U - II 1E+2S = 20M

Organic photochemistry

* The branch of organic chemistry which study the interaction of light with organic compounds is known as "organic photo-chemistry".

* In organic photochemistry light induced chemical reactions are studied.

* The organic photochemistry is concerned to the synthesis of variety of functional groups in the presence of light.

* The reactions which takes place by the absorption of light are called photochemical reactions.

$$R \xrightarrow{h\nu} \text{products}$$

* When compared to the thermal reactions it is difficult to carryout the photochemical reactions.

* Although photochemical reactions are less photochemistry has its own importance in organic synthesis.

Ex:- 1. photosynthesis

In the photosynthesis carbohydrates are synthesized from CO_2 and H_2O in the presence of light and chlorophyll.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 12O_2$$

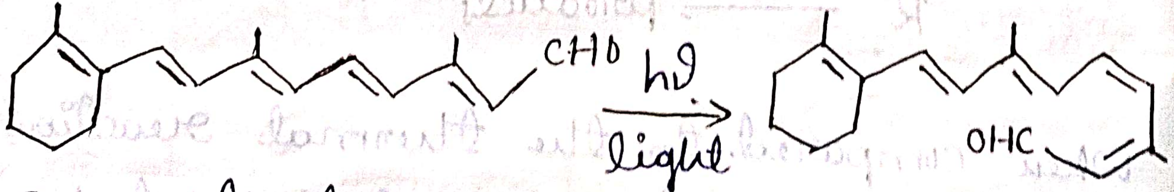
2. Natural synthesis of vit - D by the sun exposure of cholesterol.

3. Formation of ozone from oxygen in the stratosphere.

$$3O_2 \xrightarrow{h\nu} 2O_3$$

4. In vision process:-

The vision process starts by a photochemical reaction of rodospin in the eye, the conversion of trans retinal into cis rentinal takes place only in the presence of light.



Tran retinal

cis retinal

5. The synthesis of highly stained molecules which are difficult to synthesize under thermal conditions.

Photochemical reactions

* The reactions which takes place by the absorption of UV-visible radiation are called "photochemical reactions".

* In the photochemical reactions, the reactant molecules absorb light energy and gets excited, the excited molecules can convert into the products.

$$\underset{\text{reactant}}{M} \xrightarrow[\text{absorb}]{\text{"}h\nu\text{"}} \underset{\substack{\text{Excited}\\\text{molecule}}}{M^*} \longrightarrow \text{products}$$

* During the photochemical excitation reactants molecules are irradiated with the UV visible range of radiation.

* Due to the absorption of UV visible light the electronic transitions occurs and it is sufficient for bond cleavages.

* The range of UV visible radiation is 200–800nm.

Electronic transitions

The promotion of electrons from 1 molecular orbital generally bonding & non bonding molecular orbital to the another molecular orbital (antibonding molecular orbital) is called the electronic transitions.

* In general in organic compounds the following electronic transitions may takes place

1) $\sigma \rightarrow \sigma^*$
2) $\pi \rightarrow \pi^*$
3) $n \rightarrow \sigma^*$
4) $n \rightarrow \pi^*$

1) <u>$\sigma \rightarrow \sigma^*$ transition</u> :-

* The promotion of electron from σ-bonding molecular orbital to σ antibonding molecular orbital is called $\sigma \rightarrow \sigma^*$ transition.
* These transitions are possible in saturated hydrocarbons i.e, eAlkanes, cyclo eAlkanes.

2) <u>$\pi \rightarrow \pi^*$ transition</u> :-

* The promotion of electron from π-bonding molecular orbital to π antibonding molecular orbital is called $\pi \rightarrow \pi^*$ transition.

* These transitions are possible in unsaturated hydrocarbons i.e, eAlkenes, eAlkynes and aromatic hydrocarbons.

3) $n \longrightarrow \sigma^*$ transition :-

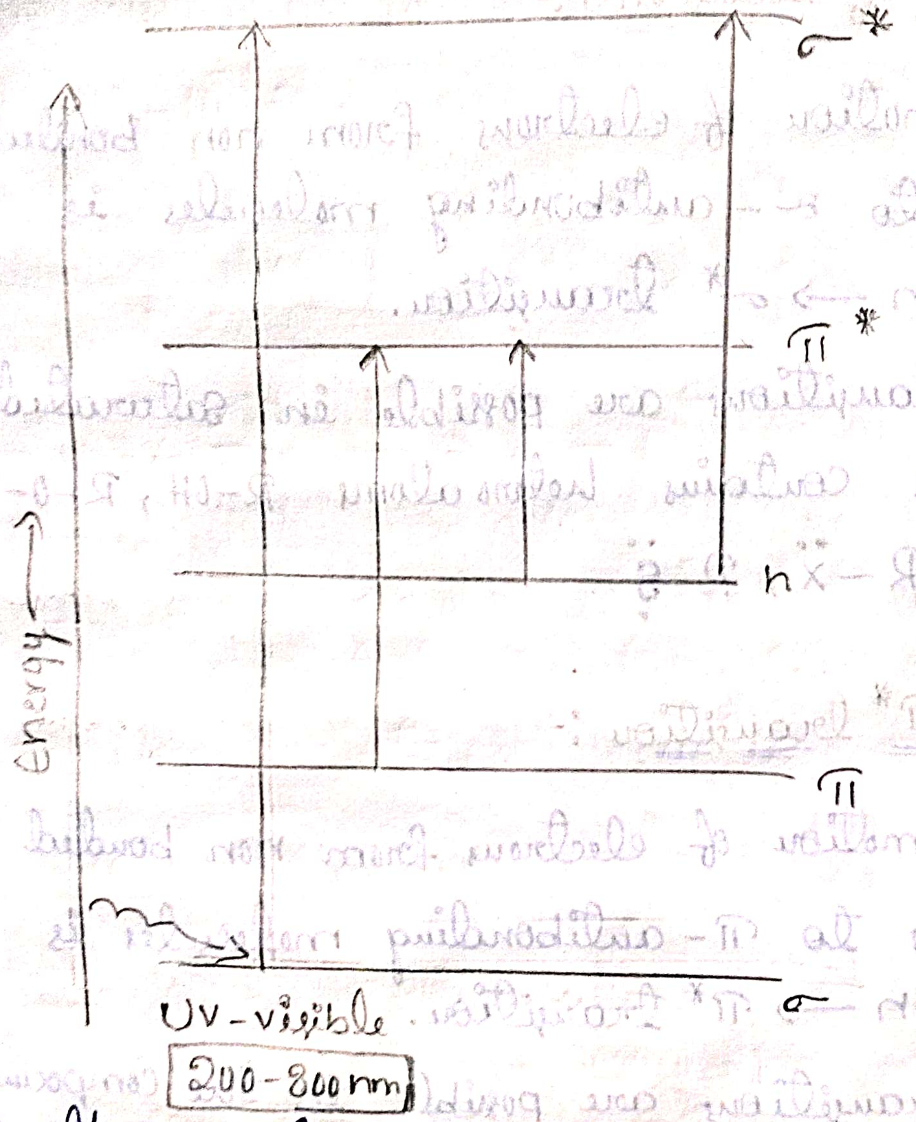
- The promotion of electrons from non bonded orbitals to σ - antibonding molecules is called $n \longrightarrow \sigma^*$ transition.
- These transitions are possible in saturated compounds contains hetero atoms $R-OH$, $R-O-R$, $R-NH_2$, $R-\ddot{X}$, $R-\overset{\cdot\cdot}{\underset{\cdot}{S}}$

4) $n \longrightarrow \pi^*$ transition :-

- The promotion of electrons from non bonded orbitals to π - antibonding molecules is called $n \longrightarrow \pi^*$ transition.
- These transitions are possible in the compounds containing multiple bonds with hetero atoms ie $R-\overset{\overset{O}{\|}}{C}-H$, $R-\overset{\overset{O}{\|}}{C}-R$, $R-\overset{\overset{O}{\|}}{C}-OH$, $R-\overset{\overset{O}{\|}}{C}-OR$.

The energy order among these 4 electronic transition is

$$\boxed{\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*}$$



In these 4 transitions the following two transitions are possible in UV visible range.

- * π – π*
- * n – π*

Electronic excited state :-

Depending on the spin multiplicity(T) the electronic excited states are derived into two types.

1) Singlet excited state
2) Triplet Excited state.

1) Singlet excited state :-

- The excited state which is formed by the " spin retention" under the UV visible radiation is called singlet excited state.
- In this state the two electrons are in opposite spins.
- It is denoted by S.
- The electrons are accamidated in a single orbital with opposite spins. So that they will experience inter electronic repulsions Hence, the singlet states are high energetic and less stable states.

Here, the total spin is $S = +1/2 - 1/2$

$$\therefore S = 0$$

Therefore spin multiplicity $J = 2S+1$

$$J = 2(0)+1$$

$$\boxed{J = 1}$$

- The singlet excited state doesn't effected by the external magnetic field. So that is shows diamagnetic behaviour.

* The Half-life period of singlet excited state is $10^{-6} - 10^{-9}$ sec.

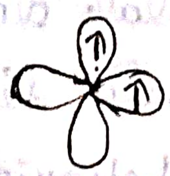
* The singlet excited state the reactant will accouired zwitter ion form

$$A \overset{\frown}{=} B \xrightarrow{h\nu} \overset{\oplus}{A} - \overset{\ominus}{B}$$

* The singlet excited state will participate in the concerted reactions like electrocyclic reactions, σ - tropic reactions etc.

Triplet Excited State:-

* The excited state which is formed by spin inversion under UV visible radiation is called "Triplet excited state."
* In this state the two electrons have same spins.
* It is denoted by "T."
* The electrons are accumidated in different orbitals in same spin. So that they will experience least repulsion forces. Hence the triplet state is low energetic and more stable state.



Here, the spin value is $S = +1/2 + 1/2$

$\therefore S = 1$

Therefore spin multiplicity $J = 2S+1$

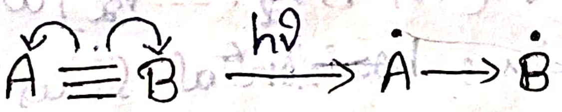
$J = 2(1)+1$

$\boxed{J = 3}$

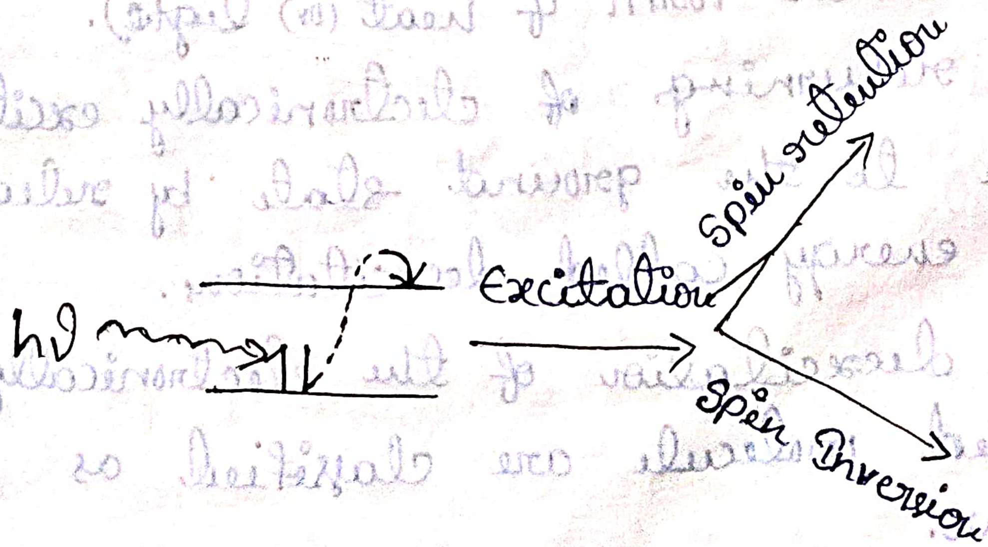
* when the external magnetic field is applied to the triplet state is splitted into 3 different states $(-1/2, 0, +1/2)$.

* Thus, it shows paramagnetic behaviour.

* The triplet state will give radical form to the reactant.



* The half life period for Triplet state is 10^{-4} sec.

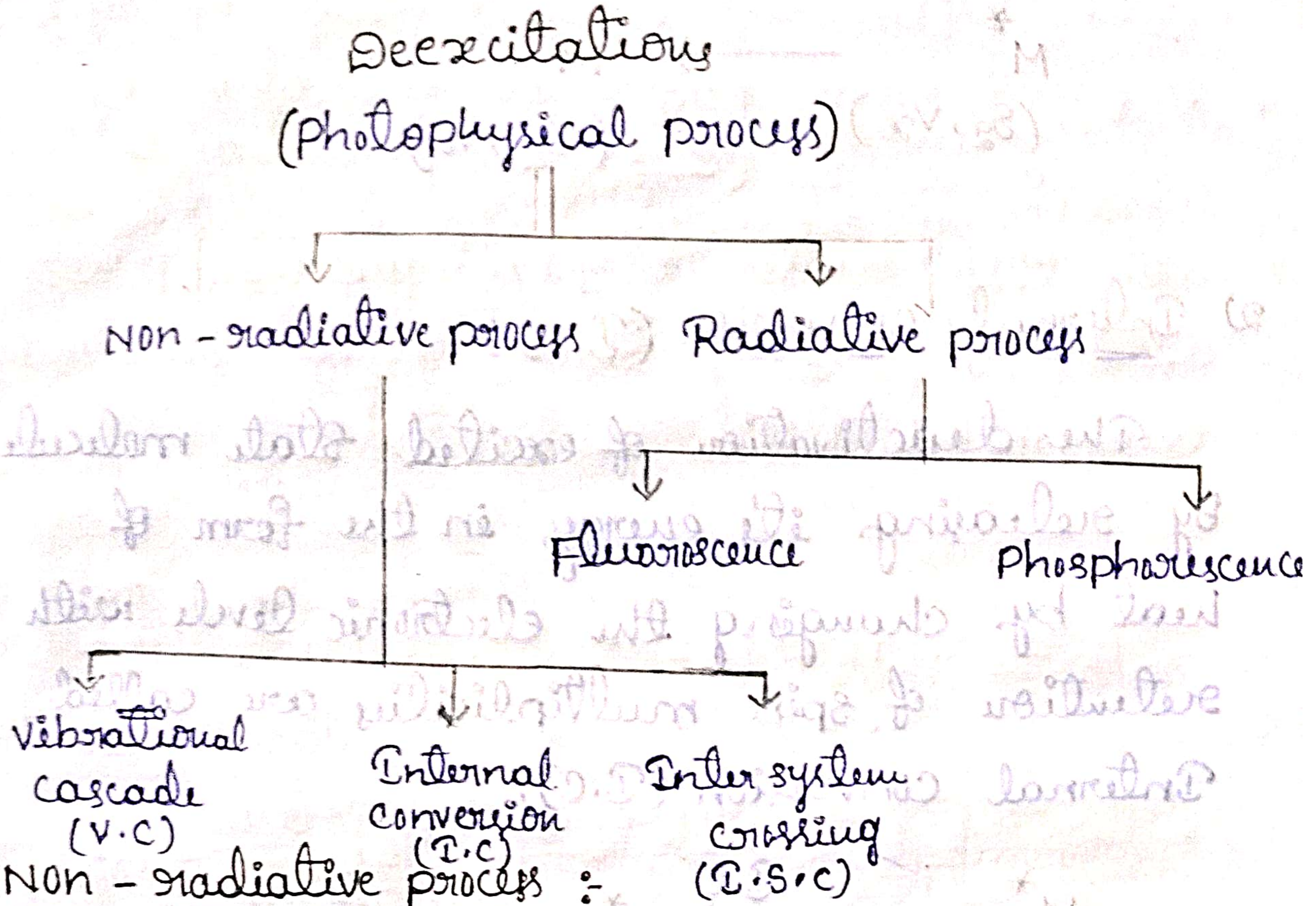


Deexcitation of electronically excited molecul

(or)

Jablouskii Diagram :-

- ∗ The Jablouskii diagram is a schematic representation of the energy transitions caused by the absorption of UV visible radiation by a molecule.
- ∗ In the Jablounskii diagram, the electronic energy states (S_0, S_1, S_2 ---- S_x) and (T_1, T_2 ---- T_x) are indicated by thick lines (▬).
- ∗ The Vibrational energy levels within the electronic states (V_0, V_1, V_2 ---- V_x) are indicat by normal lines ~~horizontal~~ lines (—)
- ∗ once formed the excited singlet & triplet states will either undergo photochemical change (or) photophysical change (loss of its energy in the form of heat (or) light).
- ∗ The returning of electronically excited state to the ground state by releasin its energy called deexcitations.
- ∗ The deexcitation of the electronically excited molecule are classified as follows.



Non-radiative process :-

* The returning of excited state molecule to the lower energy state usually ground state by loss of it's excess energy in the form of heat is called non-radiative process (or) thermal transition.

* again the non-radiative transitions are further classified into 3 types.

1) **vibrational cascade (V.C) :-**

Deactivation of excited state molecule by releasing it's energy in the form of heat by changing the vibrational levels with in the same electronic level it is called vibrational cascade (V.C).

$$\underset{(S_2, V_x)}{M^*} \longrightarrow \underset{(S_2, V_0)}{M^*}$$

2) Internal conversion (I.C) :-

The deactivation of excited state molecule by releasing it's energy in the form of heat by changing the electronic levels with retention of spin multiplicities are called Internal conversion (I.C).

$$M^*_{(S_2, V_0)} \xrightarrow[\Delta]{I.C} M^*_{(S_1, V_0)}$$

3) Inter system crossing (I.S.C) :-

The deactivation of excited state molecule by releasing it's energy in the form of heat by changing spin multiplicities it is called Inter system crossing.

$$\underset{(S_1, V_0)}{M^*} \xrightarrow[\searrow\Delta]{I.S.C} \underset{(T_1, V_0)}{M^*}$$

Radiative process :-

- * The returning of excited state molecule to the lower energy state usually ground state by loss of it's excess energy in the form of light is called radiative process.
- * The radiative processes are two types.

1) Fluoroscence :-

- * The deactivation of excited state molecule by the emission of light by retention of spin multiplicities is called "Fluoroscence".
- * It is the allowed process.
- * Fluroscence is a faster process ($10^{-6} - 10^{-9}$ sec)

$$M(S_2, v_0) \xrightarrow[\curvearrowright h\vartheta]{} M(S_0, v_0)$$

2) Phosphorescence :-

- * The deactivation of excited state molecule by the emission of light by changing the spin multiplicities is called phosphorescence.
- * It is a forbidden process.
- * The phosphorescence is a delayed process (10^{-4} sec)
- * The non-radiative transitions are indicated by wavey arrow ($\rightsquigarrow$)

- ~~All these~~
- The radiative process are indicated by normal arrow (⟶)
- All these radiative & non-radiative process are systemetically shown in the Jablonski's diagram as below.

The photochemistry of carbonyl compounds

* when the carbonyl compounds absorbs light energy in UV visible region they may undergo the following electronic transitions.

(i) $n \longrightarrow \pi^*$ Transitions

(ii) $\pi \longrightarrow \pi^*$ Transitions

* During the absorption of light the carbonyl compounds may undergo following photo-chemical reactions.

1) Photo cleavages
2) Photo cyclo additions
3) Photo rearrangements
4) Photo reductions.

1) Photo Cleavages :-

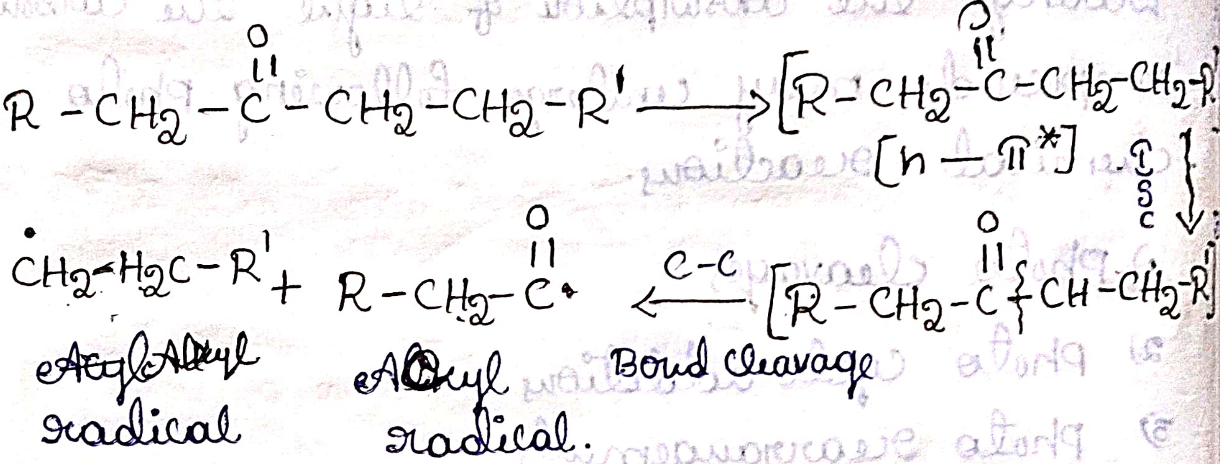
* The cleavages of C-C bond by the irradiation with light are known as "photo cleavages."

* In carbonyl compound the following photo-cleaves are observed.

1) Norrish type - I cleavages.
2) Norrish type - II clevages.

1) Norrish type - I cleavage :-

when the ketones are irradiated with light then they under go α C-C bond cleavage and forms acyl radical & alkyl radicals this process is known as Norrish type - I cleavage.



$$R-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-R' \longrightarrow [R-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-R']_{[n-\pi^*]} \xrightarrow{ISC} [R-CH_2-\overset{O}{\overset{\|}{C}}\{CH-CH_2-R']$$

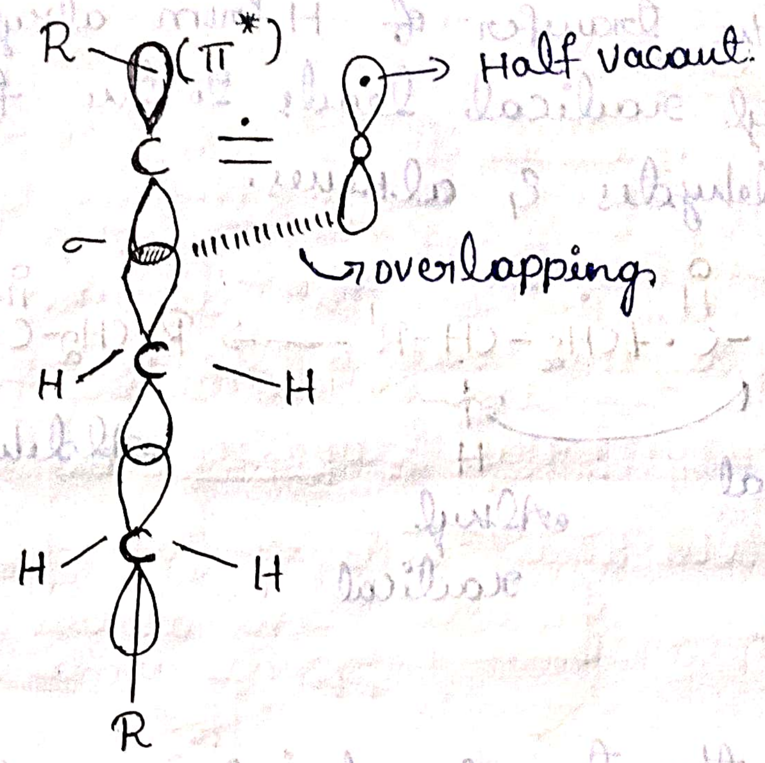
$$\dot{C}H_2-H_2C-R' + R-CH_2-\overset{O}{\overset{\|}{C}}\cdot \xleftarrow{C-C} [R-CH_2-\overset{O}{\overset{\|}{C}}\{CH-CH_2-R']$$

Explanation :-

* when the molecule absorb UV visible light then $[n \rightarrow \pi^*]^1$ and $[n \rightarrow \pi^*]^3$ states are formed.

* During the $n \rightarrow \pi^*$ transition the non-bond orbital of oxygen become half vacant and hence it is electrone deficient and it overlaps with the spacillay closed nearest α - σ bonding orbitals.

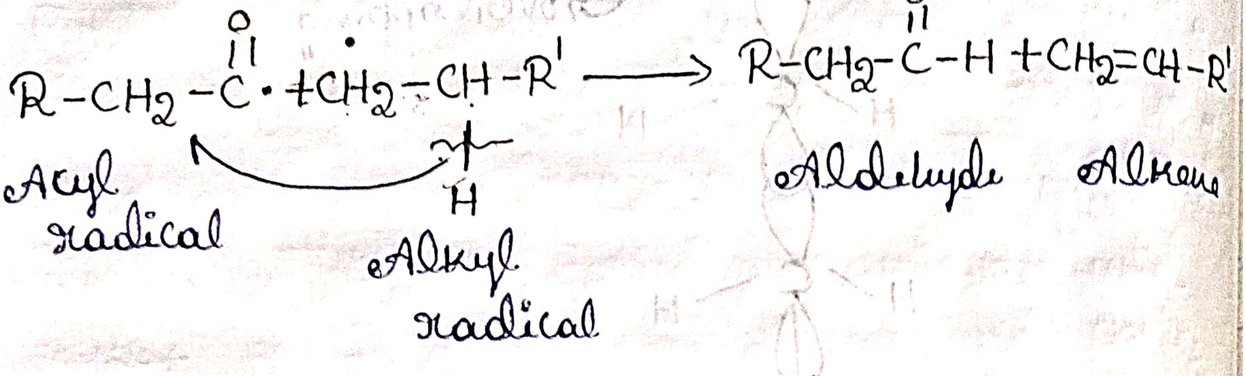
* Due to this partial transfer of electron cloud from α C-C bond to non bonding orbital makes α C-C bond weake and facilitates α C-C bond cleavage on irradiati



General features of Norrish type - I clevage :-

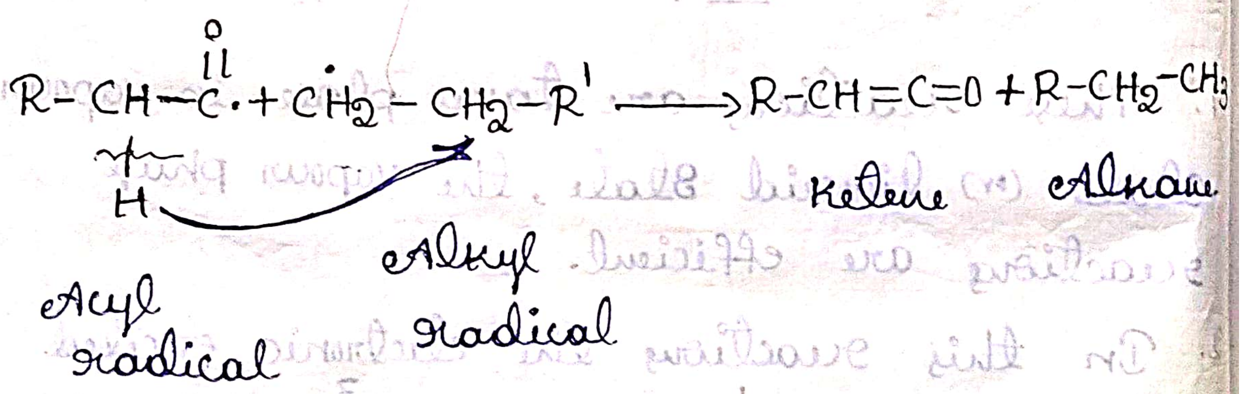
1. These reactions are takes place in vapour state (or) liacuid state, the vapour phase reactions are efficient.
2. In this reactions the electronic excited state $[n \longrightarrow \pi^*]^1$ & $[n \longrightarrow \pi^*]^3$. In these two states $[n \longrightarrow \pi^*]^3$ state reactions are efficient.
3. During the reaction the reaction intermediates are acyl radical & alkyl radicals.
4. These two radicals can be stabilised by the following roots.

A) By the transfer of $\dot{H}$ from alkyl radical to acyl radical leads to the formation of aldehydes & alkenes.



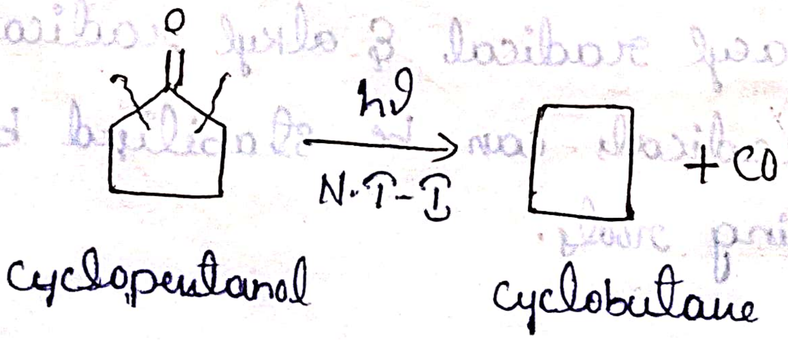
$R-CH_2-\overset{O}{\overset{\|}{C}}\cdot + CH_2-\underset{H}{CH}-R' \longrightarrow R-CH_2-\overset{O}{\overset{\|}{C}}-H + CH_2=CH-R'$

B) By the transfer of $\dot{H}$ from acyl radical to alkyl radical leads to the formation of ketenes & alkanes.

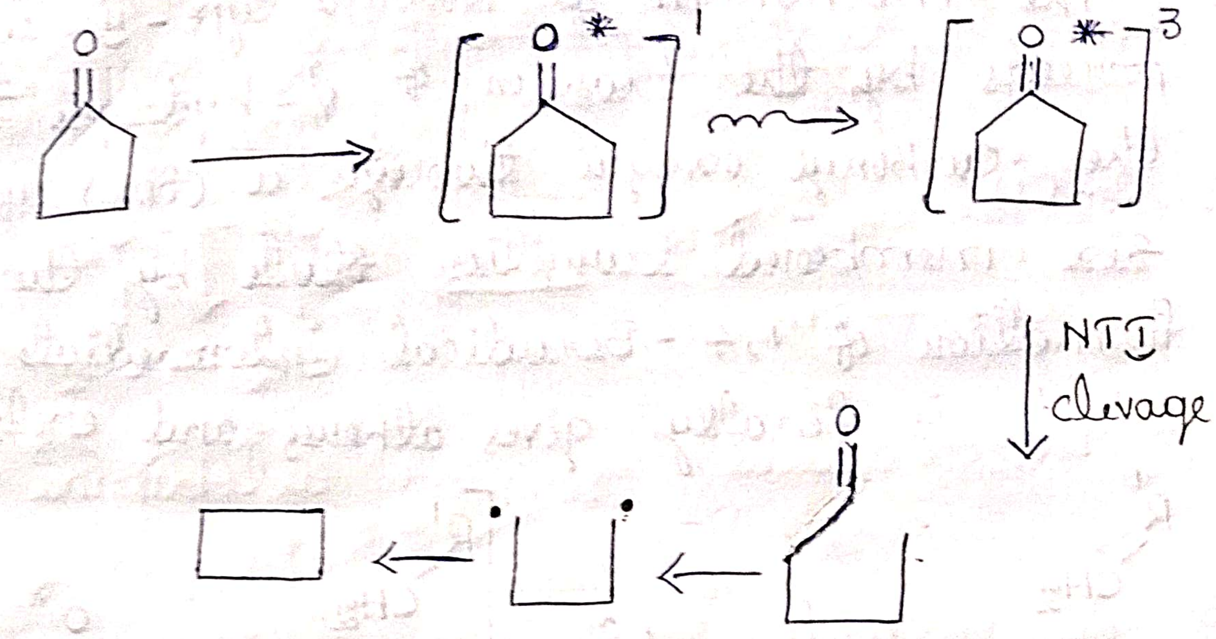


$R-\underset{H}{CH}-\overset{O}{\overset{\|}{C}}\cdot + \dot{C}H_2-CH_2-R' \longrightarrow R-CH=C=O + R-CH_2-CH_3$

5. In Norrish type- I cleavages the strained and unsaturated carbonyl compounds undergo decarboxylation process.



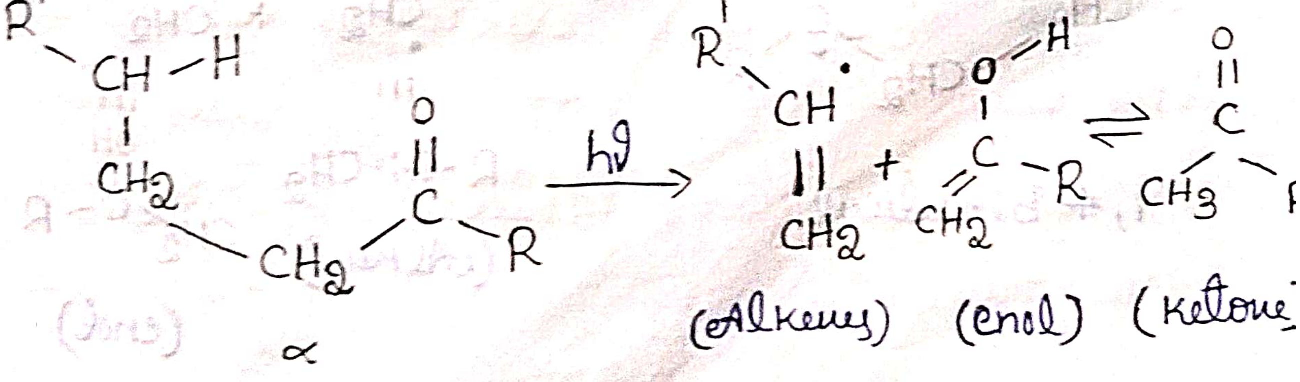
Mechanism



Norrish type - II Cleavages :-

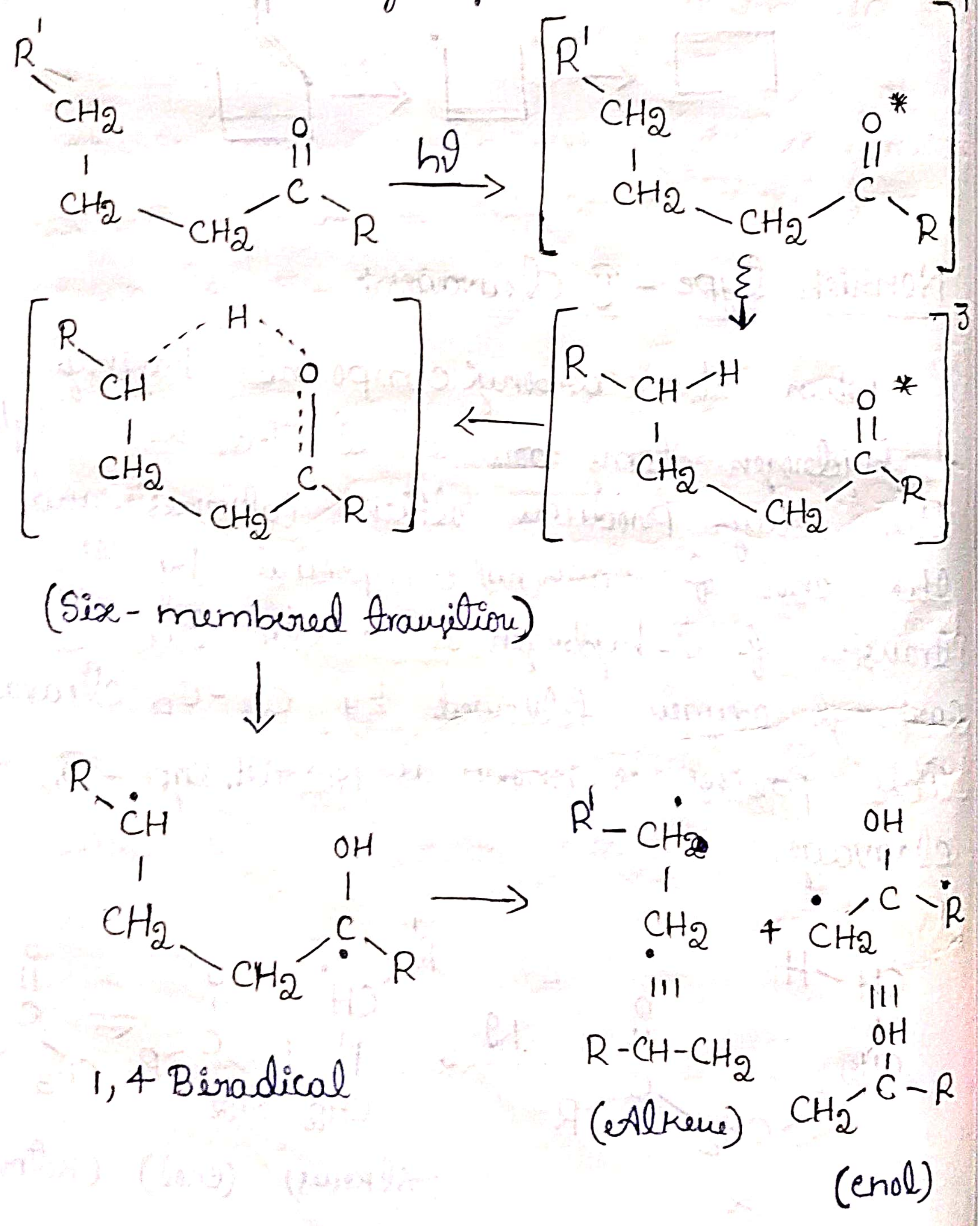
When the carbonyl compounds having γ- hydrogen atoms are irradiated with light then they produces olfiens (alkenes) and the enol of carbonyl compound by the transfer of γ- hydrogen atoms to the carbonyl oxygen followed by $C_\alpha - C_\beta$ cleavag

This process is known as Norrish type - II cleavage.



Mechanism :

The mechanism of Norrish type - II cleavage proceeds by the transfer of γ - hydrogen to the carbonyl oxygen through a (six) cyclic six membered transition state by the formation of 1,4 - Biradical intermediate which is finally gives alkenes and enols.



characterstics :-

* The carbonyl compound is irradiated at the λ_{max} of that carbonyl compound.

* In the Norrish type - II reactions, the excited states are $[n \longrightarrow \pi^*]^1$ and $[n \longrightarrow \pi^*]$

* The $[n \longrightarrow \pi^*]^1$ state, reactions are "Sterospecific."

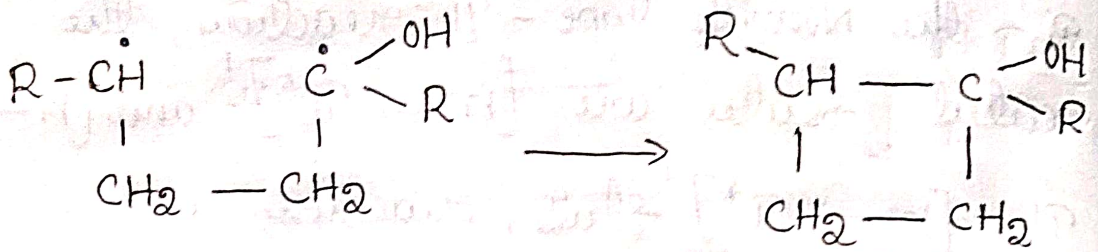
* The $[n \longrightarrow \pi^*]^3$ state, reactions are "Non- sterospecific"

* The reaction intermediates are 1,4 Biradical

* The 1,4-Biradicals are getting stabilizatio by the following roots :

(1) By the involving in $C_\alpha - C_\beta$ cleavage (Norrish - type - II cleavage) and produces eAlkenes and enols of carbonyl compound.

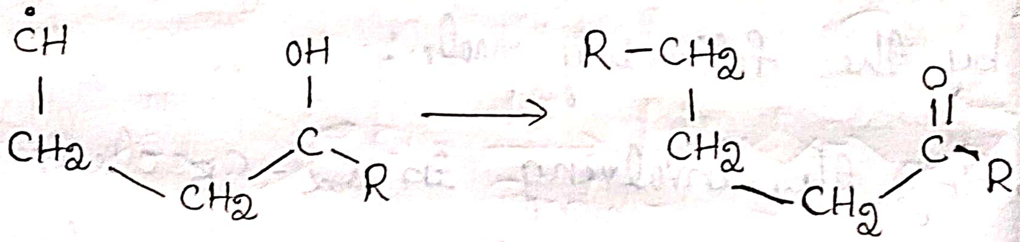
(2) By direct cyclization leads cyclobutanol derivative, this cyclization is called <u>Yang cyclization</u>



1,4 Biradical

cyclobutanol

(3) By returning into the starting material by the transfer of Hydrogen from carbonyl oxygen to γ- carbon.



1,4 Biradical

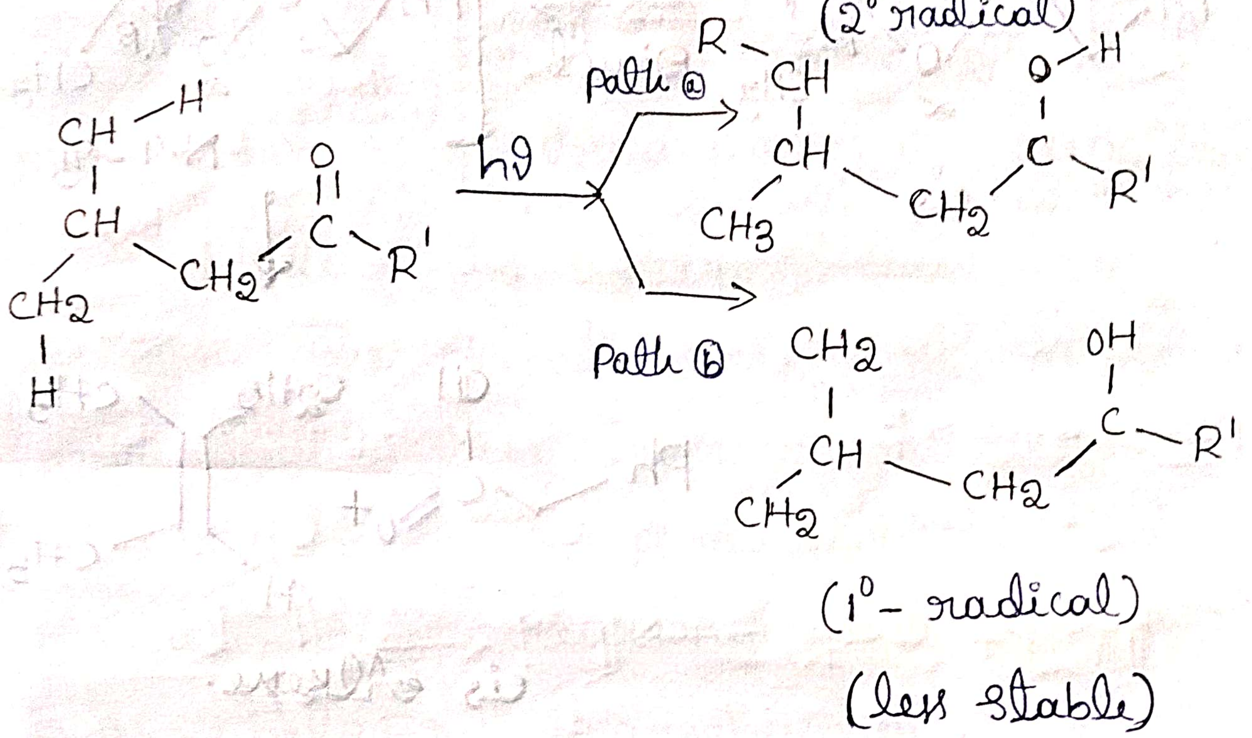
carbonyl compound

* In carbonyl compound if more than one kind of γ- hydrogens are presente the weaker γ_{C-H} bond cleavages takes place over other.

That means they produces more stable free radicals.

(i.e)

$$\boxed{3^\circ\text{-}\nu_{C-H} > 2^\circ\text{-}\nu_{C-H} > 1^\circ\text{-}\nu_{C-H} > \text{methyl } \nu_{C-H}}$$



Sterochemistry of N.T-II :

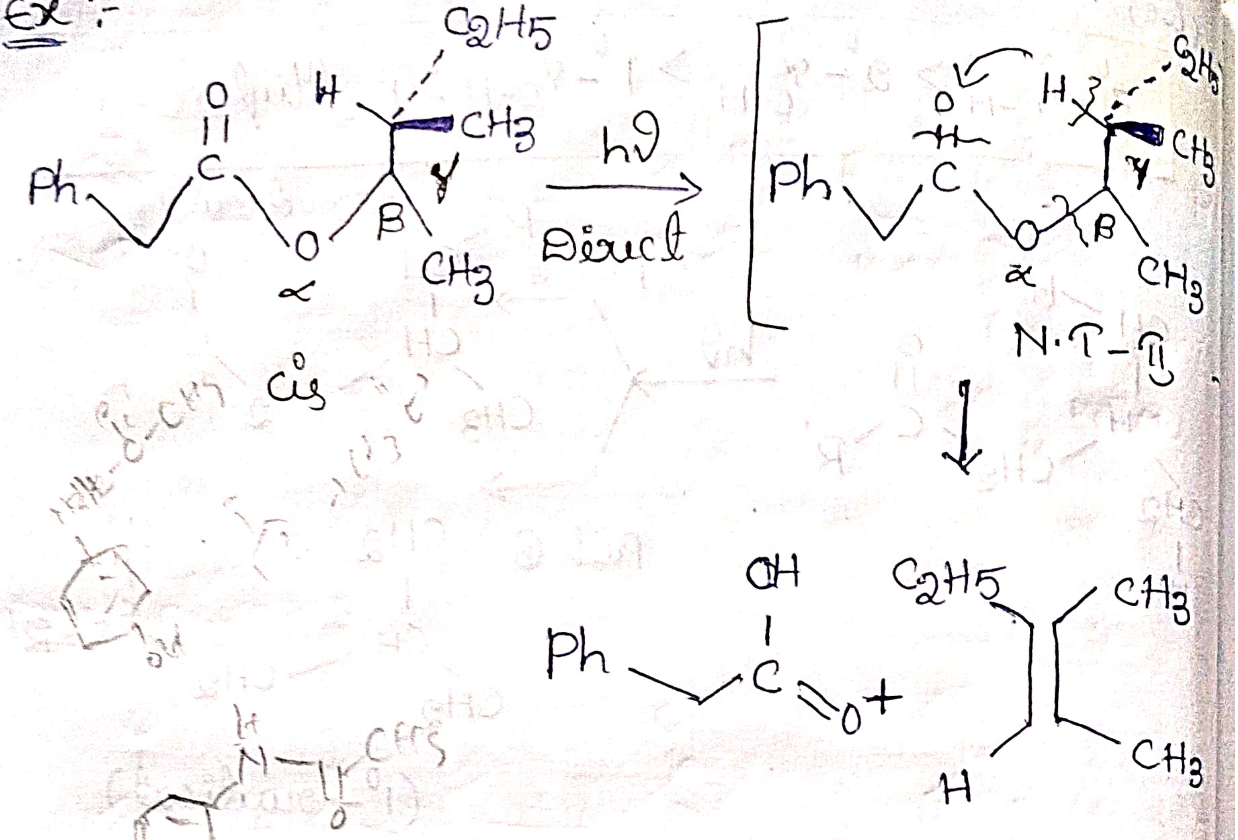
* If Norrish type-II reactions proceed through the $[n \rightarrow \pi^*]^1$ excicted (through) those reactions are sterospecific.

That means, the stereochemistry of the reactant retains in the product (alkene).

* While, the reactions proceed through $[n \rightarrow \pi^*]^3$ excited state those are Non-sterospecific.

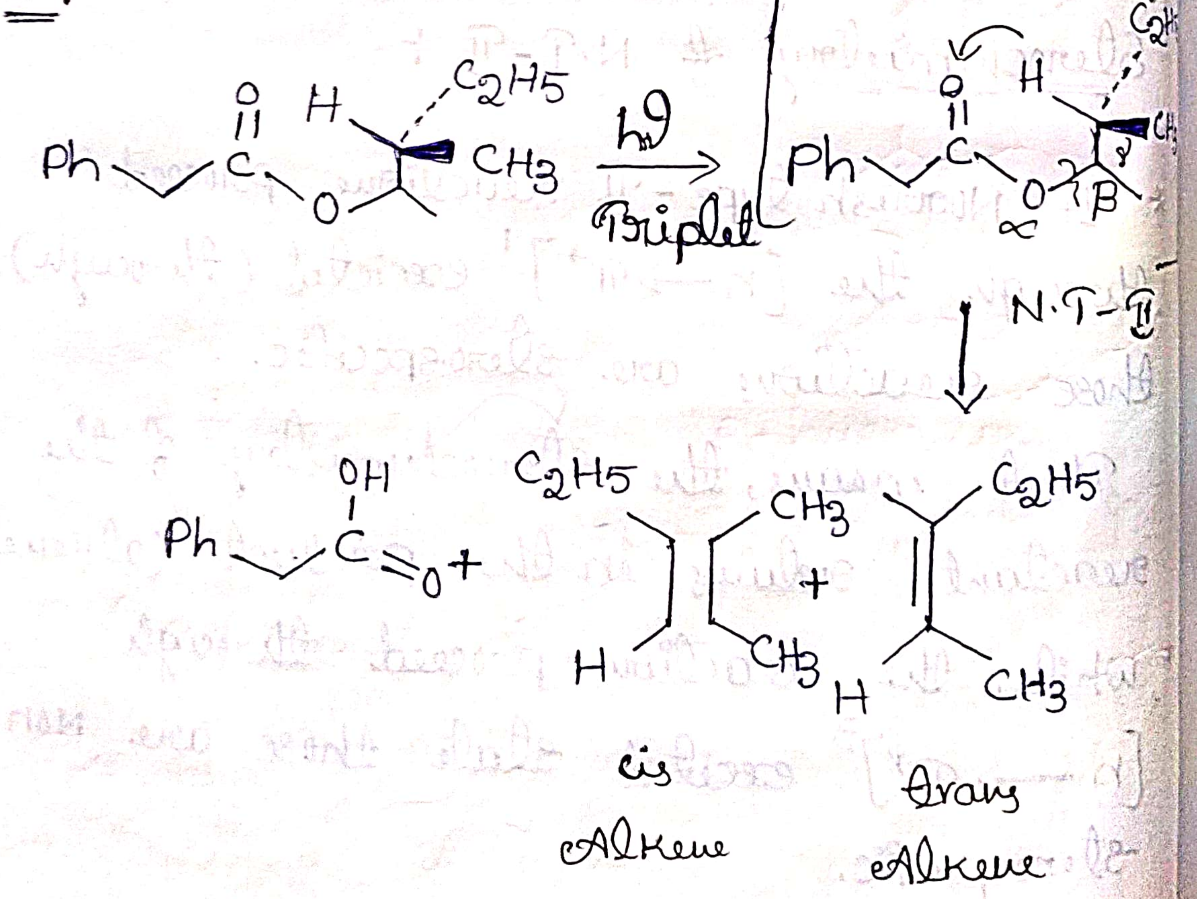
· That means, the mixture of sterochemicall-y products are obtained.

Ex:-



cis Alkene.

Ex:-

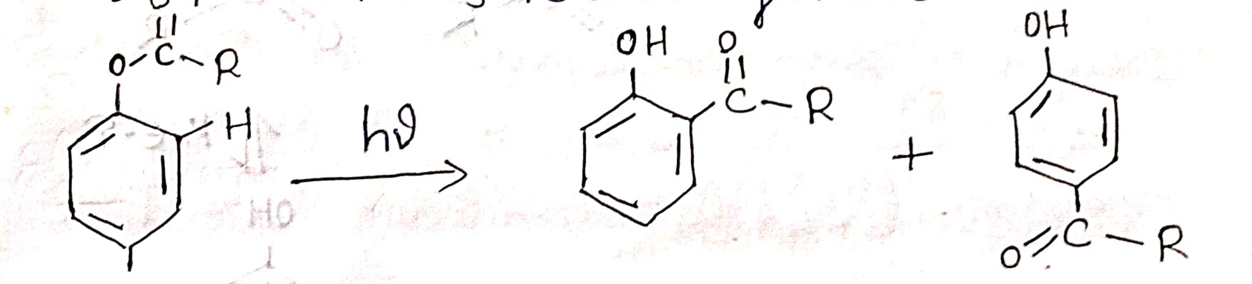


Photorearrangements

The rearrangement reactions which takes place in the presence of light are known as photorearrangement reactions.

Ex: Photo Fries rearrangement

when the phenolic esters are irradiated with light then there re-arranges to ortho - hydroxy (or) para - hydroxy acyl Ketones this rearrangement is known ~~is~~ as Photo Fries Rearrangement.



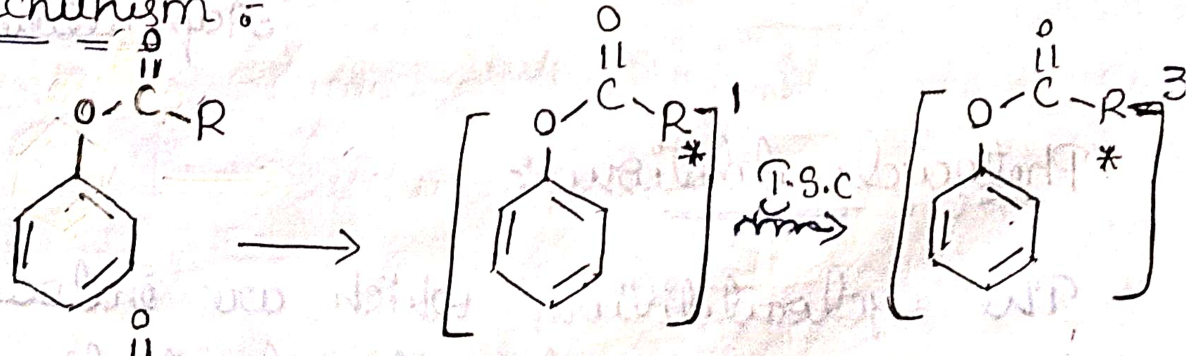
Phenolic ester

o-hydroxyl Acyl Ketone

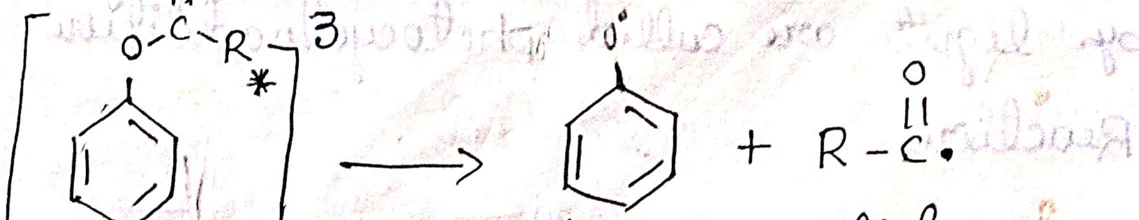
P-hydroxyl Acyl Ketone

Mechanism:

(i)



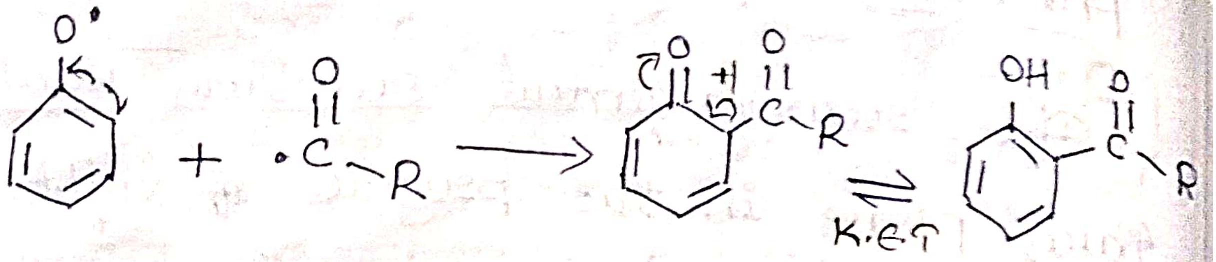
(ii)



Phenoxy Radical

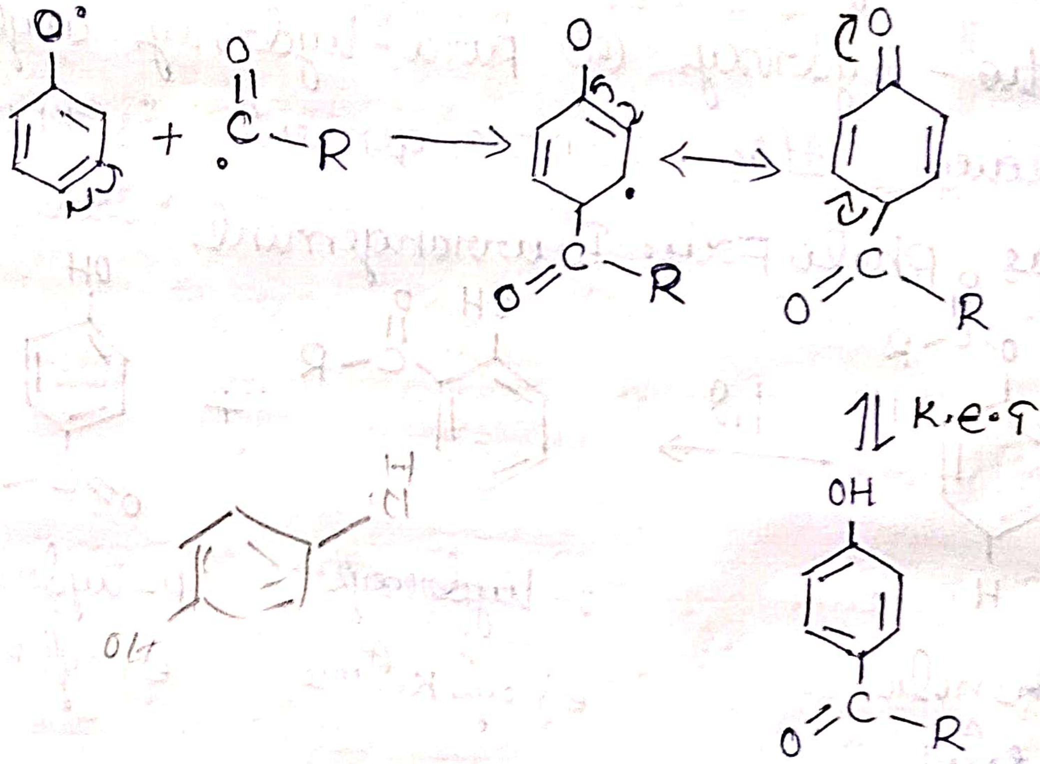
Acyl Radical

Ortho - attack :-



O-hydroxyl eAcyl ketone

Para - attack :-



P-hydroxyl eAcyl ketone

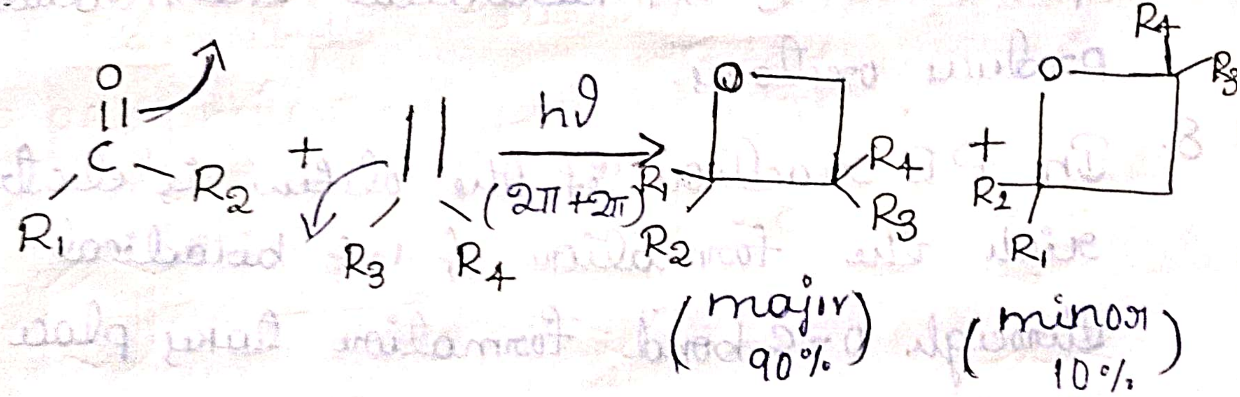
Photocycloaddition :-

The cycloaddition which are induced by light are called photocycloaddition Reactions.

Ex :-

PATERNO - BUCHI REACTION :-

The light induced $2\pi + 2\pi$ cycloaddition reaction between a carbonyl compound (aldehydes (or) ketones) and an unsaturated compounds (alkenes) leads to the formation of cyclic four-membered ether (oxetanes). This reaction is known as PATERNO-BUCHI REACTION.



characteristics :-

1. Irradiate the reaction mixture at absorption wavelength of carbonyl compound.
2. eAll kinds of ketones such as dialkyl on diaryl (or) alkyl aryl ketones as well as aldehydes under go this type of reaction.
3. Reaction excited states are $(n \rightarrow \pi^*)^1$ and $(n \rightarrow \pi^*)^3$ states

* $(n \rightarrow \pi^*)^1$ P.B reactions are "stereospecific."

* $(n \rightarrow \pi^*)^3$ P.B reactions are non-stereospe

4. The reaction intermediates are 1,4 biradica

5. Before the formation of 1,4 biradical interm-diate excited carbonyl compound develops weak charge transfer complex with ground state olefins (alkene) called "Exciplex".

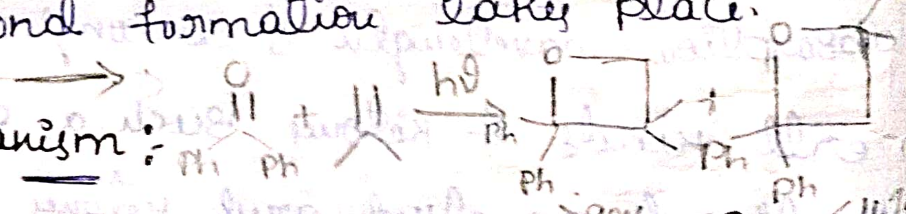
6. Reaction proceeds in such a way to produce stable 1,4 biradical intermediate.

7. Cyclisation of 1,4 biradical intermediates produces oxetanes.

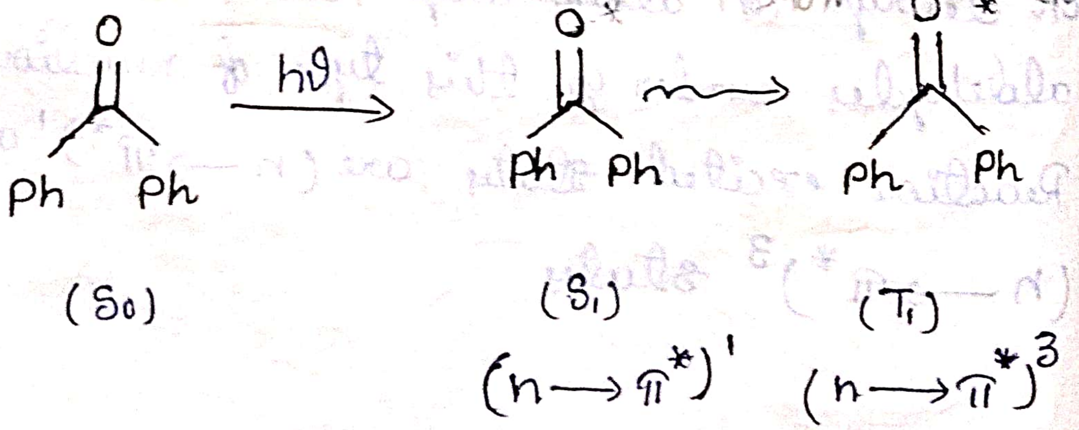
8. In P.B reaction if the olefin is electron rich the formation of 1,4 biradical through O-C bond formation takes place first.

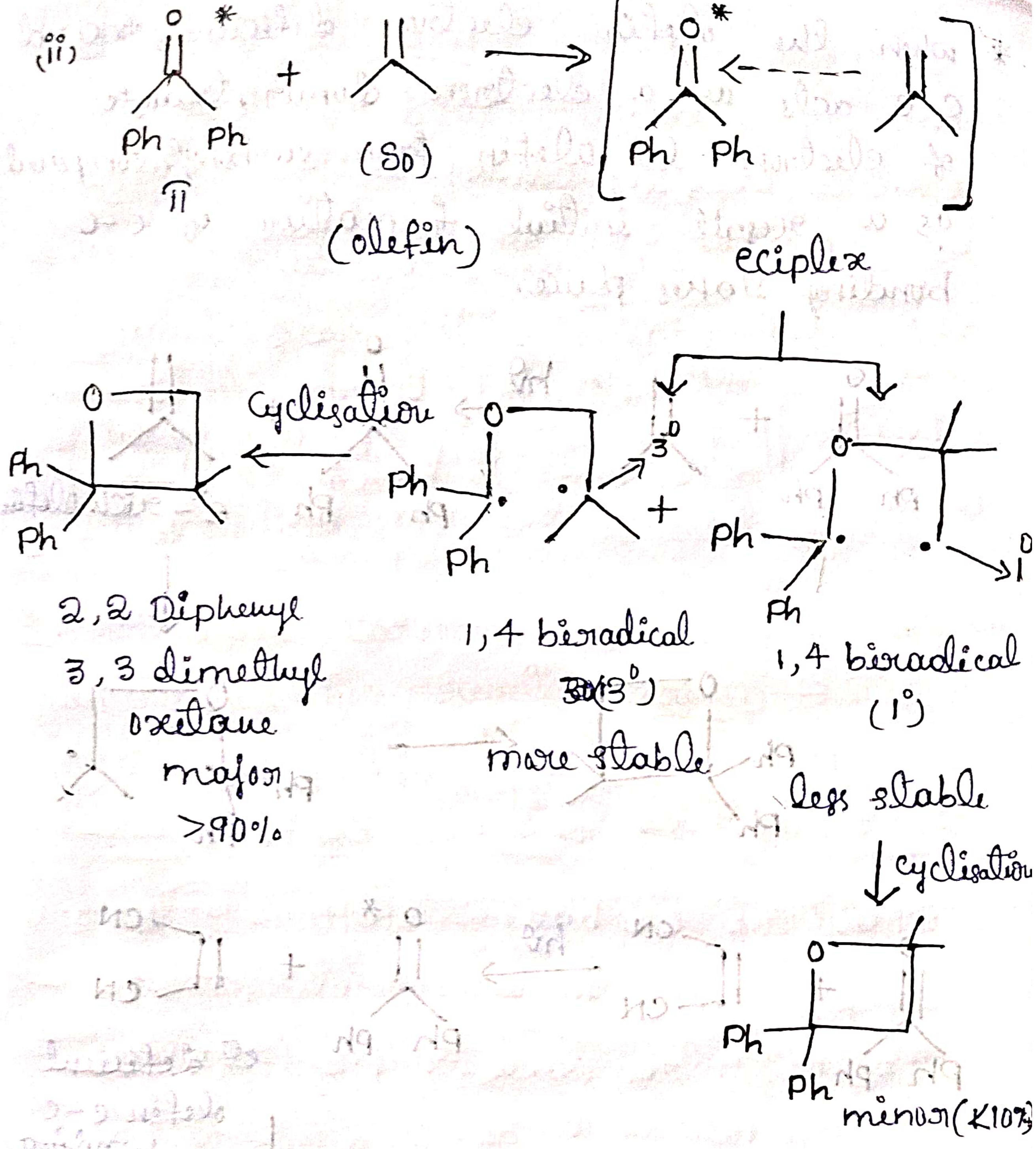
9. ~~In p~~ If the olefin is electron deficient the formation of 1,4-biradical through C-C bond formation takes place.

Mechanism :-



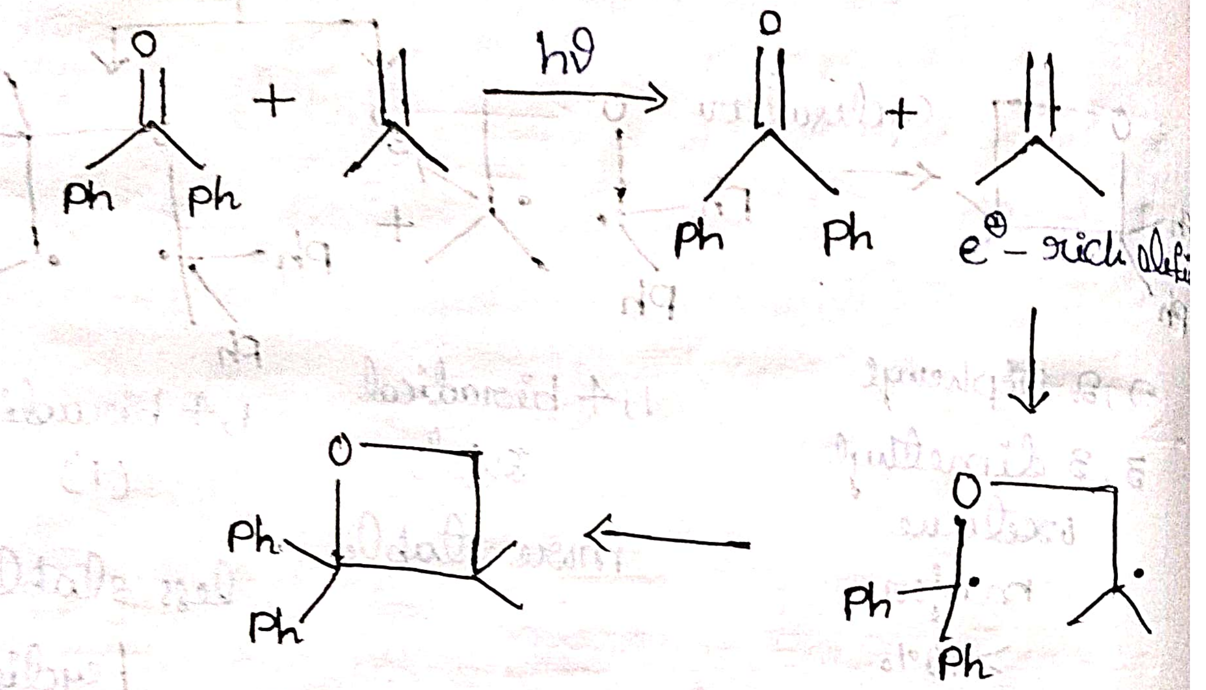
(i)

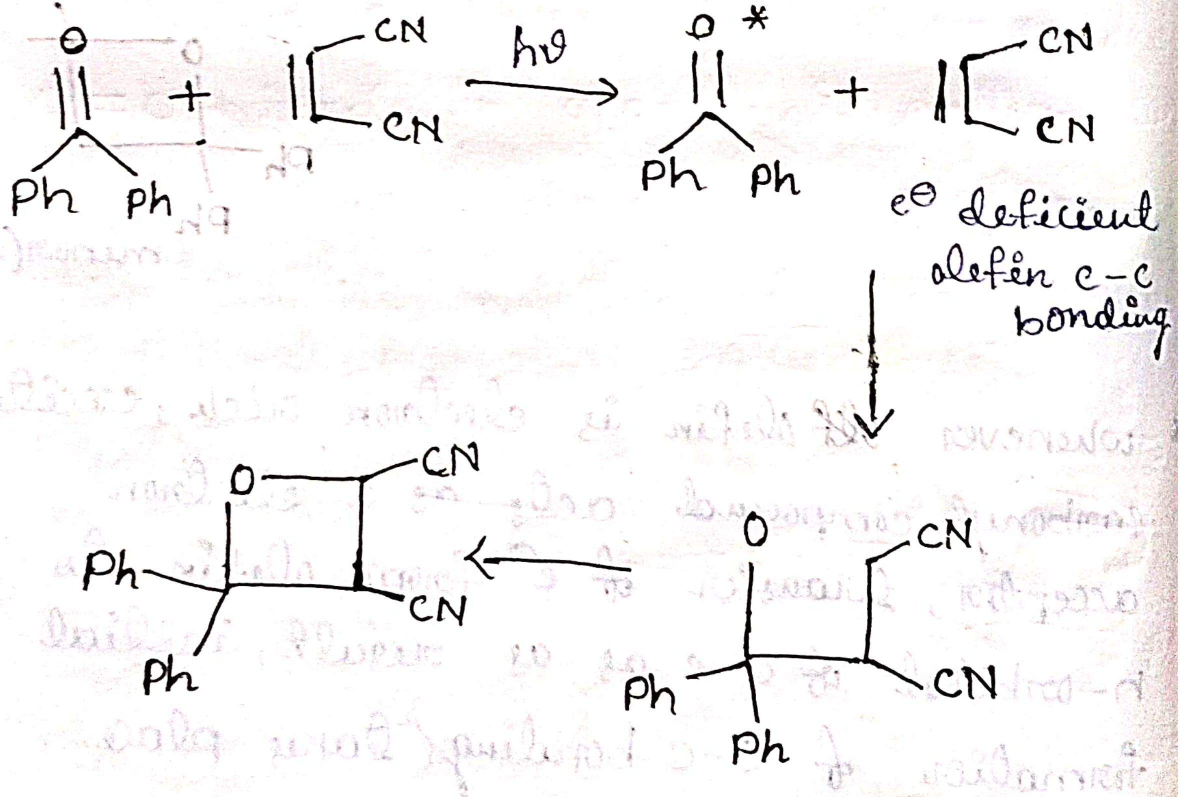




* whenever olefin is electron rich, excited carbonyl compound acts as a electron acceptor, transfer of $e^{\ominus}$ from olefin to n-orbital of C–C as a result, initial formation of O–C bonding takes place.

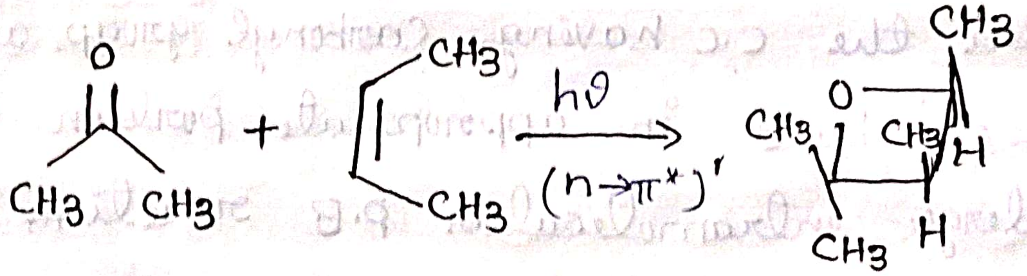
* when the olefins electron deficient, excited C-C acts as a electron donar, transfer of electrons to olefin from carbonyl compou as a result initial formation of C-C bonding takes place.



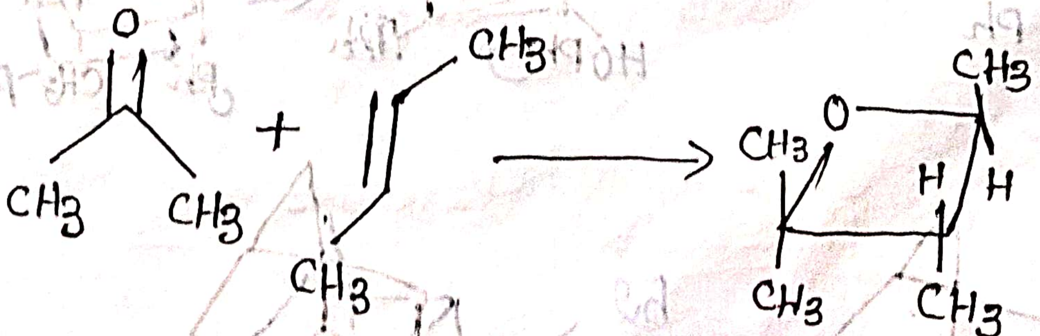


Stereochemistry of palerno-Buchi Reaction:-

- * $(n \rightarrow \pi^*)'$ singlet excited palerno Buchi reactions are "stereo-specific."
- * That means, in these P.B reactions the ground state olefin retains its stereo-chemistry in all resulting products.
- * $(n \rightarrow \pi^*)^3$ triplet excited palerno Buchi reactions are "non stereo specific."
- * Aliphatic carbonyl compounds are inefficient in I.S.C, those reactions are $(n \rightarrow \pi^*)'$ excited reaction thus the P.B reactions in aliphatic C.C are stereospecific.

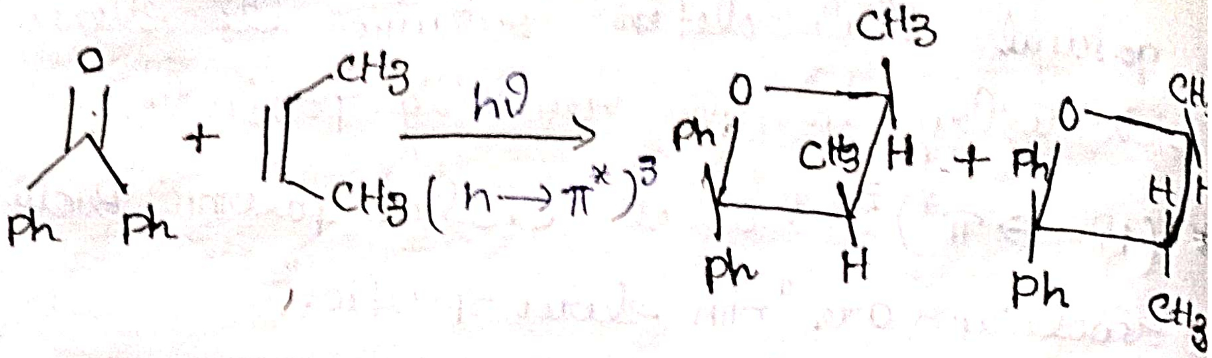


cis-2-butane (Stereo specific)



Trans 2-butane (Trans)

* aromatic carbonyl compounds are efficie in T.S.C, these reactions are $(n \rightarrow \pi^*)^3$ excited reaction. Thus the P.B reaction is aromatic C.C are non stereospecific.

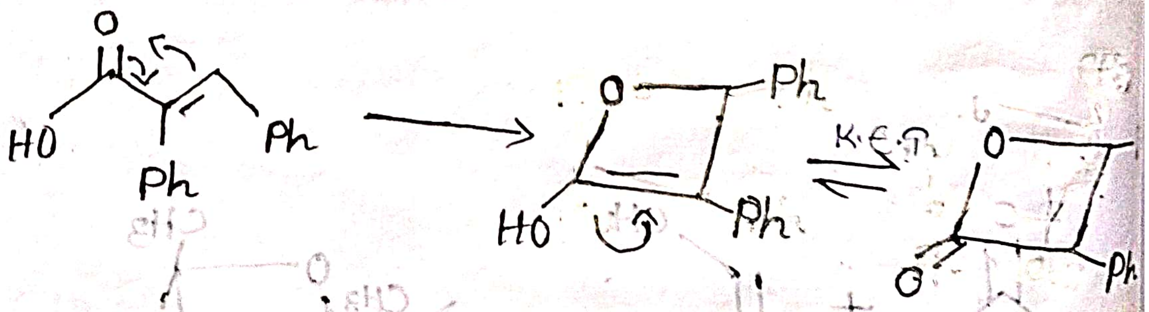


(cis) (Trans)

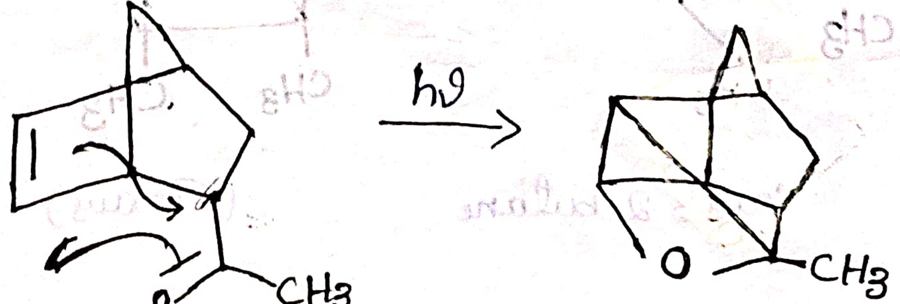
Intramolecular Paterno - Buchi Reaction:-

when the C.C having carbonyl group and "C=C" bond in appropriate portion can undergo intramolecular P.B reactions in presence of light.

Eg:-1



Eg:-2

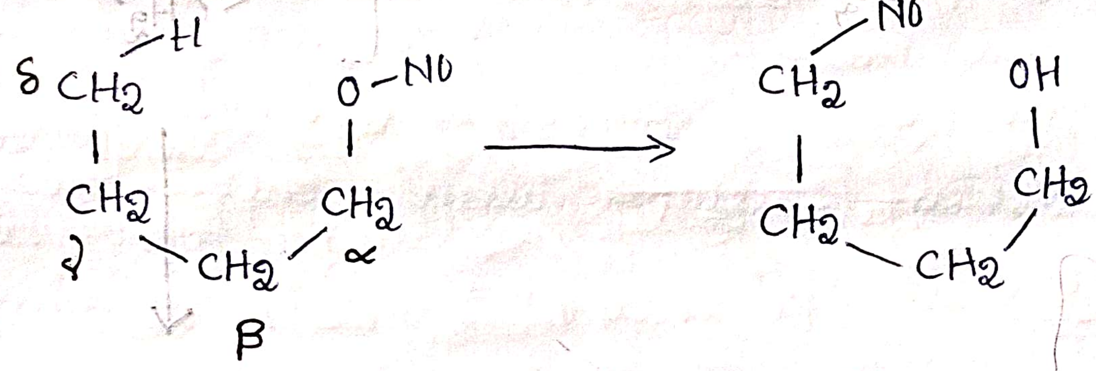


U-IV $2E + 1S = 25M$

Barton's Reaction :

The photolytic rearrangement of alkylnitrites having δ-hydrogens into nitraso alcohols is known as "barton's reaction."

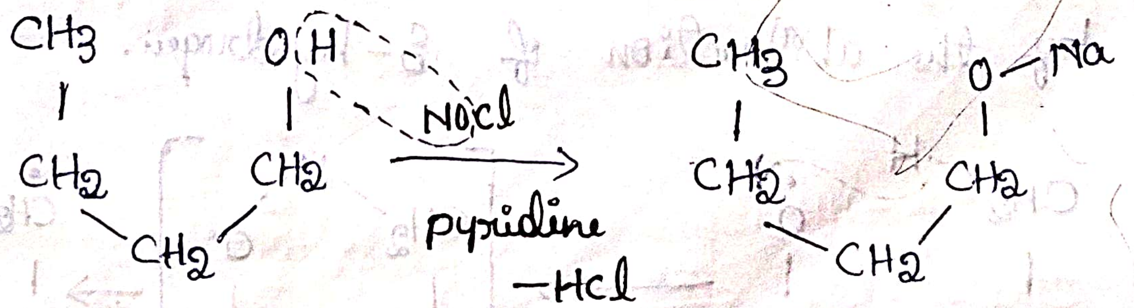
Ex :-



Alkyl nitrite
(Butyl Nitrate)

4-nitrasol-Butano
(Nitraso alcohol)

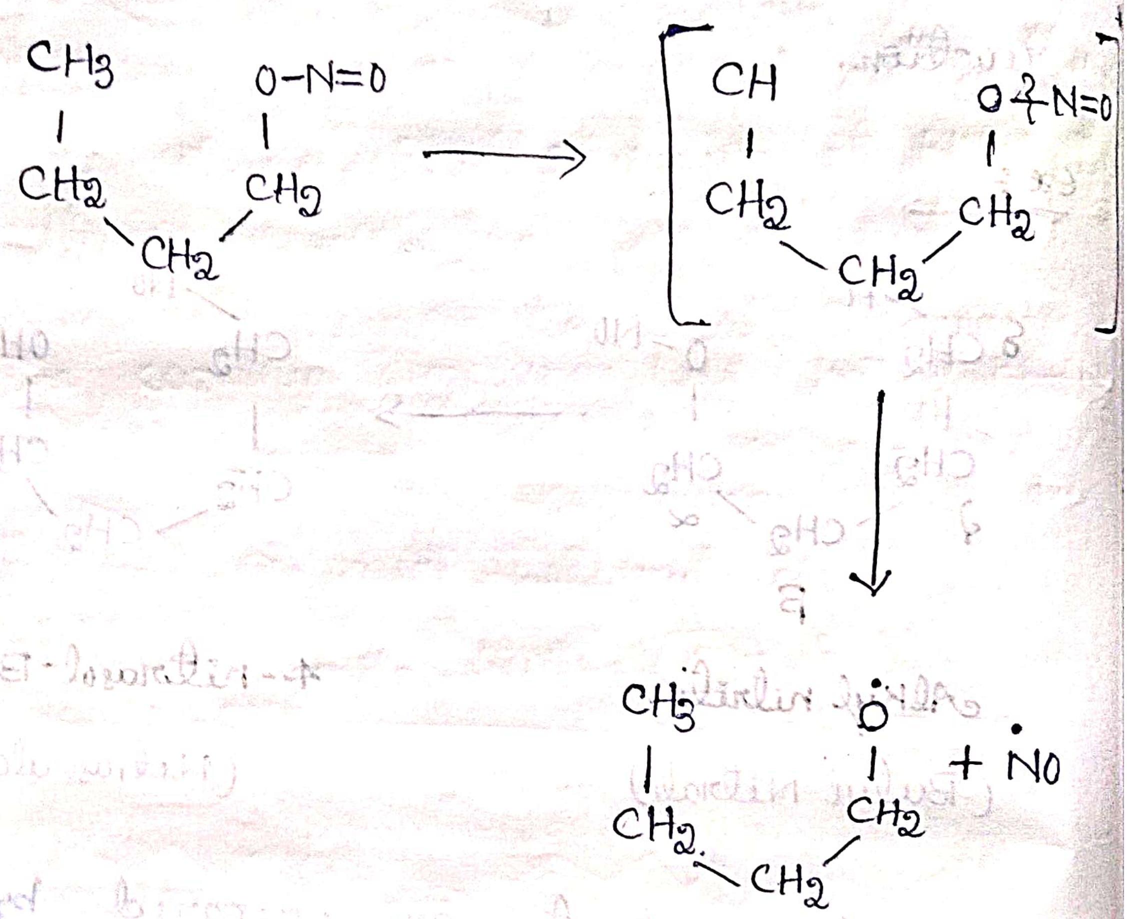
* The alkyl nitrates are prepared by the action of nitrosyl chloride (NoCl) in the presence of pyridine



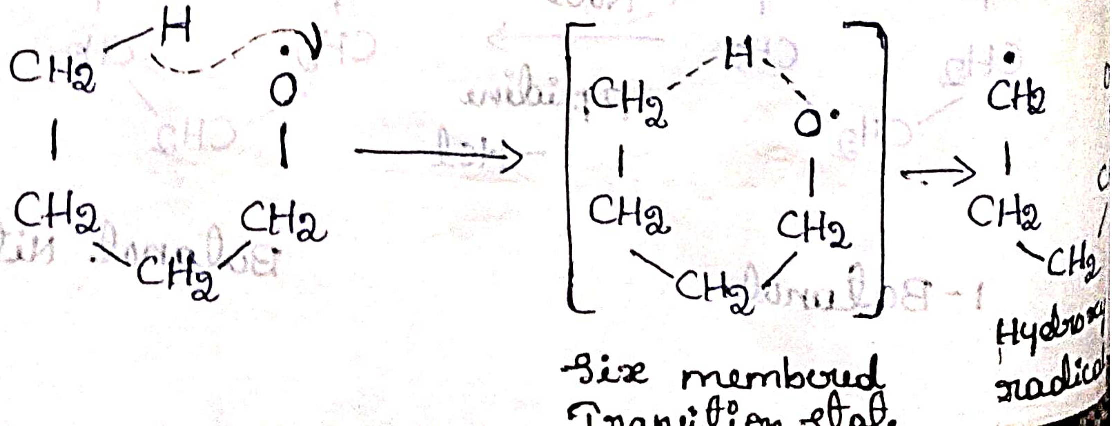
1-Butanol

Butanol Nitrite

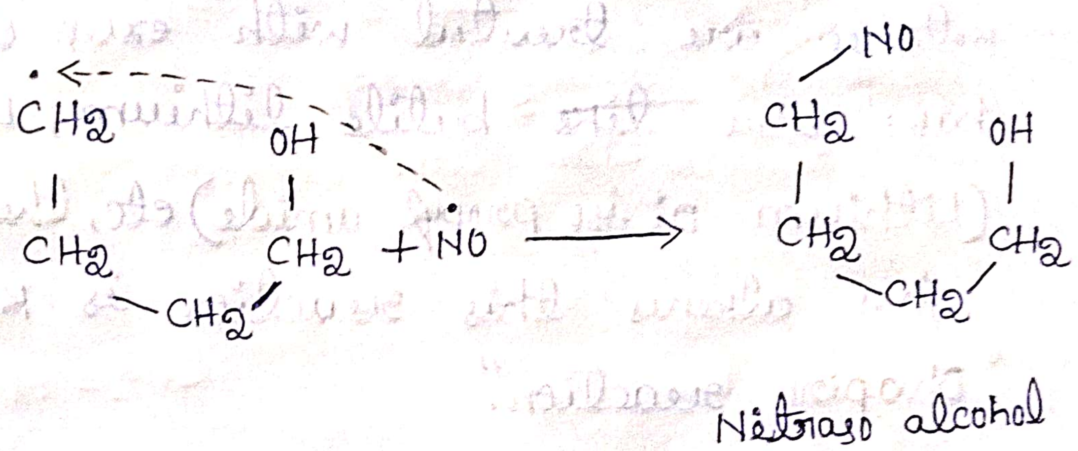
* The formed alkyl nitrite undergo homolytic cleavage through the excited state and leads to the formation of alkoxy and nitrosyl radicals.



* The formed alkoxy radical is rearranged to hydroxy radical through the six membered transition state by the abstraction of δ-hydrogen.



* Finally the hydroxy radical is combined with nitrosyl radical and forms nitroso alcohol.



* In sometimes the formed nitraso alcohol is tautomerised to oximes and is hydrolysed to carbonyl compounds.