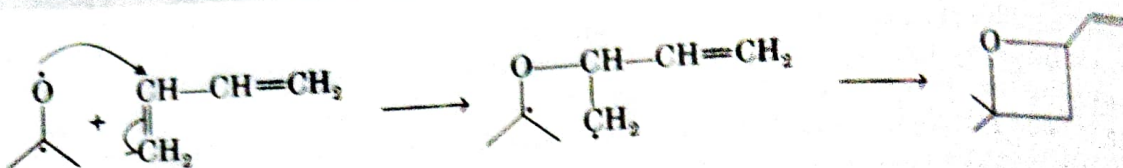
(A) With Dienes

Addition of carbonyl compounds to conjugated dienes is also feasible. The E_T of dienes is usually less than that of carbonyl compounds. However, the formation of oxetanes competes successfully with excitation energy transfer because dienes quench the T_1 ($n \rightarrow \pi^*$) state. Thus formation of oxetanes occurs from the S_1 ($n \rightarrow \pi^*$) state of the carbonyl compounds. Therefore, dienes give stereospecific reactions with dienes. Examples are as follows:

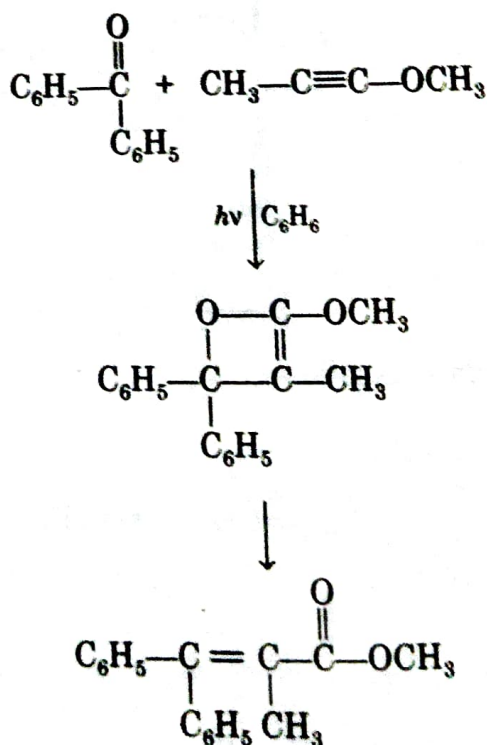
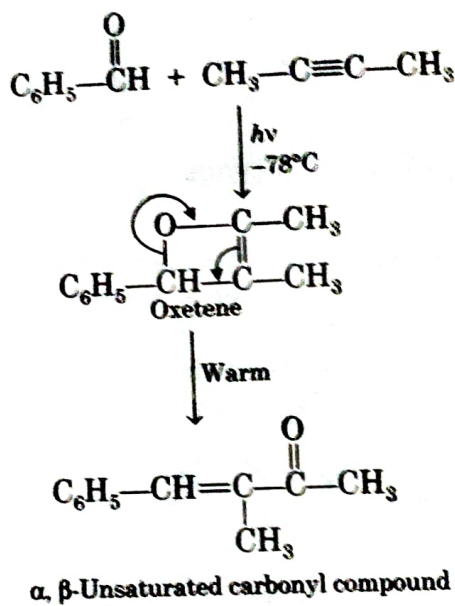


The third reaction takes place as follows:



**(B) With Alkynes**

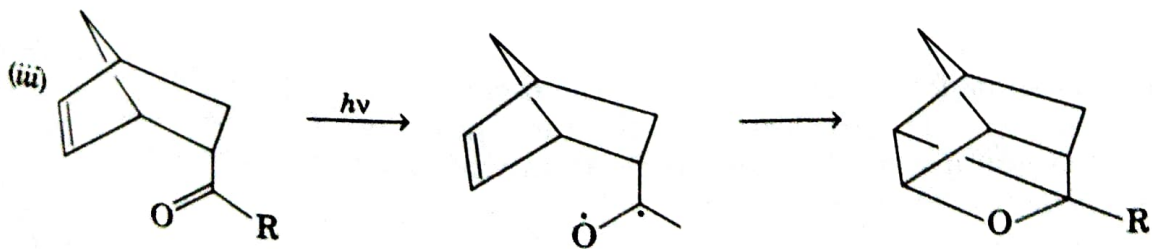
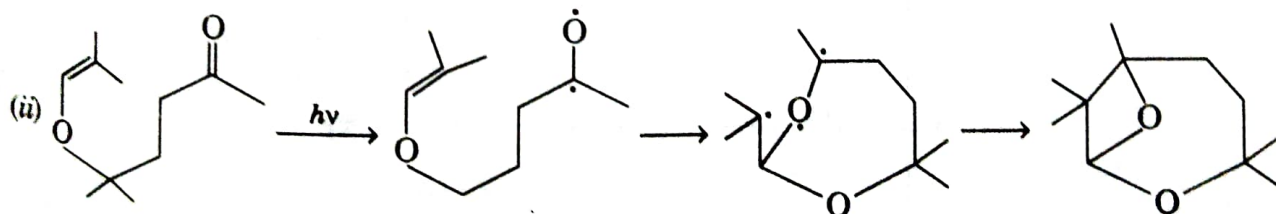
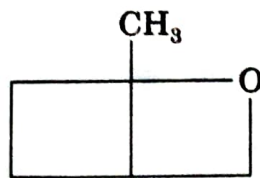
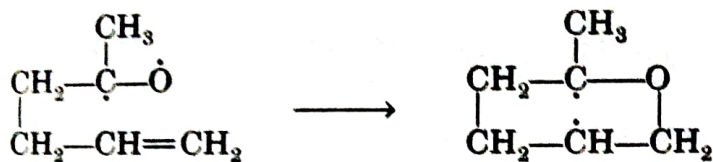
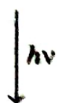
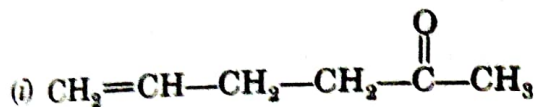
Carbonyl compounds undergo photochemical cycloaddition reaction to alkynes to give oxetenes which are usually not isolated but isomerises to α, β -unsaturated carbonyl compounds in a subsequent thermal reaction.



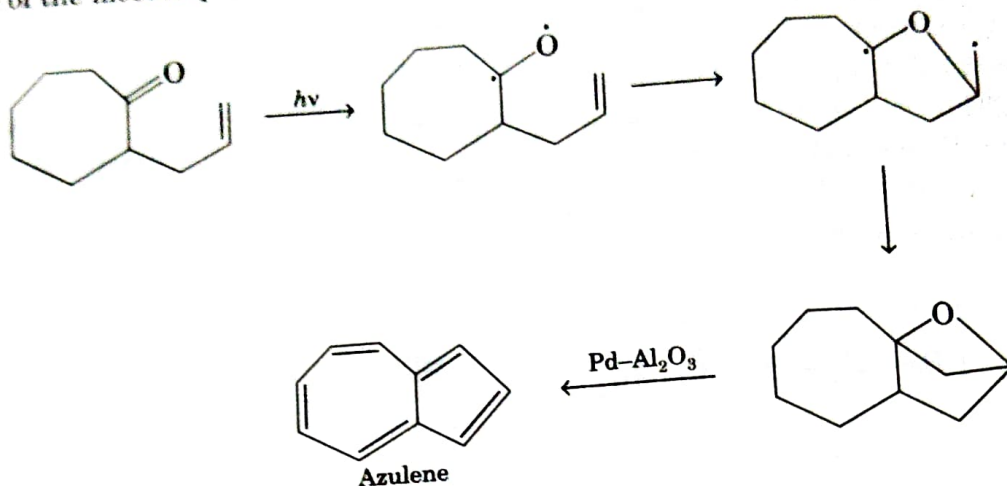
7.7.4 Intramolecular Paterno-Büchi Reaction

Intramolecular Paterno-Büchi reaction is mainly given by γ - δ -enones. The efficiency of these reactions can be attributed to the rapid rate of interaction between the excited $C=O$ group and the ground $C=C$ group. This combination of substrates allows the formation of one regioisomer. Thus yields are high and there is usually no byproduct(s). This reaction is highly efficient and versatile method for the synthesis of a variety of compounds that are difficult or impossible to be prepared by other methods.

Some examples are as follows:

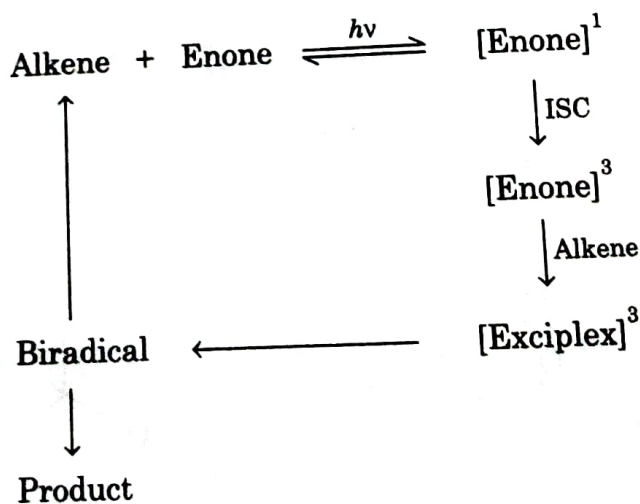


One of the most important reaction of this class is the preparation of azulene as follows:

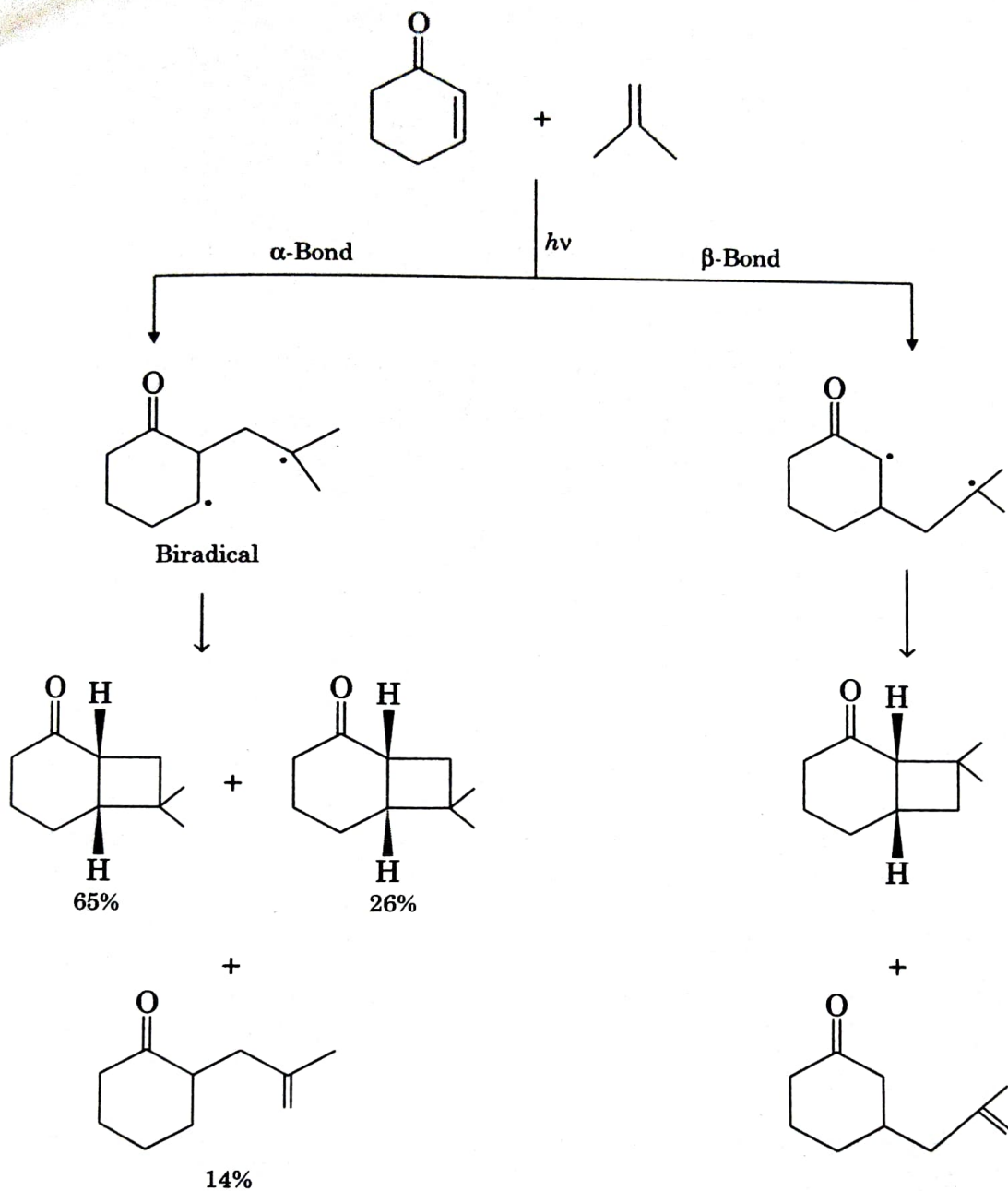


7.8 | 2 + 2 | CYCLOADDITION REACTION OF ENONES WITH ALKENES

Perhaps the most useful reaction of α, β -unsaturated enones is the | 2 + 2 | photocycloaddition reaction with alkenes which affords cyclobutane derivatives. A simplified mechanism is given below:



The biradical can be formed by bonding at the α -carbon or the β -carbon of the enone to the alkene. The reaction is stereoselective at the fused junction. *Cis*-fused 4/5, 4/6 and 5/5 systems are common and are much more stable than their *trans* isomers. 5/6 can be *cis* or *trans*. 6/6 can be *cis* or *trans* but prefers *trans*.



The reaction is regioselective with respect to unsymmetrical alkenes. Electron rich alkenes give head to tail adduct whereas electron-deficient alkenes form head to head adduct.

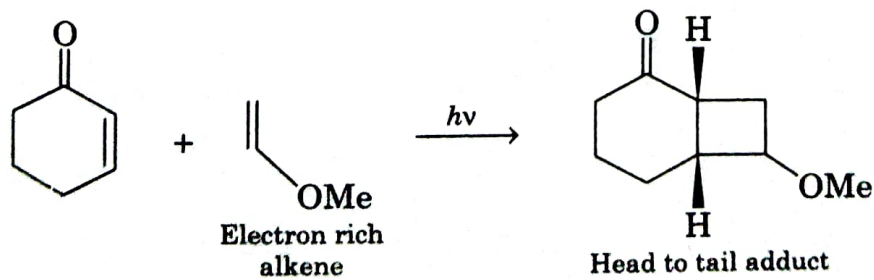
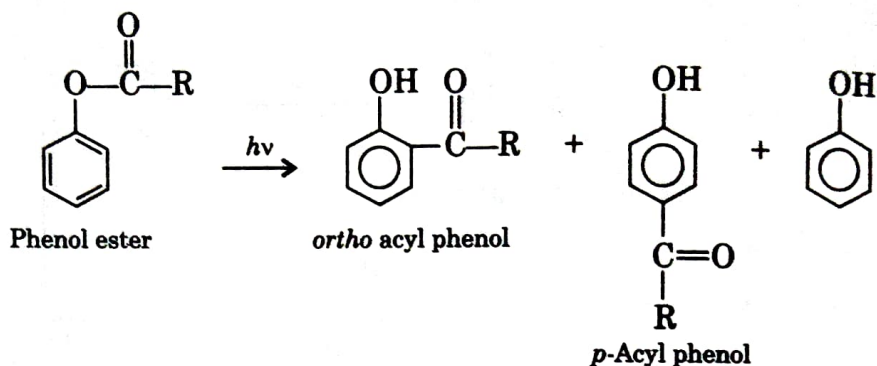
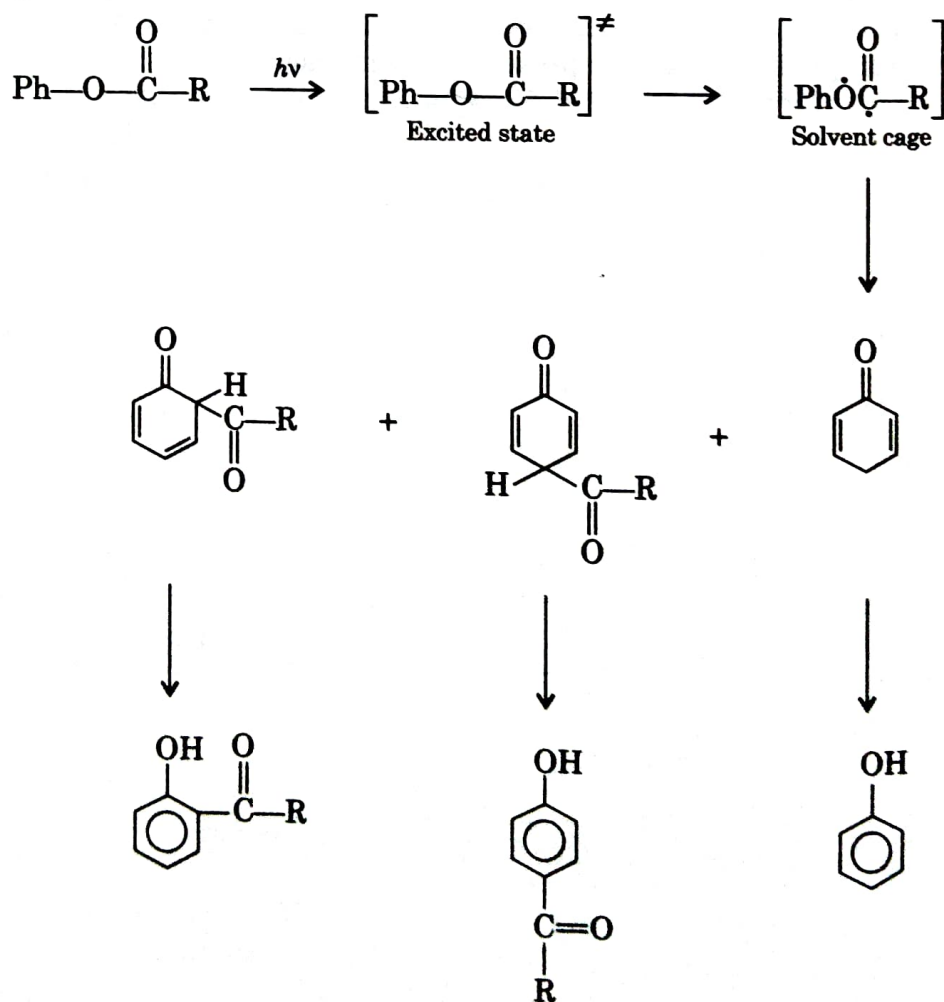


Photo-Fries Rearrangement

The most extensively investigated photo rearrangement is Photo-Fries rearrangement

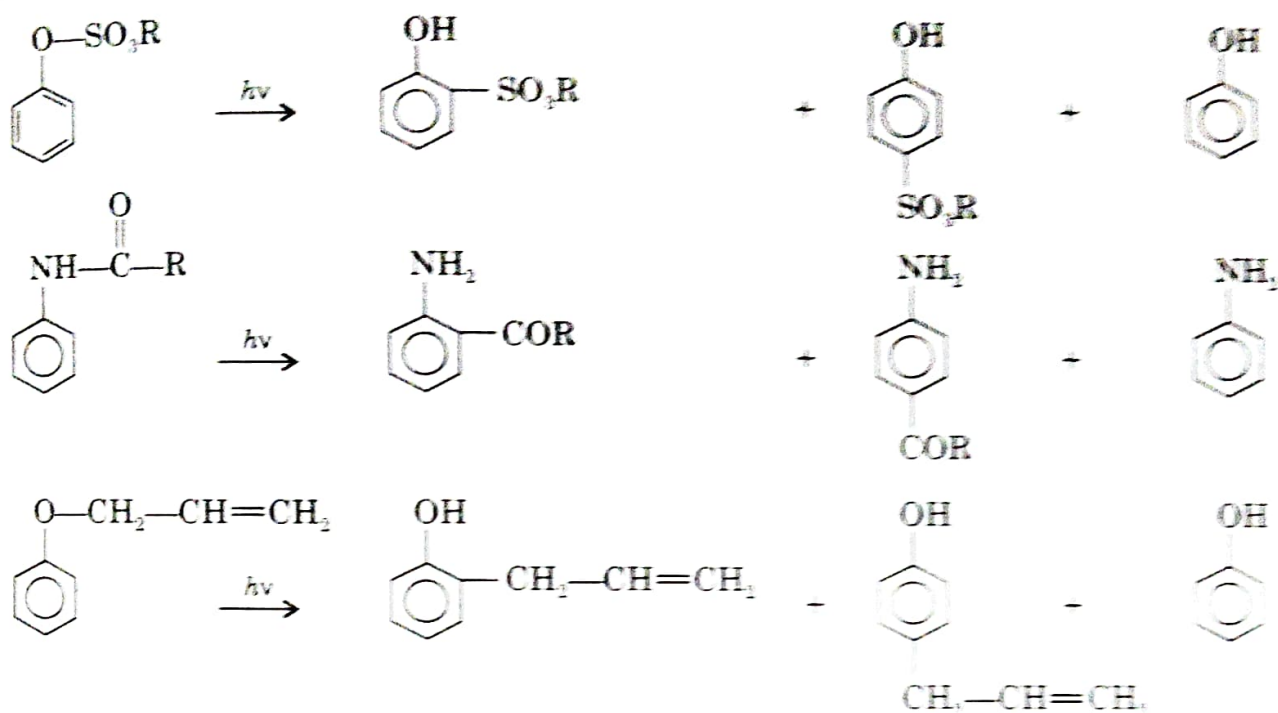


This rearrangement is an intramolecular rearrangement. In this rearrangement substrate undergoes dissociation into phenoxy and acyl radicals which combine within the solvent cage to give intermediates which on aromatisation (or enolisation) give the product. The phenol is produced by phenoxy radicals which escape from the solvent cage.



When this reaction is carried out in gaseous phase, only phenol is obtained. This confirms the formation of solvent cage.

Similar rearrangements are also obtained from the following compounds:



GLOSSARY

Photo-Fries Reaction: The formation of a mixture of *o*- and *p*-acylphenols upon photolysis of phenol ester in solution.

Di- π -Methane Rearrangement: Molecules having the *di- π -methane* moiety, i.e., having two π -systems bonded to a single sp^3 carbon atom undergo a general liquid phase photochemical transformation to vinylcyclopropane, called the *di- π -methane* rearrangement.

Oxa-Di- π -methane rearrangement: Di- π -methane rearrangement given by β , γ unsaturated ketone is known as *oxa-di- π -methane* rearrangement.

FURTHER READING

1. J.M. Coxon and B. Halton, *Organic Photochemistry*, Cambridge University Press, London, 1974.
2. P. de Mayo, ed. *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980.
3. W. Horspool and D. Arester, *Organic Photochemistry, A Comprehensive Treatment*, Ellis Horwood/Prentice Hall, 1992.
4. J. Kopecky, *Organic Photochemistry, A Visual Approach*, VCH, Weinheim, Germany, 1992.
5. J. Kargan, *Organic Photochemistry, Principles and Applications*, Academic Press, 1993.