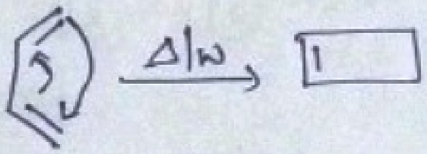
UNIT:- PERICYCLIC REACTION:-

concerted reaction by cyclic shift of e^-

Types:

1. Electro cyclic →
2. cyclo addition.
3. Sigma topic

In greek peri means peripheral and kaiklos means cyclic i.e. around cycle. There are concerted reactions (Bond forming and bond breaking occurs simultaneously with cyclic shift of e^-



1,3 butadiene.

Sailent features of pericyclic:-

1. It is a concerted reaction.
2. It involves no nucleophic (or) electrophilic reactions.
3. They does not involve any intermediate (ionic (or) radicle) Except transition state.
4. They are initiated by thermal (Δ) or photo chemical (hν).

5. They are not influenced by oxidising or reducing agents.

6. These reactions are independent of solvent and catalyst.

7. The pericycle reactions are highly stereospecific

8. These reactions are 100% atom economy reaction

✓ <u>classification</u> <u>of</u> <u>pericyclic</u> <u>reactions</u>: ✓

They are primarly classified into 3 types.

1. Electro cyclic
2. cyclo addition
3. sigma tropic reaction

6/10/2023

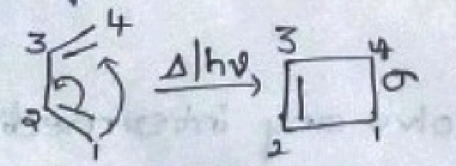
1. ✓

* <u>Electro</u> <u>cyclic</u> <u>reac^n</u>:-

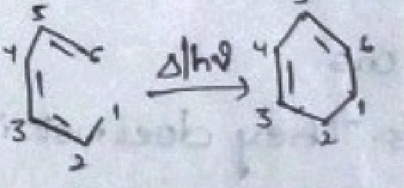
*Ring is closed in a cyclic tive conjugated System at the Expense of one π bond.

*A new Sigma bond is formed.

Ex:-



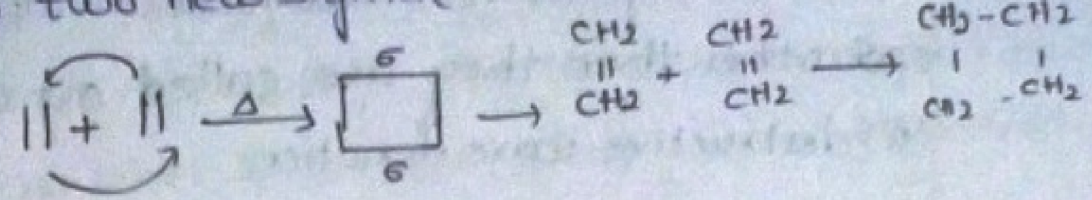
2)

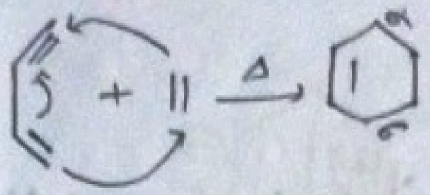


2. <u>cyclo</u> <u>addition</u>:

1. Two (8) more π conjugated A cyclic reactants added to form cyclic compounds at the expense of two(π) bonds. ie; Two(π) bonds are converted

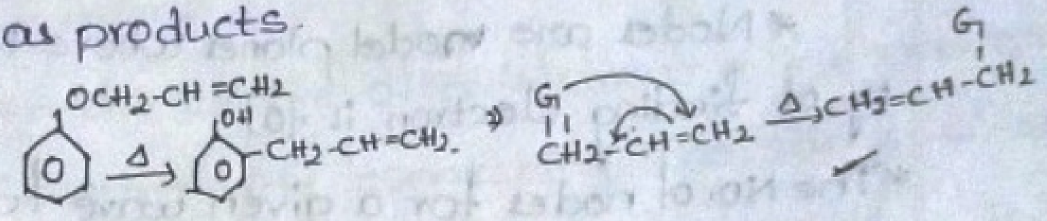
into two new Sigma(σ) bonds.

Ex:- 



3. Sigma tropic reactions:-

* In these reactions a sigma bond is migrated from one end to the other end of π bonds without changing the number of π bonds in reactants as well as products.

Ex:- 

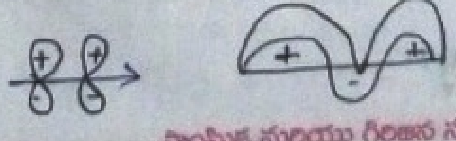
PHASE:-

1. orbitals are defined as the probability of finding electrons are maximum.

2. It is represented by mathematical term(ψ) which is a wave function.

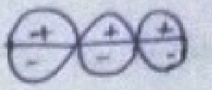
3. The number of (π) Electrons is equal to no. of carbon atoms which are equal to Number of [p] orbitals in a π conjugated system.

4. If the two lobes are same sign then it is called Inphase (or) constructive wave function



5. If the Signs of the two lobes are opposite to each other then they are called out of phase (or) destructive wave function.

Ex:



** 6. For [ψ_n] wave function if (n) is the odd then the two terminal lobes have same sign. If (n) even then the terminal lobes have opposite sign.

Node / Nodal plan:-

* Nodes are model planes where the proability of finding electron is [0]

* The No. of nodes for a given wave function ψ_n is $(n-1)$.

* If nodes is odd number it is always ~~b/w~~ centre the Orbitals.

* As the number of nodes increases Energy is also increases.

SYMMETRY:-

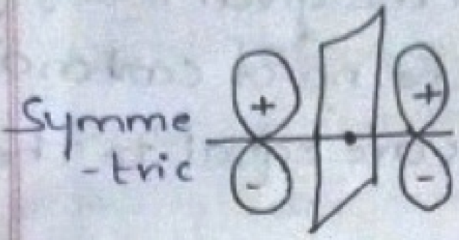
They are two types symmetries shown by molecular orbitals. They are:-

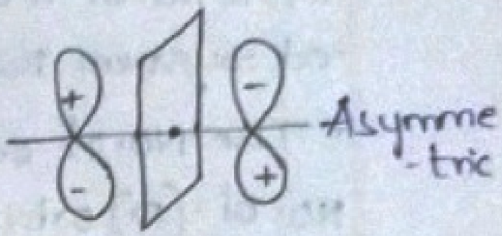
1. Mirror symmetry (m, m_R)

2. C_2 Symmetry

* Mirror Symmetry:-

1. In mirror symmetry the two lobes have mirror image relationship. when we put a mirror b/w the two lobes it is also called plane of symmetry.

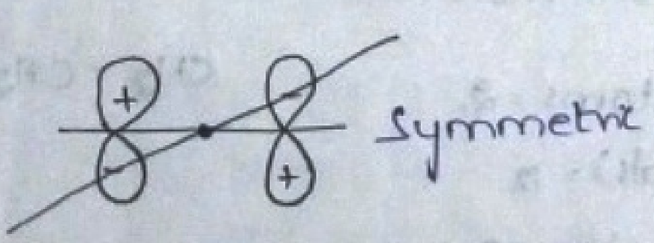


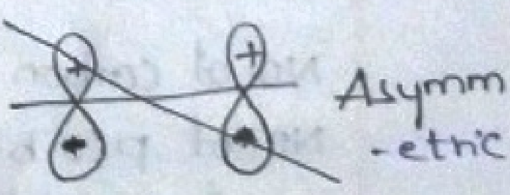


2. For ψ_n if (n) is odd the mirror symmetry is always symmetric.

<u>C_2 Symmetry:-</u>

* From the centre of axis draw a line and extent it other side connecting the same sides of lobes with equal distance from centre is called C_2 symmetry (or) If you rotate the molecular orbital along the axis of rotation at 180° and gets the same phase of molecular orbitals is called C_2 symmetry.





*If ψ_n is the wave function (n) is even number then C_2 symmetry is symmetric

Rules for writing the molecular orbitals for [π] conjugated system:

Rule:-1

*The No. of π electrons in the given π conjugated system is equal to the no. of carbon atoms

* The No. of carbon atoms are equal to the No. of [P] orbitals.

*The No. of p orbitals are equal to No. of wave function.

*The asign nodes as per rule (n-1) to the porbitals arrange the p orbitals increasing Energy order.

*If the wave function is odd the terminal lobes have same sign.

*If it is even terminal lobes have opposite sign for odd No. of nodes is place at middle of the p (orbitals). For some ψ system.

*The node is passed through orbital.

*[MO] for Ethelene molecule.

$CH_2 = CH_2$

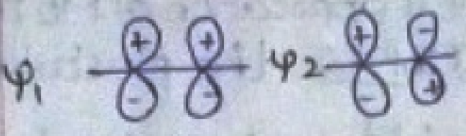
No. of carbon atoms = 2.

No. of p (orbitals) = 2.

No. of wave function = 2.

" " nodes = n-1, = 2-1 = 1

1 0 nodes.



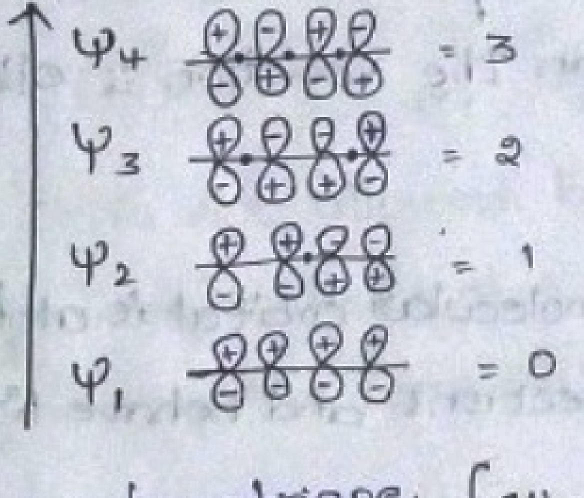
Ex: $CH_2=CH-CH=CH_2$ [1,3 butadiene]

No. of carbon atoms = 4

No. of p orbitals = 4

" " wave function = 4

" " nodes = n-1 = 4-1 = 3



1,3,5 hexatriene [$CH_2=CH-CH=CH-CH=CH_2$]

Frontier molecular theory [FMO]
* It is application of Mo theory.

* It was proposed K. FUKUI in 1952. the postulates

* The occupied orbitals of different molecules will repel each other.

* The positive charge of one molecule attracts -ve of another molecule.

* He introduced the term Orbital Symmetry conserved.

* The reactant symmetry is same as that of product symmetry than the reaction is allowed otherwise disallowed

HOMO:-

* Highest occupied molecular orbital is at higher Energy and looses Electrons and behave like nucleophile.

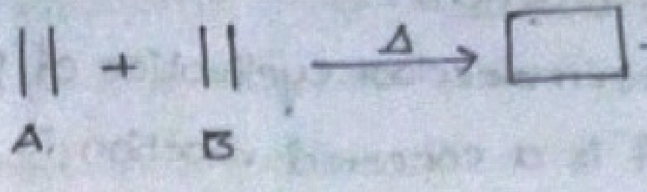
LUMO:-

* Lowest unoccupied molecular orbital

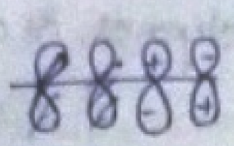
* Lowest in Energy, accepts Electrons (or) gain e- and behaves like electrophile.

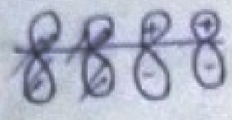
* Since the small Energy gap between homo and lumo electron transfer occurs with lowest transition state and leads to products

* According to FMO theory the symmetry of Homo should match with symmetry of lumo of other than only the reaction is allowed

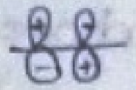


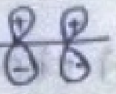
- Not allowed

ψ_2  1 A S - Lumo

ψ_1  0 S A - Homo

m C_2

ψ_2  1 A S - Lumo

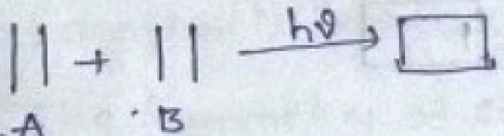
ψ_1  0 S A - Homo

m C_2

* It is not allowed, because the this reaction Symmetry of Homo of A is not similar with the Symmetry the Lumo of B.

Homo
ψ_m — Δ $\frac{n}{2}$
ψ_m — hν $\frac{n}{2}+1$

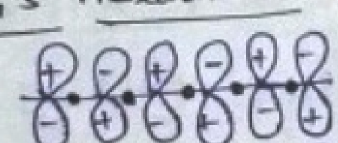
Lumo
ψ_m — Δ $n/2+1$
ψ_m — hν $n/2+2$

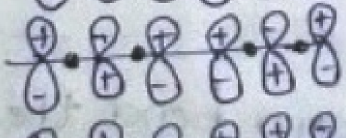


- allowed

Electro-cyclic reaⁿ

1,3,5 Hexatrienes

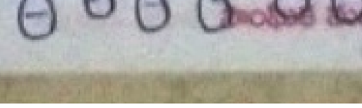
ψ_6  5 A S

ψ_5  4 S A

ψ_4  3 A S

ψ_3  2 S A ↑↓ LUMO

ψ_2  1 A S ↑↓ HOMO

ψ_1  0 S A ↑↓

M C

ψ_3 Homo
ψ_4 LUMO

Electro cyclic reaction:-

1. It is intermolecular cyclization of polyene reaction. (8) it is a concered reaction in which inter convertion of conjugated polyenes. 8l converted into cyclo alkanes.

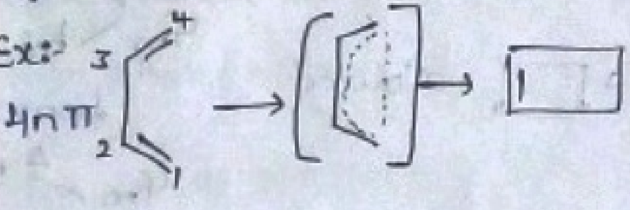
2. It is characterized by formation of new ring from Acyclic conjugated system.

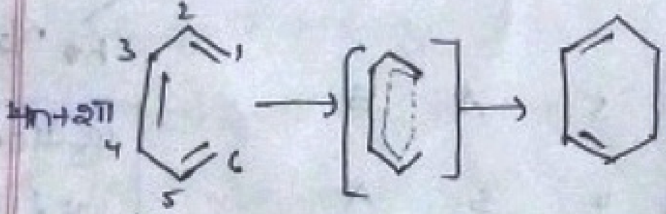
3. In this one [π] bond is broken and one (σ) ~~π~~ bond is formed

4. All reaction occurs in thermal and photochemical conditions. These reacⁿ unimolecular and reversible

5. The reversible reacⁿ is called Retro Electro cyclic reaction

Ex:-





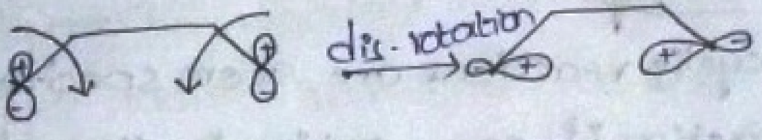
6. In order to form new Sigma bond the terminal orbitals mut rotated in con-rotating and dis rotating. Symmetric direction.

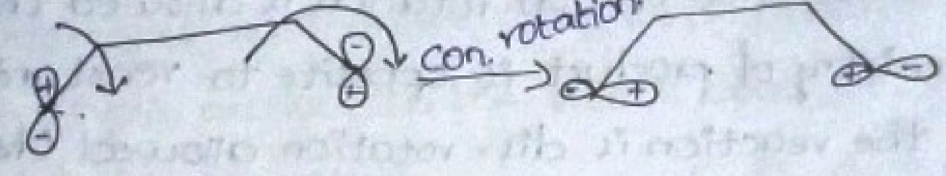
DIS- ROTATION:

* when Same sides of p-orbitals are on the Same Side of the molecule. then the two orbitals must rotated in opposite direction. That is one clock-wise and another is anti. clock wise for effecting overlapping

* The Symmetry of these orbitals is Mirror Symmetry.

Ex:





Con rotation :-

* when opposite sides of p orbitals are on the opposite side of the molecule. Then the two orbitals must rotated in same direction. That is clock-wise and another is anti-clock wise for effecting overlapping.

* The Symmetry of con. rotation is C_2.

Woodword - Hoffmann rules for Symmetry.

* For $4n\pi$ system under thermal conditions con-rotation and photochemical condition. These rotation are allowed as per orbital Symmetry.

* For $4n+2\pi$ System under thermal conditions dis-rotation and for photo chemical ($h\nu$) condition. con. rotation are allowed as per orbital Symmetry.

Application of FMO theory for electro cyclic reactions:-

* For HOMO with m (symmetric) ~~con~~ dis. rotation is allowed

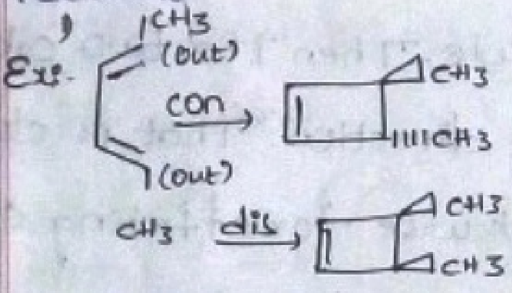
* For HOMO with C_2 symmetry con. rotation is allowed

Sterochemistry:

* Electro cyclic reactions are stero specific reactions for a reaction if con. rotation is allowed the stero chemistry of product is opposite to reactant.

* If the reaction is dis - rotation allowed then the stero chemistry of product is same as of the reactant.

Ex:- 1)



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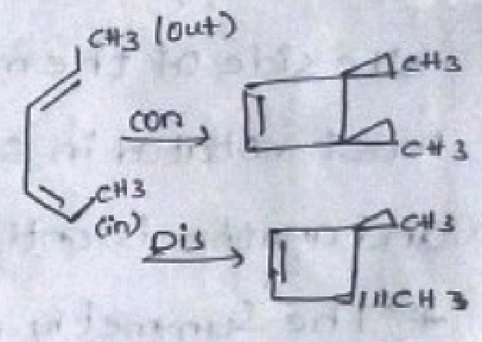
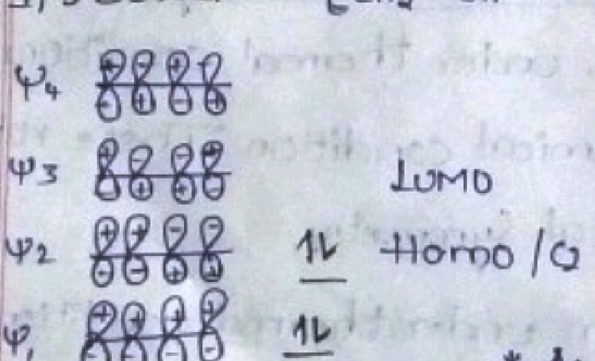
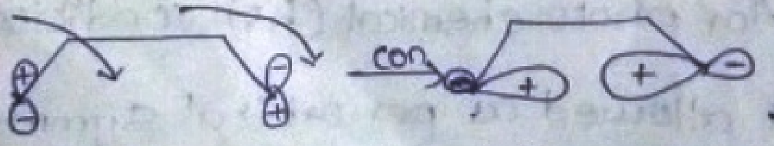


Example for Electro cyclic reaction:-

1, 3 Butadiene [$CH_2=CH-CH=CH_2$]

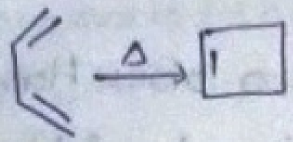




* As per FMO theory HOMO ψ_2 is C_2 symmetry Hence con-rotation is allowed as per woodword

Hoffmann Selection rule 1,3 butadiene $[4n\pi]$ System Hence con rotation is allowed in thermal condition.

* Hence



thermally allowed.

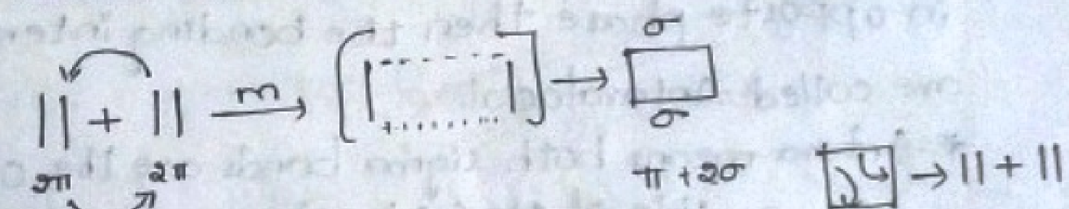
<u>cyclo addition reaction</u>:

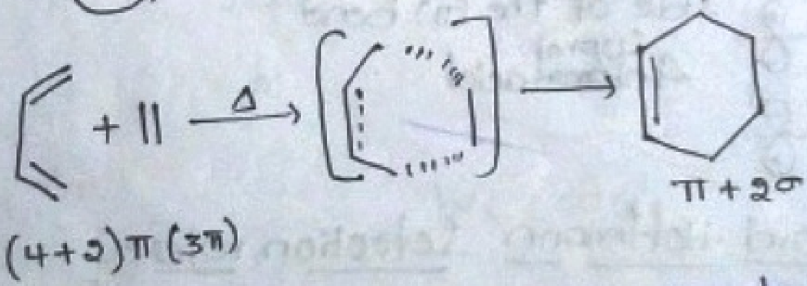
* In cyclo addition reactions two unsaturated molecules undergoes addition reaction in a conserted mechanism to give cyclic product. In this two π bond or lost and 2 new σ bonds are created.

* Since Sigma bond is stronger than π bond and their formation is Exothermic (ΔH = Negative).

* These reactions occur both thermal and photochemical conditions

Ex:





$(4+2)\pi$ (3π)

* σ bond in the product are broken to form to unsaturated compound then the reaction retrocyclo addition reaction.

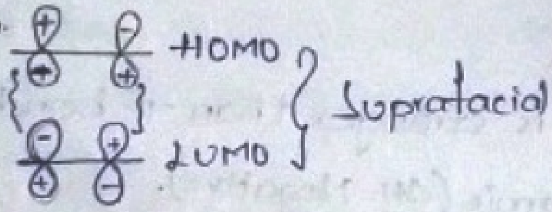
Ex:- 

Sterochemistry:-of the cyclo addition reaction:-

Suprafacial:

* If the Signs of the two lobes Homo & LUMO are in same Phase then the bonding interactions are called suprafacial.

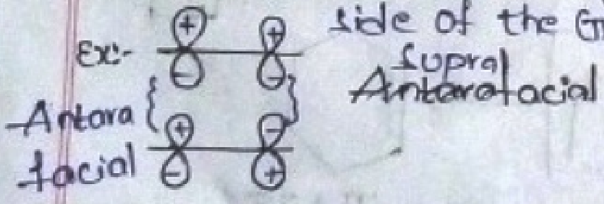
* supra means both Sigma bonds are the Same Sign.

Ex: 

Antarafacial:

* If the Signs of the two lobes HOMO & LUMO are in opposite phase then the bonding interactions are called Antarafacial.

* Antara means both sigma bonds are the opposite side of the (π) bond

Ex:- 

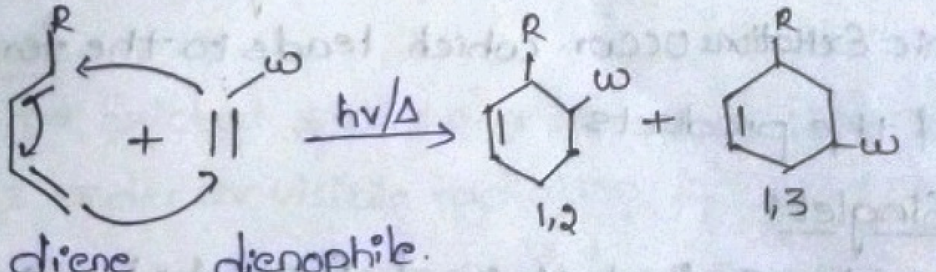
Woodword Hoffmann Selection rules:-

* For 4n π system (2+2) Supra-Suprafacial is allowed in photochemical conditions and 4n+2π system Supra-suprafacial is allowed in thermal conditions.

Regio Selectivity of Diel's-Alder reaction:-

* The diene is always substituted with a Electron Drawing group. and dienophile is always substituted with EWG. when they are added the predominant product is 1,2 disubstituted which is kinetically favour

Ex:-



R= EDG, ω=EWG

=CH_3 CH_3-NH_2, OCH_3

=CN, NO_2, CHO, COOH

* The reason for 1,2 di-substituted product is dipolar interactions in transition state.

17/10/2023 UNIT-II ORGANIC PHOTO CHEMISTRY:-

100

* It is a branch of chemistry deals with inter-action of light with chemical reactions. These reaction occurs in uv-visible region.

* when molecules absorb light Energy Electronic Extations occur which leads to the formation of the products.

Singlet:

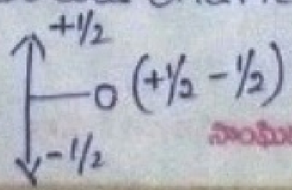
The Excited state of $e^{\ominus}$ in which spin inversion occurs under uv visible radiation is called Singlet i.e; in exicted State the two Electrons have opposite (or) anti parallel spin.

The total spin $J = 2S+1$
$= 2(+1/2 - 1/2)+1$
$= 2(0)+1$
$J = 1$

* Since electrons are paired it shows diamagnetism The life time of singlet is 10^{-9} to 10^{-6} sec.

* The structure is triangular with sp^2 hybridisation in which the two non-bonded $e^{\ominus}$s with opp spin stays in hybridised sp^2 orbital. Since $2e^{\ominus}$s are on the Same Orbital they experience high inter electronic replusions. Hence it is higher in Energy and lower in stability.

* It was unaffected by External magnetic field



* It shows Zwitter ionic character

$$A{=}B \xrightarrow[\text{singlet}]{h\nu} A^{+} + B^{-}$$

* Singlet reactions takes place in liquid state.
* Imp reactions of singlet state are decomposition, isomerisation, electro cyclic, Sigma tropic, reactions.

Triplet:

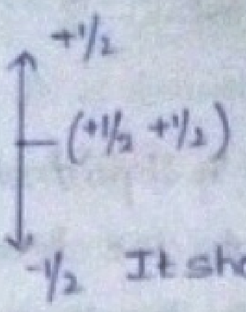
The Exicted state of $e^{\ominus}$ in which spin retention occurs under uv visible radiation is called triplet ie; in Exsited state the two $e^{\ominus}$s have same (or) parallel spin.

The total spin of triple is

$$J = 2(s) + 1$$
$$= 2(+1/2 - 1/2) + 1$$
$$= 2(1) + 1$$
$$J = 3$$

* Since the two $e^{\ominus}$ are unpaired they shows para magnetic
* It's life time is 10^{-4} to 1 sec.
* The structure is linear with sp hybridisation in which two non-bonded $e^{\ominus}$ reside in two unhybridised orbitals since two $e^{\ominus}$ are in the two different orbitals. They Experience less inter electronic replusions. Hence it is lower in Energy and higher in stability.

It was effected by External magnetic field and +1/2 gives three lines



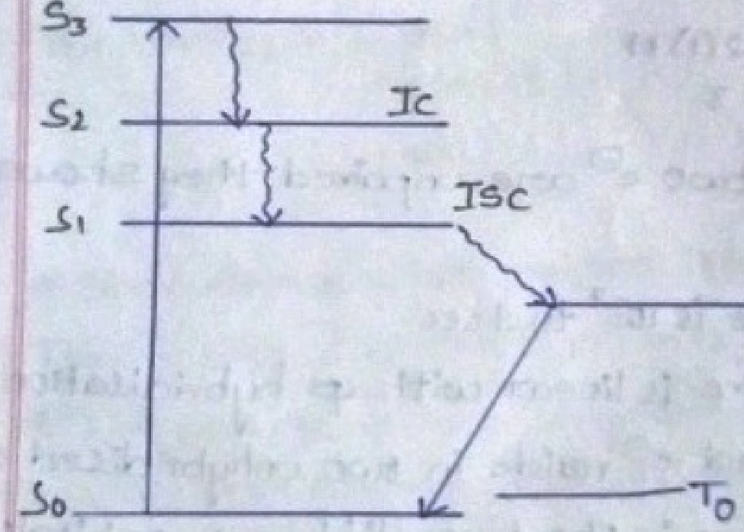
It shows radical type behaviour

$$A=B \xrightarrow[\text{triplet}]{h\nu} A^{\cdot}+B^{\cdot}$$

Triplet reactions takes place in gaseous phase as well as liquid phase.

Imp reactions are homolytic fission, hydrogen abstraction, addition to unsaturated compounds.

*JABLONSKI DIAGRAM:-



The fate of the Excited molecule transition can be explained with the help of Jablouski diagram. In this we study emmision and absorption reactions of molecule.

Inter crossing:

It is non radiative process and it occurs when an $e^{\ominus}$ returns to ground state from Excited state with release of heat Energy. It is represented by curly arrow

Eg:- Transition from $S_3 \to S_2$, $S_2 \to S_1$, $S_1 \to T_1$

Fluorosence:-

A molecule/$e^{\ominus}$ returns to it's ground state with emmision of radiation in 10^{-9} - 10^{-10} sec is called fluorosence when External light is cut off fluorosence stop at that time. The emmited wave length of light is longer than absorbed light wave length.

* It occurs in between singlet state only.

INTER SYSTEM CROSSING:-

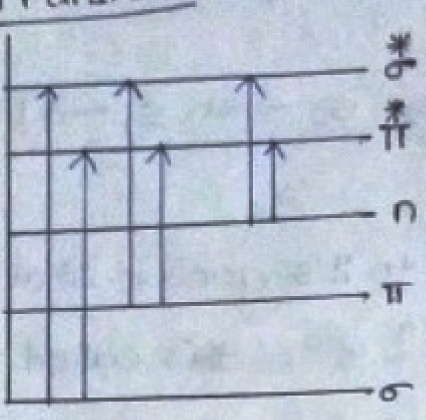
Some molecules/$e^{\ominus}$ drop from singlet state to triplet state in radiation less process, though it is forbidden Small Energy gap and overlap of vibration levels ISC occurs. Here spin inversion occurs. It takes 10^{-8} to 10^{-10} secs from singlet state to triplet state. Eg:- $S_1 \to T_1$

phosphoresence:-

The molecules/$e^{\ominus}$s drops from triplet state to singlet ground state emmission of light occurs. This phenomenon continues even when External light is cut off. The phosphoresence is observed for 10^{-3} to 10^{-4}. The emmited wave length of light is longer than incident wave length

$T_1 \longrightarrow S_0$

* Tranition *



Energy:-
$\sigma - \sigma^* > \pi - \pi^* > n - \sigma^* > n - \sigma^* > n - \pi^*$.

$\sigma - \sigma^*$ Transition:-

when a moleade absorbs uv-visible radiation the σ ē's are promoted from σ bonding orbital to σ* antibonding molecular orbital.

Ex:- Saturated hydro carbons shows σ + σ* transition

n - σ* :-

when a moleade absorbs uv-visible radiation the non-bonding e's are promoted from non-bonding orbital to σ* anti-bonding molecular orbital

Eg:- $R-\ddot{N}H_2$, $R-\ddot{O}-H$

* NORRISH TYPE-I REACTION:-

Irradiation of saturated carbonyl compo-unds under uv visible radiation undergoes

$\pi-\pi^*$ transition:-

*when a molecule absorbs uv visible radiation, the πe^-s are promoted. From π orbitals to π^* anti-bonding molecular orbitals.

Ex:- Alkanes, Alkynes, Aromatic compounds.

$n-\pi^*$ transition:
when a molecule absorbs uv visible radiation the non-bonding e^-s promoted to form non-bonding orbitals to π^* anti-bonding orbitals.

Ex:- carbonyl compounds, cyanides etc...

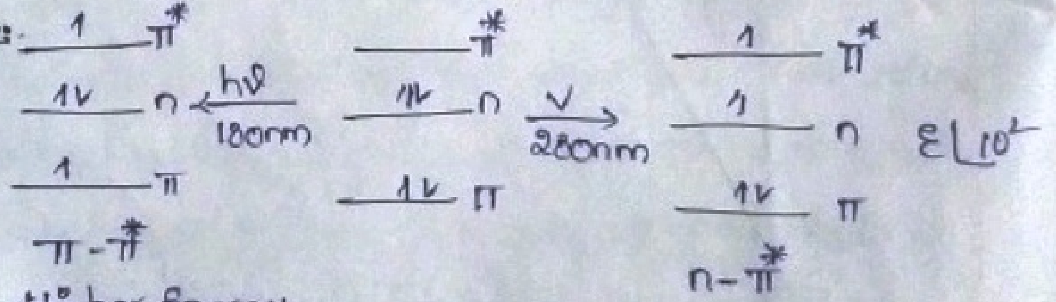
* photochemistry of carbonyl compounds:

*The normal absorption of carbonyl compoun is b/w 180-280nm.

*carbonyl compounds show two types transition

1. $\pi-\pi^*$ 2. $n-\pi^*$

Ex:-

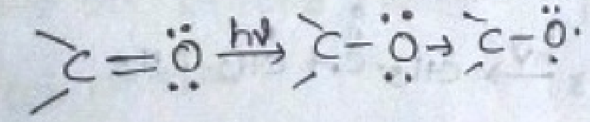


$\pi-\pi^*$
Higher Energy.
ε 10^4

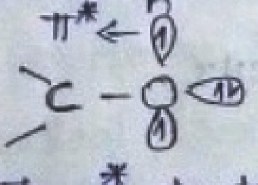
$n-\pi^*$
Lower Energy

$\pi - \pi^*$	$n - \pi^*$
1. Absorbs at low wave length.	4. Absorbs at longer wave length.
2. $\varepsilon > 10^4$ ie Absorbibiy is more	2. $\varepsilon < 10^2$ Absorbity is less
3. Tranition is allowed due to same Symmetry five orbitals	3. Tranition is forbiden due to different shapes of orbitals
4. In polar solvents its moves towards redshift (or) bathochronic shift.	4. In presence of polar solvent the absorption shifts to blue (or) hypochronic shift.
5. when uvlight ~~fa~~ falls carbonyl compounds it becomes alkoxy radical	

Ex:-



It behaves like Alkoxy radical

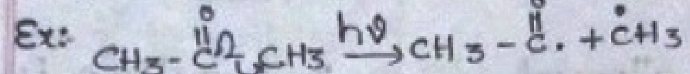


The π^* electron is distributed over c-o bond and less avabable for reaction where as the single electron in n orbital is reactive because of high electro negativity of oxygen and participate reaction like oxidation, hydrogen ~~a~~ abstraction etc- - - Ex:- $R - \ddot{O} - \ddot{N}R_3$ Increases decreases 2) $R - \ddot{O} + \dot{N}R_3$

NORRISH TYPE-I Reaction:

* when saturated ketones (cyclic (or) Acyclic) are irradiated with uv visible radiation undergoes Alph ∝-c-c Homolytic cleavage to give acyl radicals alkyl radical.

Ex:

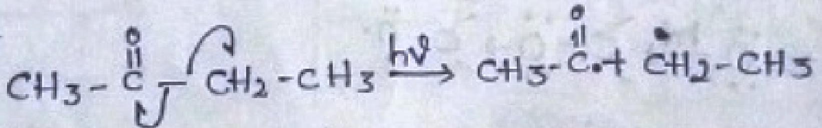


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{h\nu} CH_3-\overset{O}{\overset{\|}{C}}\cdot + \dot{C}H_3$$

In Norrish type-1 reaction the following product are formed.

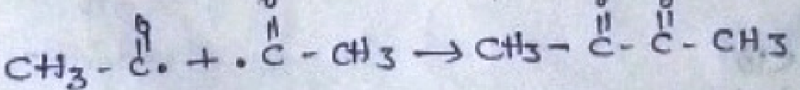
1. Recombination Acyl radical
2. Recombination alkyl radicals
3. Decarbonylation [Removal of CO]
4. Abstraction of hydrogen from alkyl radical by acyl group
5. Abstraction of hydrogen from acyl group by Alky group.

Ex:-



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{h\nu} CH_3-\overset{O}{\overset{\|}{C}}\cdot + \dot{C}H_2-CH_3$$

1. Recombination of Acyl radical:-

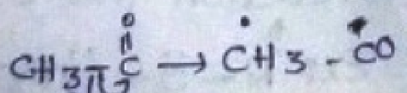


$$CH_3-\overset{O}{\overset{\|}{C}}\cdot + \cdot\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

2. Recombination of Alkyl radical:-

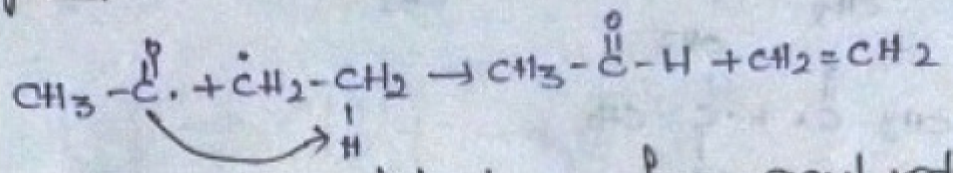
$$CH_3\dot{C}H_2 + \dot{C}H_2CH_3 \rightarrow CH_3CH_2-CH_2CH_3$$

3. Decarbonylation:



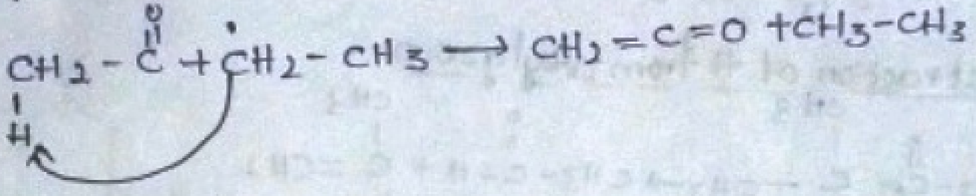
$$CH_3-\overset{O}{\overset{\|}{C}} \rightarrow \dot{C}H_3 - \dot{C}O$$

4. Abstraction of hydrogen from alkyl group by Acyl group:



$CH_3-\overset{O}{\overset{\|}{C}}\cdot + \dot{C}H_2-\underset{H}{CH_2} \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-H + CH_2=CH_2$

5. Abstraction of hydrogen from acyl radical by Alkyl group:



$\underset{H}{CH_2}-\overset{O}{\overset{\|}{C}} + \dot{C}H_2-CH_3 \rightarrow CH_2=C=O + CH_3-CH_3$

Features of norrish type-1 reaction

1\. *In norrish type-1 reaction bond b/w carbonyl carbon and Alpha carbon is weaker. Due to electron deficient Alkoxy radical draws the electron density from sigma bond of α-carbon. Hence the bond is weaker and cleavage occurs easily.

*2. Most of the norrish type-1 reactions occurs in vapour phase.

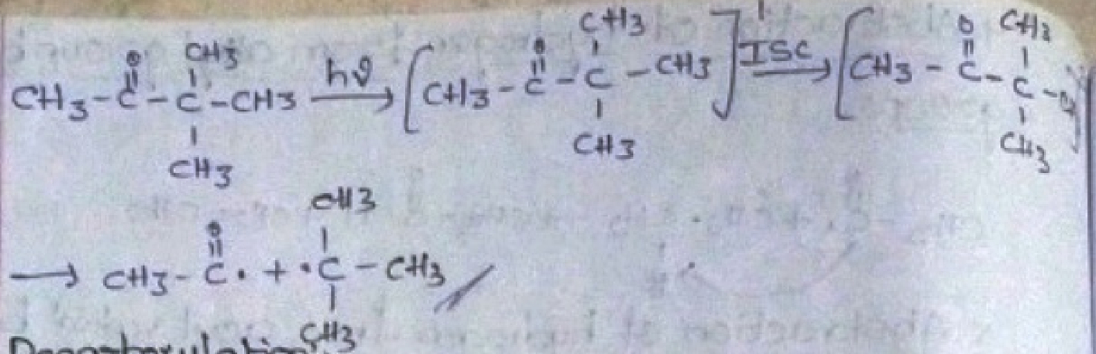
3\. At above 100°c decarbonylation favours..

4\. At below 100°c Abstraction of hydrogen by acyl radical from alkyl group to give aldehyde favours.

5\. If the carbonyl ~~carbo~~ compounds contains two different α-carbons the cleavage occurs at stable alkyl radical formation ie; cleavage occurs at more branching carbon ~~so these~~

CH3- C(CH3) -CH3 Tertiary

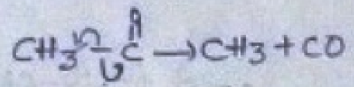
secondary CH3-C-CH3



$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{h\nu} \left[CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3\right]^1 \xrightarrow{ISC} \left[CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\right.$

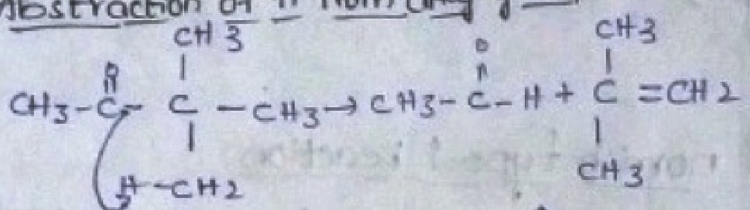
$\rightarrow CH_3-\overset{O}{\overset{\|}{C}}\cdot + \cdot\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

Decarboxylation:

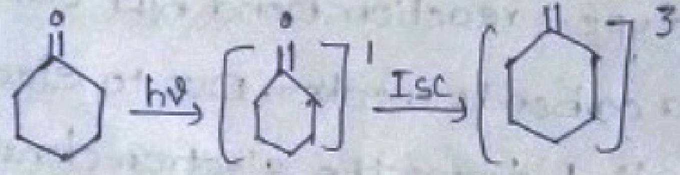


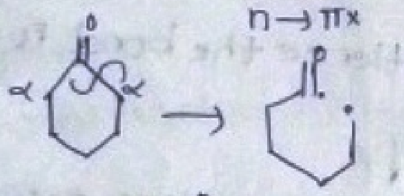
$CH_3-\overset{O}{\overset{\|}{C}} \rightarrow CH_3 + CO$

Abstraction of H from alkyl group:-

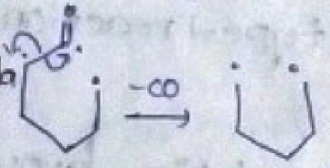


$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_2-H}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{CH_3}{\overset{CH_3}{C}}=CH_2$



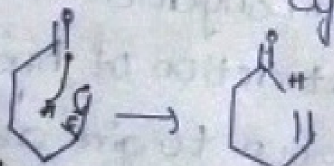


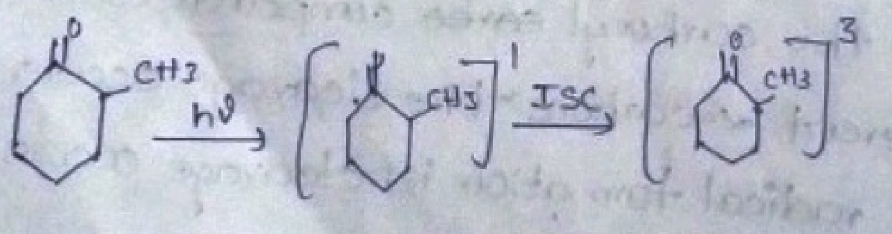
Decarbonyla -tion



Since decarbonylation given unstable primary radicals Hence cyclo pentane doesnot formed.

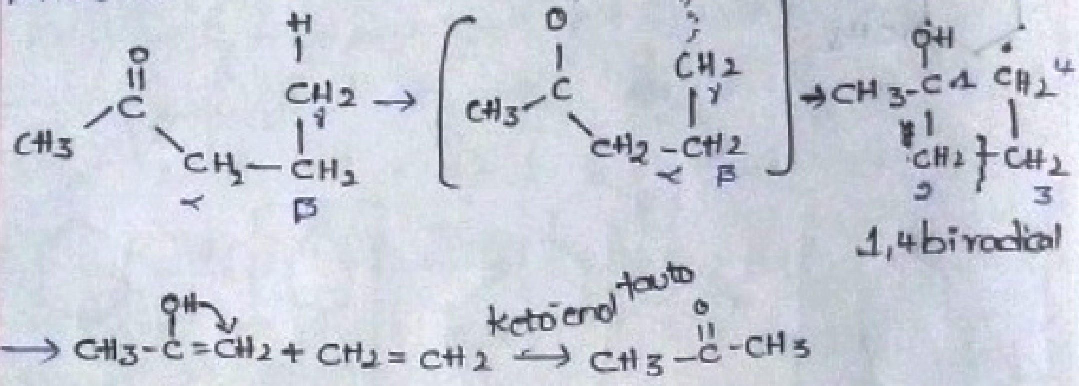
Abstraction of H from Alkyl radical





NORRISH TYPE-II REACTION:

Carbonyl compounds containing atleast one γ hydrogen on irradiation under uv visible light, the carbonyl oxygen ~~forms~~ abstracts $\overset{\gamma-}{\text{gamma}}$ hydrogen and forms 6 membered cyclic transition state which collapses into 1,4 biradical which further undergoes α, β cleavage to give keto & Alkenes



* Features of Norrish type-II Reaction:

1. most of the reactions of triplet state with $n-\pi^*$ electronic transition.

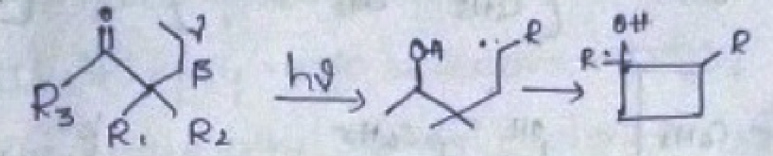
2. carbonyl compound must contain at least 1, γ-hydrogen.

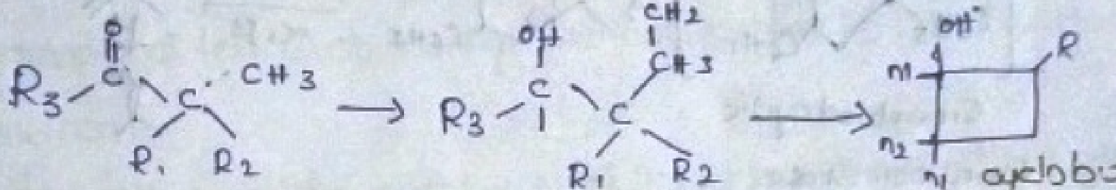
3. It must form Six membered cyclic transition state by abstracting γ- hydrogen

4. α-β cleavage must occur to give ketone and alkene.

If the α-carbon highly substituted then α, β cleavage is not favored due to Norish-II type. Hence it undergoes cycliation to give substitoted cyclo butanol derviatives. This cycliation is called Yang cycliation

Ex:-

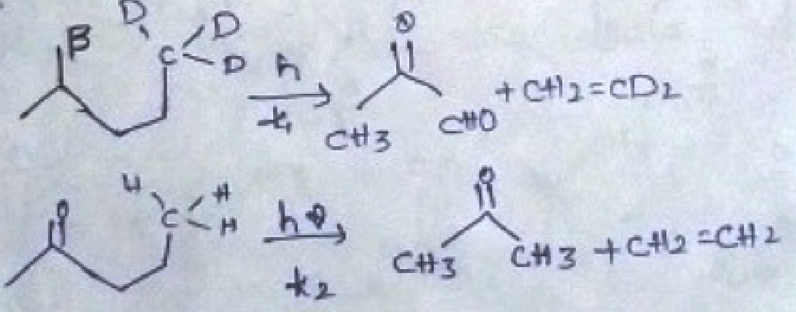




cyclobutanol

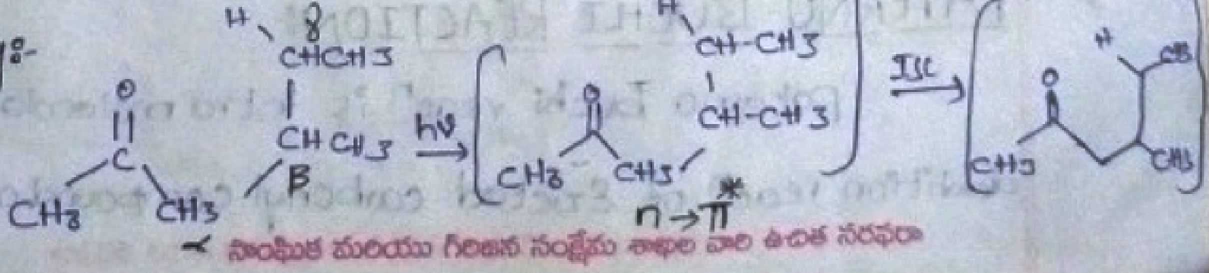
Yang cyclizatio

(The Evidence for γ-hydrogen pracipipation in norris-h type-II reac^n is obtained when we substitute γ-hydrogens by Dueterium.) Since C–D breaking is slow when compared to C–H.) Hence the rate of γ-ghydrogens is faster than rate of γ-dueterium.

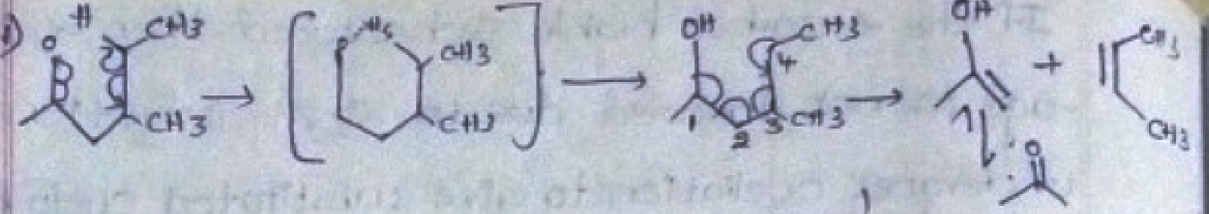


$k_2 > k_1$

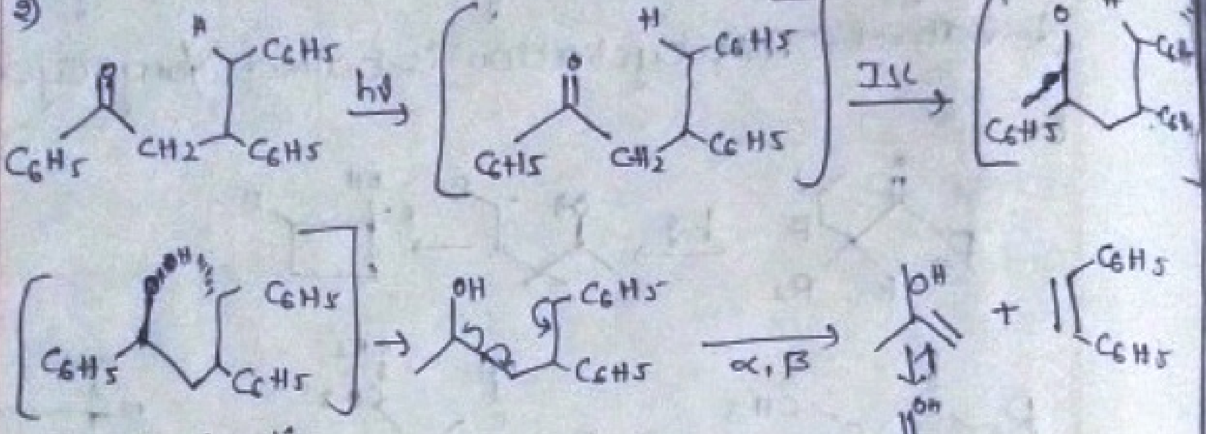
Eg:-



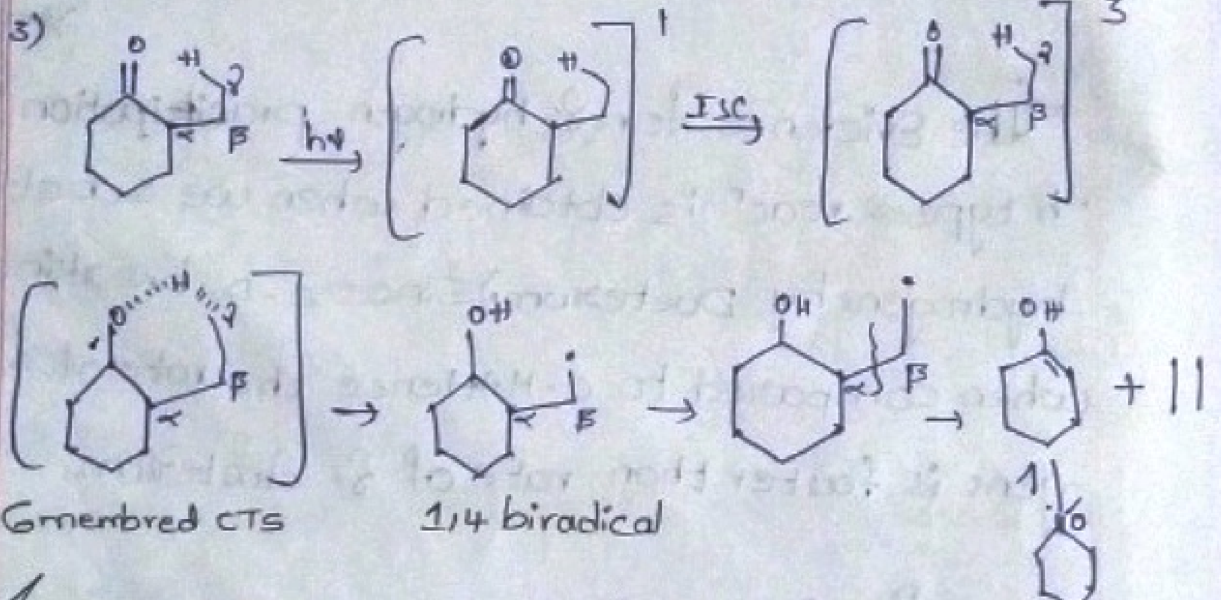
1)

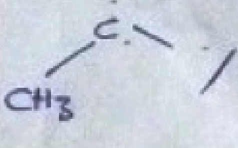


2)



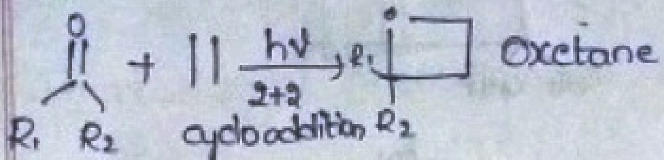
3)





PATERNO- BUCHI REACTION:-

paterno buchi reac^n is intra molecula 2+2 cyclo addition reac^n of, Exicted carbonyl compound and alkene under photo chemical conditions gives cyclic ethers (or) Oxetanes



Imp features of the reaction:-

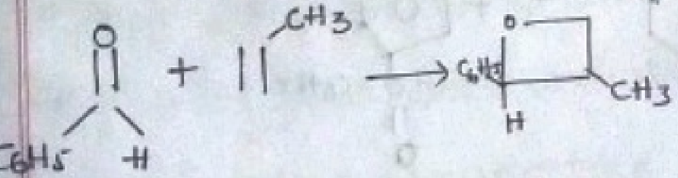
1: The carbonyl compound must be in n-π* triplet state.

2. It is highly regio selective reactivy.

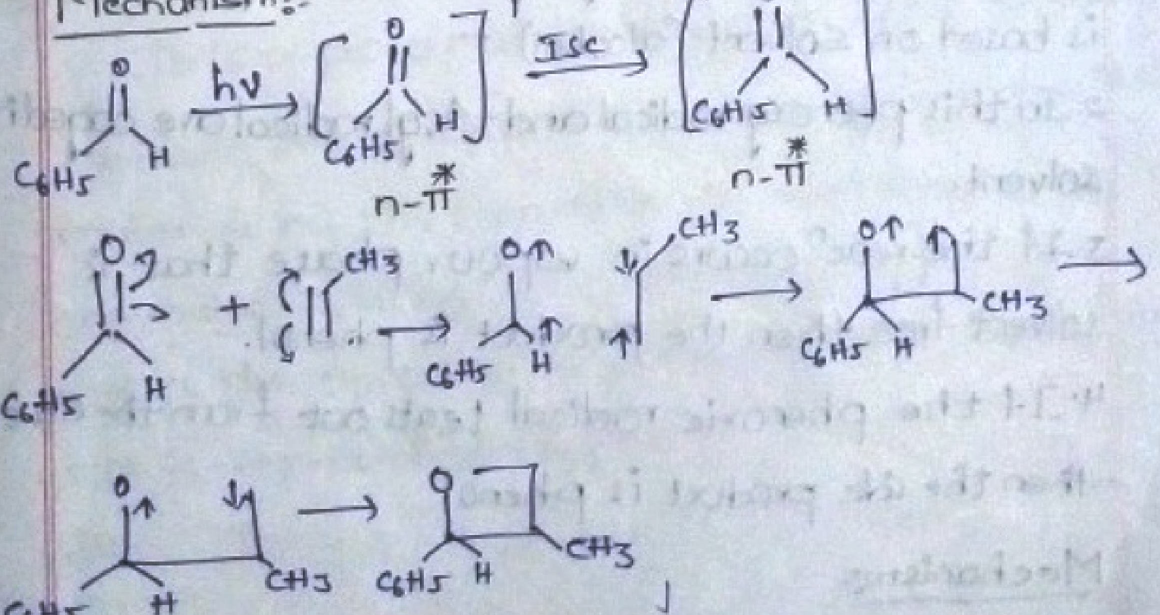
3. The stable alkyl radical prefers to bond with "c" of carbonyl group and less stable alkyl radical prefer to bond with alkoxy radical

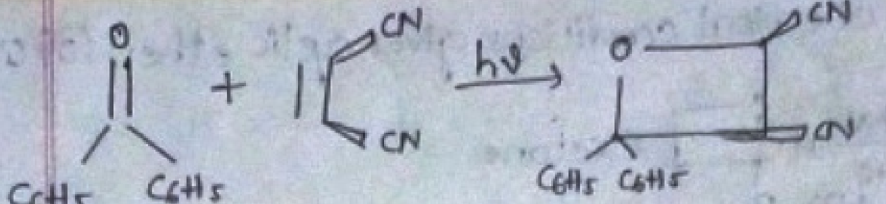
4. The alkyl radical can be stabilized by either e⁻ wd groups (or) ER Groups. This is called captodative effect.

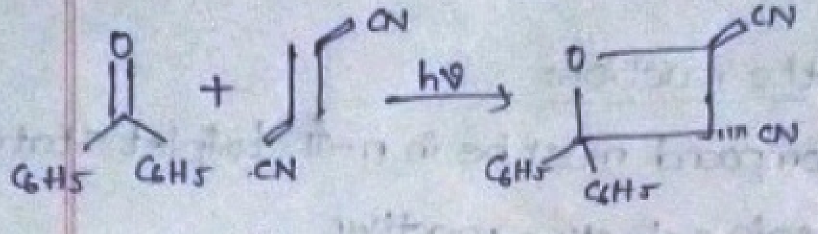
5. when alkenes are substituted by e⁻ wd groups then the reaction is sterio specific.



Mechanism:-







Eg:-

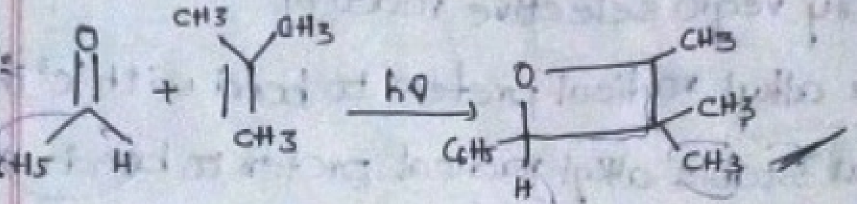
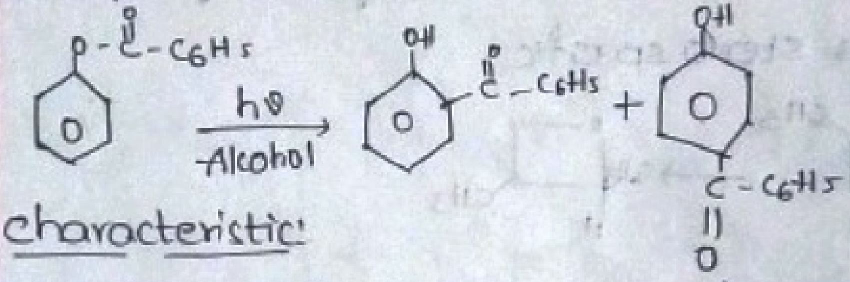


***PHOTO FRIES REARRANGEMENT:-**

under photo chemical condition, phenolic ester undergo intra molecular rearrangement to give, o, p- hydroxy acetophenones is called fries rearrangement

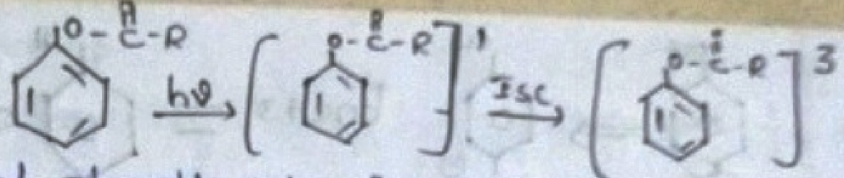


<u>characteristic:</u>

1. It does not involve any type of catalyst. This reacⁿ is based on solvent (alcohol).
2. In this phenoxy radical and Acyl radical are caged in solvent.
3. If the reacⁿ occurs in vapour phase that is solvent free then the product is phenol.
4. If the phenoxic radical leats out from the case then the side product is phenol.

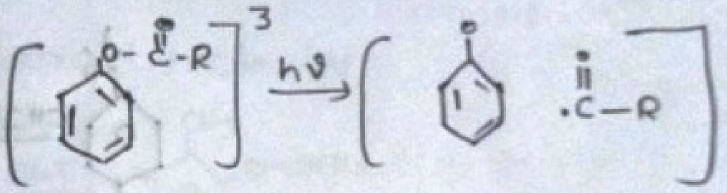
<u>Mechanism:-</u>

1 **Step:-1**



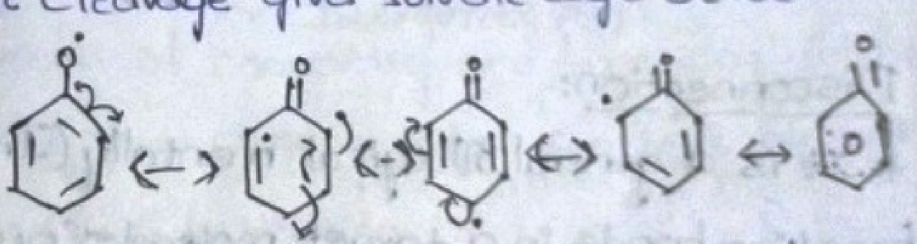
Irradiation of phenolic ester in uv radiation at 312nm

Step:-2



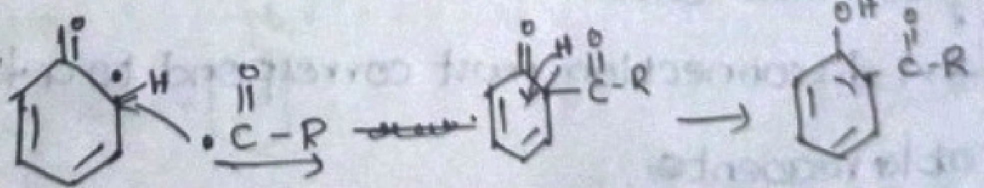
-Homolytic cleavage gives solvent cage structure.

Step:-3



Resonance stabilization of phenolic radical give high density radical • O, P, positions

Step:-4



* Acyl radical attacks o-cation followed by elimination of -H gives o hydroxy aceto derivation.

III unit

cation followed by elimination of

eriviation.

IS: III unit

reaking down bonds of target

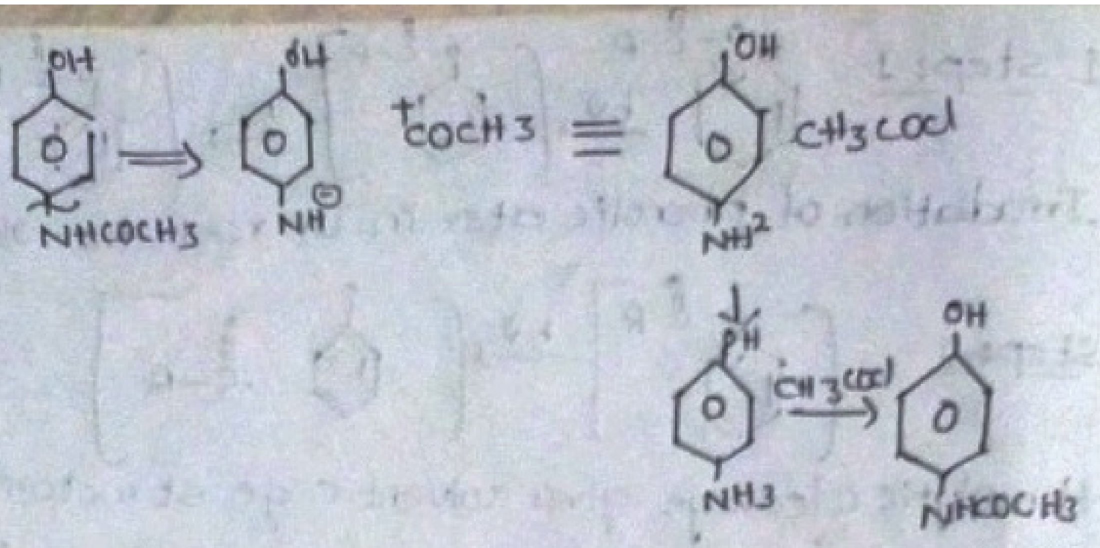
commerically available strating

ction or functional group inter

by [E.J corey]

the direction of bond formation

[⇒]



Disconnection:-

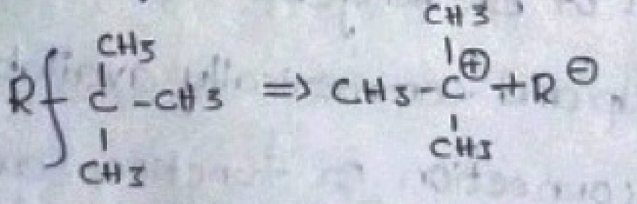
* It is a general(or) logical mentally (Imaginary) breaking bonds in a target molecule (nucleophile & electrophile) to produce fragraments are functional group interconversion.

* A disconnection must correspond to a know available reagents.

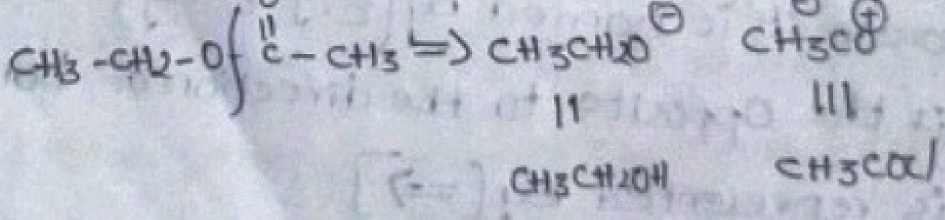
* It is represented by wiggly or curly arrow.

* The first disconnected fragments will appear in the last step of the reac^n.

* All fragments must be simple and available



$$R\wr\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \Rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + R^{\ominus}$$



$$CH_3-CH_2-O\wr\overset{O}{\overset{\|}{C}}-CH_3 \Rightarrow CH_3CH_2O^{\ominus} \quad CH_3\overset{\ominus}{C}O^{\oplus}$$

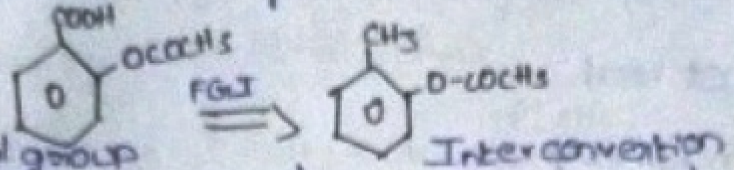
$$\| \qquad\qquad |||$$

$$CH_3CH_2OH \qquad CH_3COCl$$

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CH_2-O-\overset{\|}{C}-CH_3$$

Target molecule:-

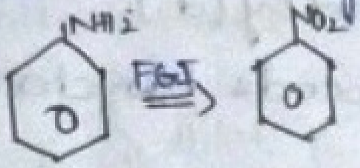
* The molecule which is to be synthesized by disconnection approach (or) functional group inter conversion is called target molecules

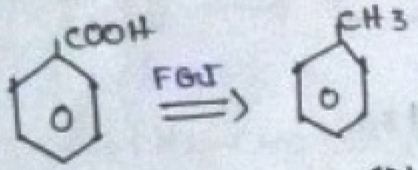


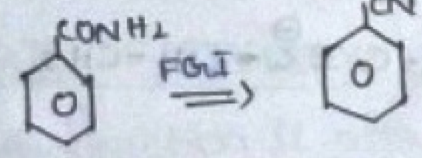
functional group Interconversion

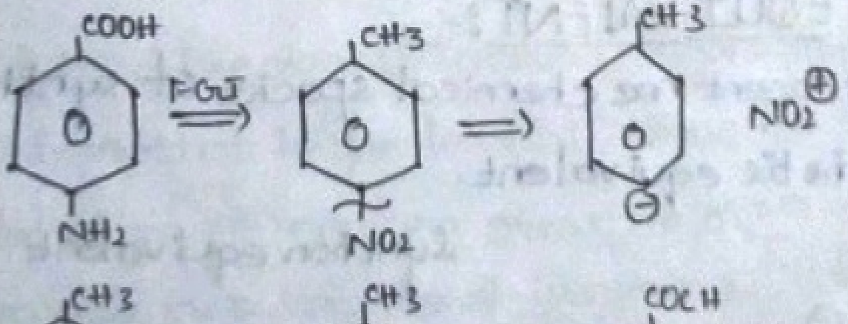
* The process of converting one functional into another functional group during retro-synthesis by oxidation (or) reduction (or) substitution.

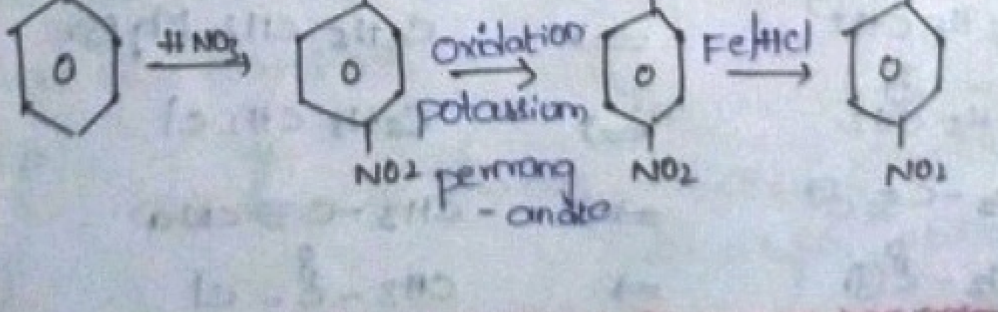
* when we donot have readly available reagents disconnection then we do functional group interconversion.











* SYNTHON:-

* The imaginary charged species or the idealized fragments formed during disconnection are called Synthons.

* They are not real.

* They are imaginary

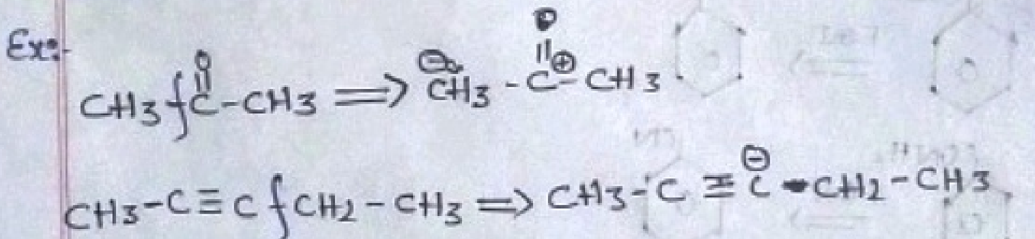
* synthons are two types:-

1. postively polarized synthon is called acceptor synthon which is denoted by (a^n).

2. The negatively charged polarized synthon is called donar synthon. it is denoted by (d^n).

* where (n) is the no. of bonds b/w charged carbon and hetero atom.

Ex:-



$CH_3 \{ \overset{O}{\overset{\|}{C}} - CH_3 \Rightarrow \overset{\ominus}{C}H_3 - \overset{\overset{\ominus}{O}}{\overset{\|}{C}}{}^{\oplus} - CH_3$

$CH_3 - C \equiv C \{ CH_2 - CH_3 \Rightarrow CH_3 - C \equiv \overset{\ominus}{C} - CH_2 - CH_3$

* SYNTHON EQUIVALENT:-

* The real reagent ~~me~~ chemical species of synthons are called synthetic equivalent.

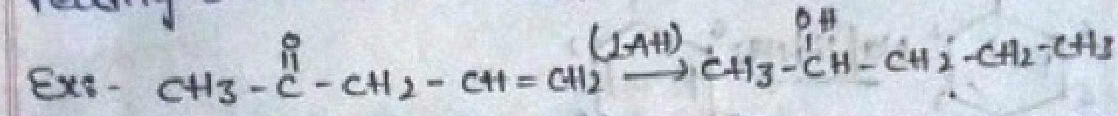
synthon		Synthon equivalent
$C_6H_5CH_2^{\ominus}$	$\Rightarrow$	$C_6H_5CH_2MgBr$
$C_6H_5\overset{\oplus}{C}H_2$	$\Rightarrow$	$C_6H_5CH_2Cl$
$CH_3 - C \equiv C^{\ominus}$	$\Rightarrow$	$CH_3 - C \equiv CNa$
$CH_3 - \overset{O}{\overset{\|}{C}}{}^{\oplus}$	$\Rightarrow$	$CH_3 - \overset{O}{\overset{\|}{C}} - Cl$
$CH_3 - \overset{OH}{C}{}^{\oplus}$	$\Rightarrow$	$CH_3 - C - H$

4/11/23
Tuesday

CHEMOSELETIVITY:-

* The affinity of reagent to react with 1 functional group in a molecule in prefference to the other functional groups ie: Reagent have affinity for a one particular functional group reacts readily overs the others.

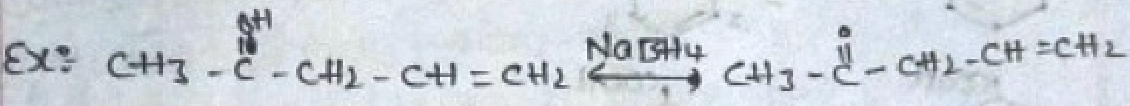
Ex:-



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH_2 \xrightarrow{(LAH)} CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CH_2-CH_3$

In the above Example (LAH) is non chemo-selective because it reduced the both ketone & Alkenes

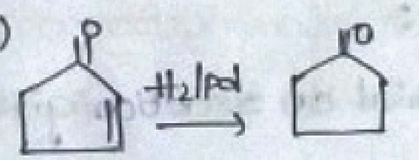
Ex:



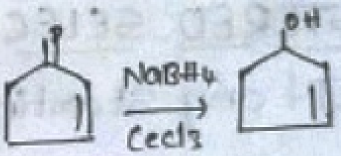
$CH_3-\overset{OH}{\overset{\|}{C}}-CH_2-CH=CH_2 \xleftrightarrow{NaBH_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH_2$

In the above Example ($NaBH_4$) reduces keto-group over the alkene. Hence it is Chemoselective reagent.

Ex:- i)



ii)

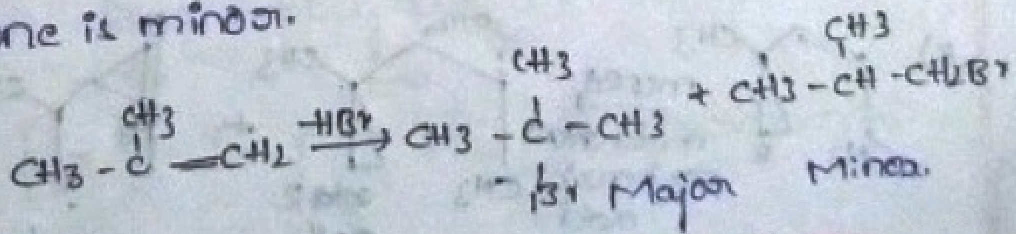


$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CHO \xrightarrow{NaBH_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH$

REGIO SELETIVITY:-

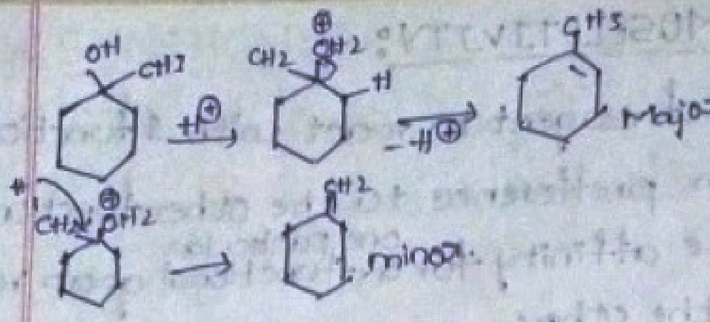
A Reaction is allowed in one direction (or) oreintation of bond breaking (or) making occurs predomiantly over the others that is preferential direction (or) oreintation of bond breaking (or) making over the other possible direction to give two structural isomers. In which one is major and one is minor.

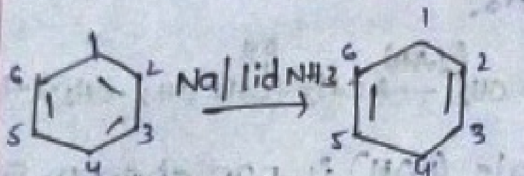
Ex:

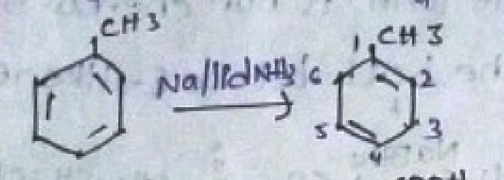


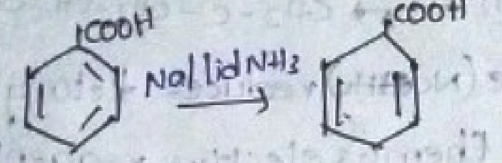
$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2Br$

Major Minor









STEREO SELECTIVITY:-

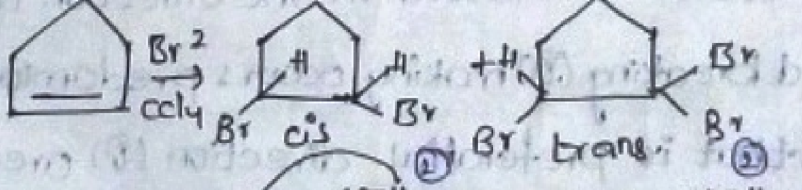
*It any Starting material on reaction gives two types of isomers in which one is major and another is minor.

∴ ie; the isomers can be cis (or) trans, D(or) L, R(or) S,

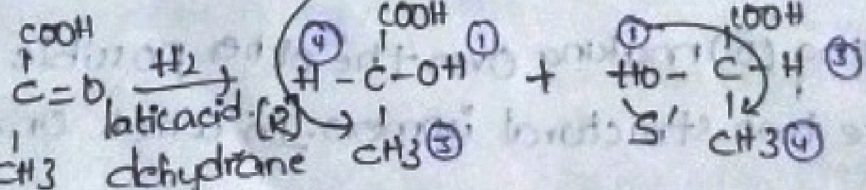
*The starting material need not be stero isomers.

Ex:-

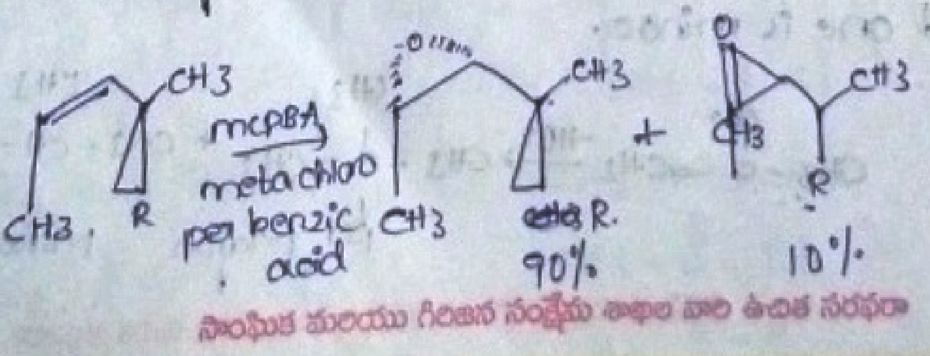
1)



2)



3)



ORDER OF EVENTS:- IN Retro synthetic analysis

The sequence in which - - - set of reaction carried out to get target molecules is called order of events

ie; Order in which reliable reacn are carried out

Order-1

1. Disconnection must be correspond to known (or) reliable reaction.

Ex:- $CH_3-O \mid CH_2 \to CH_3 \Rightarrow CH_3\overset{\ominus}{O} \quad \overset{\oplus}{C}H_2CH_3$

$|||$

$CH_3OH \quad Cl-CH_2CH_3$

Williamson's Synthesis

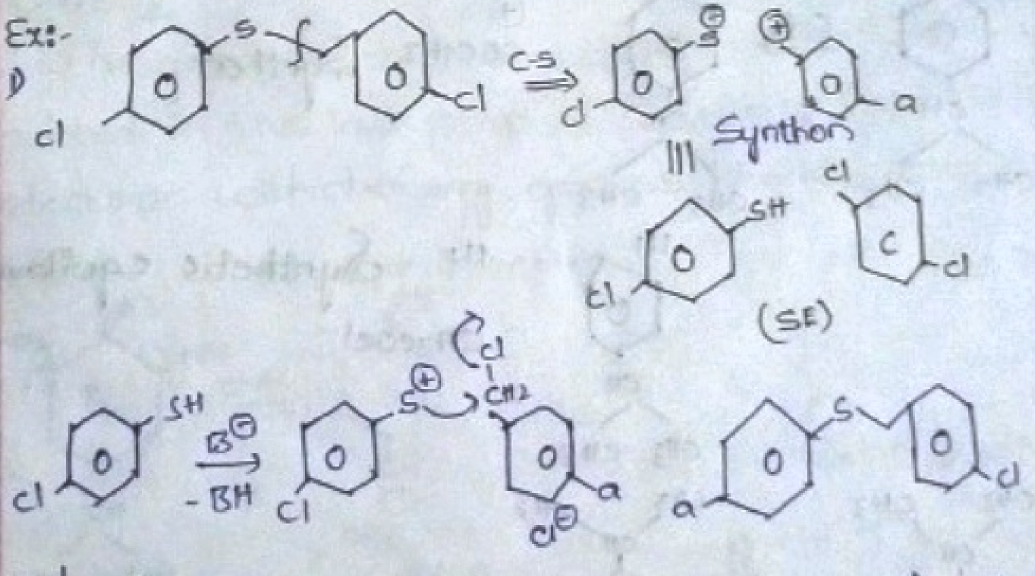
$CH_3O\boxed{Na + Cl}CH_2CH_3 \longrightarrow CH_2-O-CH_2-CH_3$

$CH_3-\overset{O}{\overset{\|}{C}} \mid O-CH_2-CH_3 \Longrightarrow CH_3-\overset{O\oplus}{\overset{\|}{C}} \quad \overset{\ominus}{O}CH_2-CH_3$

Order-2

1. Disconnection must be next to hetero atom (O,S,N) is always reliable. avoid disconnection next to benzene ring

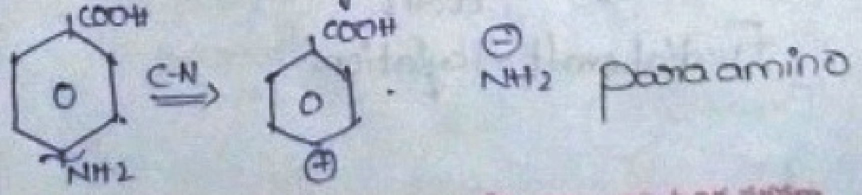
Ex:- 1)



Order-3

1. Don't disconnect group which are difficult to add

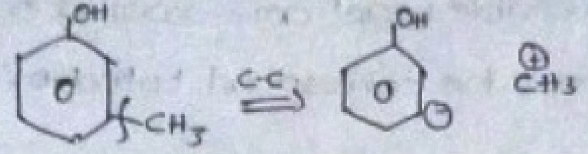
Ex:- 1)



Paraamino

In the above Example COOH group meta directing group but the target molecule is at para position Hence don't disconnect

2)



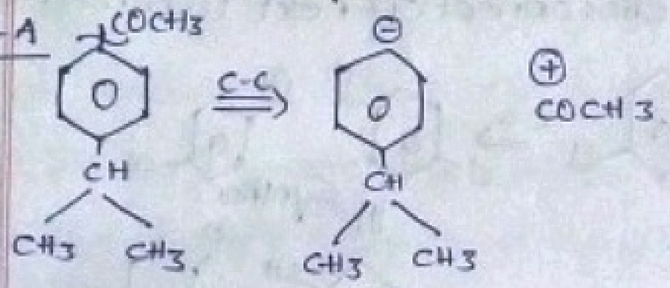
In the above Example OH group Ortho para directing but the target molecule is meta substituted Hence don't disconnect

Order: 4

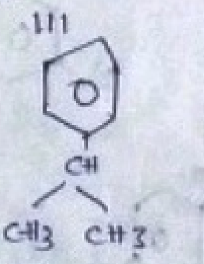
If more than one disconnection is possible then disconnect the one which gives right Orienation (or) direction of synthesis.

para isopropyl aceto phenon:-

Path A

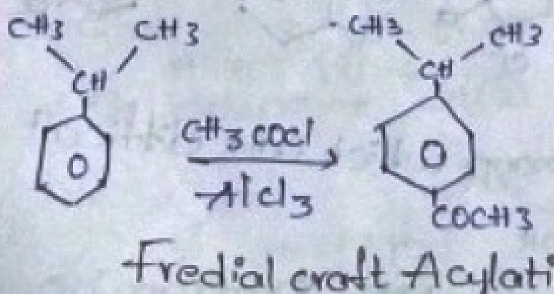


Synthon.



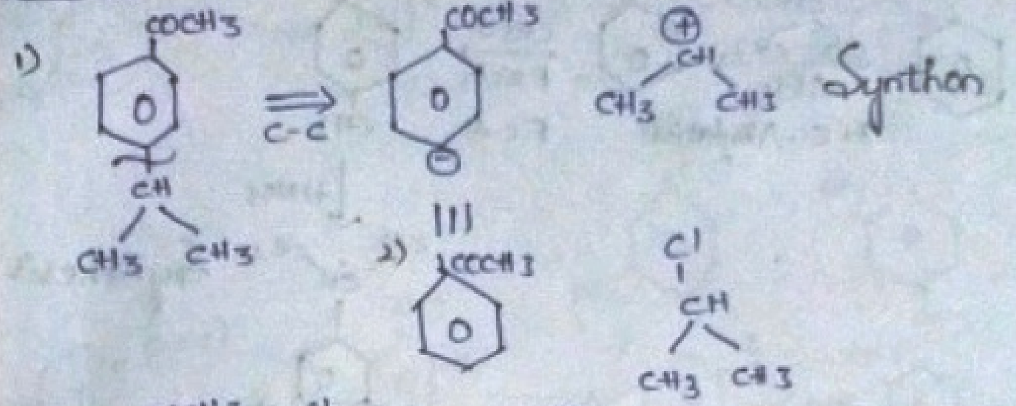
Synthetic equilovent

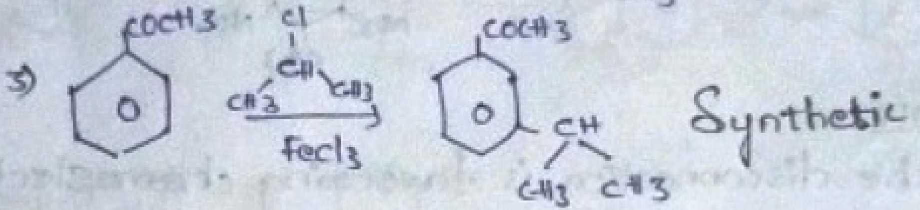
CH_3COCl



Fredial craft Acylation.

path-B

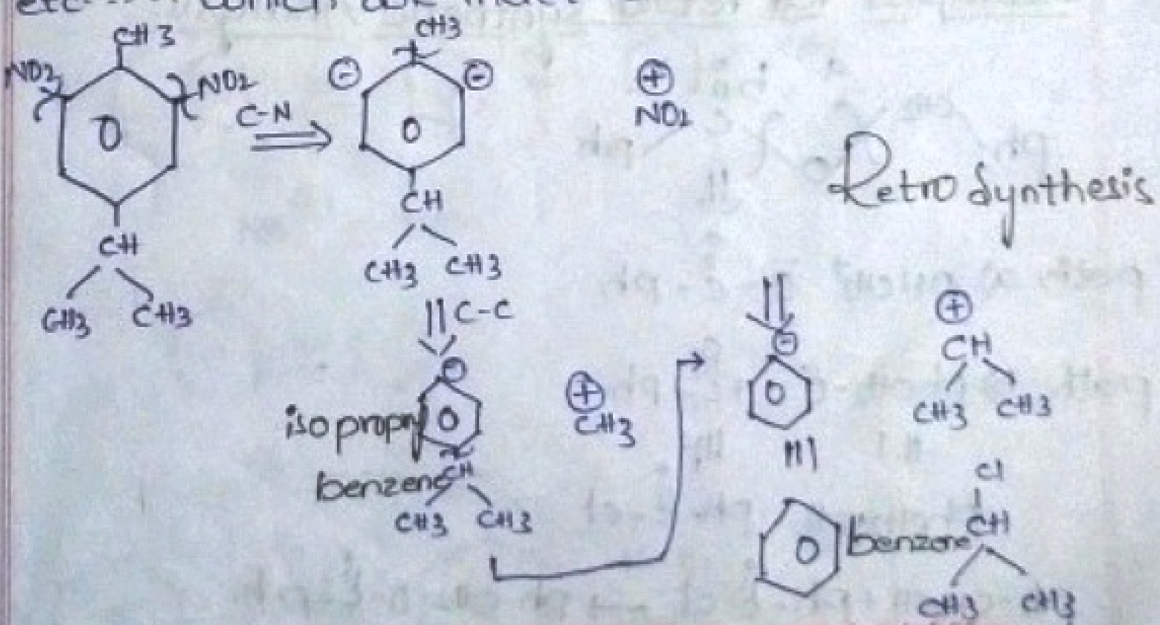


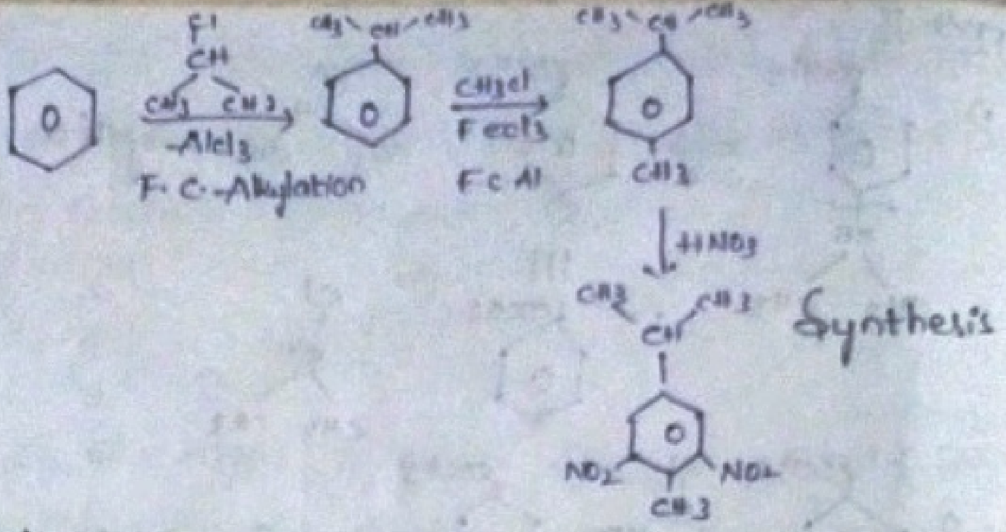


* Among above path-a disconnection gives right direction of target molecule where as path-b gives wrong direction (meta product) of the target molecule.

Orders:

1. The groups which are disconnected first will be added in the last step of synthesis. so disconnect electron withdrawing groups like NO_2, CHO, COOH, CN, etc.... which are inactive.

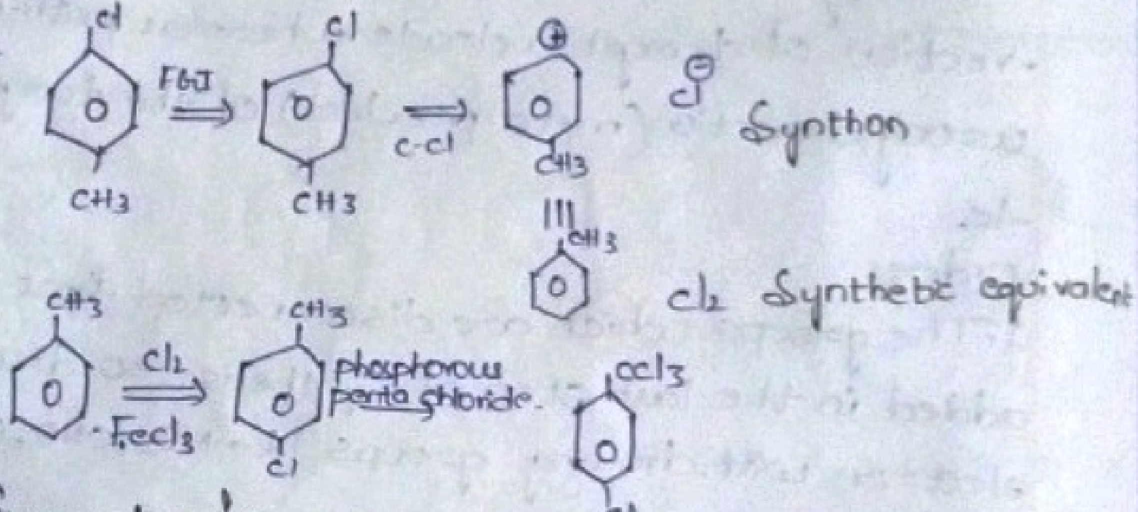




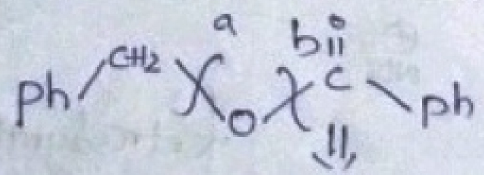
Order:6

* It the disconnection is favouring chemoslectivity problemit can be solved by functional group intercon -tion.

Ex:



Examples for retro Synthetic Analysis:



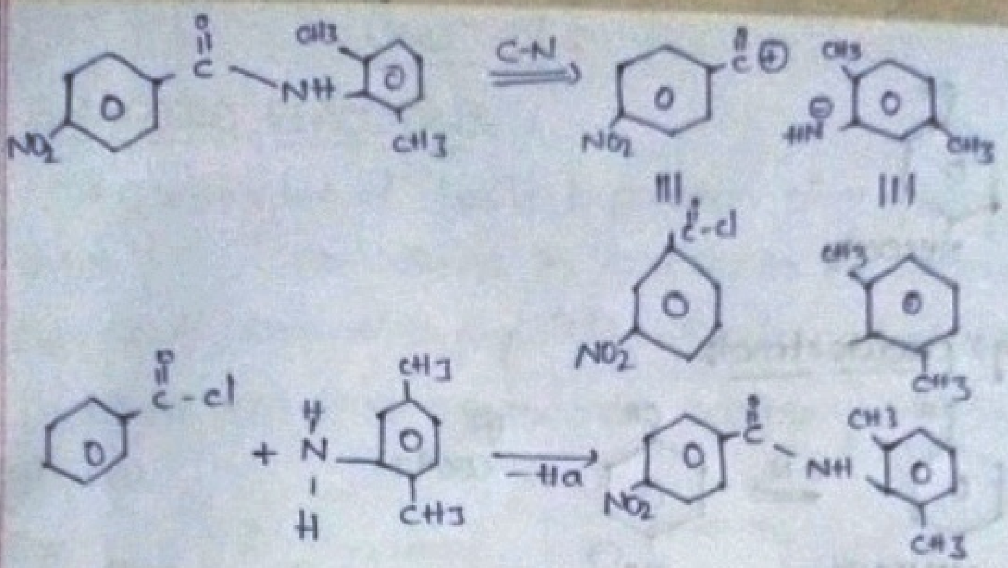
path a) $PhCH_2^{+}$ $\bar{O}-\overset{O}{\overset{\|}{C}}-ph$

path b) $phCH_2-\bar{O}$ $+\overset{O}{\overset{\|}{C}}-ph$

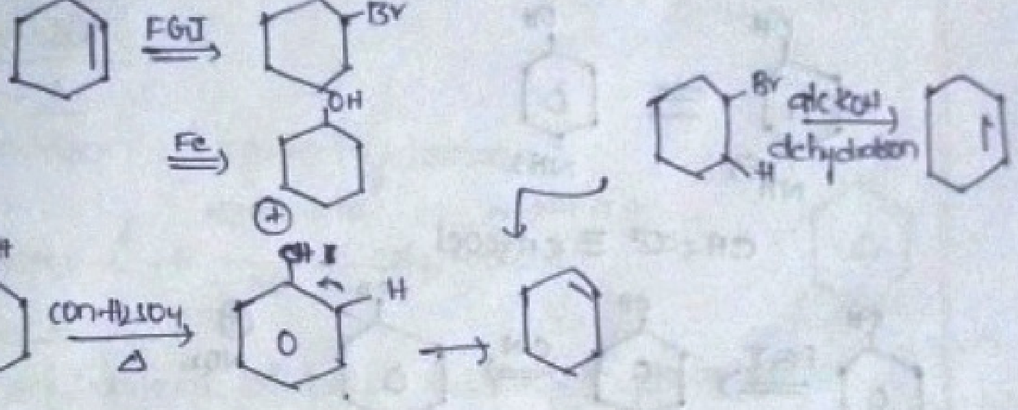
$\|\;|$ $\quad |||$

$phCH_2-OH$ $\quad ph-\overset{O}{\overset{\|}{C}}-Cl$

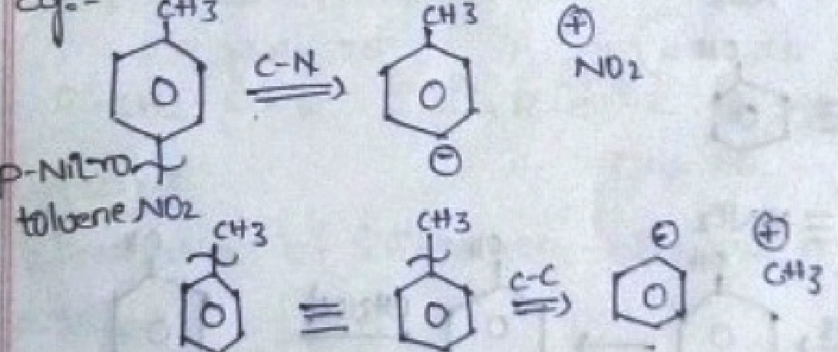
$ph-CH_2OH + ph-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow ph-CH_2-O-\overset{O}{\overset{\|}{C}}-ph$



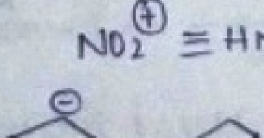
Eg:-



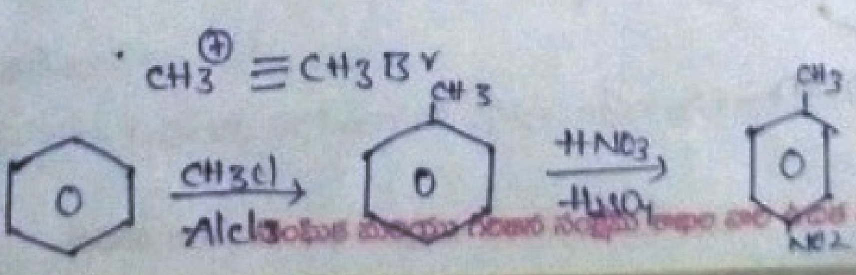
Eg:-

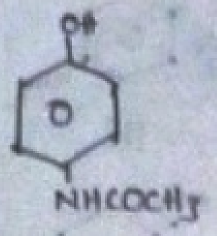


$NO_2^{\oplus} \equiv HNO_3$

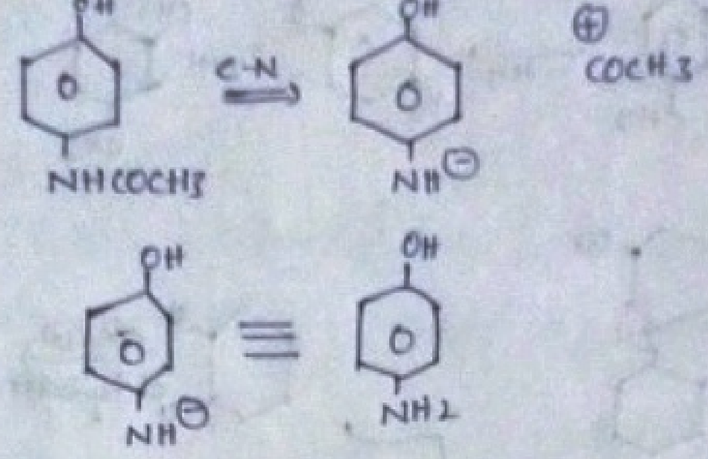


$CH_3^{\oplus} \equiv CH_3Br$

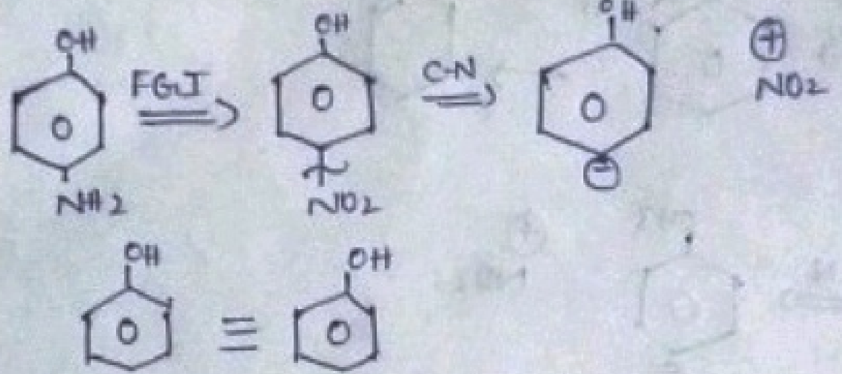




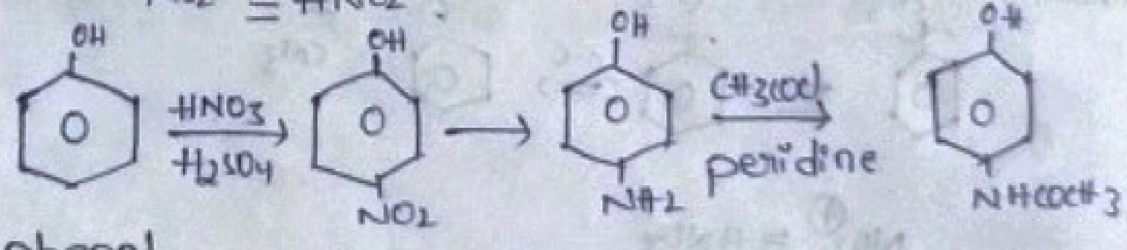
Eg: paracetmol:-



$CH_3CO^+ \equiv CH_3COCl$

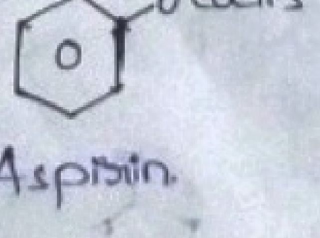


$NO_2^{\oplus} \equiv HNO_2$



phenol

Eg:-



Aspirin

4/11/23

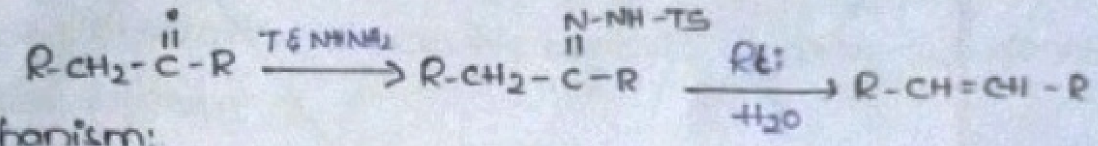
UNIT-IV :-

SHAPIRO REACTION:

*Convertion of tosile hydrozon of carbonyl compound into are alkene in presence of strong bases like (NBuli) Normal Butlyl lithium it is called shapiro Reac^n.

* In these reaction we convert carbonyl compounds into alkenes

Eg:

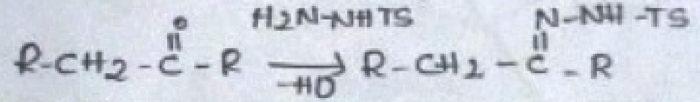


$$R\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{TS\,NHNH_2} R\text{-}CH_2\text{-}\overset{N\text{-}NH\text{-}TS}{\overset{\|}{C}}\text{-}R \xrightarrow[H_2O]{RLi} R\text{-}CH=CH\text{-}R$$

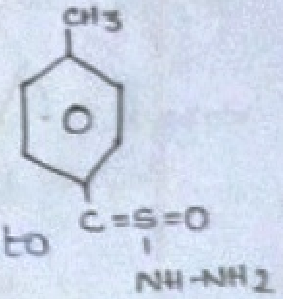
Mechanism:

step:-1

Formation of tosile hydrozen

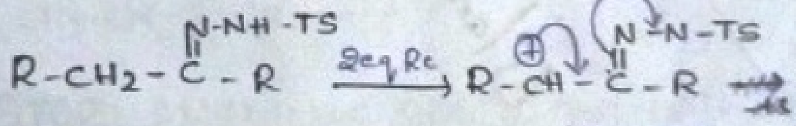


$$R\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow[-H_2O]{H_2N\text{-}NHTS} R\text{-}CH_2\text{-}\overset{N\text{-}NH\text{-}TS}{\overset{\|}{C}}\text{-}R$$



step:-2

Two equivalent of base attack hydrozon to form dianion intermediate.

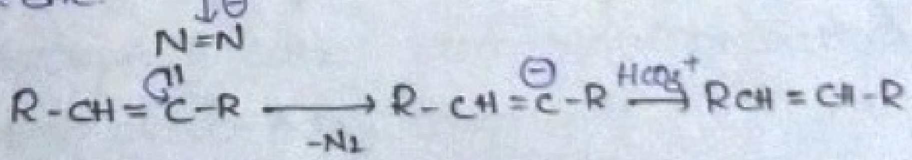


$$R\text{-}CH_2\text{-}\overset{N\text{-}NH\text{-}TS}{\overset{\|}{C}}\text{-}R \xrightarrow{2eq\,RLi} R\text{-}\overset{\oplus}{C}H\text{-}\overset{N\text{-}N\text{-}TS}{\overset{\|}{C}}\text{-}R \xrightarrow[-Ts]{}$$

Dianion

step:-3

Elimination of Nitrogen followed by hydrolysis gives alkene.



$$R\text{-}CH=\overset{N=N}{\overset{|}{C}}\text{-}R \xrightarrow[-N_2]{} R\text{-}CH=\overset{\ominus}{C}\text{-}R \xrightarrow{H_3O^+} RCH=CH\text{-}R$$

* Important bases used in shapiro reac^n of CH_3Li, NBuli $NaNH_2$, LDA. (Lithium isopropyl diamide).

Solvents:-

Higher polar solvents like dimethoxy butene.

$(CH_3O(CH_2)_4OCH_3)$

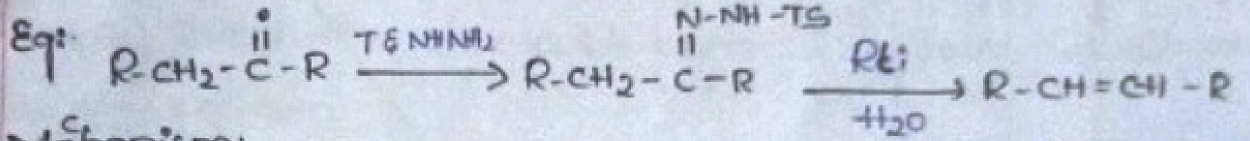
24/11/23

UNIT-IV :-

SHAPIRO REACTION:-

*Convertion of tosile hydrozon of carbony compound into are alkene in presence of Exes strong·bases like [NBuli] Normal Butly lithium it is called shapiro Reacⁿ.

* In these reaction we convert carbonyl compounds into alkenes

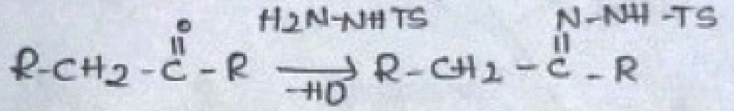


Eq: $R-CH_2-\overset{\overset{\bullet}{||}}{C}-R \xrightarrow{TS\,NHNH_2} R-CH_2-\overset{\overset{N-NH-TS}{||}}{C}-R \xrightarrow[H_2O]{RLi} R-CH=CH-R$

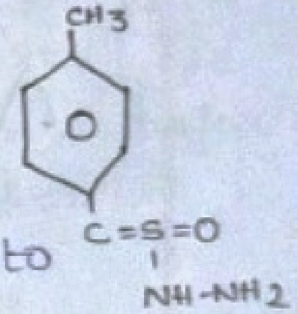
Mecānism:

step :-1

Formation of tosile hydrozen

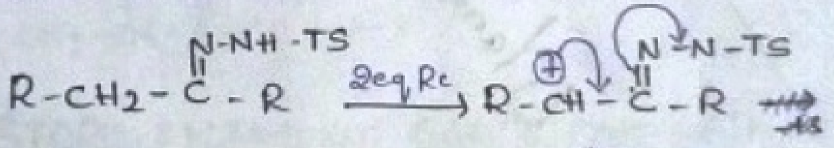


$R-CH_2-\overset{\overset{\circ}{||}}{C}-R \xrightarrow[-H_2O]{H_2N-NHTS} R-CH_2-\overset{\overset{N-NH-TS}{||}}{C}-R$



step:-2

Two equivalent of base attack hydrozon to form dianion intermediate.

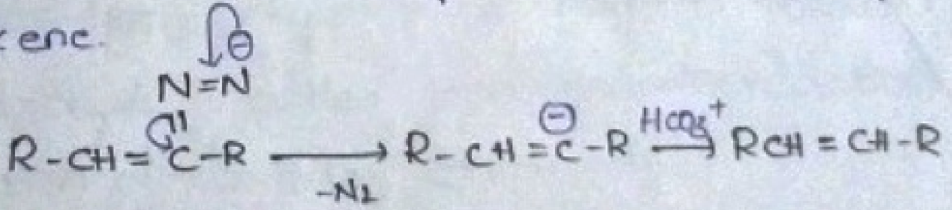


$R-CH_2-\overset{\overset{N-NH-TS}{||}}{C}-R \xrightarrow{2eq\,RLi} R-\overset{\oplus}{C}H-\overset{\overset{N=N-TS}{||}}{C}-R \xrightarrow{-TS}$

Dianion

step:-3

Elimination of Nitrogen followed by hydrolysis gives alkene.



$R-CH=\overset{\overset{N=N^{\ominus}}{|}}{C}-R \xrightarrow[-N_2]{} R-CH=\overset{\ominus}{C}-R \xrightarrow{H_3O^+} RCH=CH-R$

* Important bases used in shapiro reacⁿ of CH_3Li, NBuli $NaNH_2$, LDA. (Lithium isopropyl diamide).

Solvents:-

Higher polar solvents like dimethoxy butene. $(CH_3O(CH_2)_4OCH_3)$

* Diamine butane:-

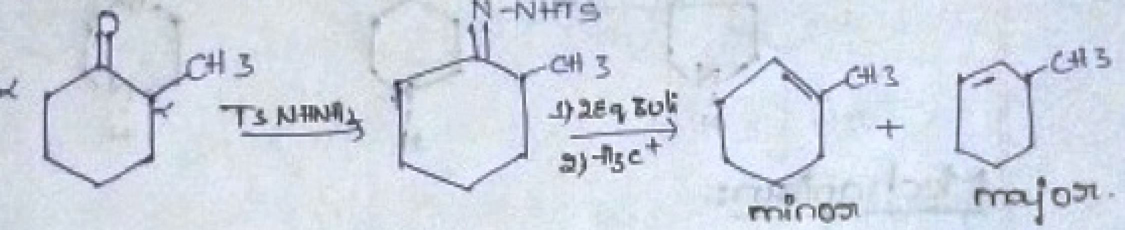
Limitations:-

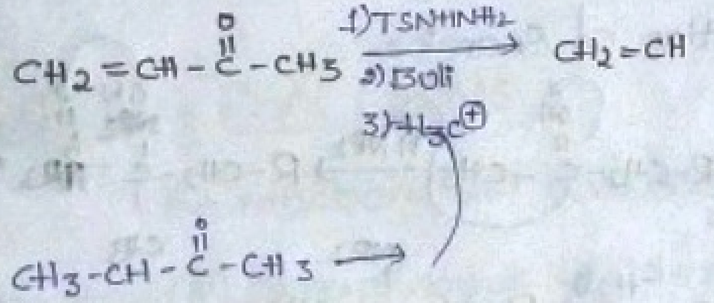
Step:-1

Formation: The carbonyl compound should contain at least one alpha (α) hydrogen.

2. It is highly regio selective.
3. In case of unsymmetrical tosile hydrogens the paido maint orientation of double bond is at less substituted at alpha carbon

Eg:-





$CH_2=CH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[2)\,BuLi]{1)\,TSNHNH_2} CH_2=CH$

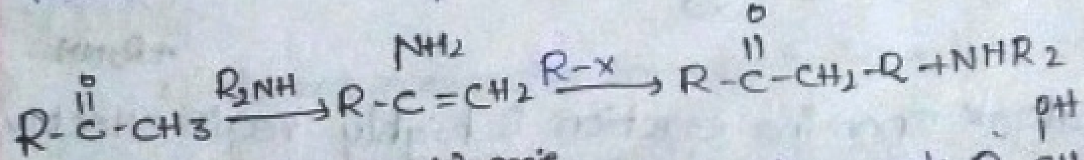
3) H_3C^{+}

$CH_3-CH-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow$

25/11/23 Saturday

STORK ENAMINE REACTION:- (Alkylation)

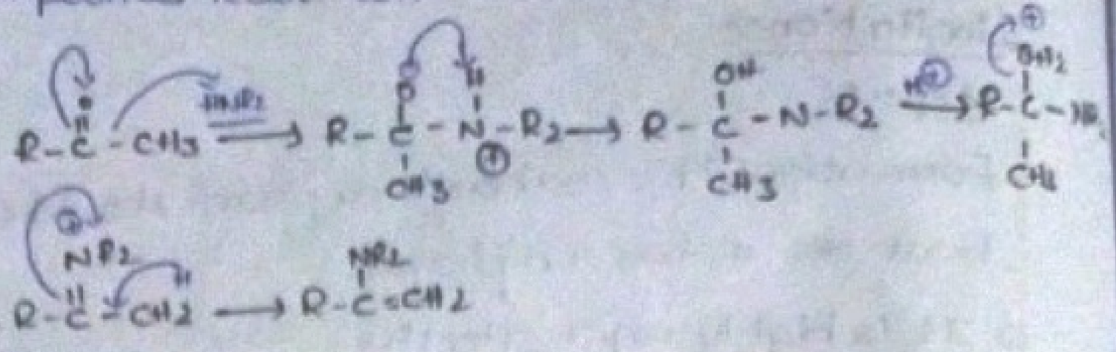
Synthesis of alpha,β unsaturated carbonyl compounds from alkylation of enamines followed by acetic hydrolysis is called stork enaminereaction ∴ ie; α, alkylation of carbonyl compounds.



$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{R_2NH} R-\overset{NH_2}{C}=CH_2 \xrightarrow{R-x} R-\overset{O}{\overset{\|}{C}}-CH_2-R + NHR_2$

ENamines are $R-\overset{NR_2\ amie}{C}H=CH_2$ enloges to enols $R-\overset{OH}{C}H=CH_2$ but more nucleophilic they are prepared when carbonyl compounds reacts with 2° amines

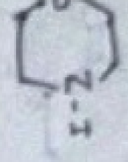
Eg:-



1°Amine

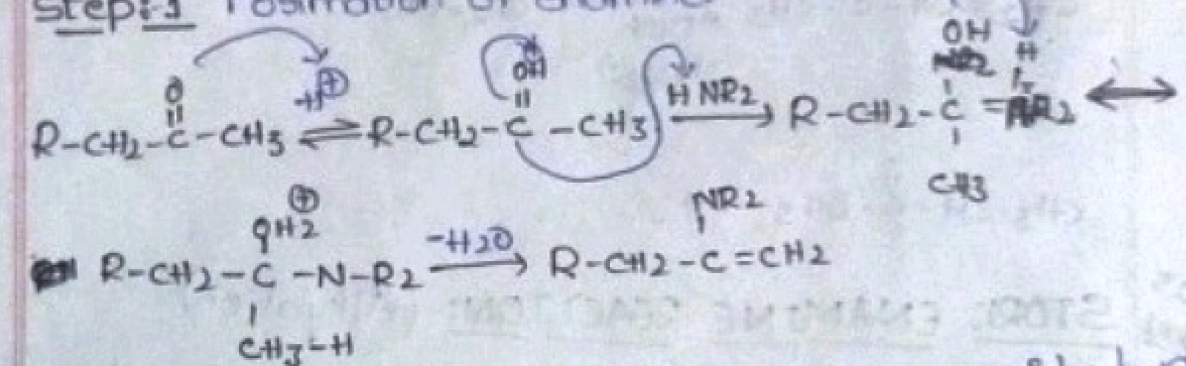
* The common 2° amines used in Stork enamine reaction of pyrrolidine, piperdiene, Morpholidine



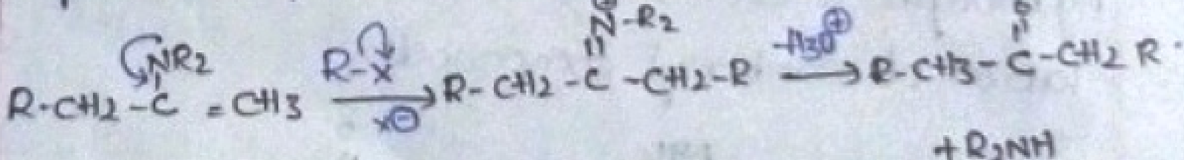


Mechanism:

Step-1 Formation of Enamine



Step-2 —Alkylation of Enamine followed by acidic hydrolysis α alkylated carbonyl compounds

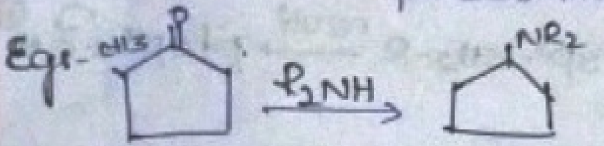


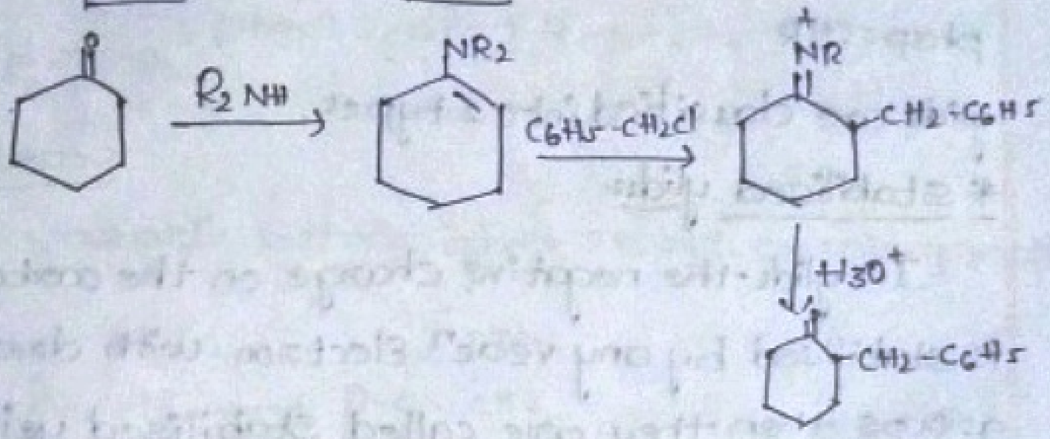
* Stork enamine reaction is highly regio selective it is always favours less substitubted double bond in enamine formation because in (less substituted)

more substituted double bond there is a replusion between 2° amine hydrogens and alkyl groops and also loss of hor co-planarity.

*Hence in stork enamine reac^n less substituted en-amine formed predominantly.

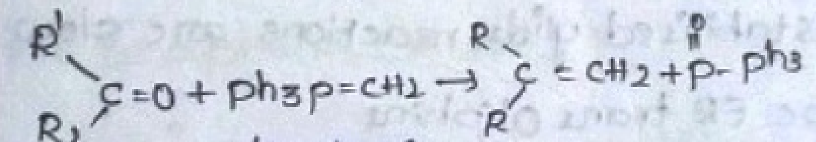
Eg:-





WITTIG REACTION:-

The reaction b/w carbonyl compounds with phosphorase (or) phosphorous yields to synthesize alkenes is called wittig reac^n. That is new C=C bond is formed.



$$\begin{matrix}R^1 \\ R_2\end{matrix}\!\!>C=O + Ph_3P=CH_2 \rightarrow \begin{matrix}R \\ R\end{matrix}\!\!>C=CH_2 + \overset{O}{\overset{\|}{P}}-Ph_3$$

phosphase

phosphus yields

YILDS:-

yilds are molecules in which to edject atoms have oppsite charge (or) separated by opposite charges.

$A^+ - B^-$

$Ph_3P = \overset{\curvearrowright}{C}H_2 \longleftrightarrow Ph_3P^+ - \overset{\ominus}{C}H_2$ unstablised yilds ylids can be prepared by the reaction ylids triphenolphasine and 1°(or) 2° alkyles aldehyde in a sn² mechanisms followed by treatment with strong bases like Nbuli

$ph_3\ddot{p} + CH_2-R \longrightarrow ph_3p^{+}-CH_2-R \xrightarrow{nBuli} ph_3p^{+}=\overset{\oplus}{C}H \longrightarrow$

$ph_3p=CHR$

ylids are clasified into 2 types.

*** Stabilised ylids:-**

In ylids the negative charge on the carbon atom is stabilised by any reacⁿ Electron with drawing groups then they are called stabilised yeilds.

$ph_3p^{+}-\overset{\oplus}{CH_2}-\overset{\overset{O}{\|}}{C}-R \longleftrightarrow ph_3p^{+}-C=\overset{\overset{O^{-}}{\|}}{C}-R$

The nucleophilicity of the ylids carbon is decreased by electron with drawing groups.

Hence stabilised ylids reactions are slow and they will be ER trans oliphins

*** unstablised ylids:.**

when they are known no Electron with drawing groups on the ylid carbon atom they are called unstablised yeilds.

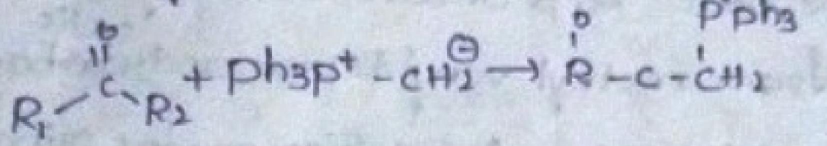
$ph_3p^{+}-\overset{\ominus}{CH_2}-CH_3$

They are very reactive and forms cis (or) G-alkenes

Mechanism:-

Step:-1

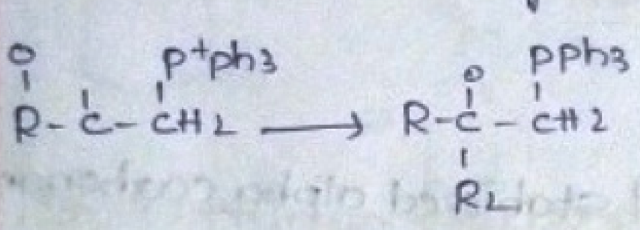
Nucleophilic addition by ylid carbon at carbonyl carbon gives unstable Betane.



$$R_1-\overset{\overset{O}{\|}}{C}-R_2 + ph_3P^+-CH_2^{\ominus} \rightarrow R-\overset{\overset{O}{|}}{C}-\overset{\overset{P^+ph_3}{|}}{CH_2}$$

Step:-2

Unstable Betane gives stable oxaphosphatane



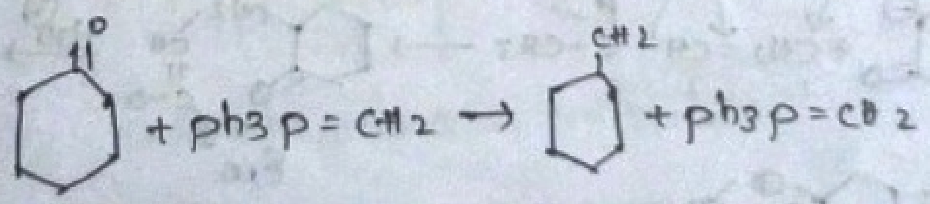
$$R-\overset{\overset{O}{|}}{C}-\overset{\overset{P^+ph_3}{|}}{CH_2} \longrightarrow R-\underset{\underset{R_2}{|}}{\overset{\overset{O}{|}}{C}}-\overset{\overset{Pph_3}{|}}{CH_2}$$

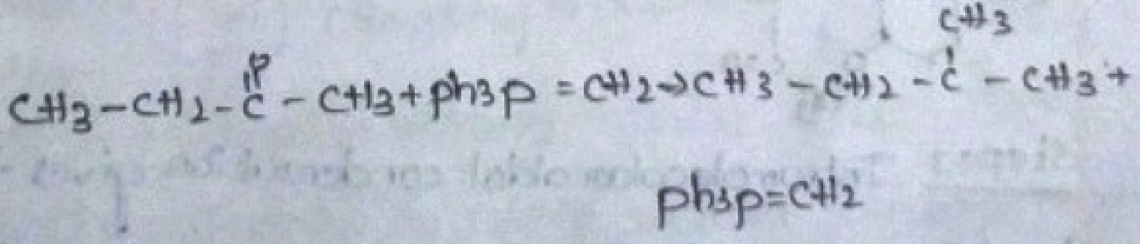
Oxophosphatene.

Step:-3

The Driving force for this reaction formation of a bond b/w phosphorus and oxygen give alkene and phosphone oxidize.

Ex:-



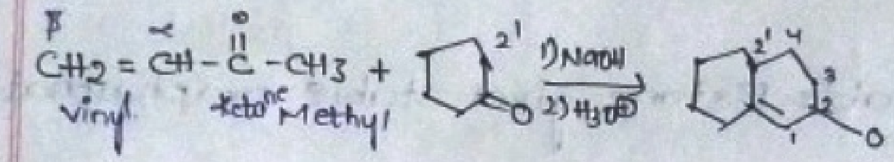


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3+ph_3P=CH_2 \rightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}-CH_3+ ph_3P=CH_2$$

ROBINSON ANNULATION:-

The sequencial process of micaheladdition (1,4 addition) followed by intra molecular Aldol condensation leads to form six membered cyclic ring is called Robinson Annulation.

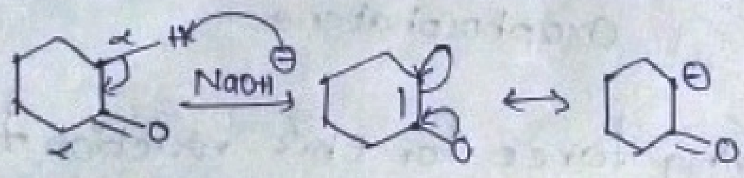
In these reac^n α, β unsaturated cyclic ketones (or) obtained from methyl venyl ketone and cyclic carbonyl compounds the condensation. Annulation means ring forming



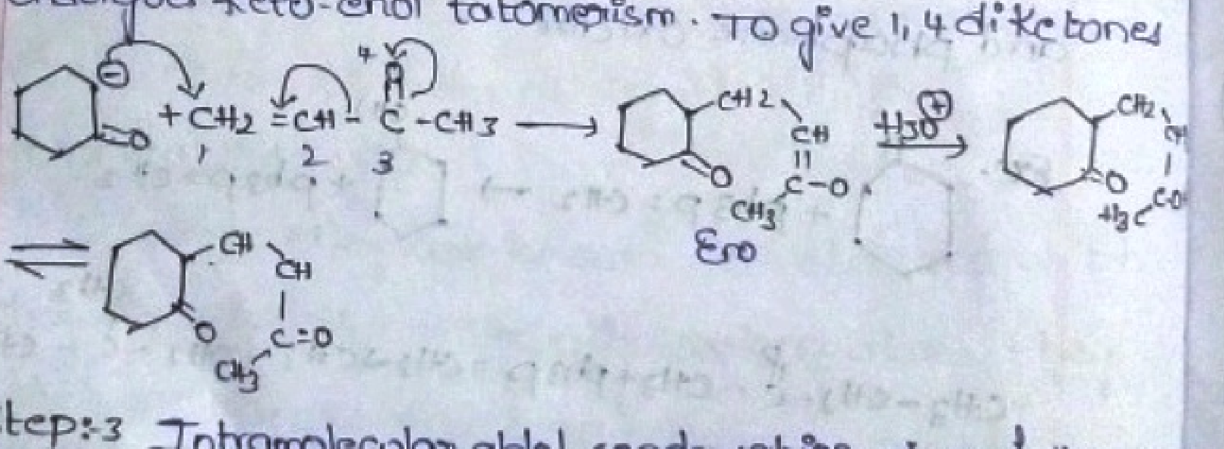
Mechanism:-

Michael addition:-

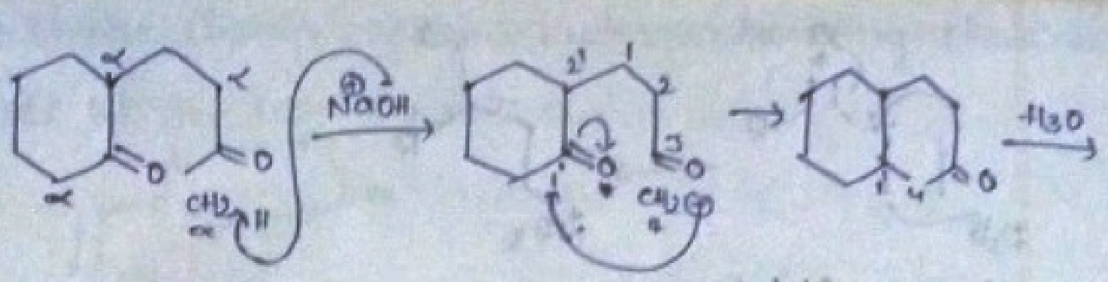
Step:-1 formation of stabilized alpha carbonanion

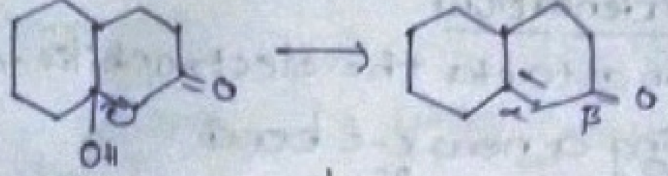


Step:-2 1,4 nucleophilic addition gives Enol which further undergoes keto-enol tatomerism. To give 1,4 diketones

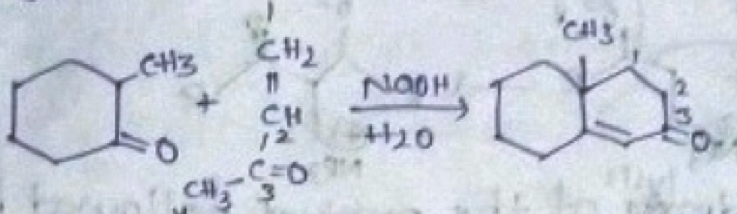


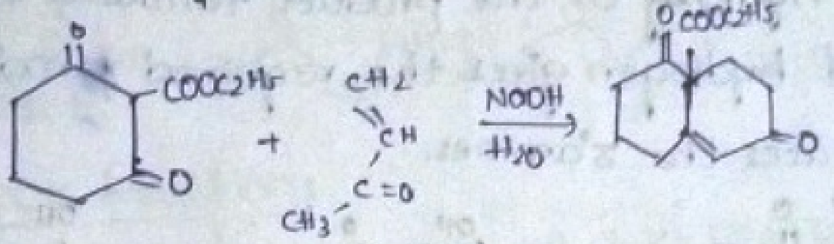
Step:-3 Intramolecular aldol condensation. gives followed by dehydration gives α, β unsaturated bi cyclo ketones





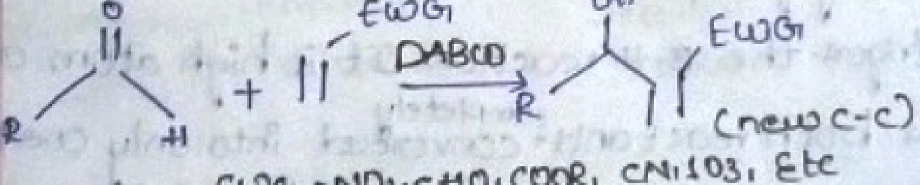
Eg:





/12/23. **Baylis - Hilman Reaction:-** (DABCO) Di-aza-Bicyclo octane

* convention of activated alkenes into hydroxy in alkylene (acrobic compounds), developing new c-c bond at alpha position of ~~aldehydes 3°amines~~ carbon in presence of unhinden 3° amines like DABCO



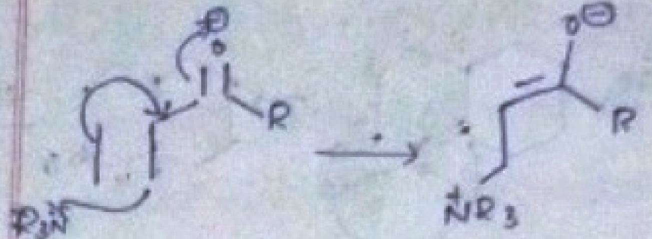
EWG = NO_2, CHO, COOR, CN, 103, Etc

DABCO =  Diarabicyclo octane.

Mechanism:

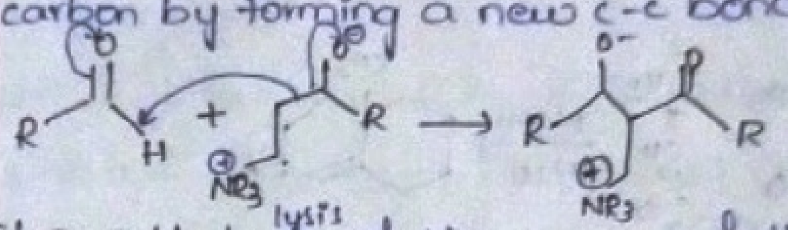
Step:-1 Michael addition:-

In these 3°amine in DABCO attacks β-carbon atom and forms zwitterion like enolate anion.

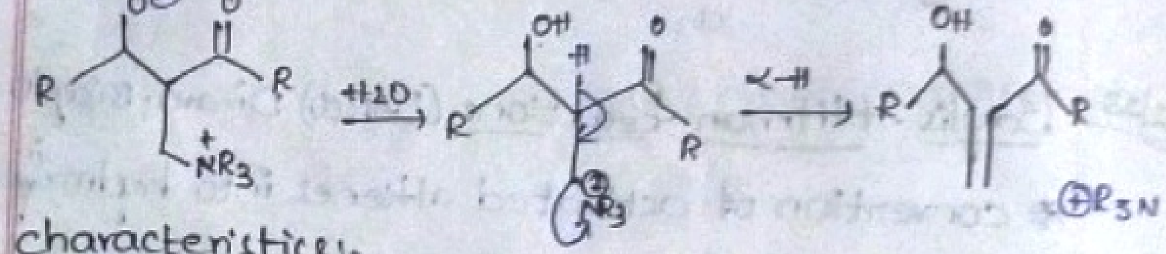


Step:2 Aldol condensation:-

The Enlate anion attacks the electrophilic Aldehyde carbon by forming a new c-c bond.



Step:3 Hydrolysis of the product followed by Elimination of hydrogen gives the required product and regenerates the 3°amines.



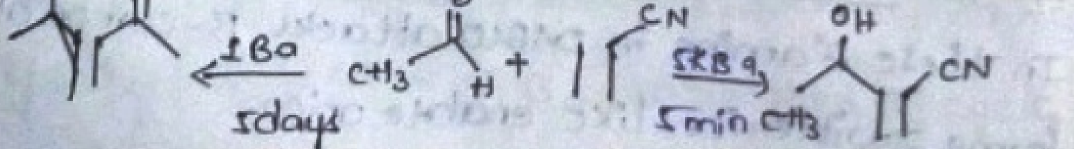
Characteristics:-

* DABCO plays as a good nucleophile as well as good leaving group.

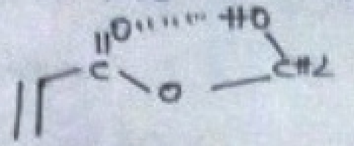
* Its trigers the B-H reaction It is high atom aconomy reactions both reactants completely converted into only one product

* This reac^n rate can be increases at high temperatures.

* At high pressure also the rate of reac^n increase

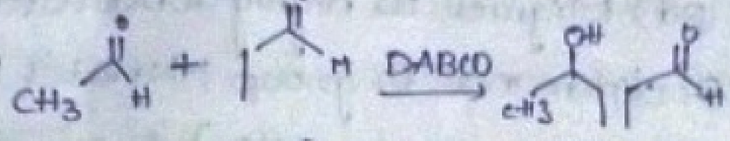


* If the oliphin contains hydrogen bonding then also rate of the reac^n increases.

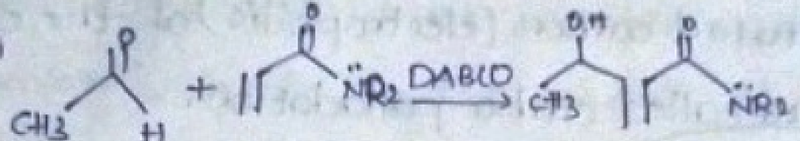


Examples:-

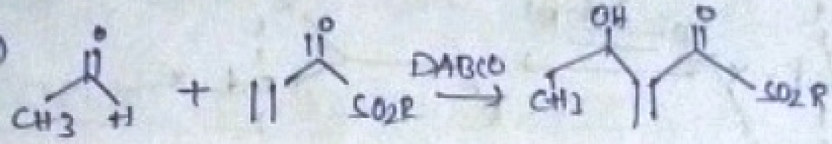
1)



2)



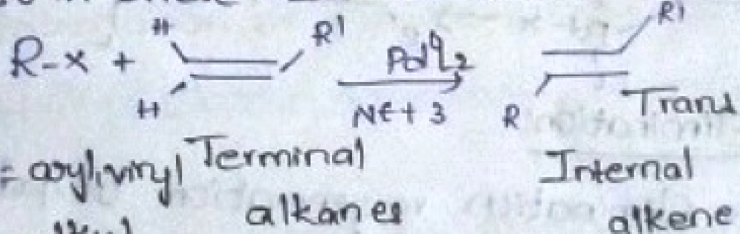
3)



1/12/23 day

HECK Reaction:

Formation of new c-c bond b/w halo organo compound (R-x) and oliphins in presence of pd° complex & base ∴ The hydrogen is substituted aryl (or) alkyl group so in these reac^n convertion terminal alkenes into internal alkenes occurs.



R = aryl, vinyl alkyl

X = Cl, Br, I, etc - - -

R- = Any Electron with drawing group.

L = OAc, Cl, PPh3 Etc - - -

1) Mechanism:-

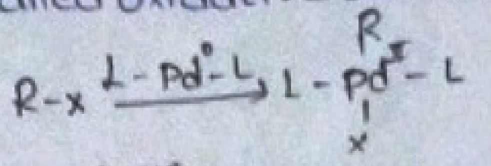
1) oxidative additions

when a two atoms of a molecule dissociates to

సాంఘిక మరియు గిరిజన సంక్షేమ శాఖల వారి ఉచిత సరఫరా

form to new σ bonds with Electron difficent meta

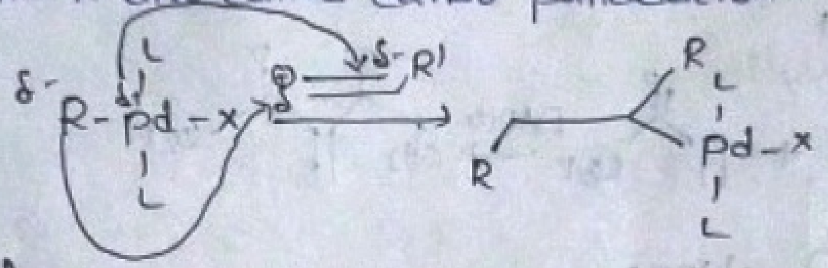
is called oxidative addition.



$$R{-}X \xrightarrow{L-Pd^{0}-L} L-\underset{X}{\overset{R}{Pd^{II}}}-L$$

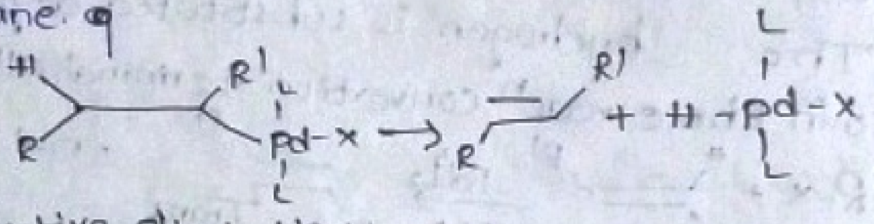
2) SYN addition:

In this (pd) Migraes to highly substituted carbo (nucleophilic) of oliphareand R. group Migrates to the less substituted carbon (electrophilic) of the oliphane. This is also called carbo palladation.



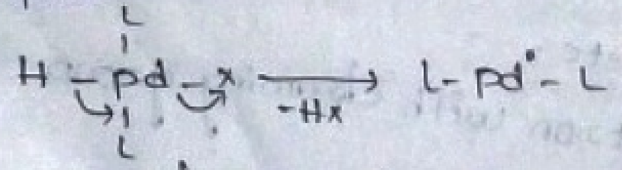
3) β-Hydrogen Elimination:-

Elimination of β. hydrogen by base gives substituted Oliphane.



4) Reductive Elimination:

ON Reductive Elimination regeneration of pd complex



$$H-\underset{L}{\overset{L}{Pd}}-X \xrightarrow[-HX]{} L-Pd^{0}-L$$

Important features of this reaction:-

- * Starting materials are little expensive.
- * Recovery of palladium is very low.

*Aryl halides Reacts slowly when compared to other.

*It is a stero-selective reac^n and always gives trans Oliphane.

*If the ligands and phosphorous are bulky. (PPh_3) the rate of reac^n also increases

*This reac^n is catalysed by silver salts.

*The important bases in this reac^n are triethyl amine, K_2CO_3, Ag_2CO_3 the solvents of the reac^n are [THF], DMF. (Dimethyl formaide)

SUZUKI COUPLING: Reaction:

* Coupling reactions are when two hydro carbon fragments are coupled. (combine) with aid of catalyst
* pd catalysis cross coupling of aryl (or) alkyl halides with organo boro derivatives, which leads to the formation of new c-c bond with high regio selectivity & stero selectivity is called Suzuki coupling reac^n.

$$R-x + r'-B(OH)_2 \xrightarrow[2)\,NaOEt]{1)\,Pd^0L_2} R-r'$$

where, R= Aryl, alkyl, alkenyl, alkynyl, allyl

x = Cl, Br, I

Base = $NaOC_2H_5$, KOH etc - - -

Solvents = Benzene, Ether Etc - - -

Characteristics:

* All starting materials are readily available & cheap.

* All reactants are non-toxic and can easily hand

* It give 100% only one product

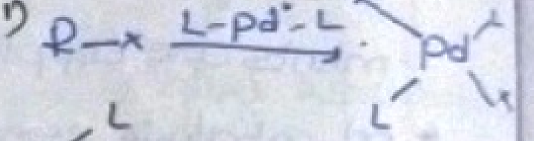
* The Bi-products easily removed

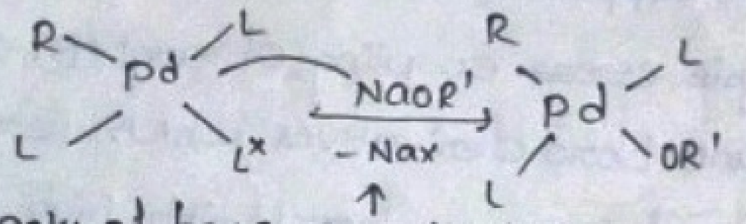
* stero-chemistry of the reactant is retained

Mechanism:-

Oxedative addition:-

pd inserts between R & x and oxide state pd increased from 0 to 2 is called oxdative addition

1) 

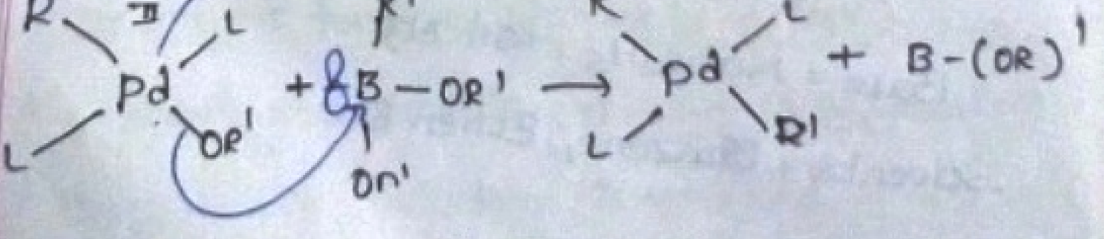
2) 

Attacks of base on palledium

Base attacks pd & removes a halide anion.

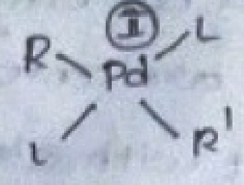
Trans-metalization:-

Transfer alkyl group from boron to pd trans metalition. since Electro negativity of carbon & pd is same the migration occurs

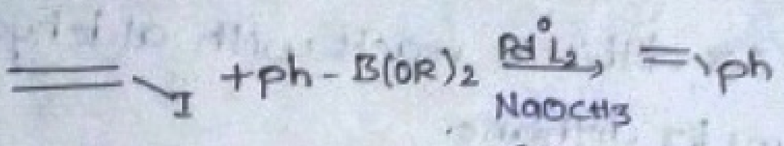


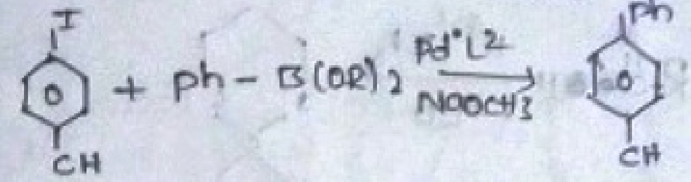
Reductive Elimination :-

Reductive elimination it gives coupled product & regenerates (pd) catalyst.

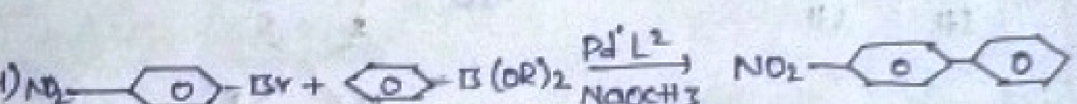


Examples:-

1)


2)


3) $C_6H_5-CH_2-Br + C_6H_5-B-(OR)_2 \xrightarrow[NaOCH_3]{Pd^{\circ}L^2} C_6H_5-CH_2-C_6H_5$

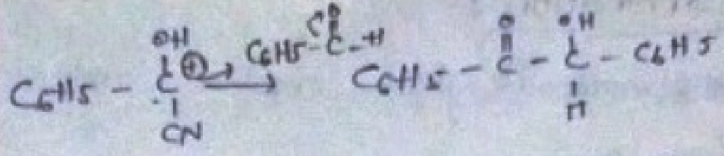
4)


UMPOLUNG:-

It is German word means Rervse of polarity given by see back in

$\overset{\delta+}{R}-\overset{\delta-}{X}$. $\overset{\delta-}{R}\overset{\delta+}{Mg}X$

In benzoic condition the reache electrophilic carbon of carbonyl compound becomes nucleophilic carbon.

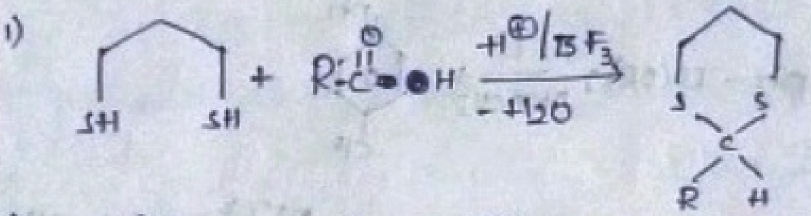


*Normally carbonyl carbon is electrophilic nature; Hence can react with electrophiles but using umpol concept when carbonyl compounds are convert into 1,3 dithiene anion which can react with electrophil.

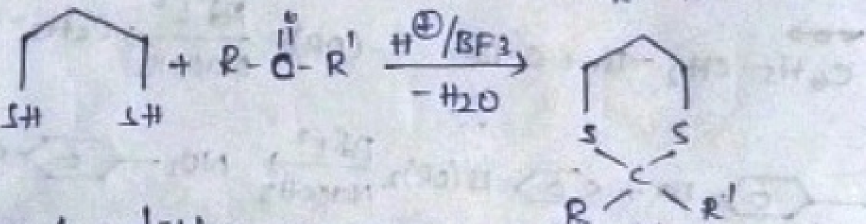
Preparation of 1,3 dithiane:-

* propane 1,3 dithione reacts with aldehydes & ketones forms 1,3 dithiane.

1)

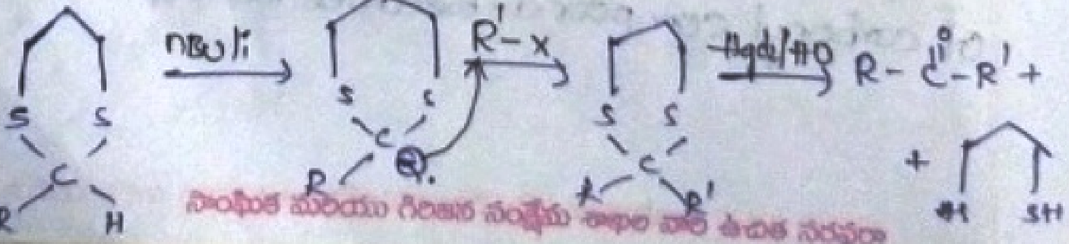


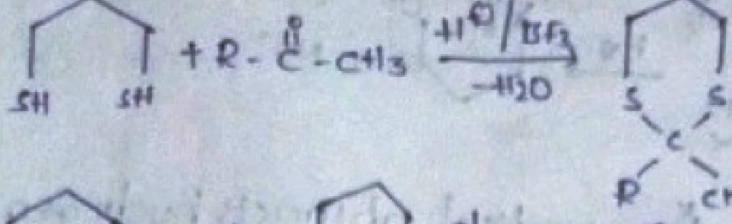
2)

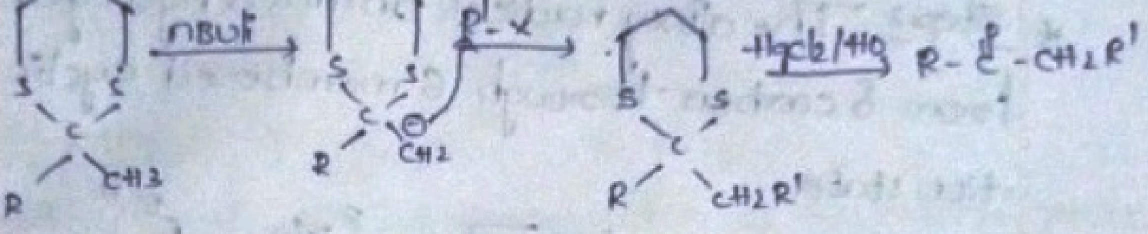


* when 1,3 dithiane reacts with strong bases like (nBuLi) forms carbonion that is electrophilic carbon is convert into nucleophilic carbon which on treated by Alkylation followed by hydrolysis with Mecuric salts gives alkyloted carbonyl compounds.

Step:-2







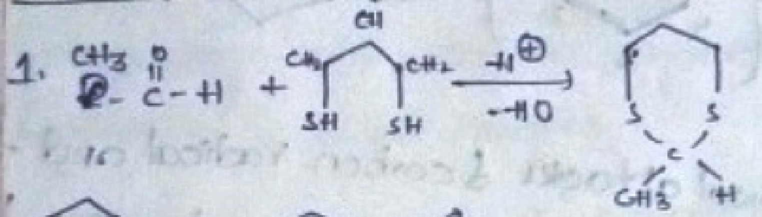
* Applications of 1,3 dithiane:-

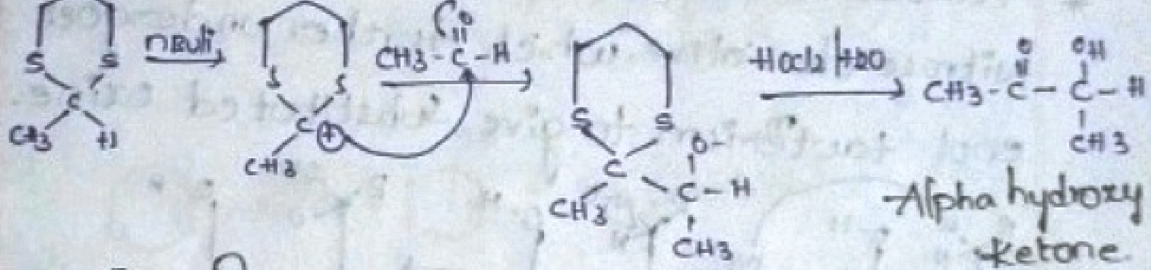
R-NO-Nitroso

R-ONO- Nitrite

R-NO3- Nitrate

R=NOH Oxine.

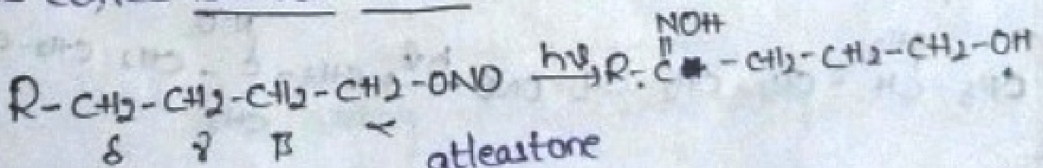
1. 



Alpha hydroxy ketone.

Barton:- Reaction:-

* Converition of Nitrites with (δ-H) atom into hydroxy subtituted oxines under the influence of (UV) radiation is called Barton reacⁿ.



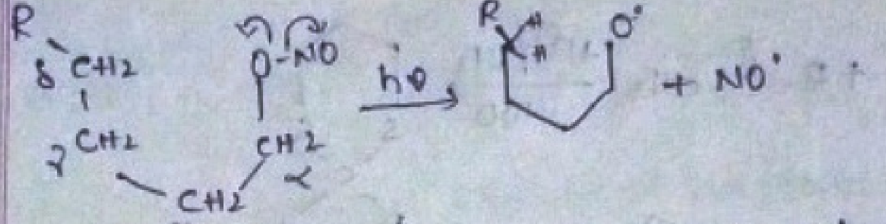
$$R-\underset{\delta}{CH_2}-\underset{\gamma}{CH_2}-\underset{\beta}{CH_2}-CH_2-ONO \xrightarrow{h\nu} R-\overset{NOH}{\overset{\|}{C}}-CH_2-CH_2-CH_2-OH$$

atleastone

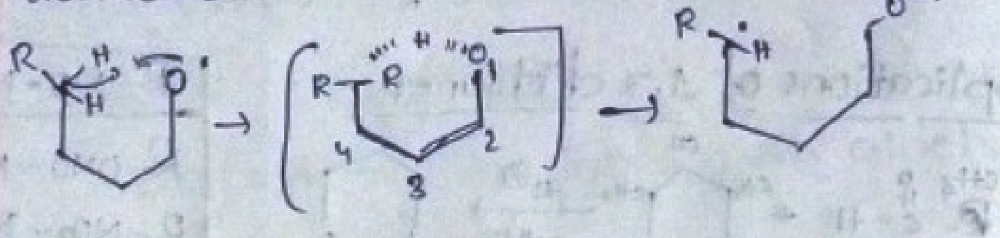
* In barton reacⁿ δ hydrogen is necessary it introduces by functional groups (OH) alchol, oxines

Mechanism:-

Step:-1 Homolytic cleavage of nitrite gives alkoxy radical & Nitrose radical.

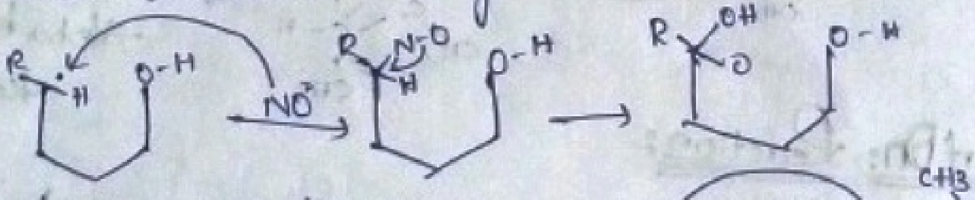


* Step:2 : The alkoxy radical abstracts hydrogen radical from δ carbon through 6 membered cyclic transition state.

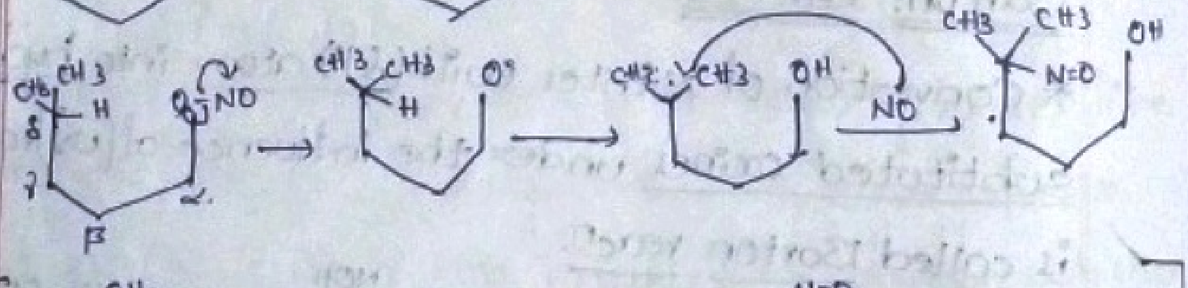


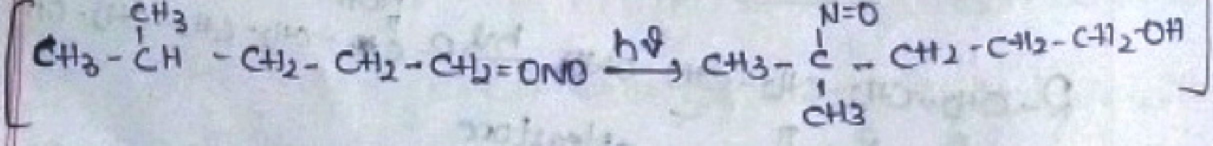
Step:3

* Nitrose radical attacks δ carbon radical and forms Nitrose derviative, which further undergoes keto-enol tautomerism to give substituted oxime



2) Ex:

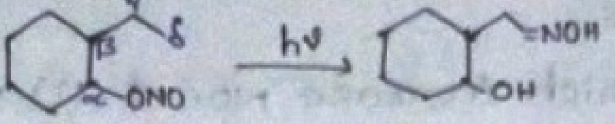




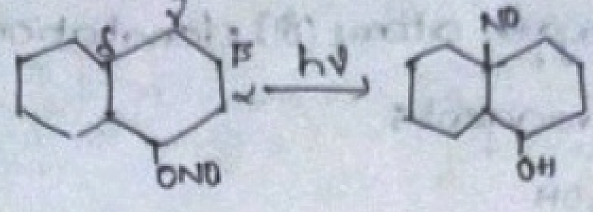
$$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-CH_2=ONO \xrightarrow{h\nu} CH_3-\underset{CH_3}{\overset{N=O}{C}}-CH_2-CH_2-CH_2-OH$$

* Since there is no δ hydrogen, no tautomerism takes place and hence the product is nitrose product in~~sadent~~stead of oxime.

1)

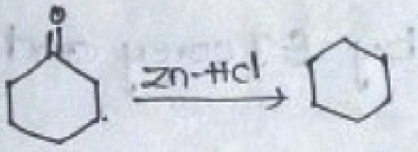


2)

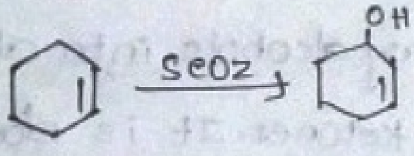


Synthetic reagents:-

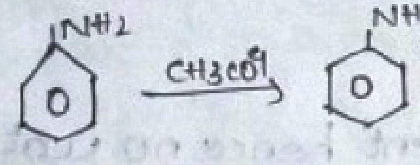
Any chemical Substance adds as functional group Elimination (or) functional group addition (or) functional group inter-conversion in organic reaction (or) organic synthesis is called reagent



- FG Elimination



- FG addition



- FG conversion

*These reagents are classified into two types:

Reagents

1) oxidizing

2) Reducing

1. OXIDIZING Reagent:

*Any reagent which increases number of oxygen atoms (or) decreases number of hydrogen atoms (or) withdraws Electrons is called oxidizing reagent.

Ex: $RCHO \xrightarrow{KMnO_4} RCOOH$ 2) $RCH_2OH \xrightarrow{PCC} RCHO$

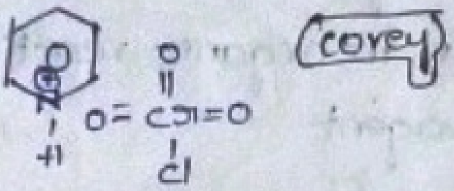
2) Reducing reagents:

* Any reagent which increace NO. of (H) atoms (or) decreases NO. of oxygen atoms (or) donatation Elect is called reducing reagents.

Ex: $RCHO \xrightarrow{NaBH_4} RCH_3OH$

$RCHO \xrightarrow{Zn \cdot HCl} RCH3$

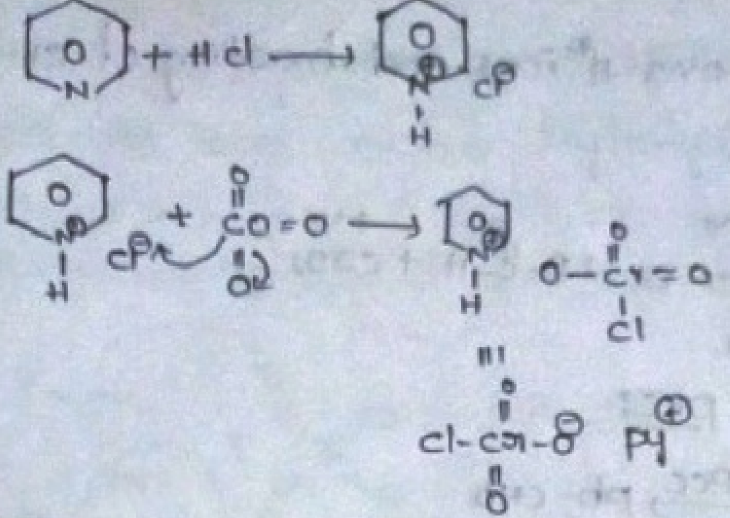
* PCC (pyridinium choloro chromate)



* It was synthesized by E J corey and very selective reagent.
* It is oxidises primary alcohols into aldehydes, secondary alcohols into ketones. It is doesn't oxidise tertiary alcohols.
* It is Anhydrus reagent hence no water is required.
* It is acetic group sensitive reagent it may be affect acetic group hence to avoid buffer solution like sodium acetate. is used.

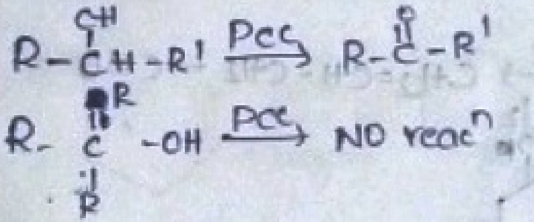
Preparation:

* It is prepared by mixing pyridine, Hcl followed by chromium trioxide.



Reactions:

$R-CH_2OH \xrightarrow{PCC} RCHO$



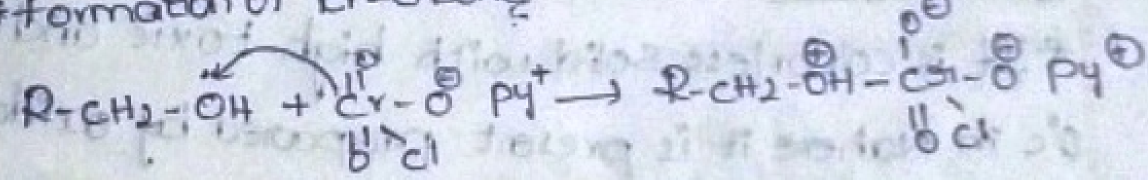
$R-\overset{OH}{C}H-R' \xrightarrow{PCC} R-\overset{O}{\overset{\|}{C}}-R'$

$R-\overset{R}{\underset{R}{C}}-OH \xrightarrow{PCC} \text{NO reac}^{n}$

Mechanism:

Step:1

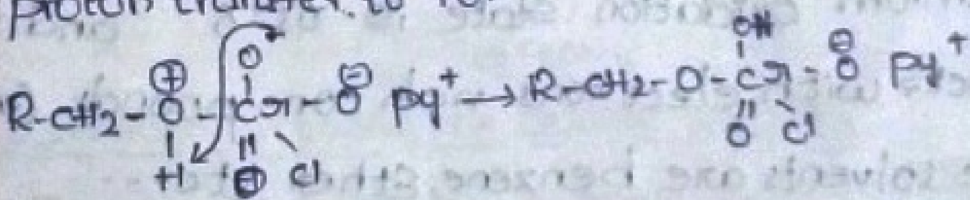
*Formation of Cr–O bond



$R-CH_2-\ddot{O}H + \overset{O}{\underset{O\ \ Cl}{Cr}}-\overset{\ominus}{O}\ Py^+ \longrightarrow R-CH_2-\overset{\oplus}{O}H-\overset{O^\ominus}{\underset{O\ \ Cl}{Cr}}-\overset{\ominus}{O}\ Py^\oplus$

Step:2

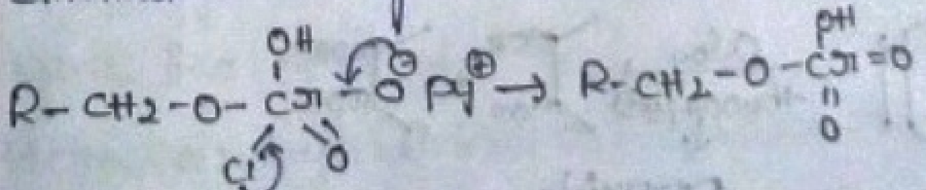
proton transfer to for



$R-CH_2-\overset{\oplus}{\underset{H}{O}}-\overset{O}{\underset{O^\ominus\ \ Cl}{Cr}}-\overset{\ominus}{O}\ py^+ \longrightarrow R-CH_2-O-\overset{OH}{\underset{O\ \ Cl}{Cr}}=\overset{\ominus}{O}\ Py^+$

Step:3

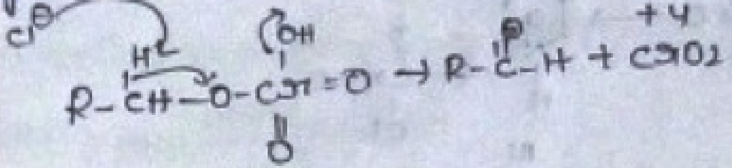
Elimination Cl⁻ gives Chromate Ester



$R-CH_2-O-\overset{OH}{\underset{Cl\ \ O}{Cr}}-\overset{\ominus}{O}\ Py^\oplus \longrightarrow R-CH_2-O-\overset{OH}{\underset{O}{Cr}}=O$

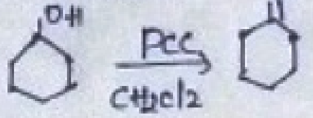
Step:-4

* Cr^{-} ions Removes $H^{\oplus}$ ions and breaking of cr-o bon
gives aldehyde.

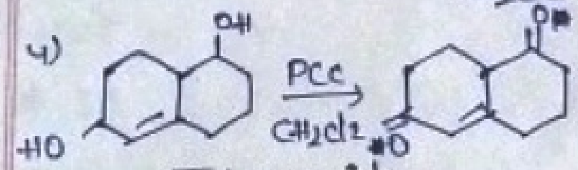


14 * **Examples for pcc:-**

1) $Ph\text{-}CH_2OH \xrightarrow[CH_2Cl_2]{PCC} Ph\text{-}CHO$
1°alcohol

2) 

3) $CH_2=CH-CH_2-CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_2=CH-CH_2-CHO$

4) 

Tetraoxide

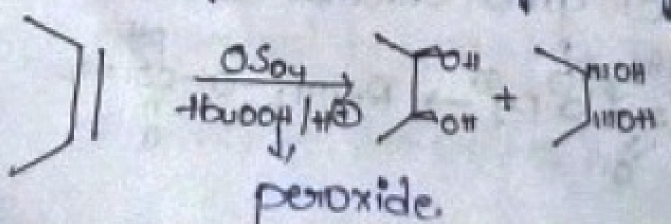
* **Osinium (OsO_4) (colourless solid compound):-**

* It is colourless solid with high toxic and (woltile
0°c in Nahere it is present prepared by oxidation
of osmium. $\left[Os^{-} + 2O \longrightarrow O^{-}sO_4 \right]$

* osamium oxidation state is Os^{+8} and here it reacts with electrons rich compounds (alkane)

* The solvents are benzene, Ether etc...

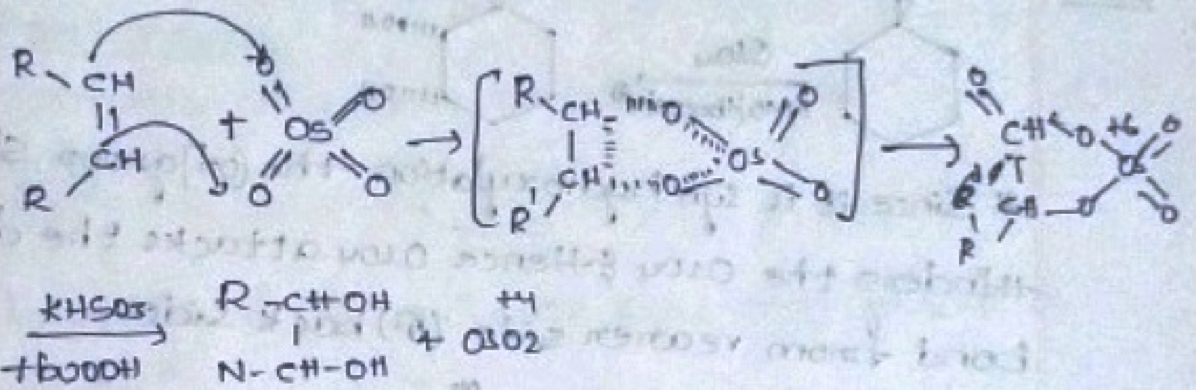
* It is mainly used for sym hydroxylation of alke

Ex:- 

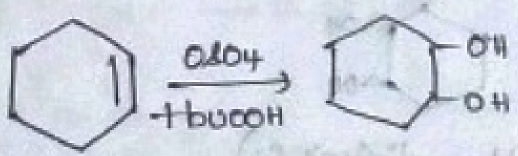
Mechanism:-

1) * It undergoes 3+2 cyclo addition mechanism to form osmate Ester which on hydrolysis by $KHSO_3$ (or) +buOOH Etc..

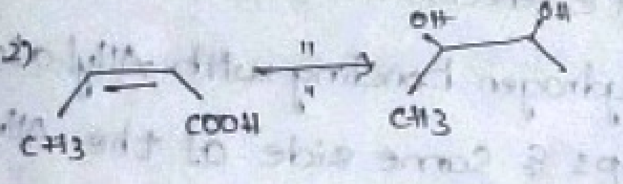
* Breaks Os-O bond which are weaker than C-O bonds



1)

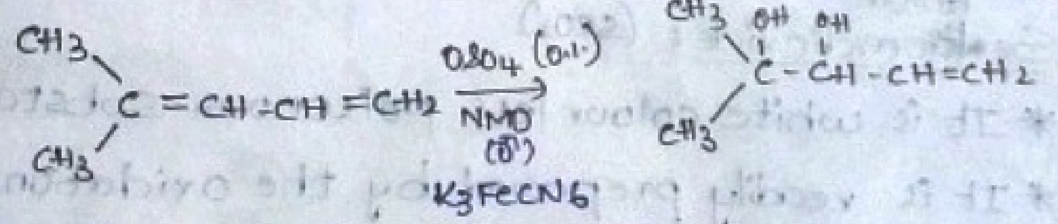


2)



2) [NMO-] - (N-methyl morphelene oxyene)

Ex:-1)

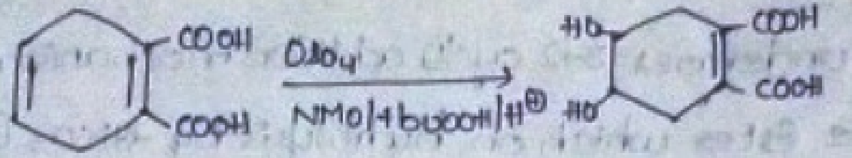


* Osmium attacks the double bond *.

* Due to high price & toxic nature osmium is used in as catalytic amounts in presence of other oxidising agents like [NMO], [K_3FeCN_6]

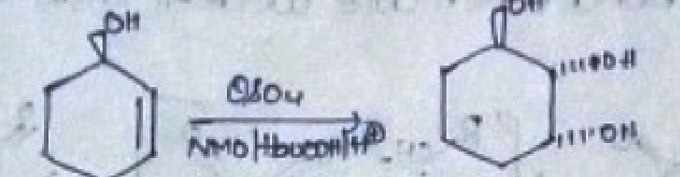
* OsO_4 always attacks high substituted double bonds.

Ex:2



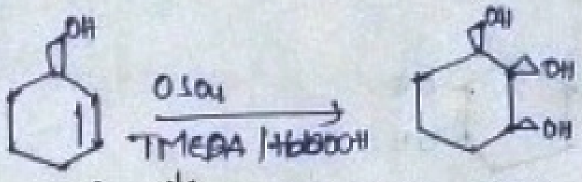
*OsO4 always attacks Electron rich double bond.

Ex:3



* Since it is syn hydroxylation the (OH) group Sterically hinders the OsO4 & Hence OsO4 attacks the double bond from rearer side (or) back side.

Ex:-4



(TetraMethyl EthenediAmine.)

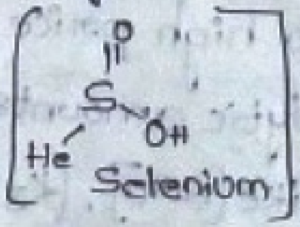
*TMEDA forms hydrogen bonding with Allyl alcohol and places two OH groups & same side of the Allylic(OH) group.

* Seleniumdioxide :- (SeO_2)

* It is white colour less poisonous substances.

* It is readily prepared by the oxidation of se. but the actual reactive reagent is H_2SeO_3 (Selenous acid)

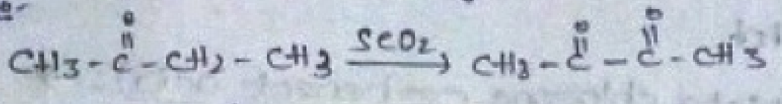
Eqs. $SeO_2 + H_2O \rightarrow H_2SeO_3$



* It converts Alpha methelene group adjacent to carbonyl group. into dicarbonyl compound.

* This is called Riley oxidation reaction.

Eg:-

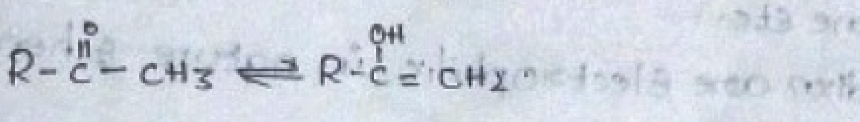


$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{SeO_2} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

* solvents for the reaction are benzene, CH_3COOH Etc....

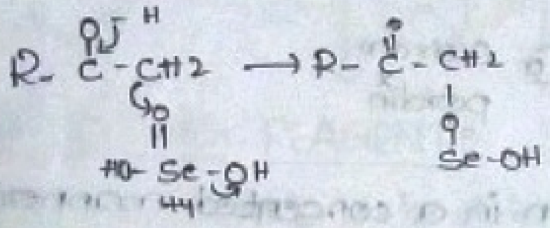
Mechanism:-

Step:-1 conversion of carbonyl carbon into enol

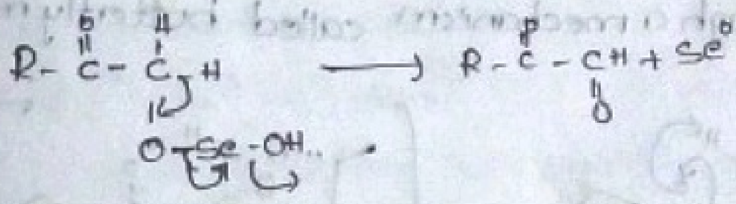


$R-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons R-\overset{OH}{\overset{|}{C}}=CH_2$

Step:2 formation of c-o bond with elimination of water



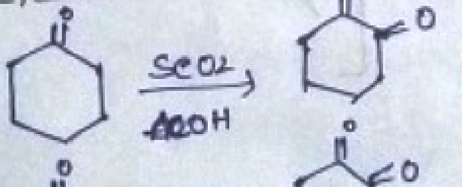
Step:3 cleavage of SeO bond gives product



$R-\overset{O}{\overset{\|}{C}}-CH\overset{\|}{O}+Se$

Examples:-

1)



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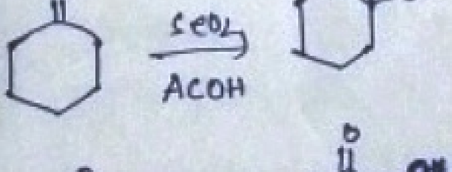
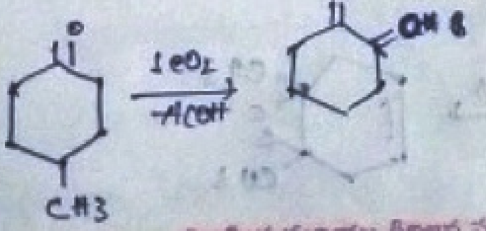
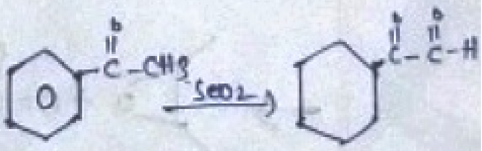


3)



4) $Ph-CH_2-Ph \xrightarrow[C_6H_6]{SeO_2}$

5)



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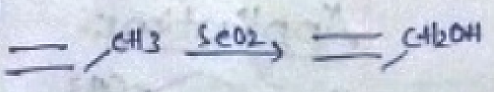


* It also converts allyl group ithe allylic carbon into allylic alcohol

* MCPBA (Meta chlorone perbenzoic acid):- *

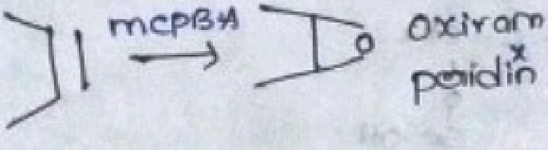
* It converts alkenes into Epoxides sides oxyranes

* It is reasonably reactive reagent. cheaper & stable. The solvents ~~per~~ for this reagent are Ether, benzene etc....

* peridixn are Electrophilic in nature & hence they attacks the

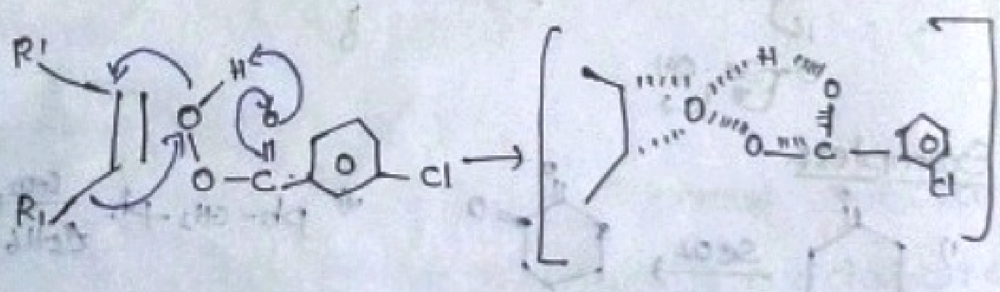
Ex:-

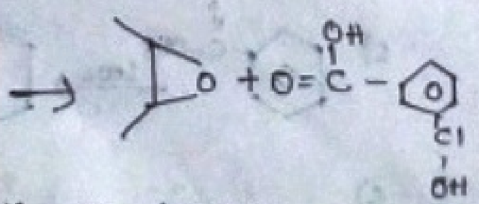
1)



1) It is sign addition in a concerted manner.

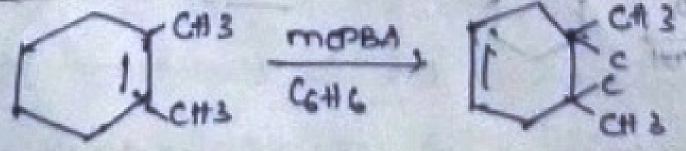
2) In which electrophilic oxygen is formation Epoxide with alkene through a mechanism called butterfly mechanism



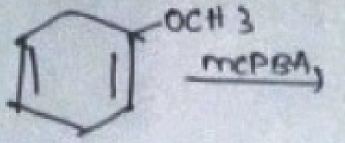


Applications:-

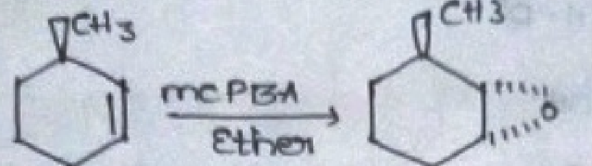
*

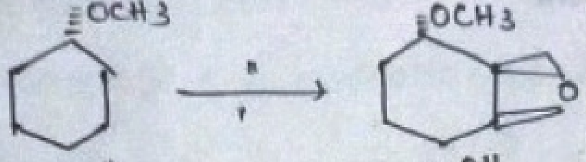


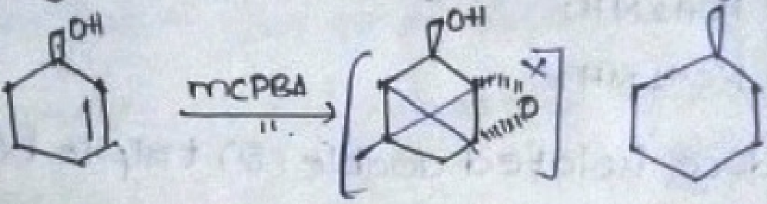
* MCPBA always attacks the highly substituted double bond.



Eg:-







* REDUCING REAGENT:-

Lithium aluminum hydride:-

* AlH_3 is Lewis acid with incomplete octate and electron deficient compound.

* $AlH_3^{\oplus} + H^{\ominus} \longrightarrow AlH_4^{\ominus}$

* In order stabilize its negative charge, Li^+ is added. ie: $LiAlH_4$ is formed. But it releases $H^{\ominus}$, very easily that it is $H^{\ominus}$ ions source and nucleophile and attacks any electrophilic centres.

Preparation:.

* It is prepared.

$LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$

* It is white colour solid compound and decomposes moisture in readily.

$LiAlH_4 + 2H_2O \longrightarrow LiOH + AlOH_3 + H_2 + Energy$

* It is very powerful reducing agent

1) $R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{LAH} RCH_2OH$

2) $R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{LAH} R-\overset{OH}{\overset{|}{C}}H-R'$

3) $R-\overset{O}{\overset{\|}{C}}-OR' \longrightarrow R-CH_2OH$

$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow RCH_2-OH$

$R-NO_2 \rightarrow RNH_2$

$R-CN \rightarrow RCH_2NH_2$

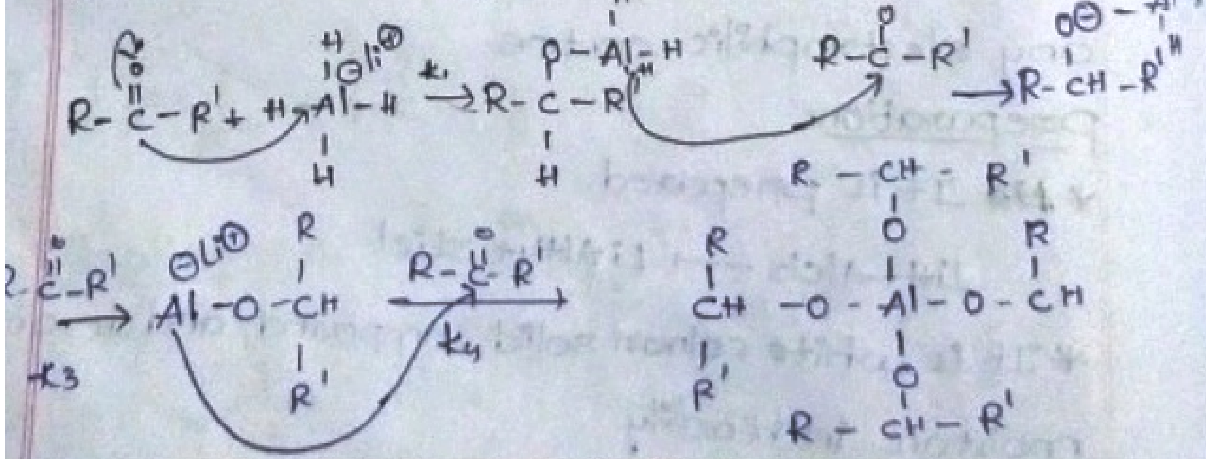
$RCONH_2 \longrightarrow RCH_2NH_2$

* It can't reduce isolated double (or) triple bond. But it can reduce conjugated double bonds like alpha, Beta unsaturated carbonyl compounds.

* At elivated temperatures.

Mechanism:

step:-1 Nucleophilic hydrate attacks carbonyl carbon compound and forms alkoxy aluminate which further reacts with three molecules of ketone successively & finaly form tetra alkoxy aluminate



$\xrightarrow{+H_3O^{\oplus}} R-\overset{OH}{\overset{|}{C}}H-R' + Al(OH_3) + LiOH$

Thus one equalent of LAH Reduces four equalents of ketones

*The Rate of reduction of Lithium-Alumnium is $k_1 > k_2 > k_3 > k_4$ This is due to $I^{\ominus}$ effect of alkoxy group of Alumnium decreases rate of release of hydride ion.

Application of Lithium Alumium hydrides.

1) $C_6H_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow[EtO]{LiAlH_4} C_6H_5-CH_2OH$

2) $ph-CH_2-Br \xrightarrow[(C_2H_5)_2O]{LiAlH_4} ph-CH_3$

3) $ph-CH=CH-CHO \xrightarrow[EtO\ 35^{\circ}C]{LiAlH_4} ph-CH_2-CH_2-CH_2OH$

4) $ph-CH=CH-CHO \xrightarrow[EtO]{LiAlH_4} ph-CH=CH-CH_2OH$

5) $C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[C_2H_2CH_3]{-18^{\circ}C \; LAH_4} C_6H_5-\overset{OH}{\overset{|}{C}}H-C_6H_5$

Sodium borohydride:-

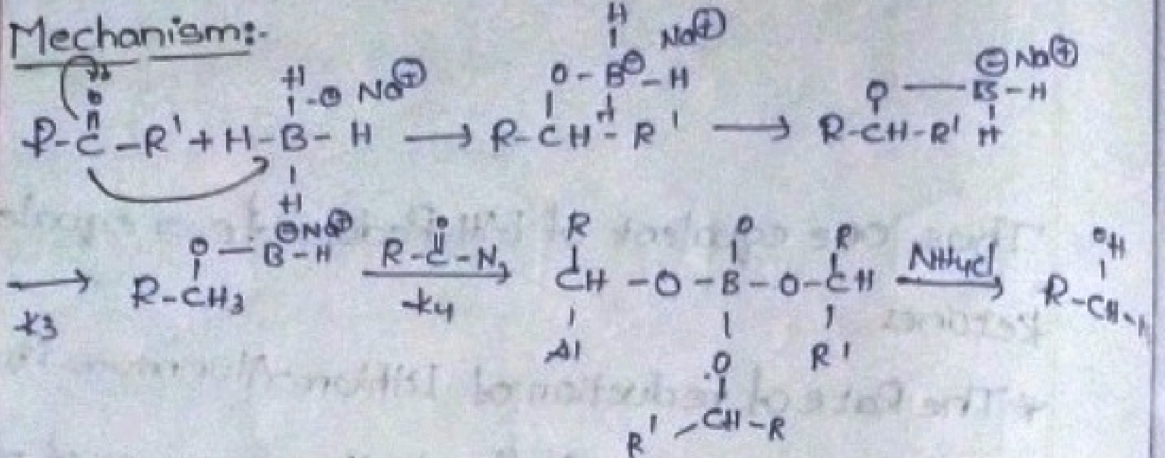
* It is less powerful than $LiAlH_4$ & more selective because boron is polar atom and it is more Electro negative than hence can't release $[H^-]$ readily

*It is white colour solid Stable at room temp and reacts under protoic & approtic solvents.

preparation:-

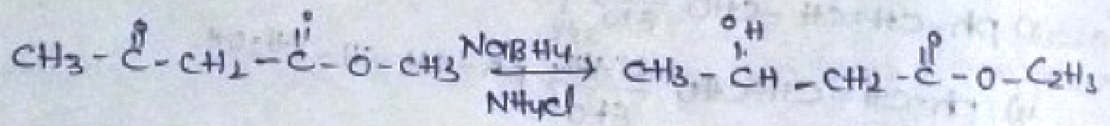
$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3CH_3ONa$

Mechanism:-



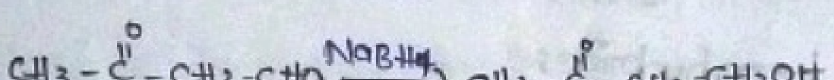
* Nucleophilic hydride attacks (or) ketone produces alkoxy borate which further reacts with three equi-lents of ketone and produces tetra alkoxy borate which on hydrolysis by NH_4Cl gives four equalents secondary alcohols

* Appilication of sodium boro hydride:-

1) 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-\ddot{O}-CH_3 \xrightarrow[NH_4Cl]{NaBH_4} CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_3$

2) $CH_3-CH=CH-CHO \xrightarrow[NH_4Cl]{NaBH_4} CH_3-CH=CH-CH_2OH$

3) 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CHO \xrightarrow[NH_4Cl]{NaBH_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH$

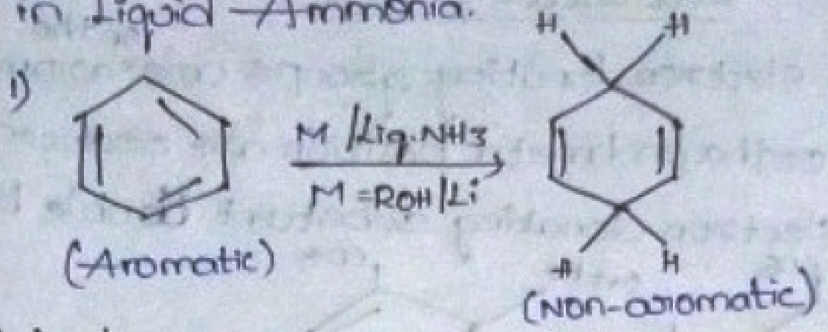
Birch reduction:-

→ It is one type of meta dissolving reducing agent

* In which aromatic hydro carbons undergoes partial reduction to form 1,4 unconjugated cyclo hexadiene in presence of sodium (or) Li metal

in Liquid Ammonia.

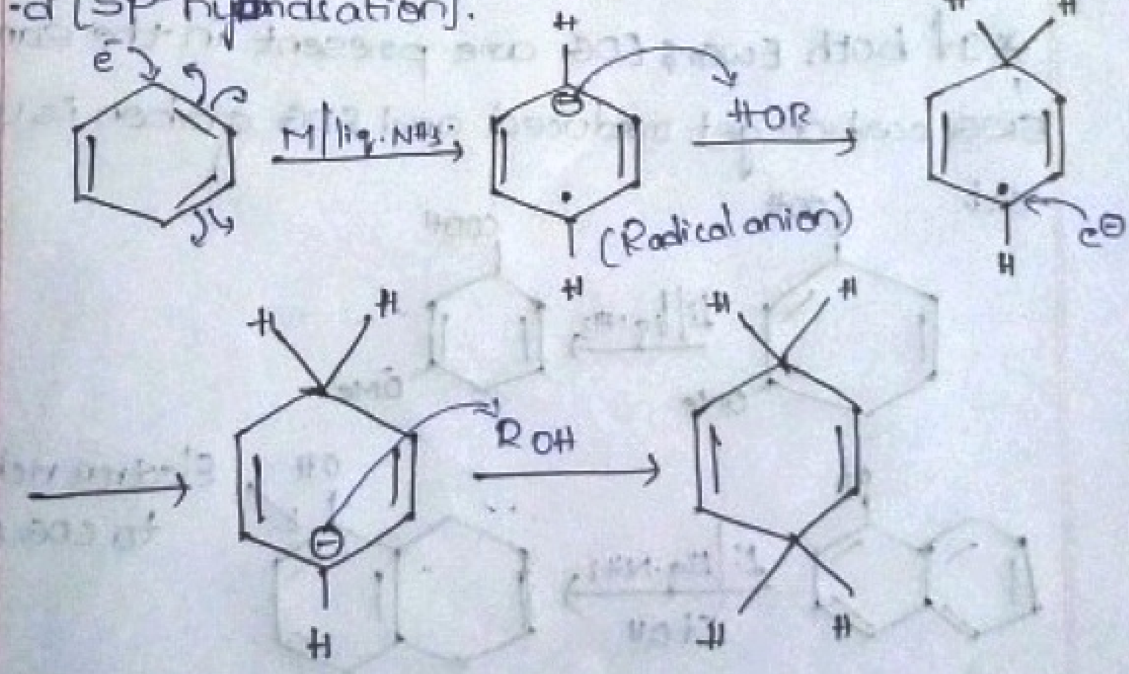
1)



Mechanism:-

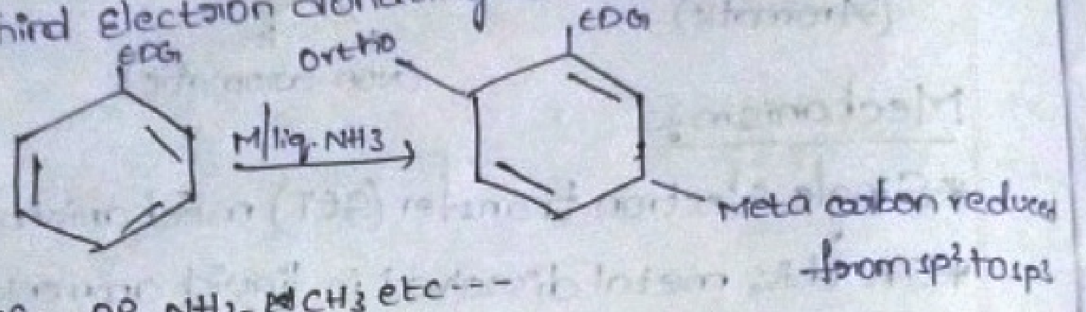
*Single Electron transfer (SET) mechanism.

*In this metal dissolved in liquid ammonia produces Solvated Electrons. one Electron from this attacks the aromatic compounds forms radical anion. This anion picks up protons to alcohols and get reduced. Another Electrons attacks the carbon electron and forms carbanion. Again this Abstracts proton from alcohol and get reduced. In this way 1,4 position are reduced [SP^3 hybridisation].



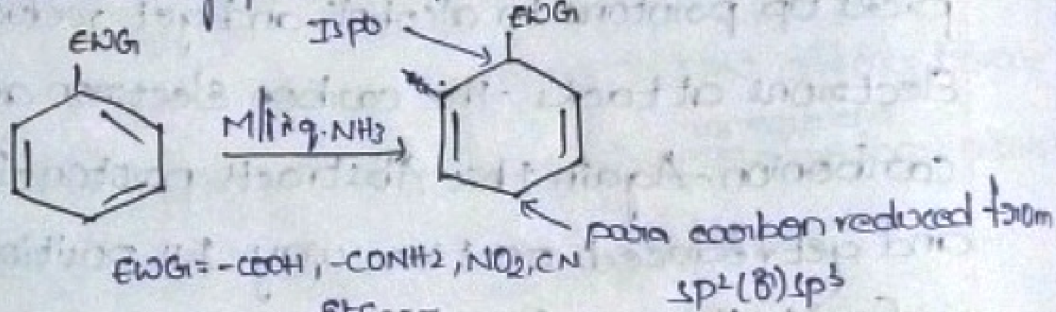
REGIOSELECTIVITY:-

* when electron donating groups are on the aromatic carbon ortho and meta position are reduced leavi behind electron donating substuent double bond.



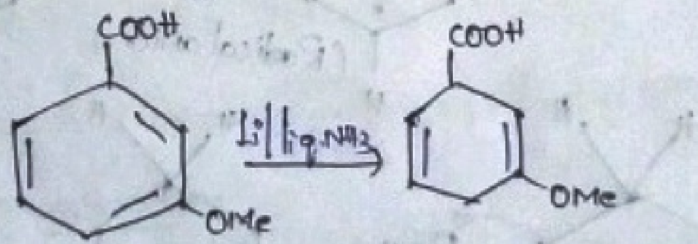
EDG = -OR, NH_2 - CH_3 etc ---

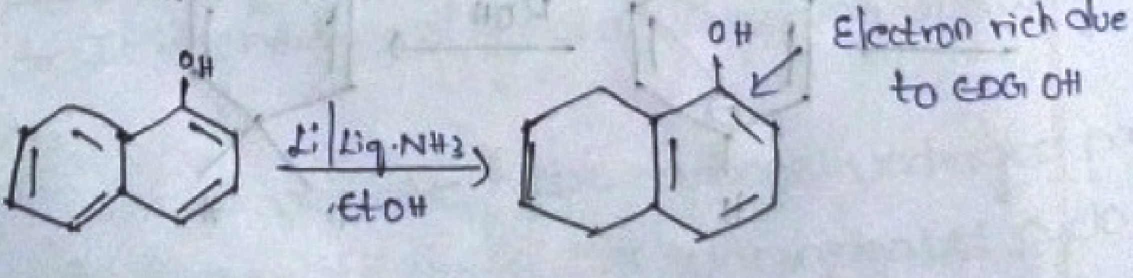
* If electron withdrawing groups presented on the aromatic ring ipso and para carbon atoms are reduced

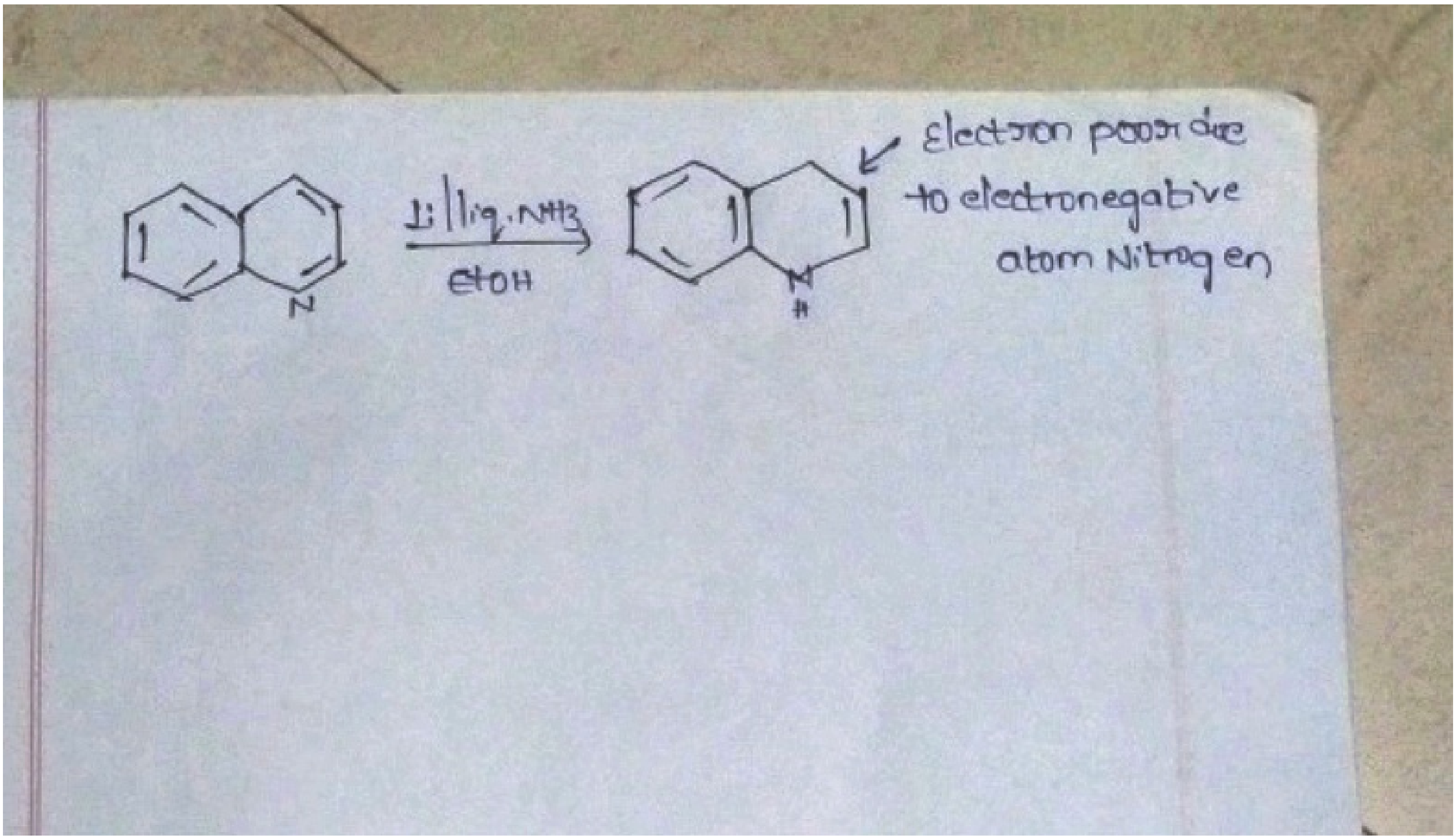


EWG = -COOH, -$CONH_2$, NO_2, CN etc ---

* If both EWG & EDG are present in the same ring EWG carbon get reduced and EDG carbon is unredu -ced.







Electron poor due to electronegative atom Nitrogen