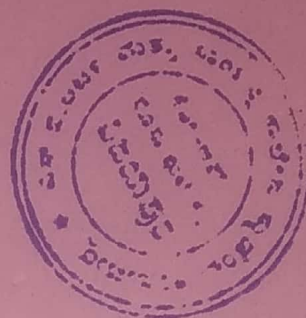


B.L.D.E. Association's

**S. B. Arts & K.C.P. Science College,  
VIJAYAPUR- 586 103.**



# ASSIGNMENT

For B.A./ B.Sc. <sup>3<sup>rd</sup></sup> Semester  
2019 - 2020

Name of the Student DANESHVAR, WALDMARDDA

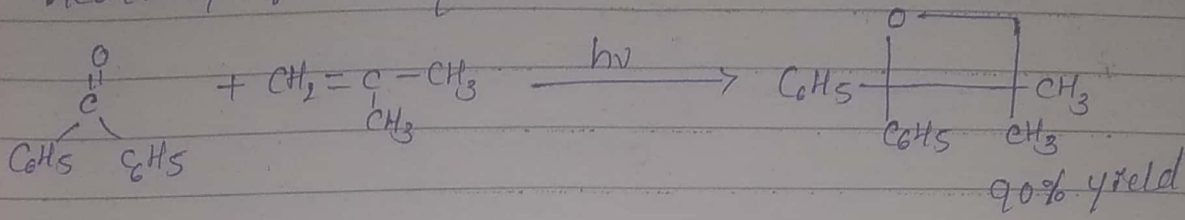
Roll No. 10 R.C.U. Seat No. CH182007

Subject ORGANIC CHEMISTRY

Assignment No.	Date	Marks Assigned	Marks Obtained	Name and Signature of Teacher	Remarks
1					
2					
3					
4					

## Paterno-Buehi Reaction:-

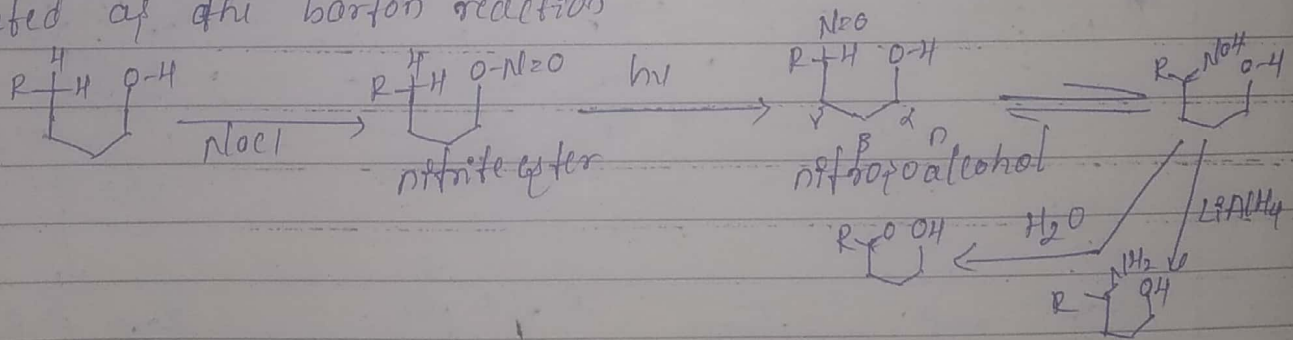
In the presence of olefin, photo excited ketone add to it and yields oxetane the reaction is known as paterno-Buehi reaction. It is one of the first photocyclo addition reactions to be studied



This addition takes place by the absorption of the light in the region of absorption of carbonyl group hence it takes place by the excitation of carbonyl group rather than that of olefin bond

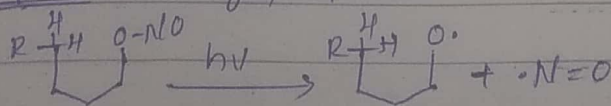
## Barton Reaction:-

Photolytic decomposition of organic nitrites to the alkoxy radicals followed by regioselective intramolecular hydrogen abstraction by the alkoxy radical & the recombination of the resulting carbon radicals with nitric oxide radical produced to form nitroso alcohol is designated as the Barton reaction



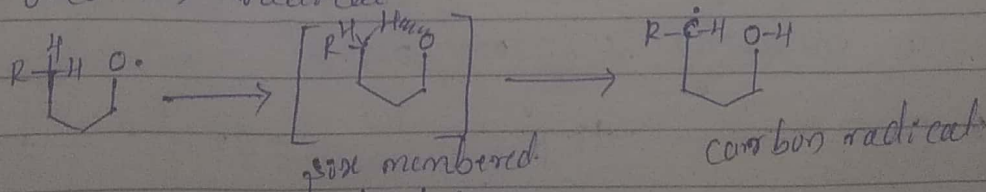
### Mechanism:-

Step-I Homolysis of the nitrite ester on photo irradiation

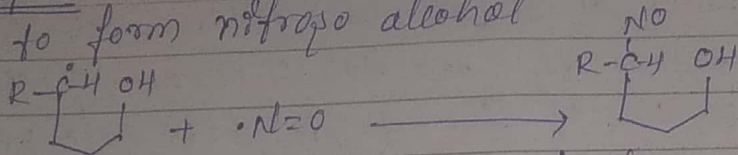


Nitric oxide radical is a stable & long lived radical

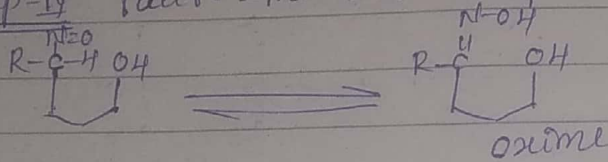
Step-II Intramolecular hydrogen abstraction from  $\delta$  carbon via a six membered cyclic transition state & generation of  $\delta$ -carbon radical



Step-III Recombination of Carbon radical & nitric oxide to form nitroso alcohol



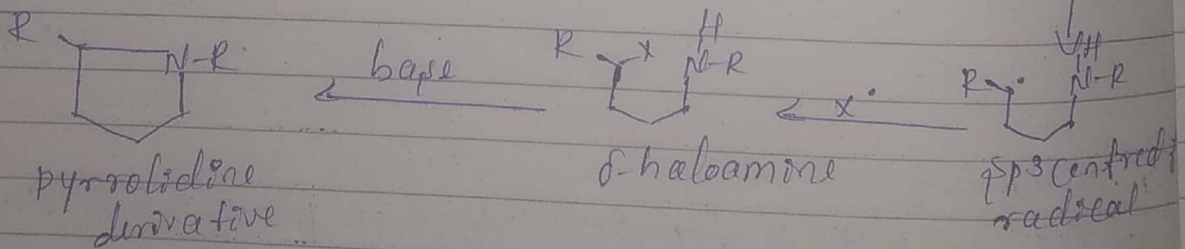
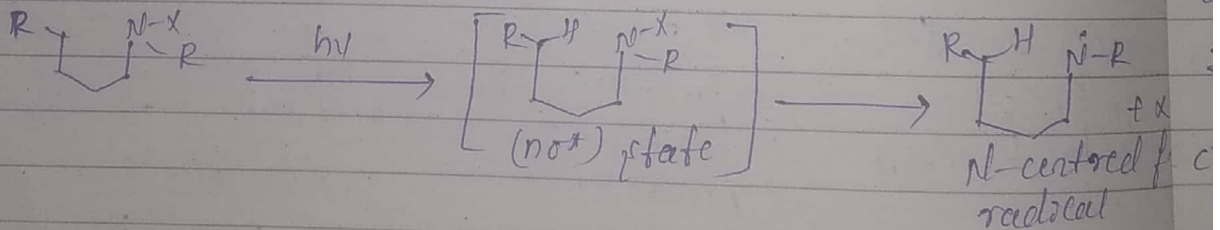
Step-IV Tauto-merization of the nitroso alcohol to an oxime



03) Hoffmann-Löffler-Freytag reaction?

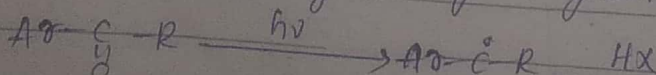
It is heterocyclization reaction involves intramolecular free radical reaction

N-haloamines on irradiation with UV light in a acid solution undergo photooxidation to  $(n\pi^*)$  state which splits off a halogen availability of a  $\delta$ sp<sup>3</sup>-C atom in this free radical leads to an sp<sup>3</sup>-C centred free radical due to intramolecular abstraction of  $\delta$ -H atom the  $\delta$ -halogenated amine obtained from the sp<sup>3</sup>-C centred free radical can be easily cyclised to pyrrolidine derivative with a base



04) photo reduction? (Hydrogen atom abstraction)

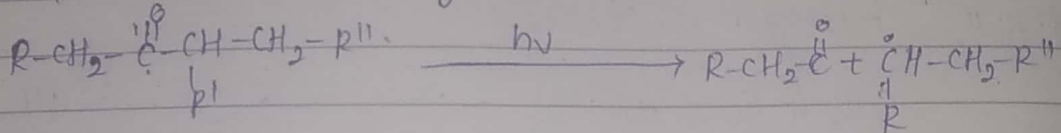
Many aromatic ketones react by hydrogen atom abstraction from solvent or some other hydrogen donor to give diols as the stable products formed by the coupling of the resulting  $\alpha$ -hydroxybenzyl radicals





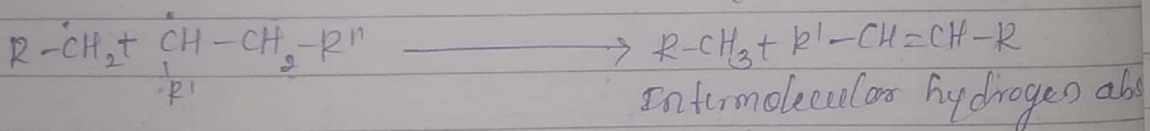
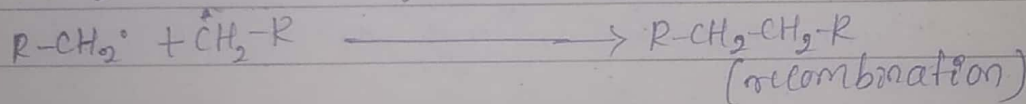
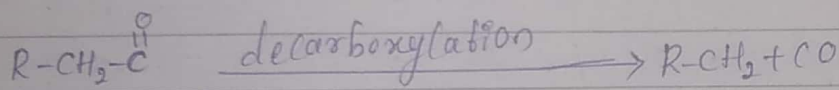
\* Norrish type-II process gives by acyclic saturated before saturated carbonyl compounds under photo irradiation in the gas phase, this process was first observed by R.G. Norrish & it is known as Norrish type-II cleavage process.

01) primary process:- Norrish type-II cleavage is characterized initial cleavage of the carbonyl carbon & the alpha carbon bond to give an acyl & an alkyl radicals this process is known as primary photo-chemical process

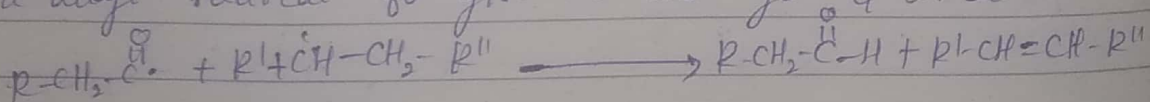


02) secondary process:-

a) Decarboxylation of acyl radical to give carbon monoxide & an alkyl radical this alkyl radical can recombine to give an alkane or can undergo intermolecular hydrogen abstraction to form an alkene & an alkane



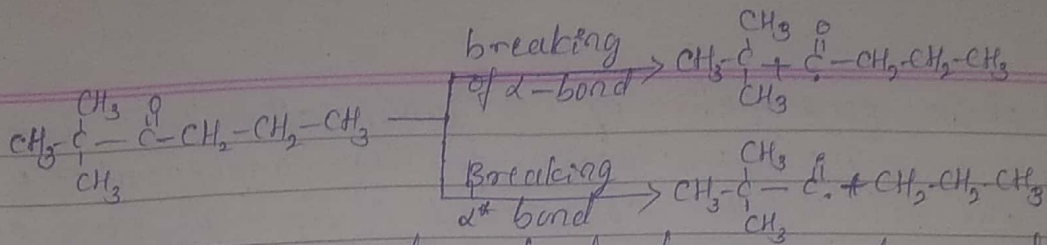
b) Intramolecular hydrogen abstraction by the acyl radical & the alkyl radical to give an aldehyde & an alkene



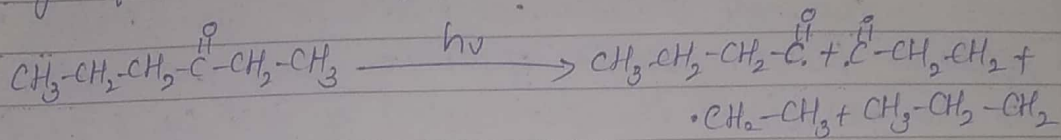
this process can only be possible if alkyl radical has at least one beta-hydrogen

c) Intermolecular hydrogen abstraction by the acyl radical from the alpha-carbon of the alkyl radical to form a ketone & an alkene



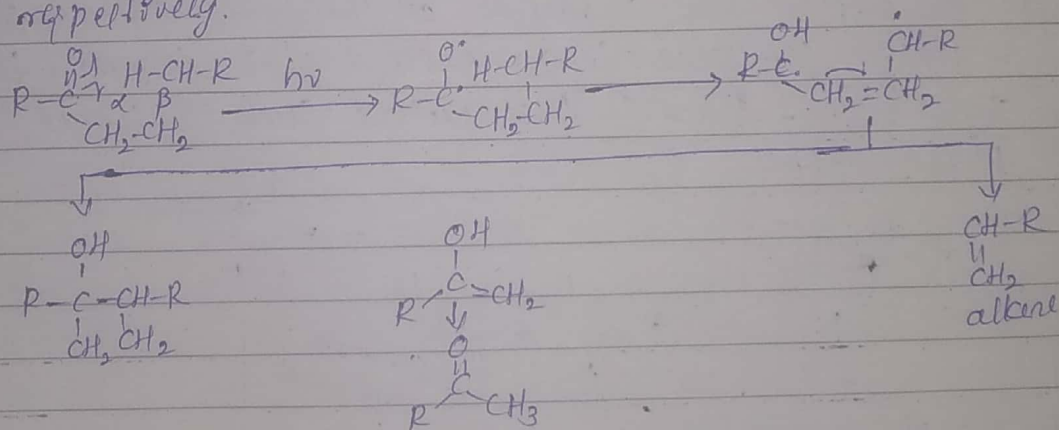


In above case only  $\alpha$ -bond cleavage undergoes if both alkyl substituents are same then there is little selectivity of bond cleavage

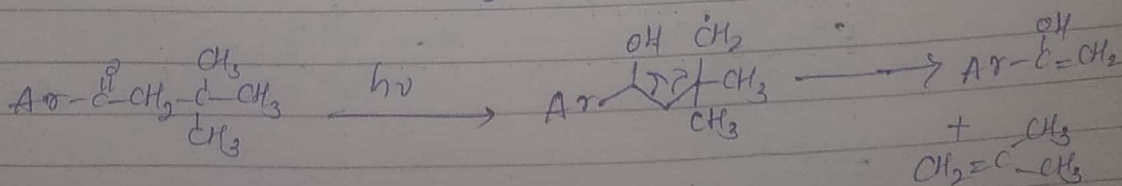
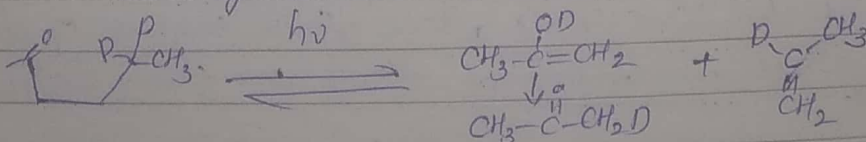


### Norrish type-II Reaction or $\beta$ -Cleavage

If the carbonyl compound contains at least one H-atom at  $\gamma$ -carbon atom. intermolecular abstraction of the  $\gamma$ -hydrogen atom occurs followed by cleavage on cyclisation of diradical to form cyclobutanol derivative respectively.

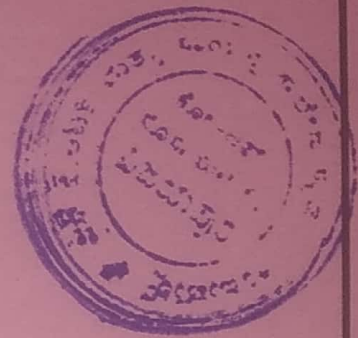


The  $\gamma$ -hydrogen transfer to the oxygen has been shown to be intermolecular the transfer involved a five membered cyclic transition state 5,5-dideuterohexan-2-one on irradiation gives 2-deuteropropene



This singlet state photoelimination reaction occurs with a high degree of stereospecificity in three syntho form of helms

S. B. Arts & K.C.P. Science College,  
VIJAYAPUR- 586 103.



# ASSIGNMENT

For B.A./ B.Sc. .... Semester  
20 - 20

Name of the Student B. S. Pattanashetti

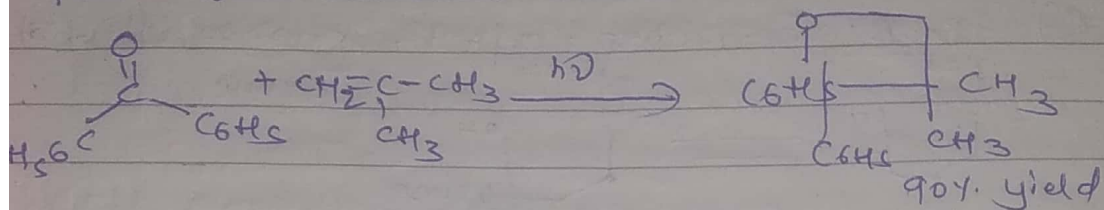
Roll No. 14 R.C.U. Seat No. CH 18 2005

Subject Organic chemistry

Assignment No.	Date	Marks Assigned	Marks Obtained	Name and Signature of Teacher	Remarks
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4					

## 01) Paterno Buchi Reaction?

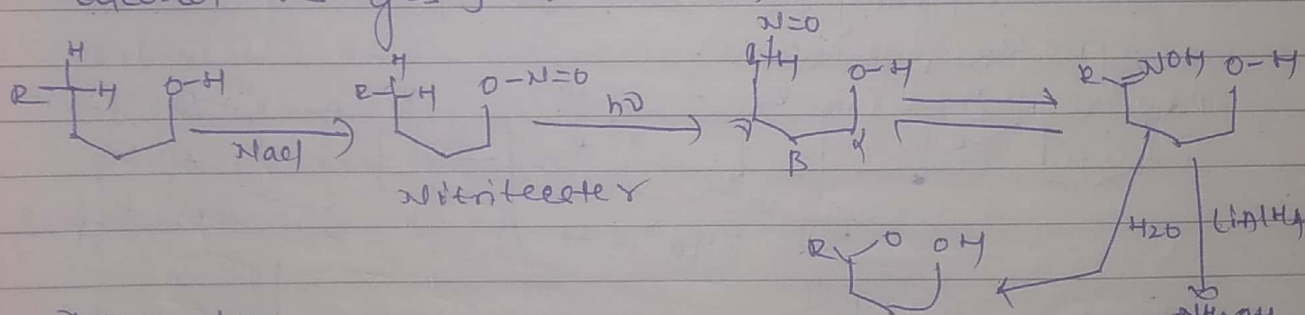
⇒ In the presence of olefin, photo excited ketone add to it and yields oxetone the reaction is known as paterno Buchi reaction. It is one of the first photo cyclo addition reactions to be studied.



This addition takes place by the absorption of the light in the region of absorption of carbonyl group hence it takes place by the excitation of carbonyl group rather than that of olefinic bond.

## 02) Barton Reaction?

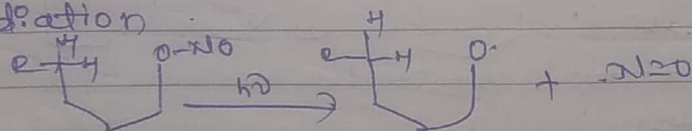
⇒ photolytic decomposition of organic nitrites to the alkoxy radicals followed by regioselective intramolecular hydrogen abstraction by the alkoxy radical & the recombination of the resulting carbon radicals with nitric oxide radical produced to form nitroso alcohol is designated as the barton reaction.



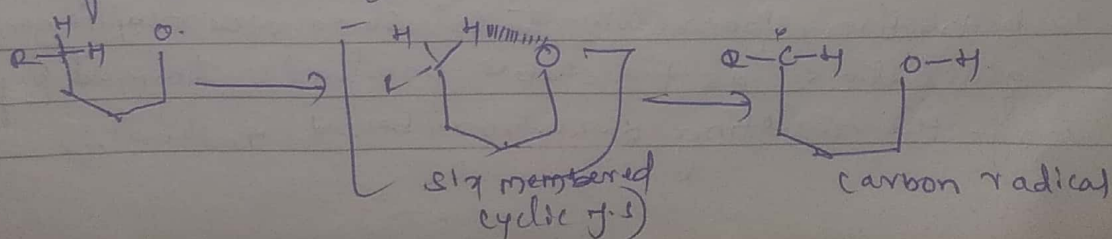
### Mechanism

Step-I) Homolysis of the nitrite ester on photo

irradiation

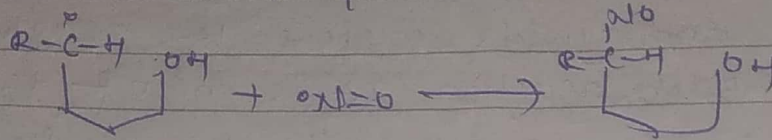


Step-II) Intramolecular hydrogen abstraction from  $\beta$ -carbon via a six membered cyclic transition state, generation of  $\alpha$ -carbon radical.

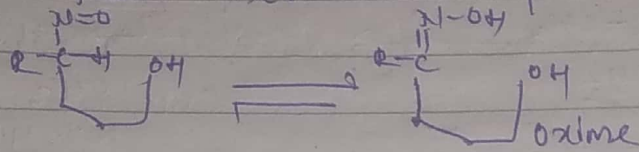




Step-III) Recombination of carbon radical & nitro oxide radical to form nitroso alcohol.



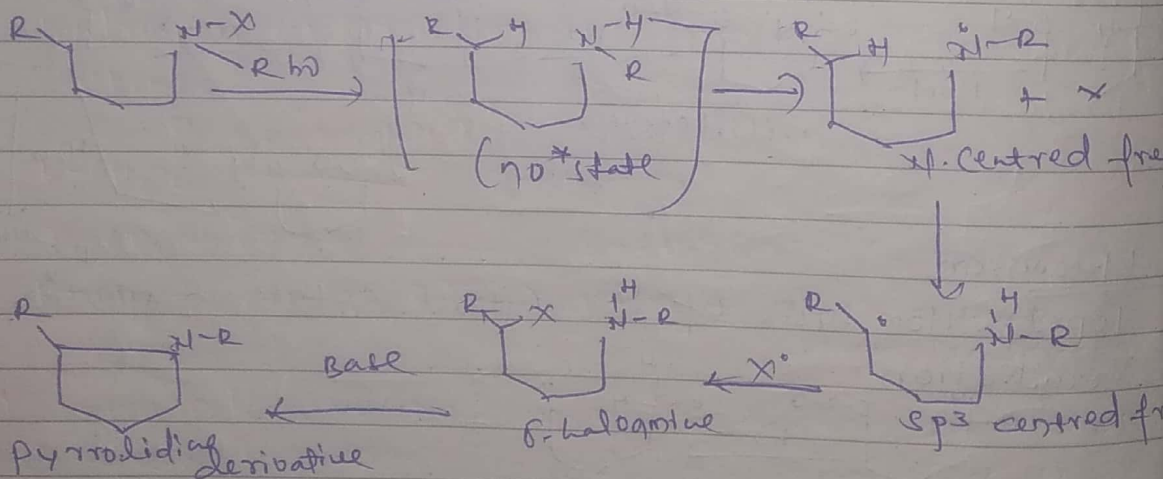
Step-IV) Tauto merization of the nitroso alcohol oxime



03) Hoffman - (b) effler fregtag reaction?

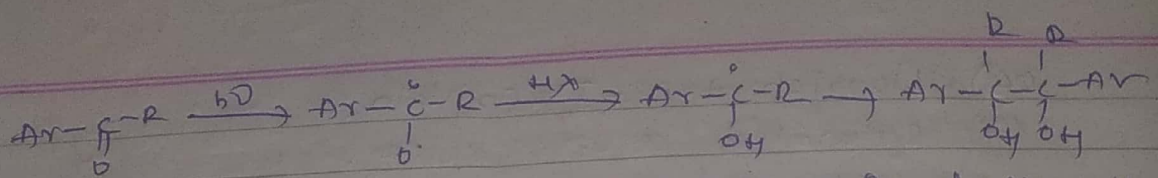
⇒ It is heterocyclization reaction involving intramolecular free radical reaction.

N-haloamine on irradiation with visible acid solution undergo photoexcitation to  $(n\pi^*)$  which splits off a halogen availability of  $\delta$  atom in this free radical leads to an  $sp^3$ -free radical due to intramolecular abstraction  $\delta$ -H atom the resulting  $\delta$ -halogenated amine obtained from the  $sp^3$ -centred free radical can be easily cyclised to pyrrolidine derivative with a base



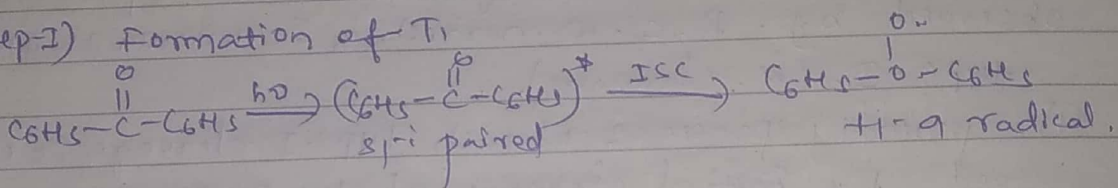
04) photo reduction (Hydrogen atom abstraction)

Many aromatic ketones react by hydrogen abstraction from solvent or some other hydrogen donor to give diols as the stable products formed by the reaction of the resulting  $\alpha$ -hydroxybenzyl radicals.

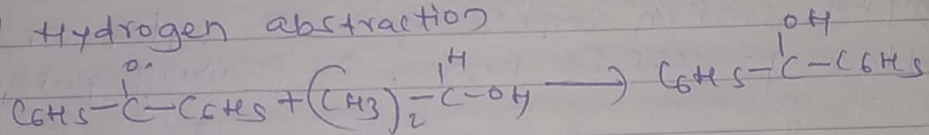


→ An aryl ketone eg. Benzophenone on irradiation in the presence of a hydrogen donor like a secondary alcohol brings about a reductive coupling reaction. The initial excited singlet state goes to a triplet state the triplet contains two compared electrons & thus is a diradical.

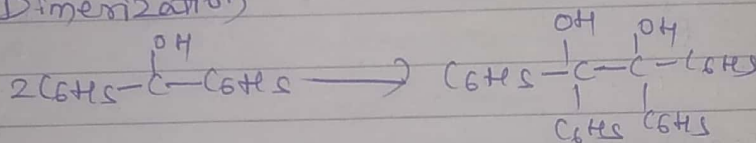
Step-I) Formation of T<sub>1</sub>



Step-II) Hydrogen abstraction

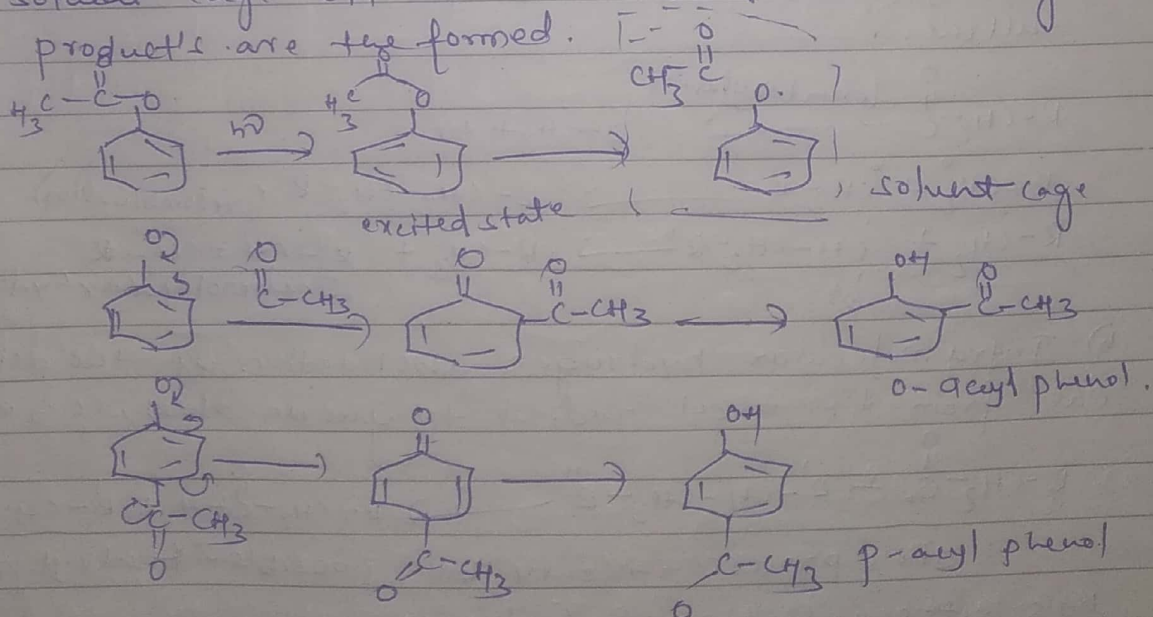


Step-III) Dimerization



5) photo Fries Reaction?

phenol esters in solution on photolysis give a mixture of o & p-acylphenols. In the gas phase where solvent cage effects are not operative many other products are formed.

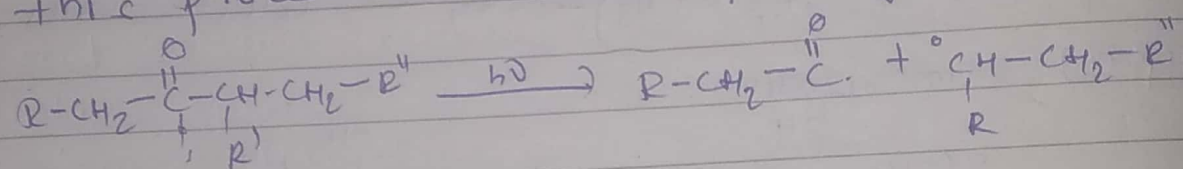


06) Norrish type-I explain.

- 1) saturated alicyclic ketones
- 2) saturated cyclic ketones.
- 3)  $\beta$ - $\gamma$ -unsaturated ketones.

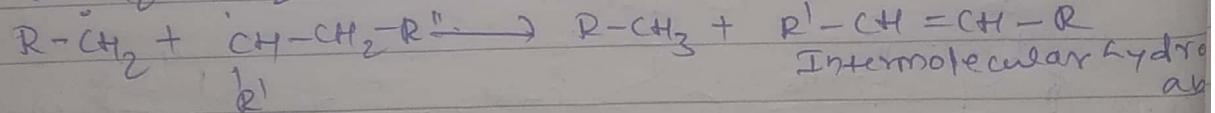
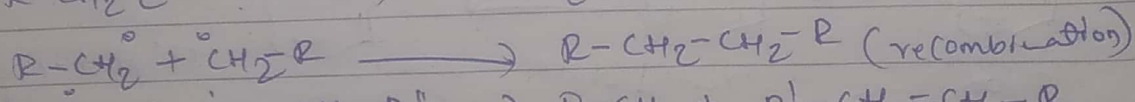
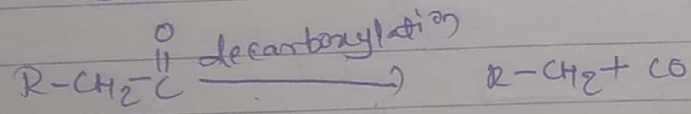
\* Norrish type-I  $\Rightarrow$  process given by acyclic saturated carbonyl compounds under photochemical decarboxylation in the gas phase. This process was observed by R. G. W. Norrish & is known as Norrish type-I. ( $\alpha$ -cleavage).

\* primary process: Norrish type-I cleavage is characterized by initial cleavage of the carbonyl carbon  $\alpha$ -carbon bond to give an acyl & an alkyl radical. This process is known as primary photochemical process.



02) Secondary process:

$\Rightarrow$  Decarboxylation of acyl radical to give carbonyl & an alkyl radical. This alkyl radical can recombine to give an alkane. (or) can undergo intermolecular hydrogen abstraction to form an alkane & an alkene.



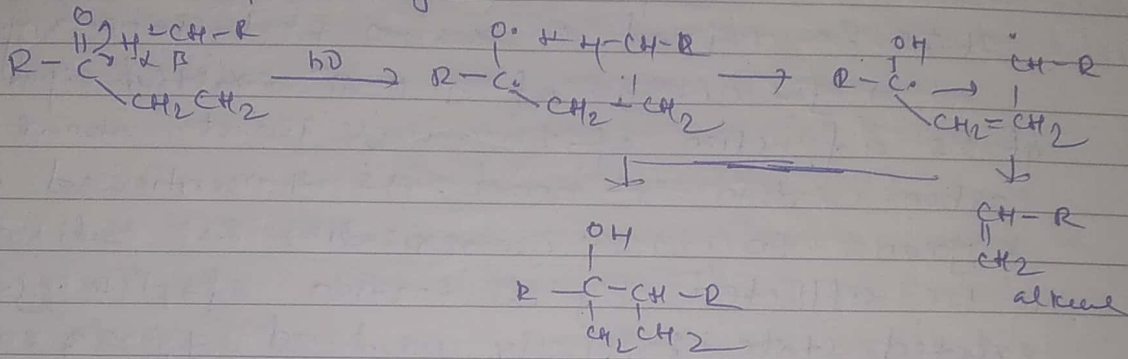
b) Intramolecular hydrogen abstraction by the acyl radical from the alkyl radical to give an aldehyde & an alkene.



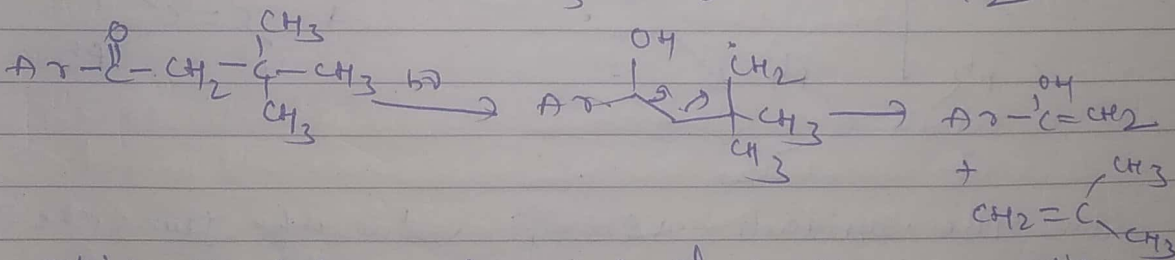
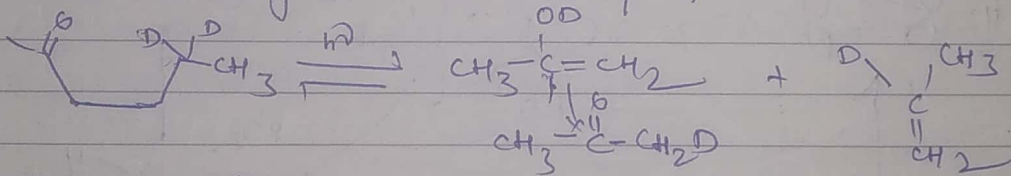
This process can only be possible if alkyl radical has at least one  $\beta$ -hydrogen.

67) Norrish type-II) Reaction &  $\beta$  cleavage

$\rightarrow$  If the carbonyl compound contains at least one  $\beta$ -atom at  $\gamma$ -carbon atom. Intermolecular abstraction of the  $\gamma$ -hydrogen atom occurs followed by cleavage (i) cyclization of diradical to form cyclobutanol derivative respectively.



The  $\gamma$ -hydrogen transfer to the oxygen has been shown to be intermolecular the transfer involved a six membered cyclic transition state. s-s diacetoferohexan 2 one an irradiation gives 2-deuterio propene



This singlet state photo elimination reaction occurs with a high degree of stereospecificity in trans & erythro form of ketone

68) photo isomerization of cis-trans alkene

The isomerization for the simplest alkene is difficult to achieve as a result of the high energy absorption however with more substituted alkenes the UV as a result of the pushed above 200nm so a direct excitation can be more readily achieved