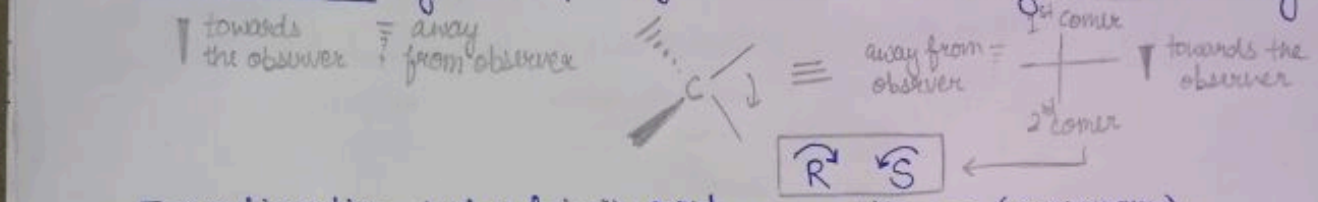
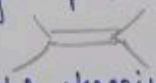
MODULE 4: ORGANIC

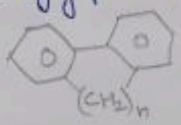
- **Optical isomers**: compound that rotates ppl
  - **Criteria for optical activity** - 1) at least one chiral center
    2) Non superimposable mirror image
    3) No POS, COS
  - **Enantiomers** - Chiral molecules that are mirror image of each other but non superimposable
  - **Diastereomers** - Non superimposable (differ in spatial arrangement), not mirror images
  - **Priority rules** - Directly attached to chiral center → Atomic no. ↑ Priority ↑
    If same, move to next, Double bond C=C implies C(C)(C)
  - **R-S Nomenclature** - get lowest priority on horizontal line through even exchanges



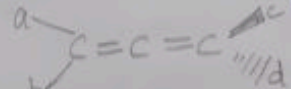
  - **E-Z configuration** - highest priority group → same side → Z (zussamann)
    opp side → E (Entgzin)



  - **Atropisomerism** - Isolable stereoisomers, arise from hindered rotation about single bond
    ex- (i) Biphenyls (with bulky grps on ortho)
    (ii) Bridged biphenyl

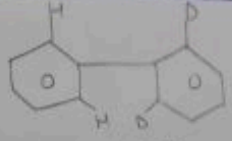


    (iii) Binaphthols.
  - **Optical isomerism in Allenes** - Non superimposable mirror image
    optically active when a ≠ b & c ≠ d

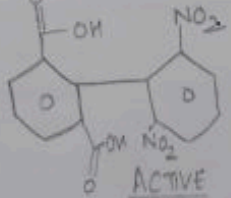


  - **Optical isomerism in Spiranes** - 2 rings fused with 1C atom
    active when a ≠ b and c ≠ d

  - **Optical isomerism in biphenyls** - arises due to restricted rotation of phenyls due to hindrance



free rotation of phenyls allowed coz H & D are very small.



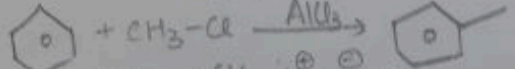
No free rotat" coz of -COOH, & $-NO_2$ being large & bulky

- **Carbocation**: Intermediate, 6 e^- in octet

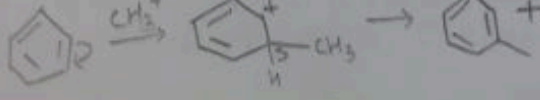
$$\text{hybridization}, H = \frac{1}{2}[V + M - C + A]$$

V: valence e^- in central atom; M: Monovalent atom

- **Formation**:
  - * **Alkylation** -

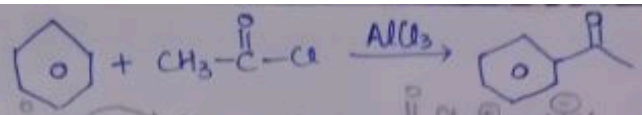


Mech: $CH_3-Cl + AlCl_3 \rightarrow CH_3-Cl^{\oplus}-AlCl_3^{\ominus}$

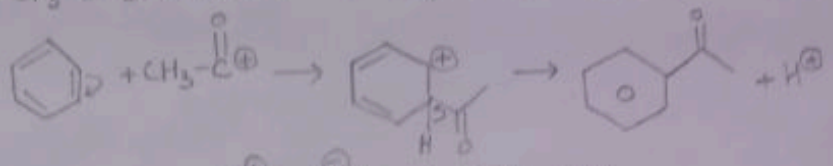


$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

* Acylation-



Mech: $CH_3-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}{}^{\oplus}\cdots Cl^{\ominus}-AlCl_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}{}^{\oplus} + AlCl_4^{\ominus}$

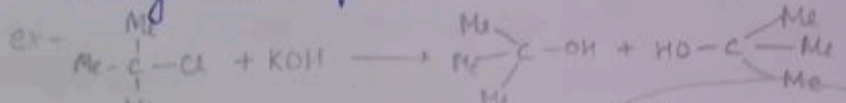


$H^{\oplus} + AlCl_4^{\ominus} \longrightarrow AlCl_3 + HCl$

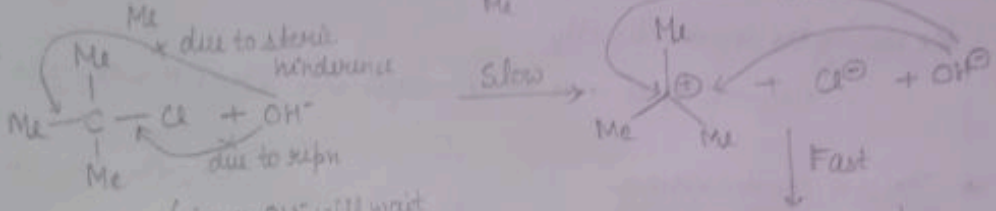
* SN^1 Rxn - (α stab of $C^{\oplus}$) Unimolecular $Nu^{\ominus}$ subs^n

3° alkyl halide + aq KOH $\longrightarrow$ subs^n

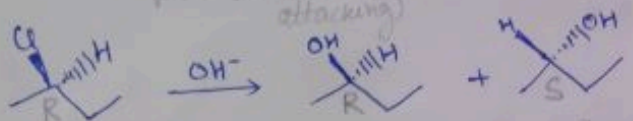
ex-



Mech:



ex-



[* Retension & inversion both taken place]

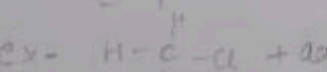
* SN^2 Rxn - (α — steric hindrance) Bimolecular $Nu^{\ominus}$ subs^n

1° alkyl halide + $Nu^{\ominus}$ in polar aprotic solvent $\longrightarrow$ subs^n

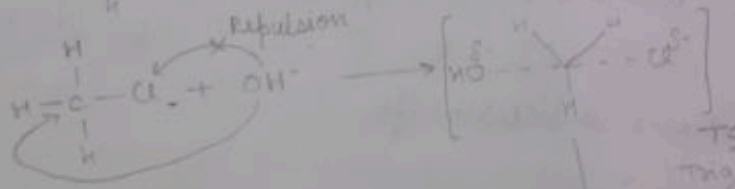
NaI/Acetone
aq KOH
NaOH, DMF

[* proceeds with inversion of configuration (R→S, S→R)]

ex-

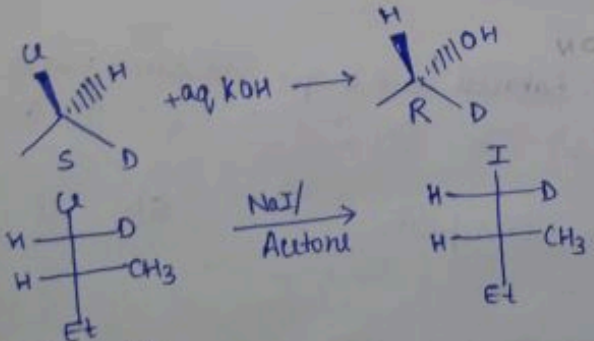


Mech:



SN^2 Rxn doesn't give intermediate
It's a single stepped rxn
hence doesn't belong to the reacting form of α

ex-



- Carbanion: 8e⁻ in octet
  - Formation:
    * Aldol condensation- aldehyde/ketone + aldehyde/ketone $\xrightarrow[\text{base}]{\text{strong}}$ β hydroxy aldehyde (Aldol)

[aldehyde + alcohol]

one of these must contain α-H

alc KOH, dil NaOH

ex- $2CH_3CHO \xrightleftharpoons{OH^-} CH_3CH(OH)CH_2CHO$

Mech: $CH_3CHO + OH^- \rightleftharpoons CH_2^-CHO + H_2O$

$CH_3-\underset{H}{\overset{O}{\overset{\|}{C}}}-H + CH_2^-CHO \rightleftharpoons CH_3-\underset{H}{\overset{O^-}{C}}-CH_2CHO \xrightleftharpoons{H_2O} CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO$

When base is in excess, multiple aldol take place

$CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO \xrightarrow[\text{(ii) } CH_3CHO]{\text{(i) } OH^-} \text{(twice)}$ $CH_3-\underset{OH}{CH}-\underset{CH-CH_3}{\overset{OH}{\underset{|}{C}}}-CHO$ +

Rxn may still occuyon if aldehyde of base available, without αH, Cannizzaro mechanism will be followed

[for writing the answer directly,

$CH_3-\underset{H}{\overset{O}{\overset{\|}{C}}}-H + H_2-CH-CHO \longrightarrow CH_3-CH=CH-CH$

$\downarrow -H_2O$

$CH_3-\underset{OH}{CH}-CH_2-CHO$] TRICK

* Claisen condensation -

(self condensation occurs) Esters having αH $\xrightarrow[\text{alc KOH, } C_2H_5ONa]{\text{strong base}}$ β-keto esters

ex- $2\,CH_3-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{\text{alc KOH}}$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt$

Mech:

$CH_3-\overset{O}{\overset{\|}{C}}-OEt + KOH \longrightarrow \bar{C}H_2-\overset{O}{\overset{\|}{C}}-OEt + H_2O$

$CH_3-\overset{O}{\overset{\|}{C}}-OH + \bar{C}H_2-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow CH_3-\underset{OEt}{\overset{O^-}{\underset{|}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt$

- Carbene: six(6) e^- in octet, with 2 radical on C

- Singlet Carbene - Radical e^-s are in opp. spin, spin multiplicity is one

$:CH_2\downarrow\uparrow$ - $1s^2 2s^2 2p^2$ GS ↑↓ | | | ES ↑↓ | ↑ | ↑

$[sp^2]$

V shape

* Singlet carbene is stereospecific.

ie while addn of carbene into alkene, cis forms cis product, trans trans

ex- Cis $\xrightarrow{CH_2\downarrow\uparrow}$ cis

trans $\xrightarrow{CH_2\downarrow\uparrow}$ trans

- Triplet carbene - Both e^- in parallel spin & spin multiplicity is 3

$\cdot\dot{C}H_2\downarrow\downarrow$ - $1s^2 2s^2 2p^2$ GS ↑↓ | | | ES ↑ | ↑ | ↑

$[sp]$

* Triplet Carbene non stereospecific

ie while addn both cis trans product observed.

ex Cis $\xrightarrow{CH_2\downarrow\uparrow}$ cis + trans

- Formation of carbenes -

1- from chloroform and base(NaOH)

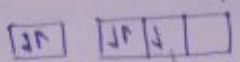
$OH^- + H-C(Cl)(Cl)(Cl) \longrightarrow H_2O + \bar{C}(Cl)(Cl)(Cl) \xrightarrow{Na^+} :C(Cl)(Cl) + NaOH$

2- from strong heating or Irradiating with light. Diazomethane

$CH_2=N_2 \xrightarrow{h\nu} \dot{C}H_2 + N_2\uparrow$

- Nitrene: 6e⁻s in octet

- Singlet Nitrene - $R-\ddot{N}: \quad 1s^2 2s^2 2p^3$



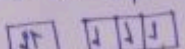
$[sp^2]$

Linear

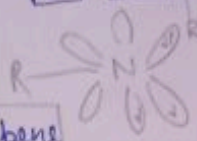
s, total spin quantum = 0

spin multiplicity = 1 $(2s+1)$

- Triplet Nitrene - $R-\dot{N}-\dot{N}\cdot \quad 1s^2 2s^2 2p^3$



$[sp]$



Linear

s, total spin quantum = 1

spin multiplicity = 3

* Triplet is more stable than Singlet for both carbene and nitrene

exception arises in case of back bonding (in nitrenes)

ex- $CH_3-\ddot{O}-\ddot{N}\uparrow\uparrow$ (singlet) $>$ $CH_3-\ddot{O}-\ddot{N}\uparrow\downarrow$ (triplet) (stab.)

- Formation of Nitrenes:

1- from Acyl Azide

$RCON_3 + RCON_3 \longrightarrow R-\underset{\underset{O}{\|}}{C}-N + N_2\uparrow$

(Nitrene) (triplet) (No back bonding)

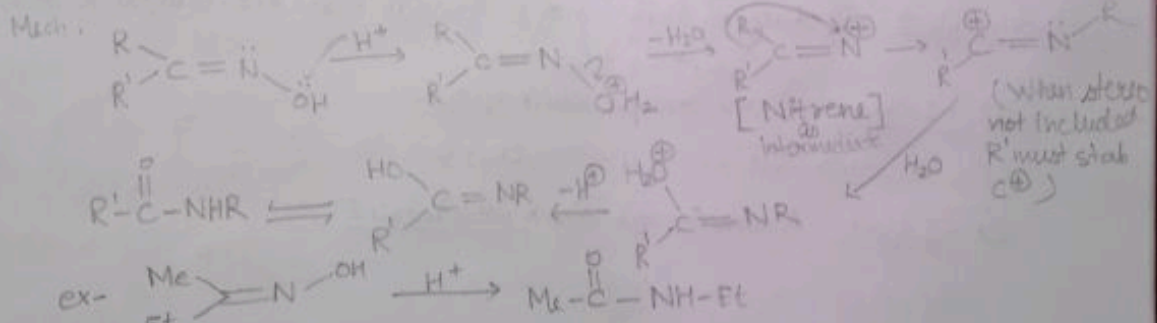
2- Beckmann Rearrangement:

Acid catalysed conversion of ketoximes to N substituted amides

$RR'C=NOH \xrightarrow{H^+} RCONHR'$ or $R'CONHR$

* rxn is stereospecific, migrating grp is always trans to -OH grp.

Mech:



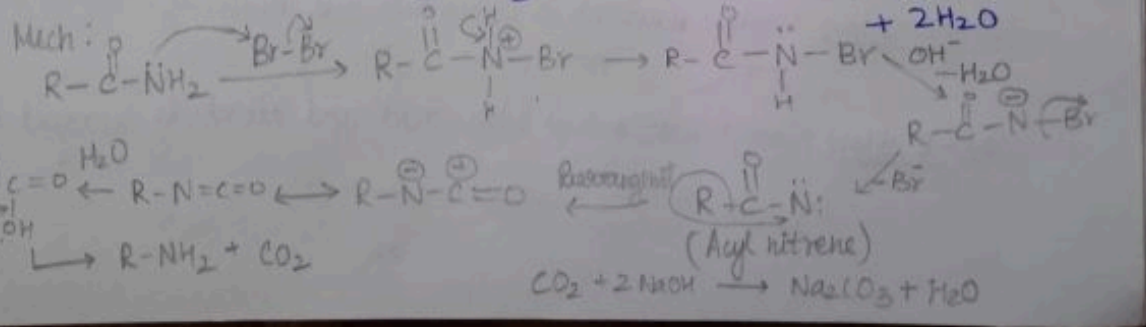
ex- $Me-C(=N-OH)-Et \xrightarrow{H^+} Me-C(=O)-NH-Et$

3- Hofmann Rearrangement or Hofmann bromamide Rxn:

Conversion of amide into a primary amine with one Carbon less by action of Br_2 or Cl_2 / NaOH.

$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + N_2CO_3 + 2H_2O$

Mech:



$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

4- Curtius rearrangement:

Decomposition of acyl azide in an inert solvent by gentle heat to isocyanate.

$RCON_3 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-\ddot{N}: \longrightarrow R-N=C=O$ (intermediate: nitrene)

$\downarrow H_2O$

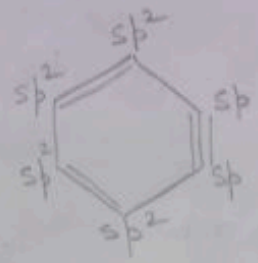
$R-NH_2 + CO_2$

Mech:

$R-\overset{O}{\overset{\|}{C}}-\ddot{N}=\overset{\oplus}{N}=\overset{\ominus}{N}: \leftrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \xrightarrow{-N_2} R-\overset{O}{\overset{\|}{C}}-\ddot{N}: \rightarrow R-\ddot{N}=C=O$

$RNH_2 + CO_2 \leftarrow$

- Benzynes:



Schmidt rearrangement:

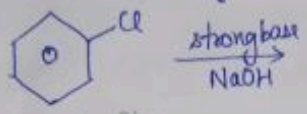
$RCOOH + N_3H \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$

$R_2CO + N_3H \xrightarrow{H_2SO_4} RCONHR + N_2$

$RCHO + N_3H \xrightarrow{H_2SO_4} RCN$ (Major) $+ RNHCHO$ (minor)

- Formation -

1- from haloarenes / Aryl halides (Dow process)



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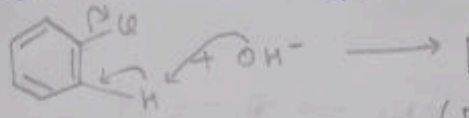
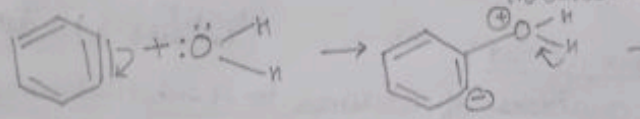
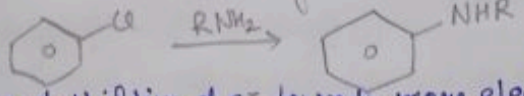


(Benzyne intermediate)



Similar mechanism when strong base is RNH_2



- Inductive effect: Tendency of shifting of e^- towards more electronegative atom

$C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow X$

1) +I effect: Atoms/Groups which release e^-

$CH_2^- > NH^- > O^- > CH_3-\overset{CH_3}{\overset{|}{C}}- > CH_3-\overset{CH_3}{\overset{|}{C}}H > -CH_3$

2) -I effect: Atoms/Groups which withdraw e^-

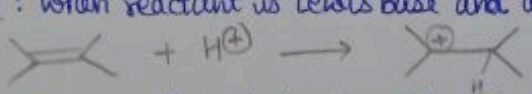
$-\overset{R}{\overset{|}{\overset{\oplus}{N}}}-R > -NO_2 > -CN > -CHO > -\overset{O}{\overset{\|}{C}}- > -COOH > F > -Cl > -Br > -I$

$> -OR > -OH > -NH_2 > -C_6H_5 > -CH=CH_2$

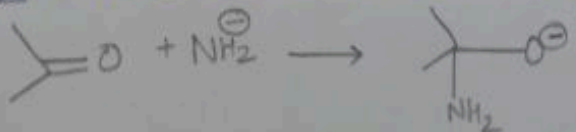
- Electromeric effect - phenomenon of movement of e^- from one atom to another at the demand of attacking reagent

* arises when attacking species ionises the neutral species in rxn mechanism

1) +E effect: when reactant is Lewis base and attacking reagent is Lewis acid.



2) -E effect: when reactant is Lewis acid and attacking reagent is Lewis base.



- Mesomeric effect : defined as the polarity produced in the molecule by interaction of two π bonds or b/w π bond and lone pair of e⁻ present on an adjacent atom

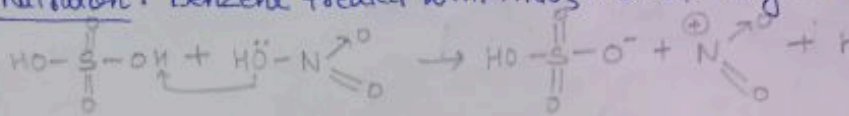
1) +M effect - When group or atom donate the e⁻ pair to the conjugate π system

2) -M effect - When group or atom attracts the lone pair of e⁻ from system.

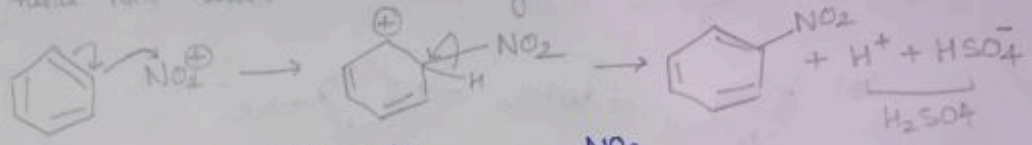
- Aromatic electrophile subs^{n} Rxn :

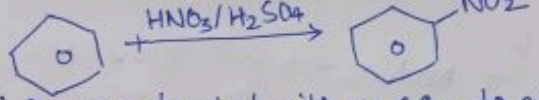
Replacement of hydrogen atom by E^+ is electrophilic subs^{n}:

1- Nitration : Benzene treated with HNO_3/H_2SO_4 to give nitrobenzene.

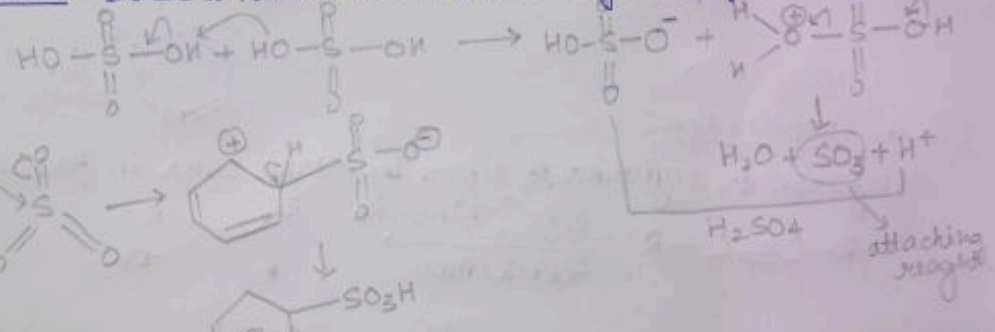


hence $NO_2^{\oplus}$ attacks benzene ring





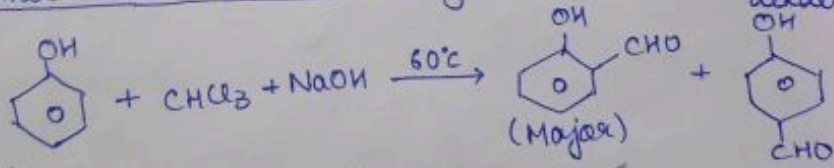
2- Sulphonation : Benzene treated with H_2SO_4 to give sulfonic acid



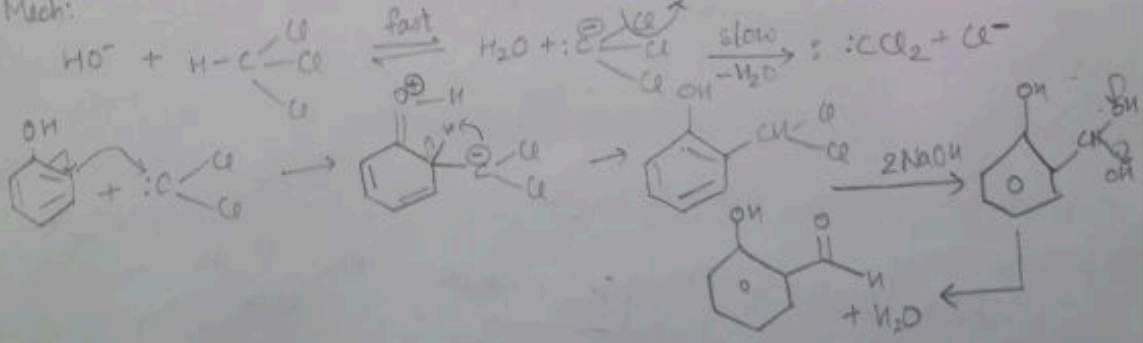
3- Friedel Craft Rxn : Benzene treated with alkyl halide ~~or acyl halide~~ in presence of $AlCl_3$ to give alkyl benzene.

exception  $\xrightarrow[AlCl_3]{R\text{-}Cl}$ No rxn Phenol $\xrightarrow[AlCl_3]{R\text{-}Cl}$ No rxn [rearrangement ✓]

4- Reimer-Tiemann reaction : Formylation of phenols with chloroform in alkaline solution



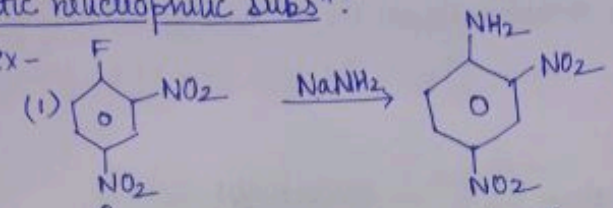
Mech:

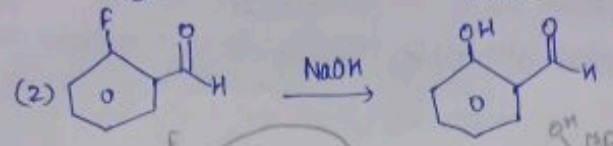


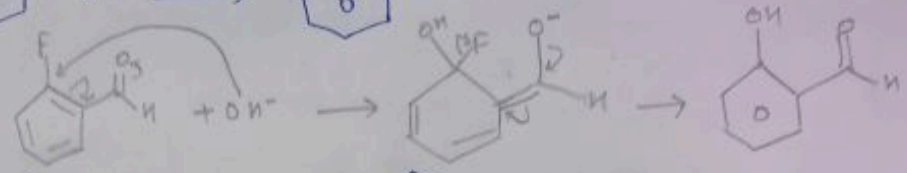
- Nucleophilic subs^n : 1- S_N1
  2- S_N2] explained earlier

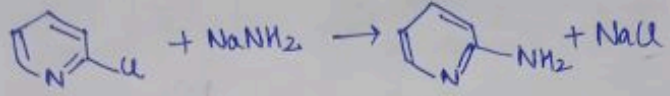
- Aromatic nucleophilic subs^n :

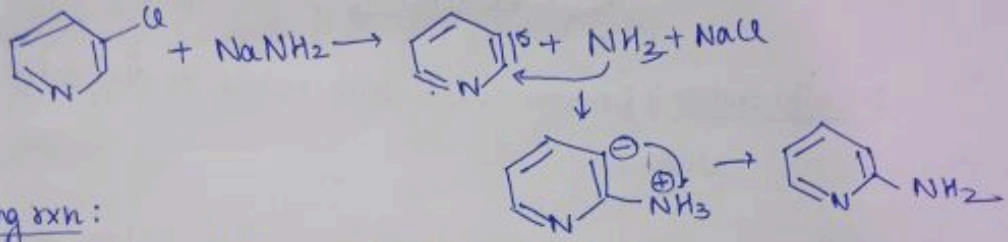
ex-

(1) 

(2) 

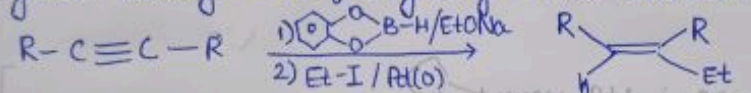
mech: 

(3) 

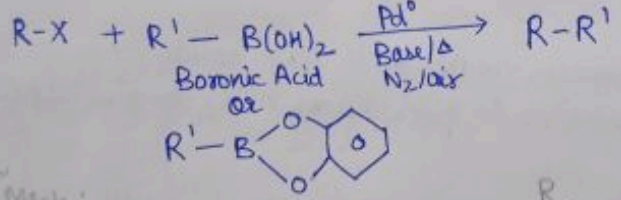
(4) 

- Suzuki Coupling rxn :

Alkylation or arylation of alkyne by boronic ester in presence of Pd(0) and base



means Pd is in OS = 0



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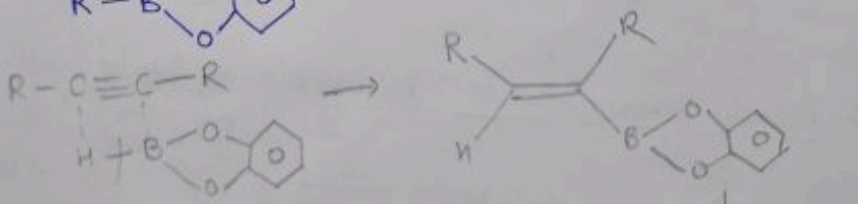
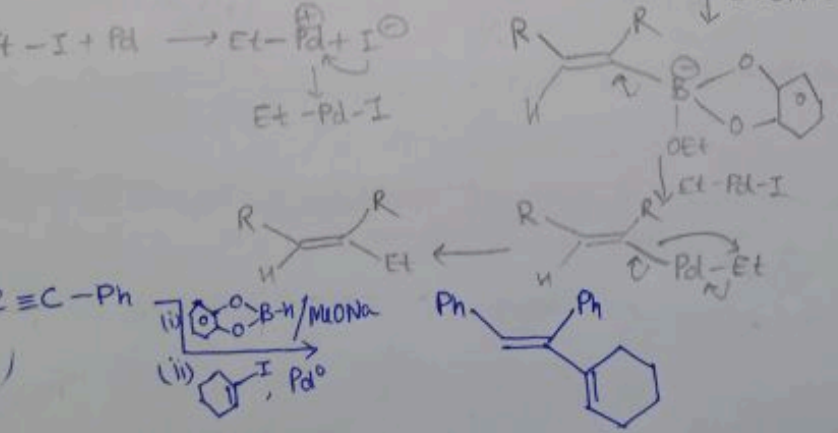
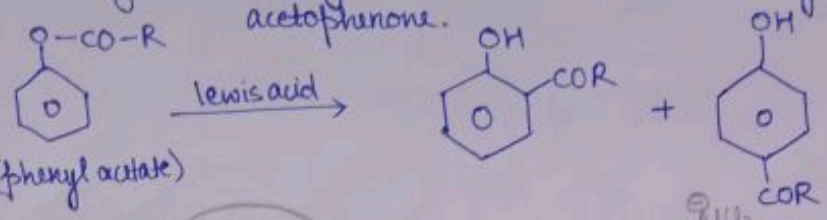


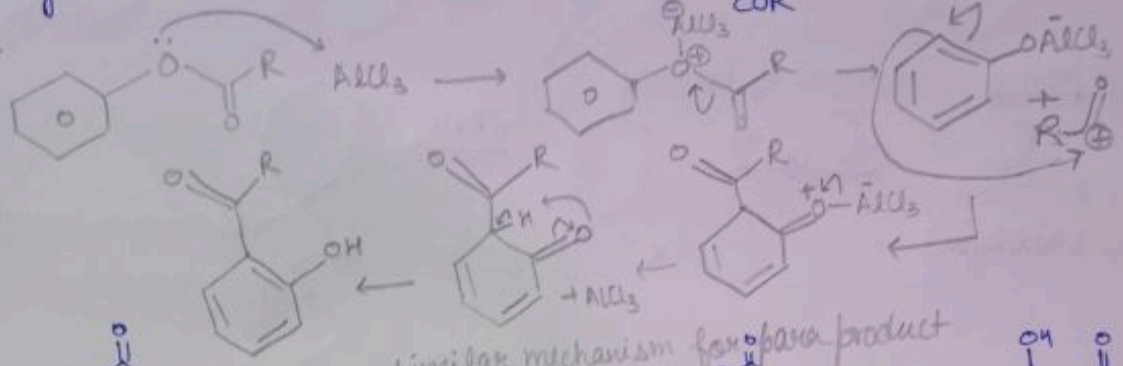


ex- Ph-C≡C-Ph

- **Fries Rearrangement**: Phenyl acetate treated with $AlCl_3$ to give ortho & para hydroxy acetophenone.

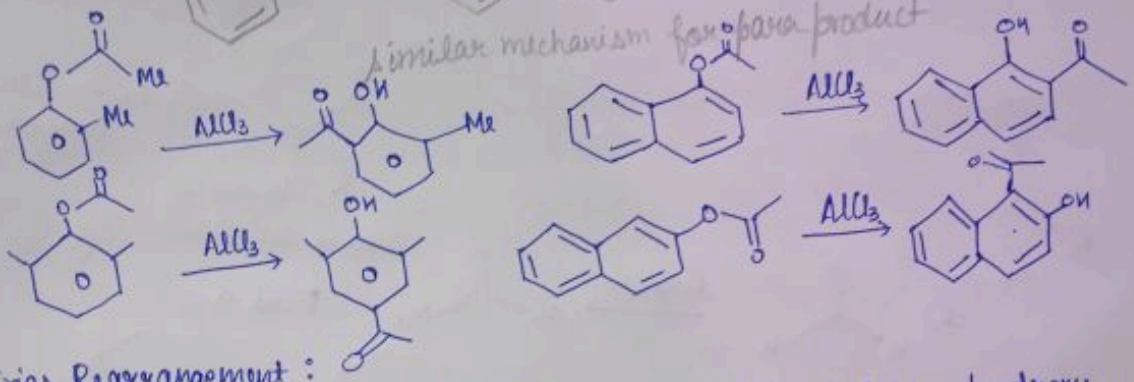


Mech:

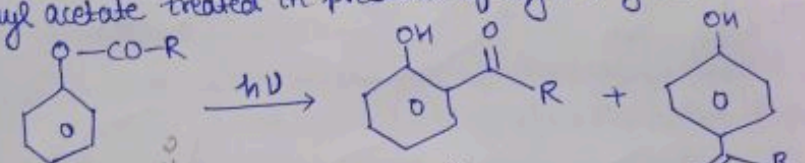


similar mechanism for para product

ex-



- **Photo Fries Rearrangement**:
Phenyl acetate treated in presence of light, gives ortho and para hydroxy acetophenon



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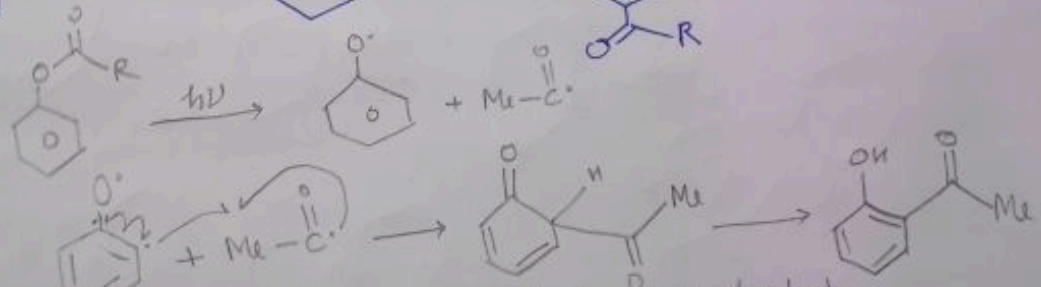
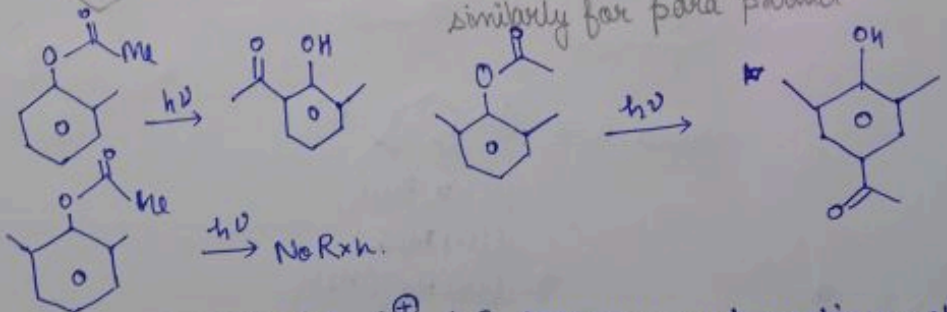


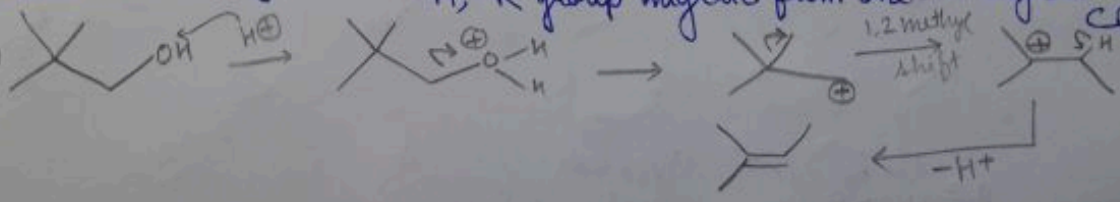
similarly for para product

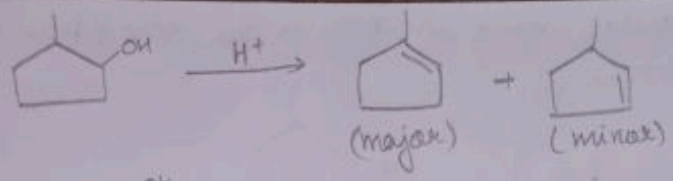
ex-

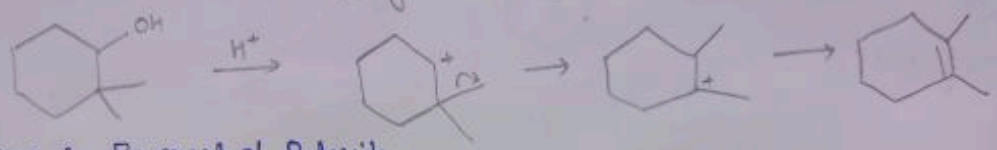


- **Wagner Meerwein rearrangement**: $C^{\oplus}$ 1,2 rearrangement reactions where -H, -R group migrate from one C to neighbouring C

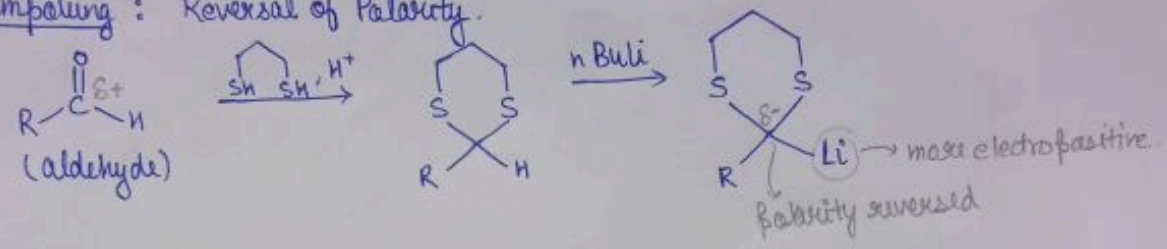
ex - 1)



2) 

3) 

- Umpolung : Reversal of Polarity.

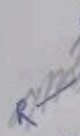


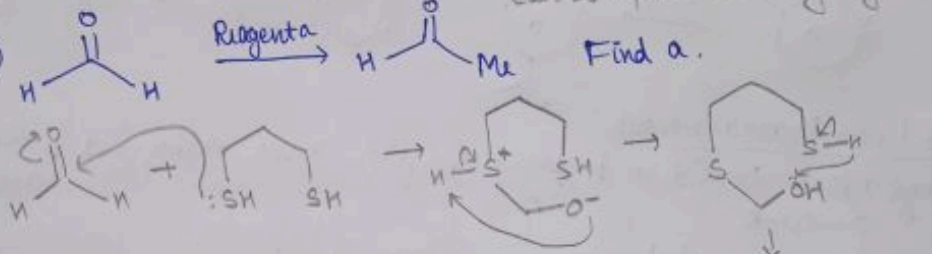
now  will be the attacking reagent.

Dithiane

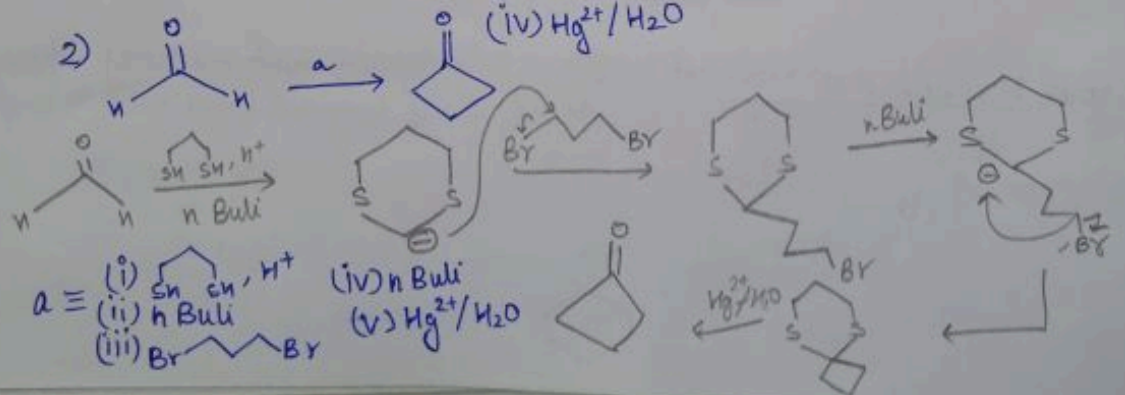
Can be deprotonated by Hg^{2+}/H_2O

~~Similarly.~~

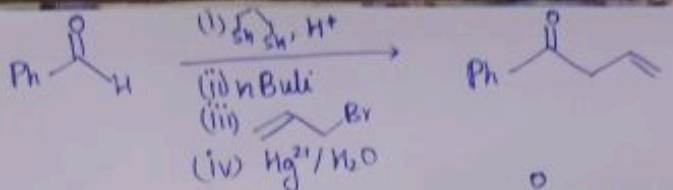


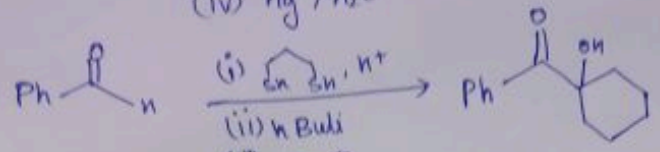
ex → 1) 

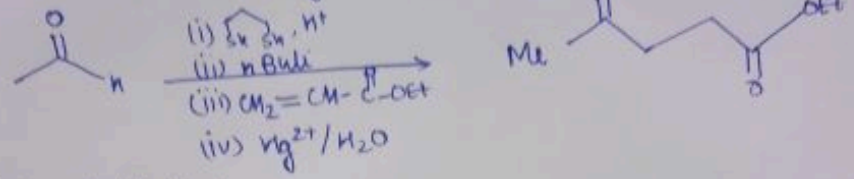
hence a ≡ (i) SH SH, H+
(ii) n Buli
(iii) MeI
(iv) Hg^{2+}/H_2O

2) 

a ≡ (i) SH SH, H+
(ii) n Buli
(iii) Br Br
(iv) n Buli
(v) Hg^{2+}/H_2O

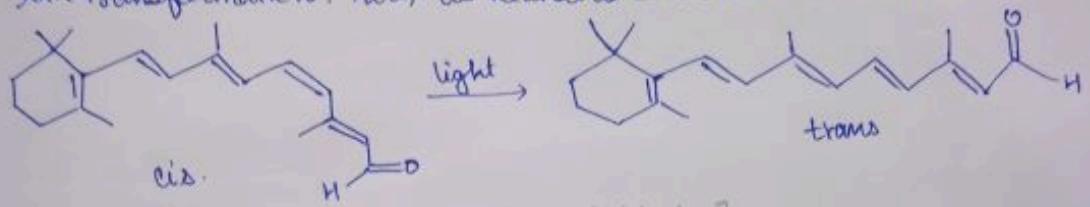
(3) 

(4) 

(5) 

- Chemistry of Vision :

As light strikes the eye, brain recieves a signal that something is there. The vision is possible because brain carries out direct and uncomplicated, purely chemical ~~sun~~ transformation. here, cis Ritinal is converted to trans retinal.



- Circular Dichroism: [stereochemistry ka topic hai]

Circular dichroism is an adsorption spectroscopy, that uses circularly polarised light to investigate structural aspects of optically active chiral media. It is mostly used to study biological molecules, their structure and interactions with metals and other molecules.