

SBG STUDY

Reduction!

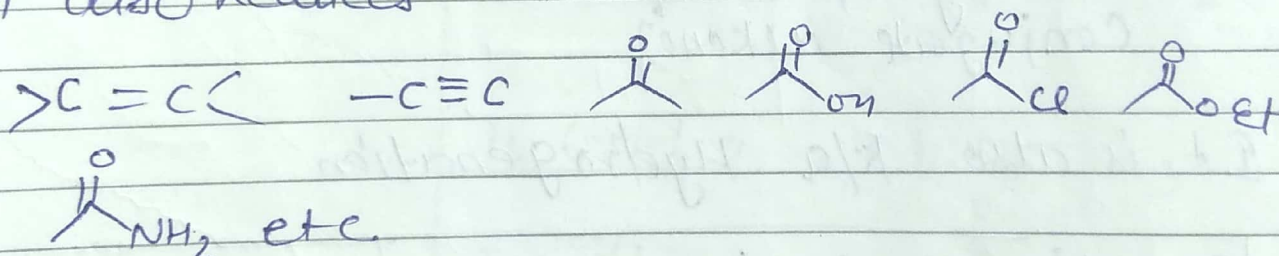
* Reduction!

- Addition Hydrogen
- Removal of oxygen
- (+)ve charge ↓ (±)
- (-)ve " ↑ (±)

* Reduction by H_2 / cat! (Ni or Pt or Pd)

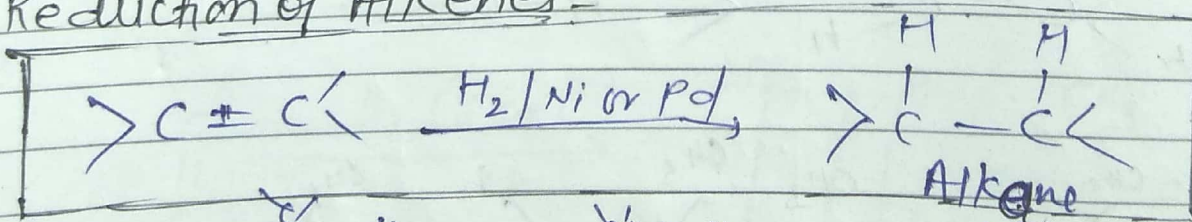
It reduces all those group which have π Bonds

It also reduces R-X.

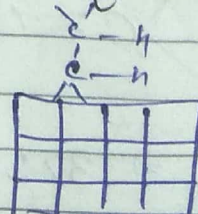
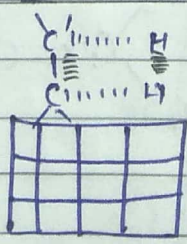
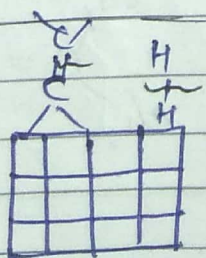


* Reduction of Alkene and Alkynes!

* Reduction of Alkenes!



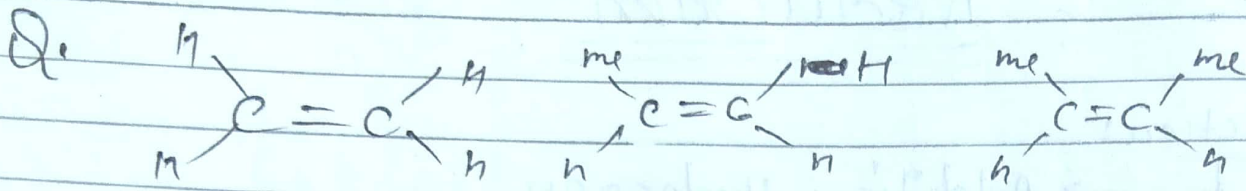
Mech ^{m!}



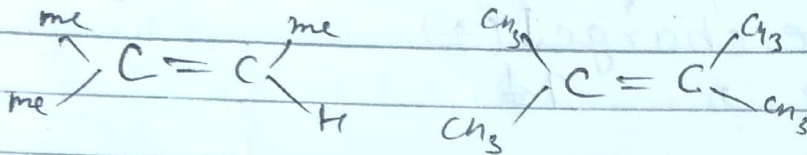
4m cts ✓

orb-electrophilic

Its adsorption phenomenon



R.O of above alkenes



1 > 2 > 3 > 4 > 5

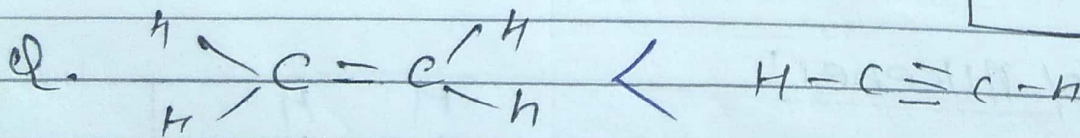
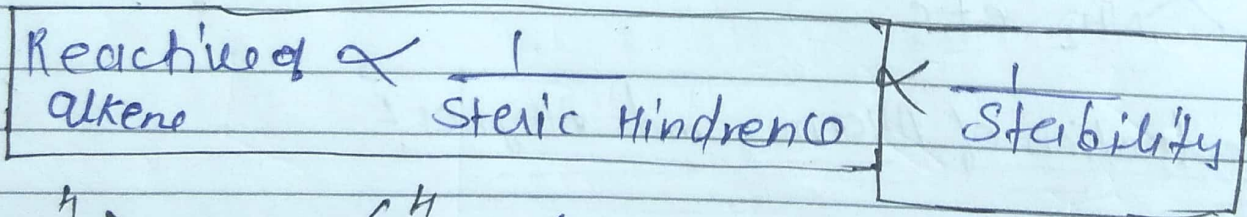
* Its syn addition process (SAP)

Cis-alkene → Erthro
Trans-alkene → Threo

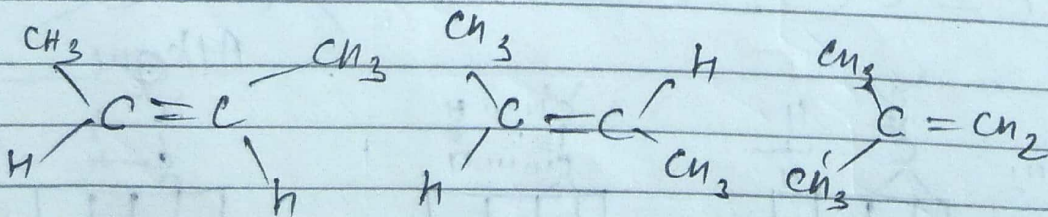
* It occurs by formⁿ of π -m.c.t.s (for non conjugate alkenes)

* It is also k/a Hydrogenation

*



Ques!



SO ⇒ 3 > 2 > 1

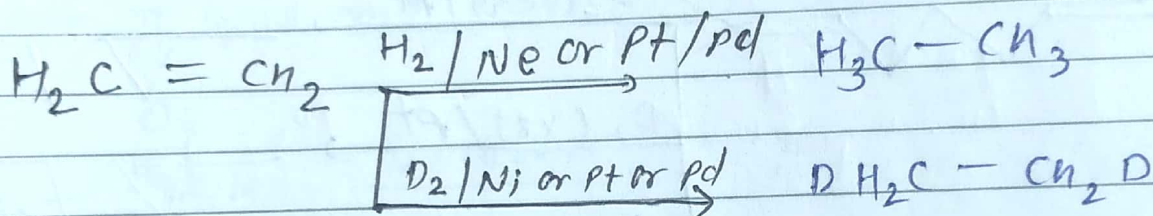
R.O = 1 > 2 > 3

HOH = 1 > 2 > 3

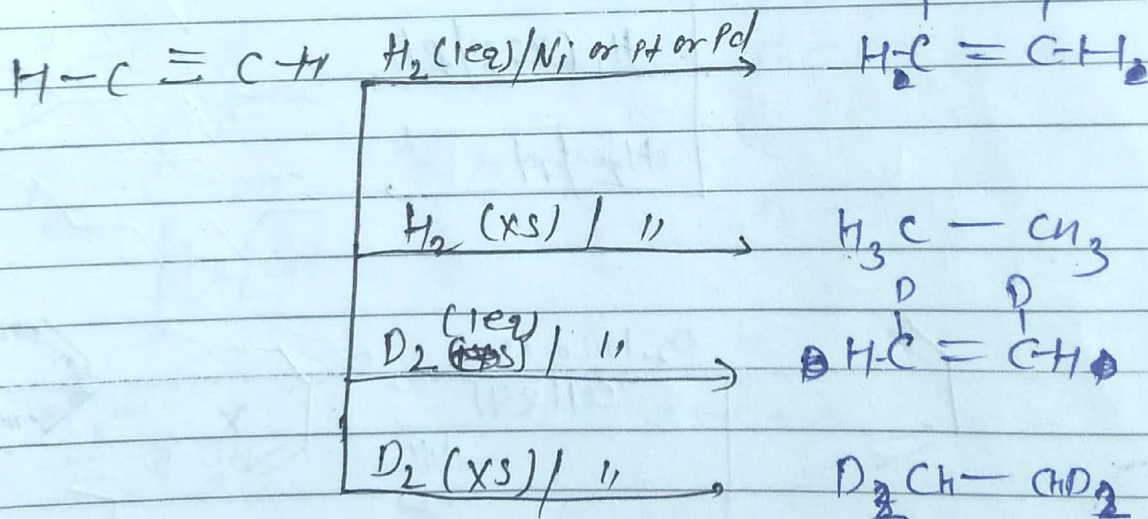
In this Rxⁿ Heat evolve which is known as Heat of Hydrogenation (H_{OH}) (in kcal)

* Similar reduction can also be done 1 mole of Hydrogen converted alkyne to alkene, 2 mol of H converted alkyne to alkane

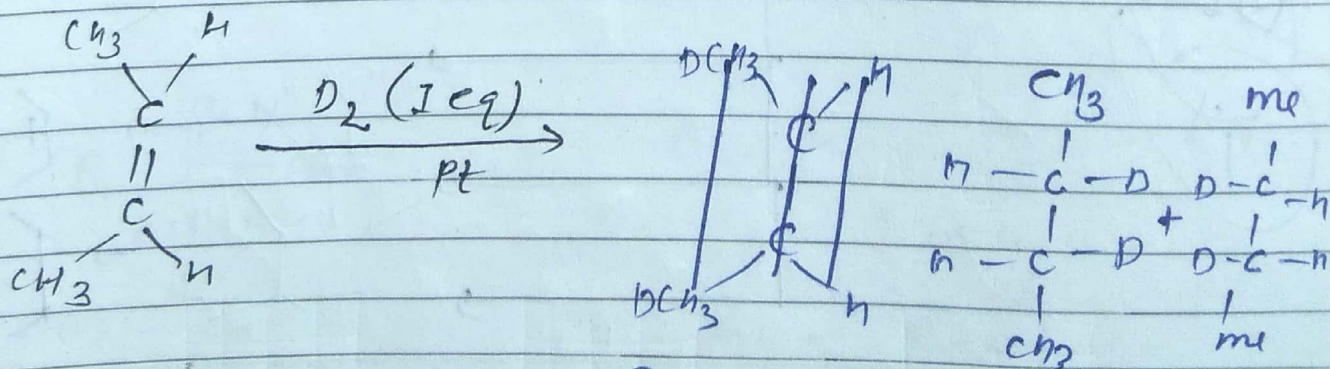
Q.1



(2)



(3)



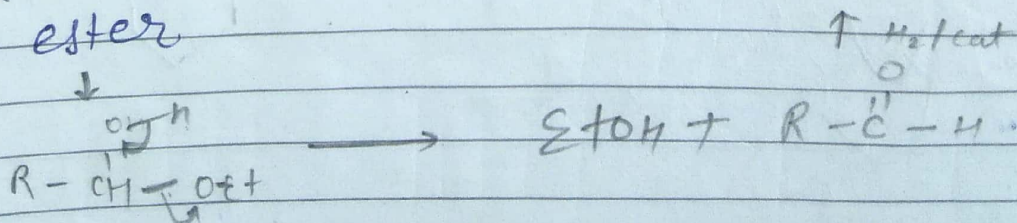
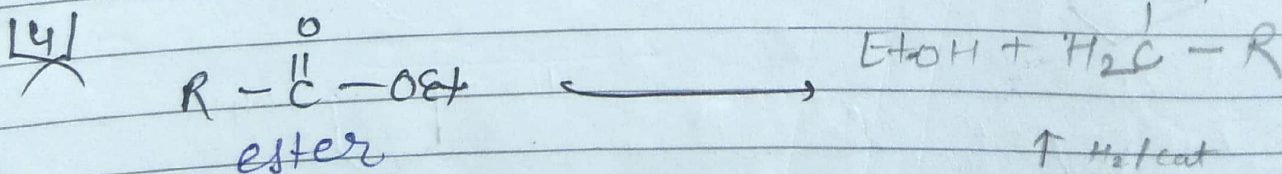
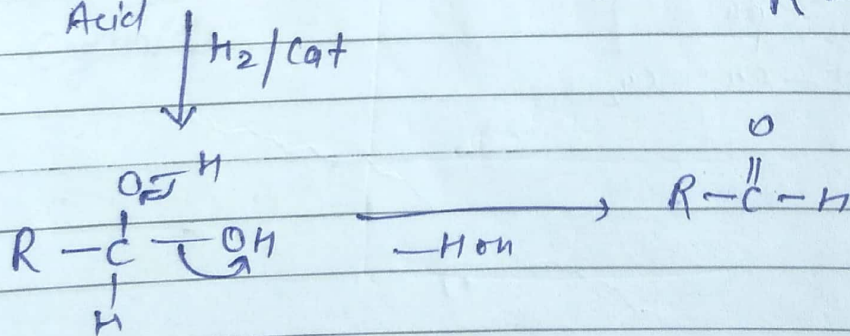
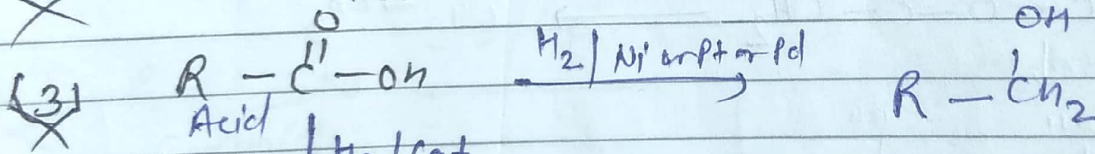
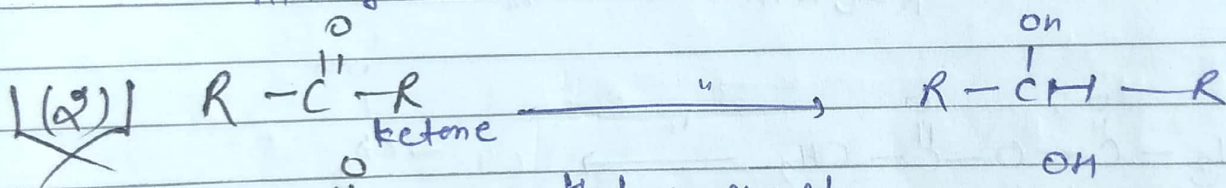
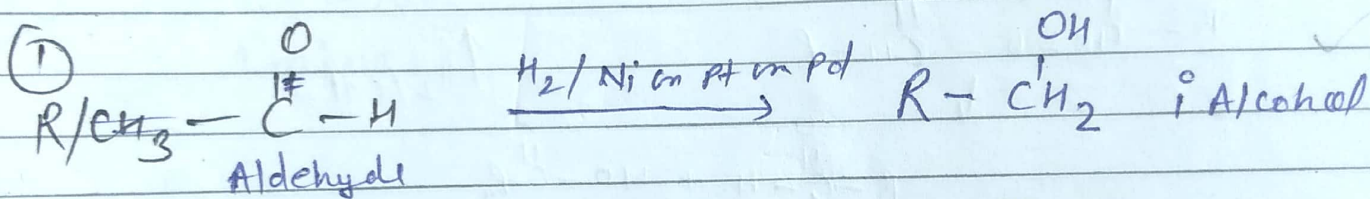
Erythro pair:

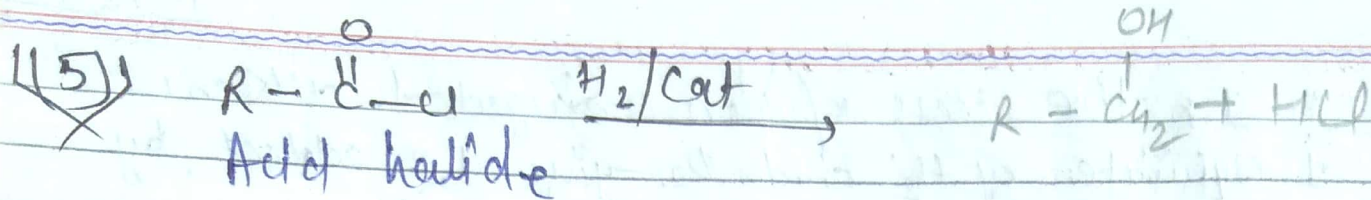
Meso Pair

Note - In the case of Non-conjugated alkene
 1 equivalent of H_2 and D_2 give 1,2 adduct by
 formation of 4 MCTS

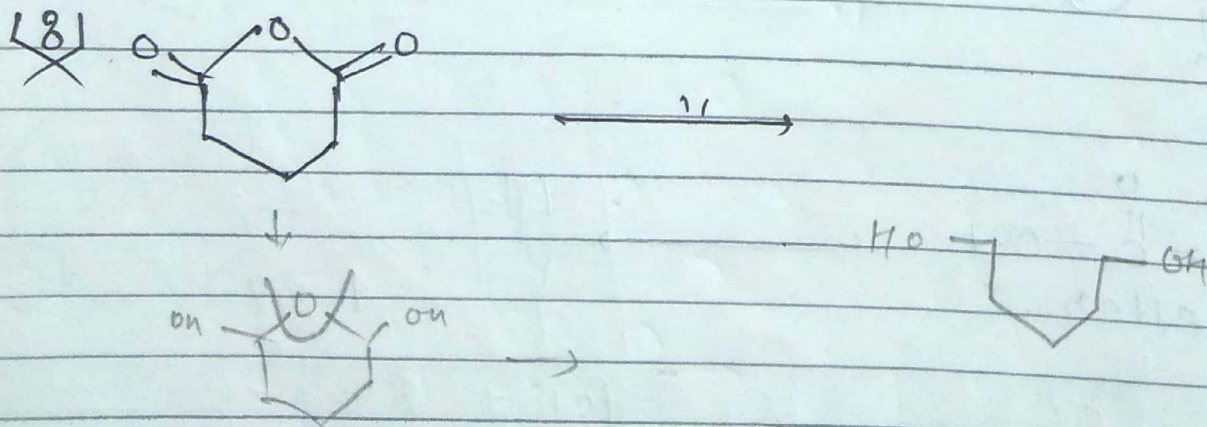
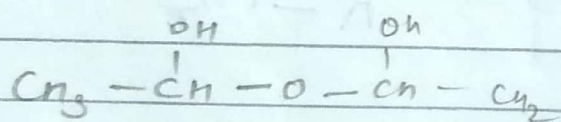
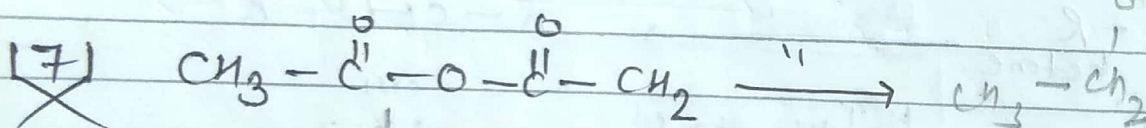
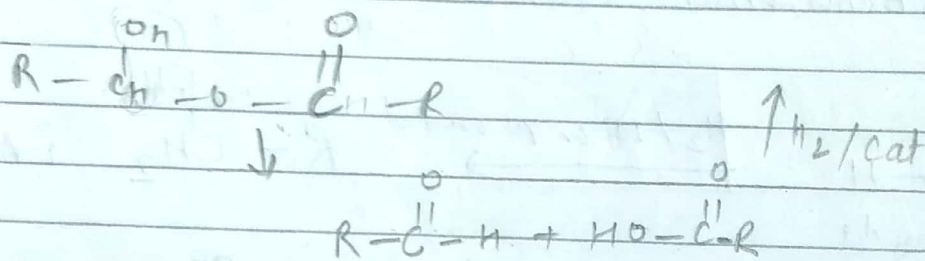
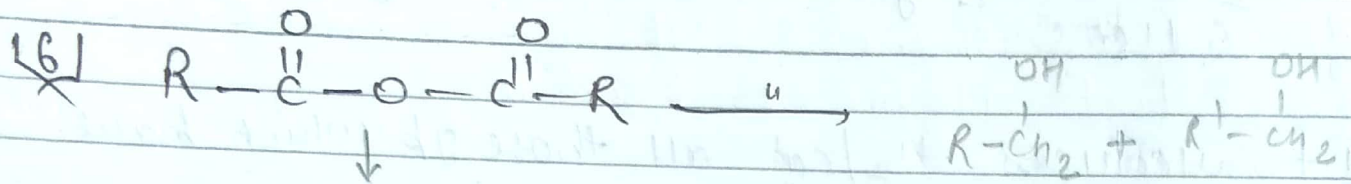
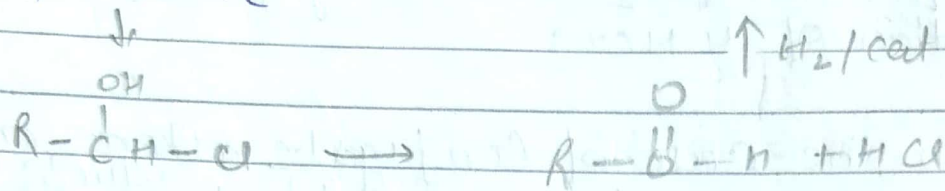
But in the case of Conjugate alkene one eq of
 H_2 and D_2 give 1,4 adduct ^{due to} formation
 of 6 MCTS

It reduces H_2 /cat all those gp which have
~~weak~~ π bond and polar weak bond.

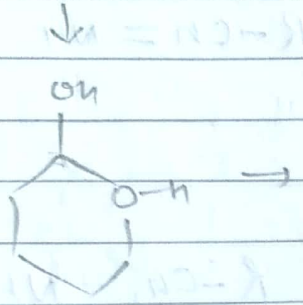
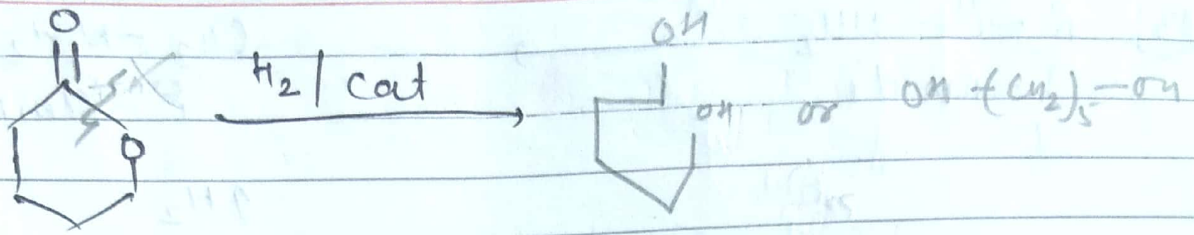




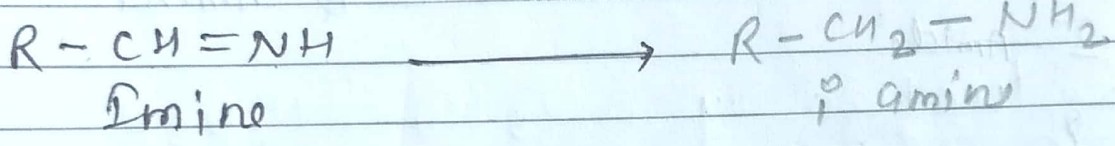
Acid chloride



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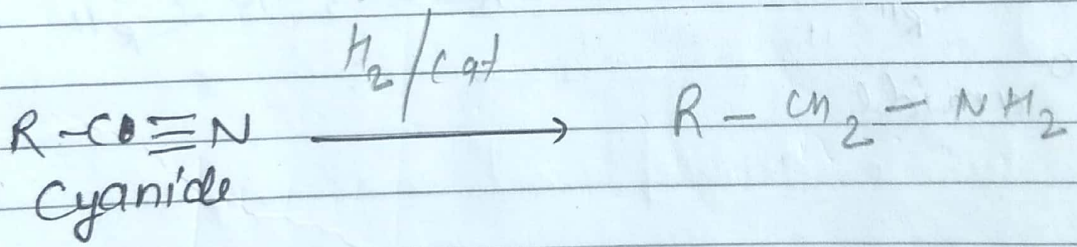


110

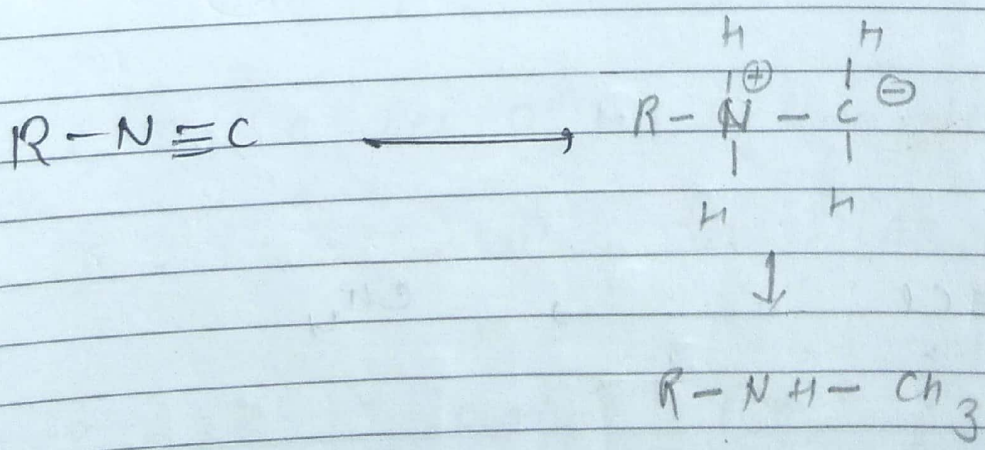


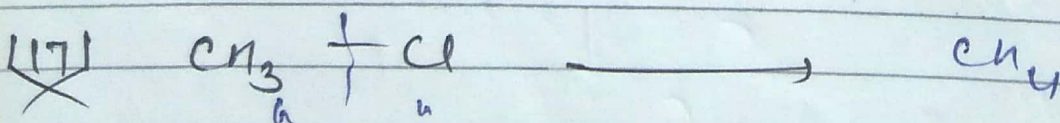
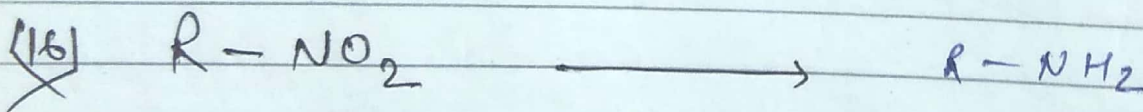
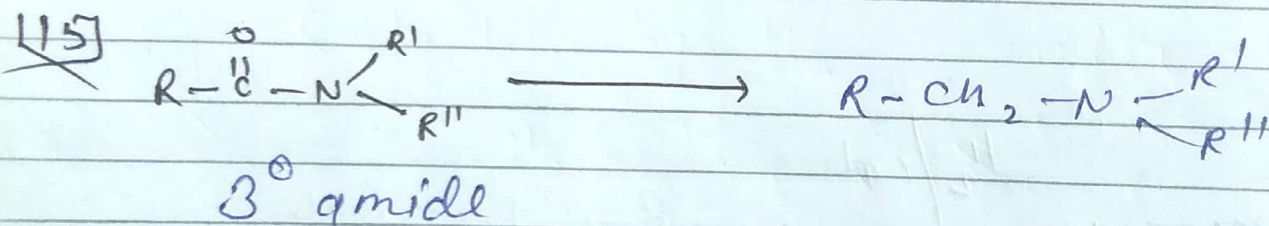
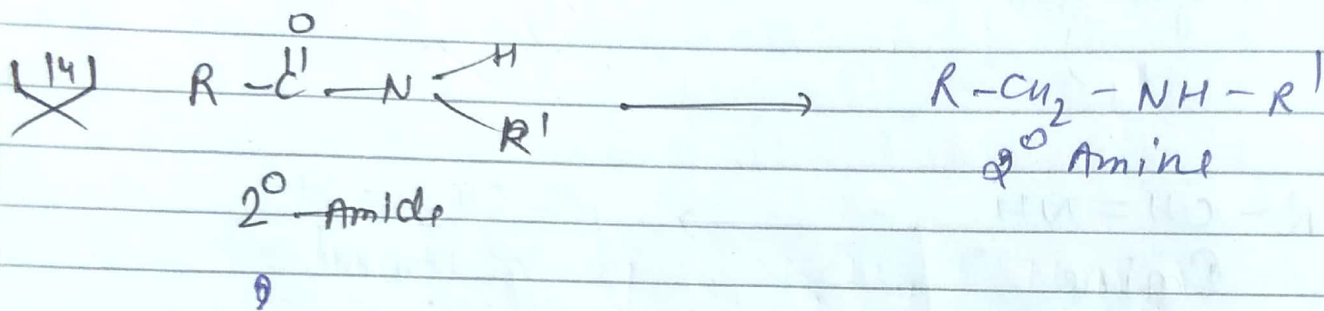
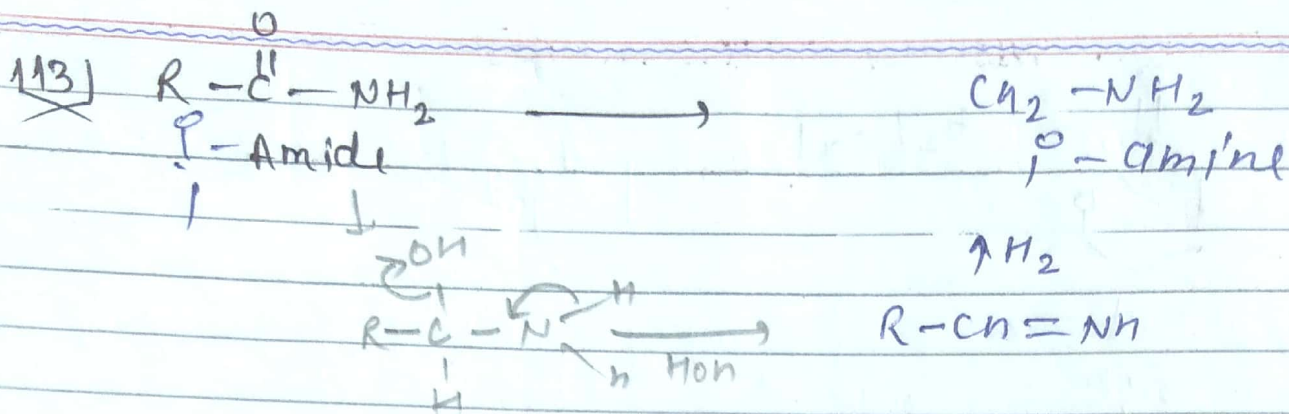
R-

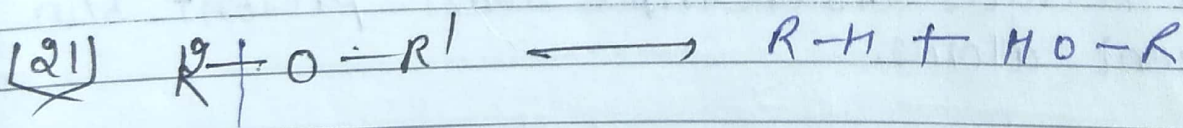
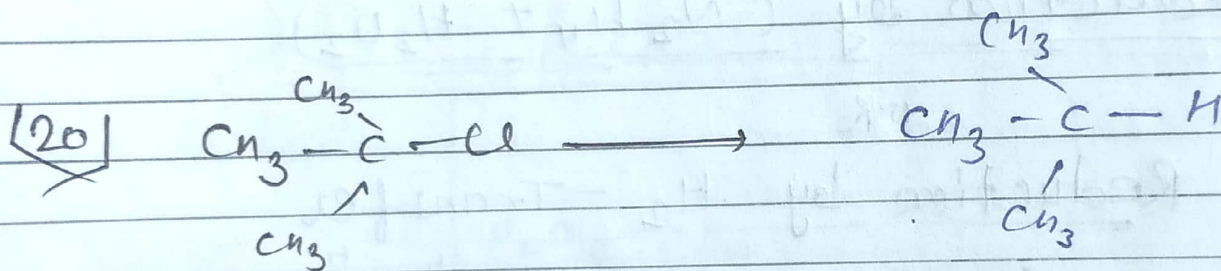
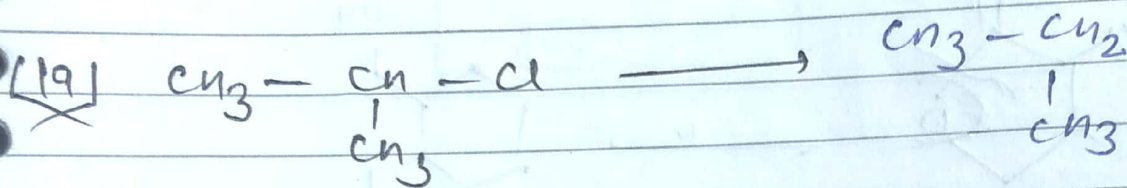
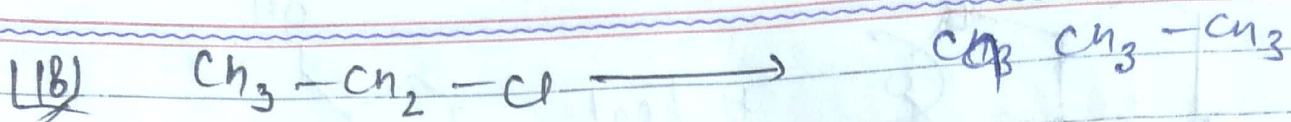
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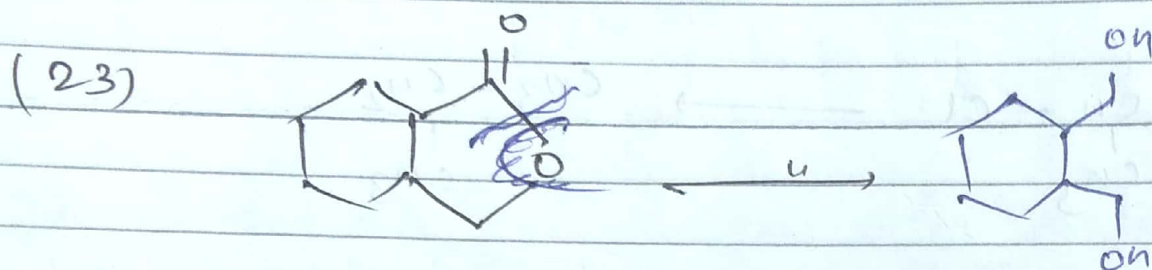
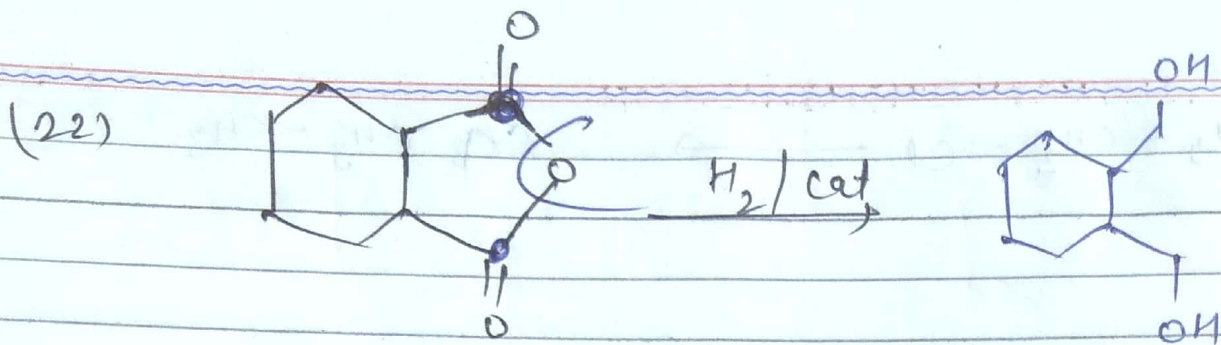
112







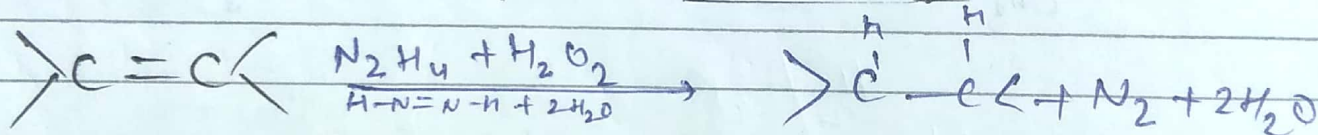
→ Jis 'C' per 'O' HO to Hua alcohol 😊
 → " " " 'N' " " " Amine 😊
 → " " " 'Dono' " " " " "



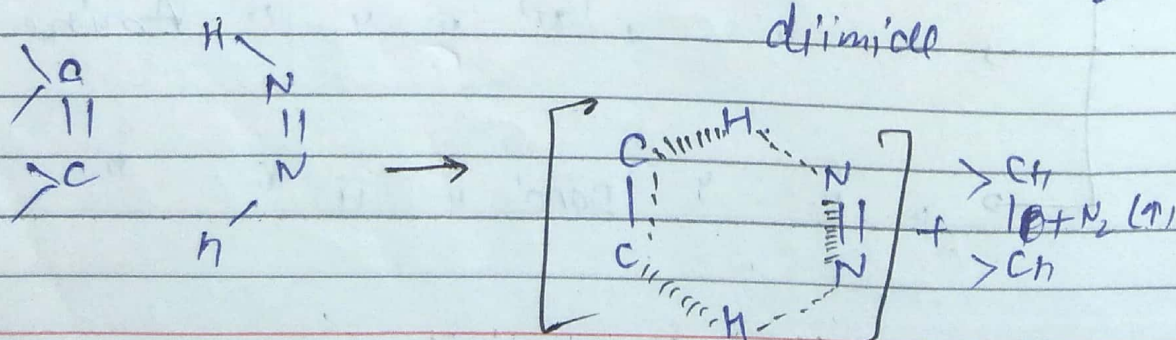
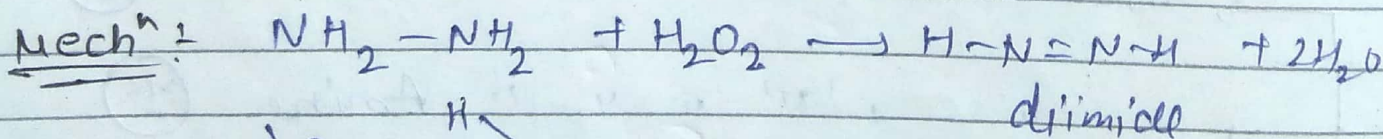
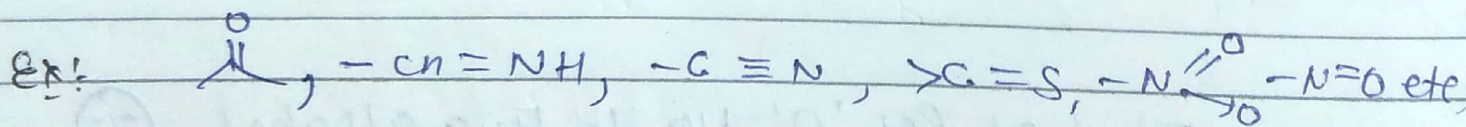
* Reduction by $\text{N}_2\text{H}_4 + \text{H}_2\text{O}_2$

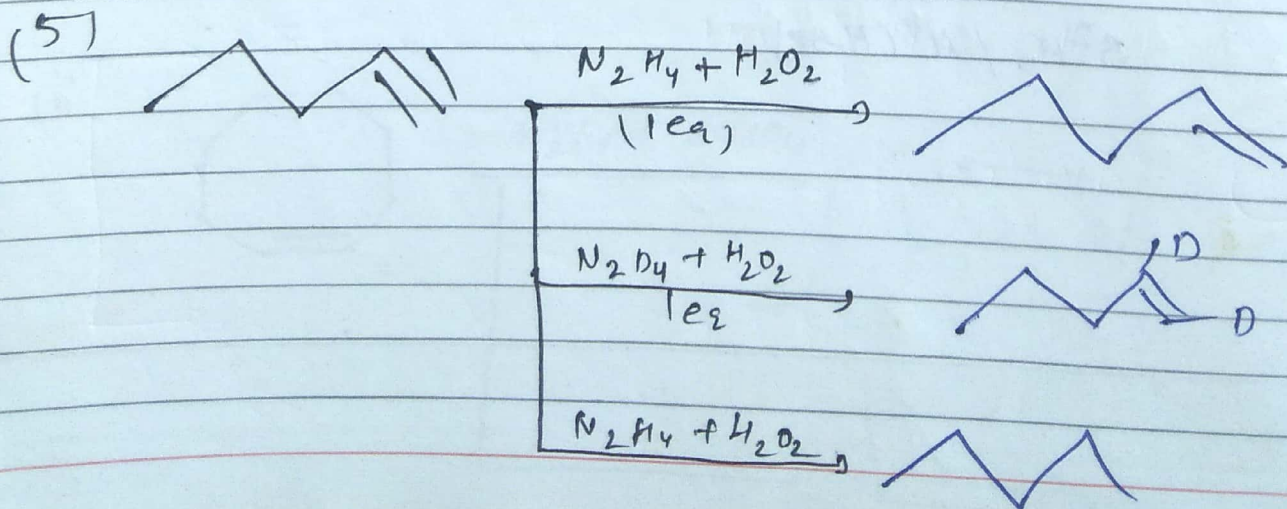
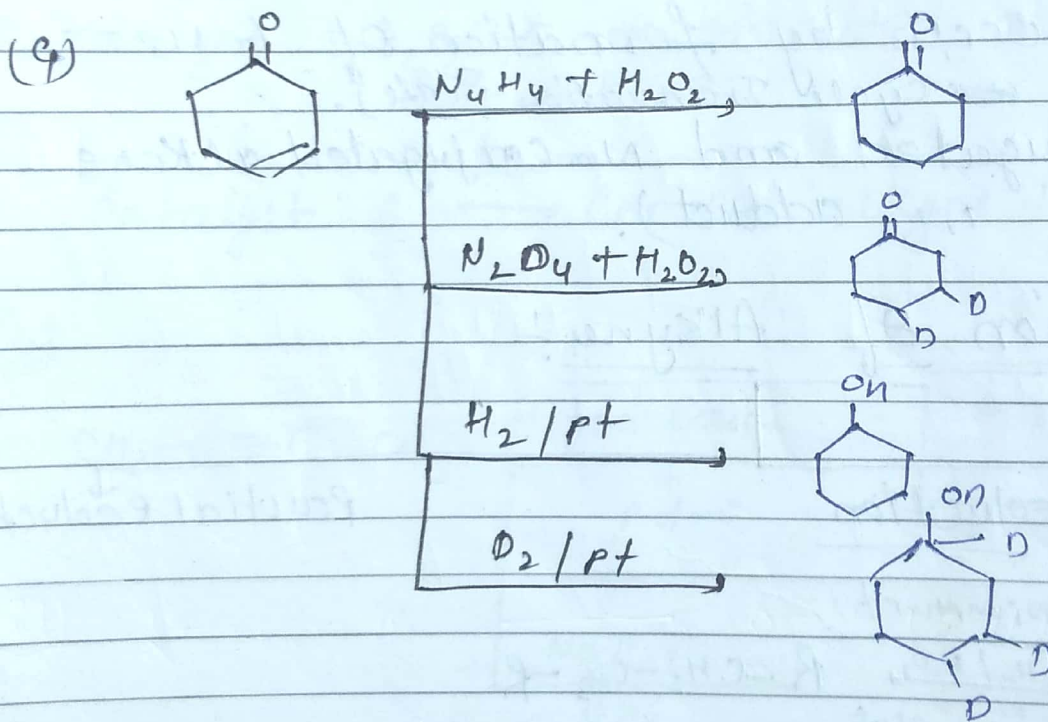
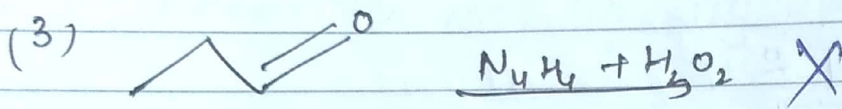
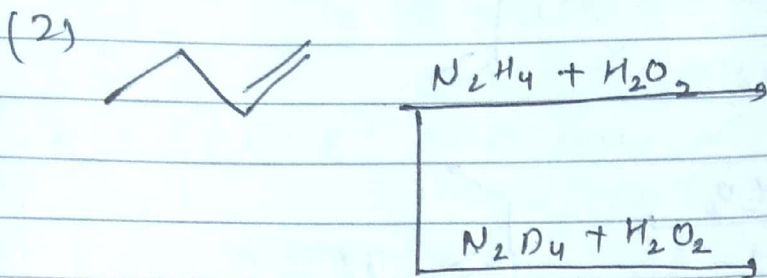
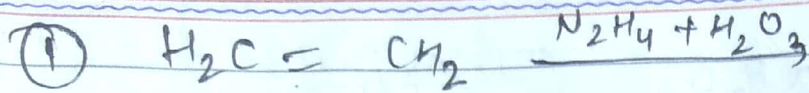
OR

Reduction by H_2 - Transfer

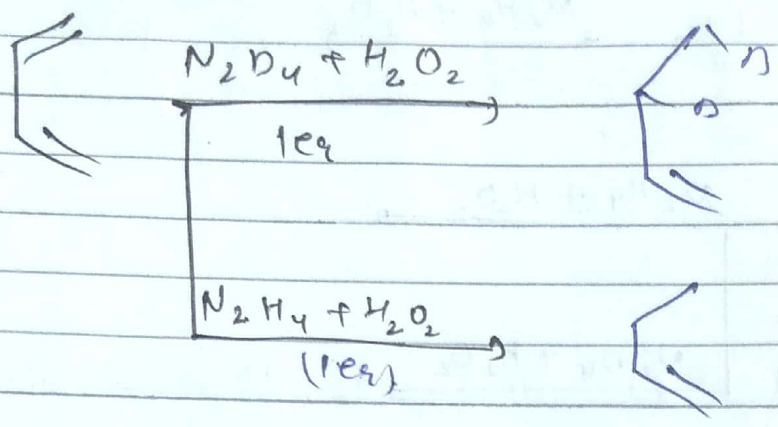


- It Reduces double bond and triple bond present in alkene / Alkyne.
- It not Reduces db or triple bond present b/w different atoms.





6



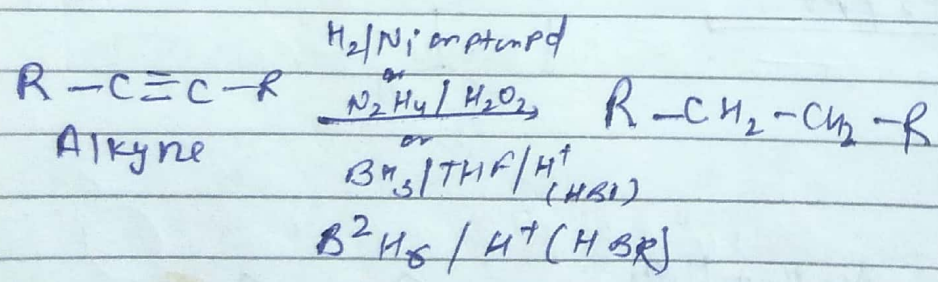
* Important point

- * This Rxⁿ occur by formation of 6 M.E.T.S (6 member ~~is~~ cycle Transition State).
- * with conjugated and non-conjugated alkyne it form 1,2 adduct.

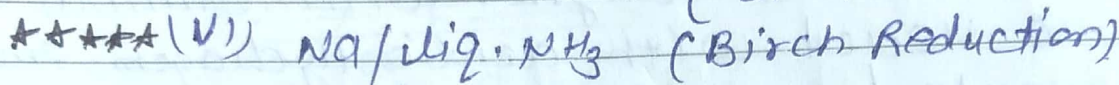
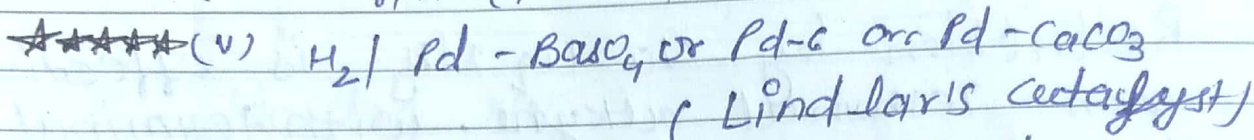
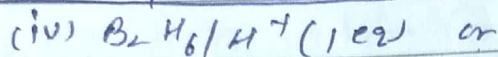
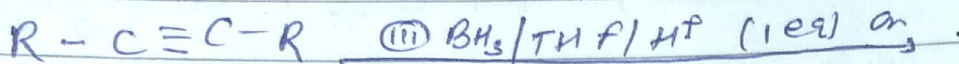
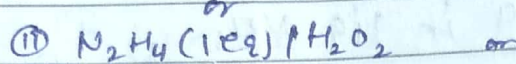
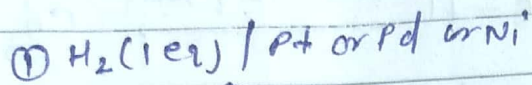
* Reduction of Alkyne!

1) Complete Reduction

Partial Reduction



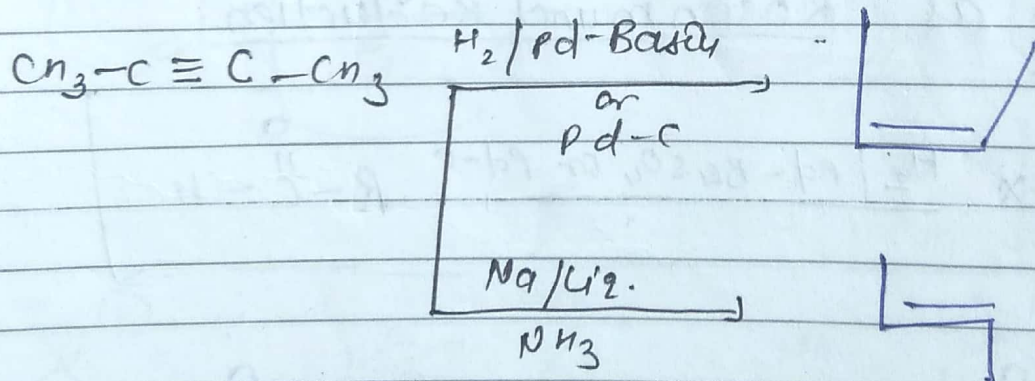
Partial Reduction:



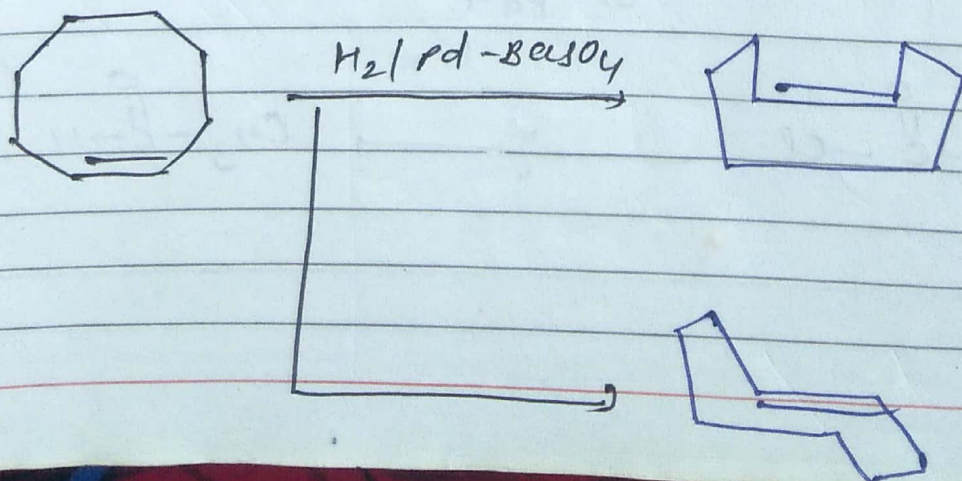
* Catalyst 1, 2, 3, 4, 5 \rightarrow Converted alkyne to cis-alkene

catalyst 6 \rightarrow Convert alkyne to trans alkene

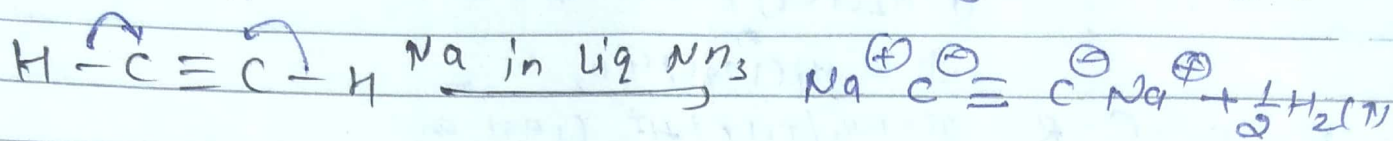
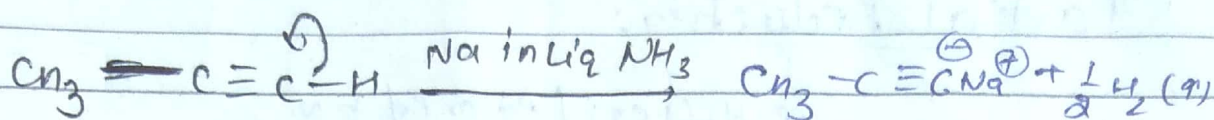
Q.1



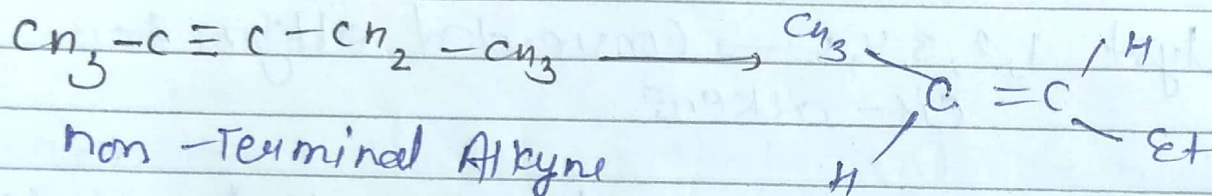
(ii)



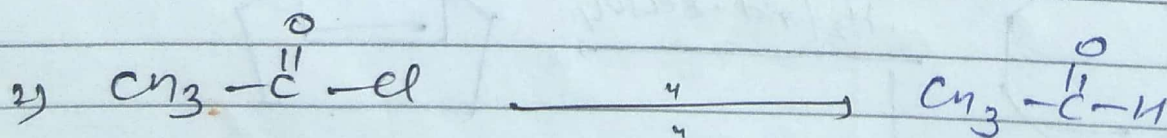
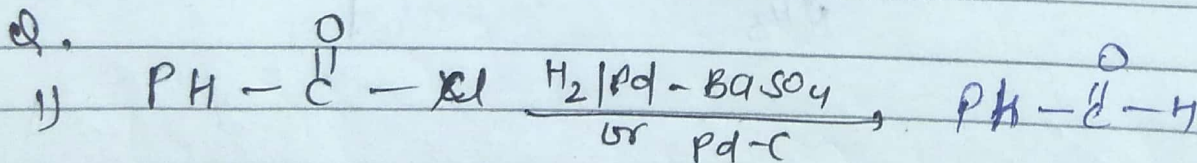
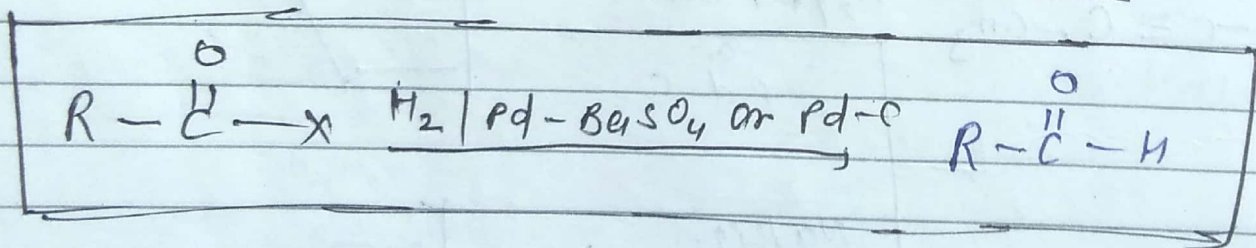
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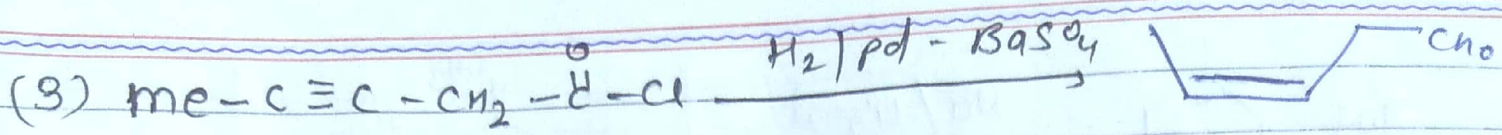


Reduction by Na liq NH₃ is effective with non-terminal alkyne. With terminal alkyne Na reacts with acidic hydrogen and converted to salt of alkyne.



* Lindlar Catalyst (H₂ / Pd-BaSO₄ or Pd-C) also reduces Acid halide partially and reduction is known as Rosenmund Reduction.

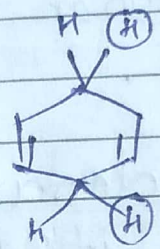
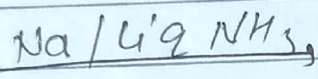
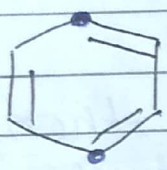




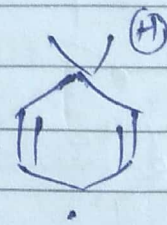
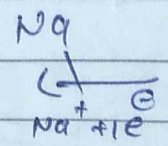
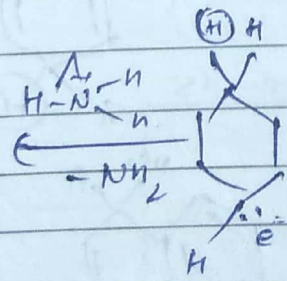
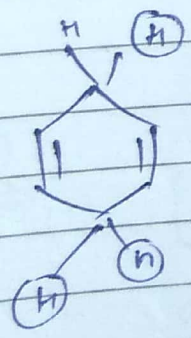
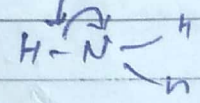
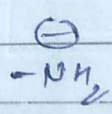
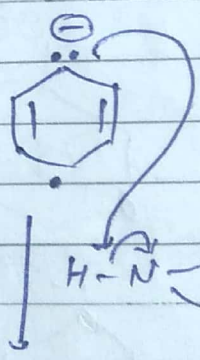
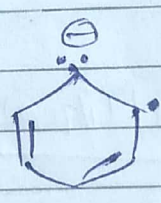
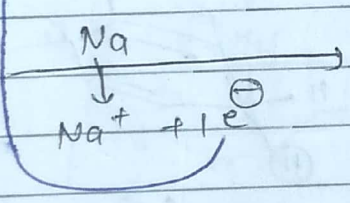
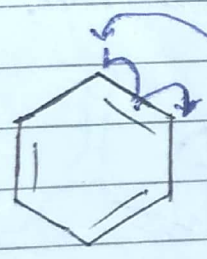
* Na/liq. NH₃ also reduces Aromatic Compounds

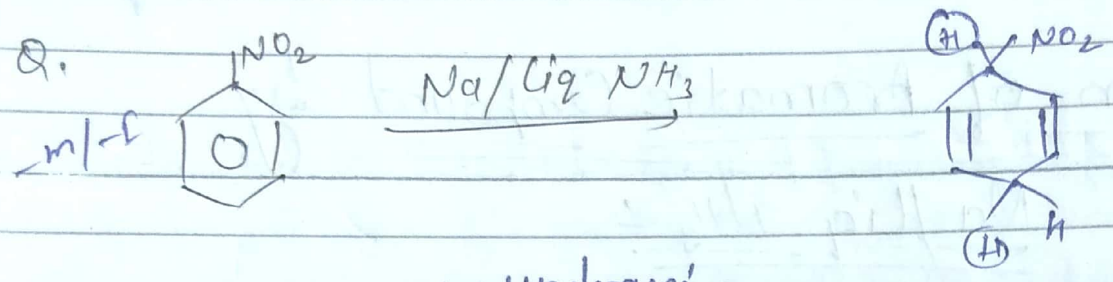
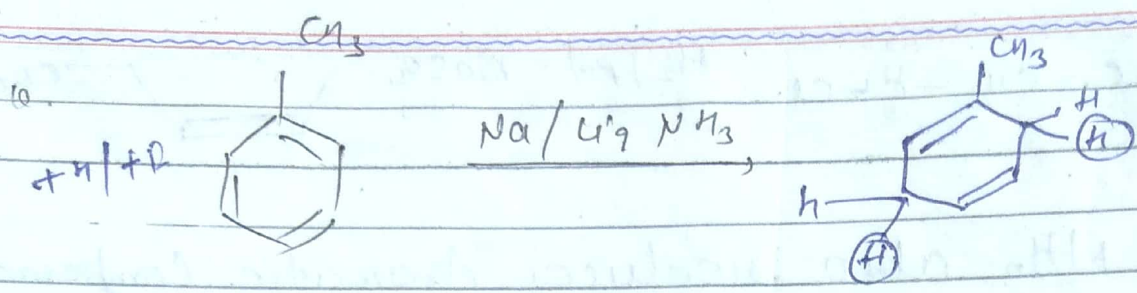
* Reduction of Aromatic Compound by

Na/liq. NH₃ :
or
Birch Reduction :



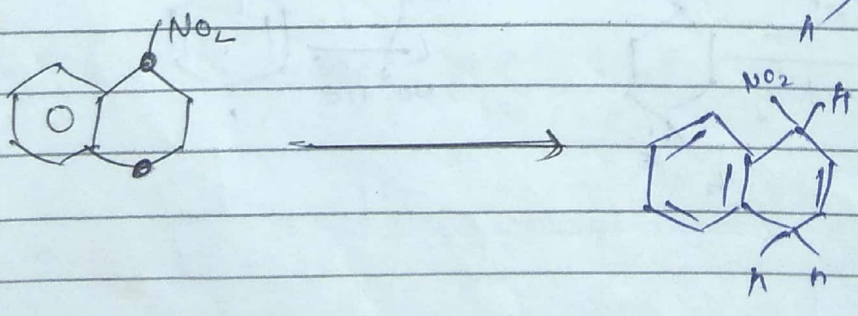
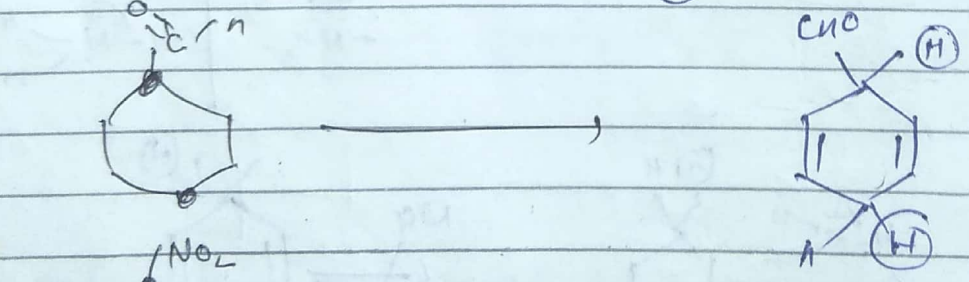
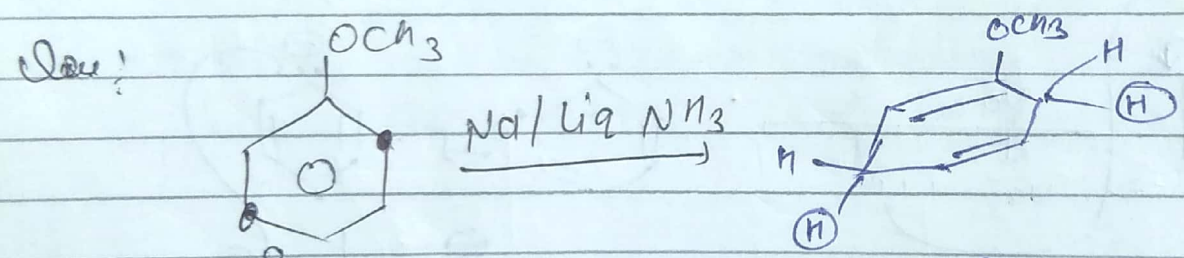
1,4-Adduct.





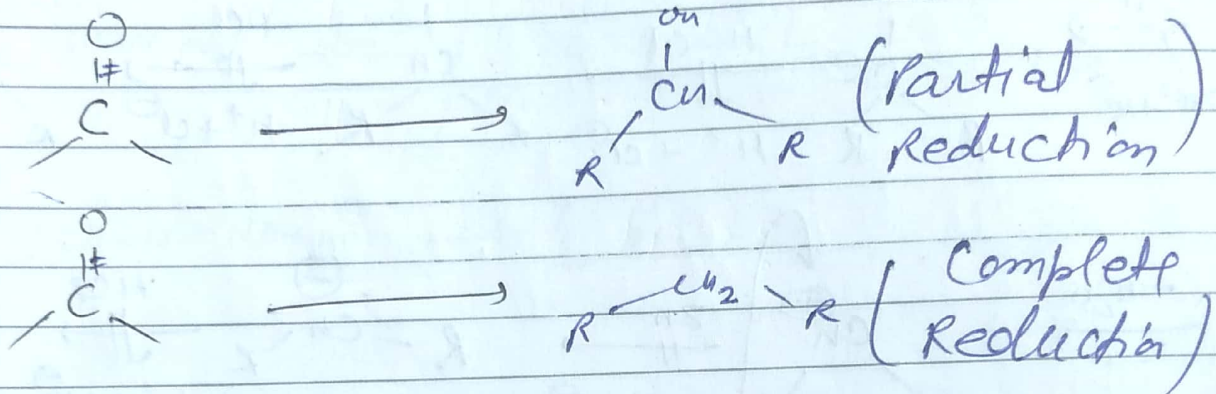
* When e^- withdrawing gp present on Benzene Ring then Reduction occur on same atom and para-atom.

* When e^- donating gp present on then Reduction occur on its ortho and meta position.

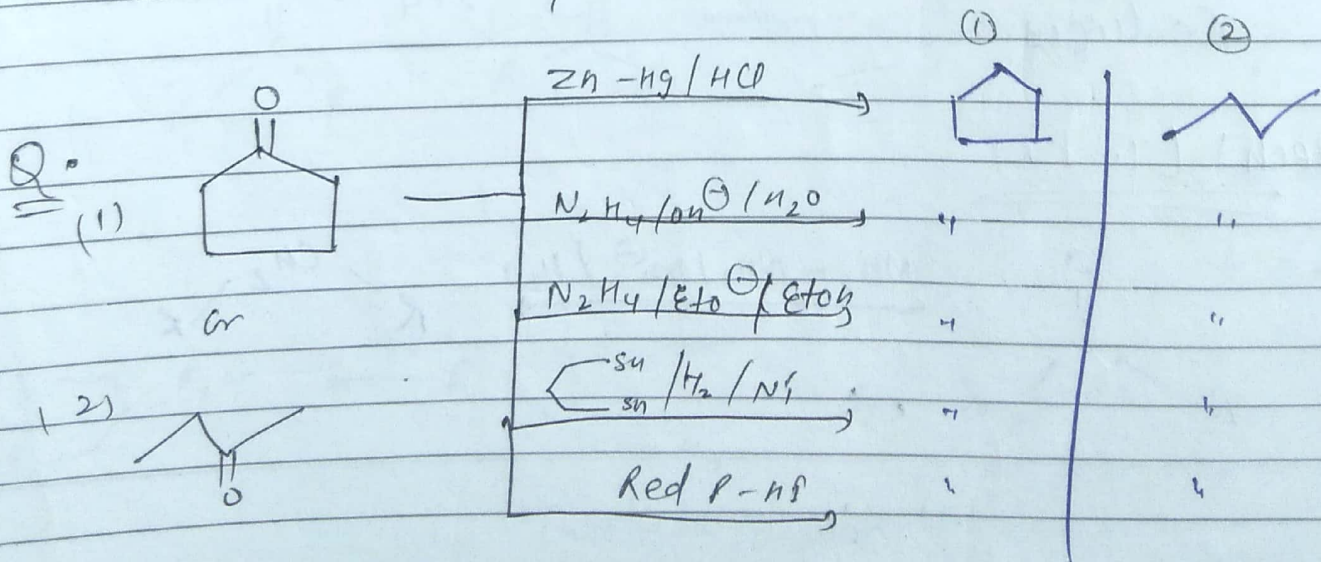
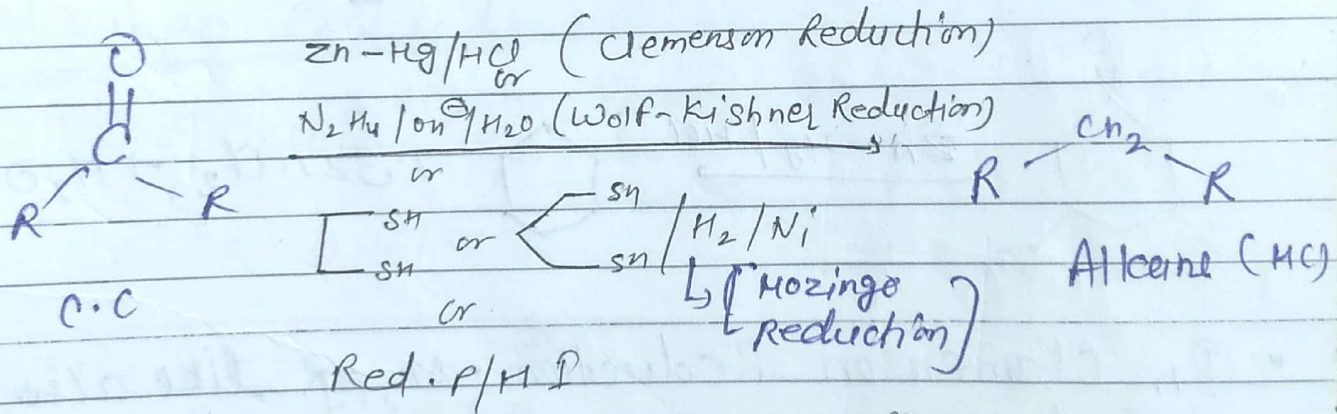


* Reduction by LiAlH_4 Hydride :

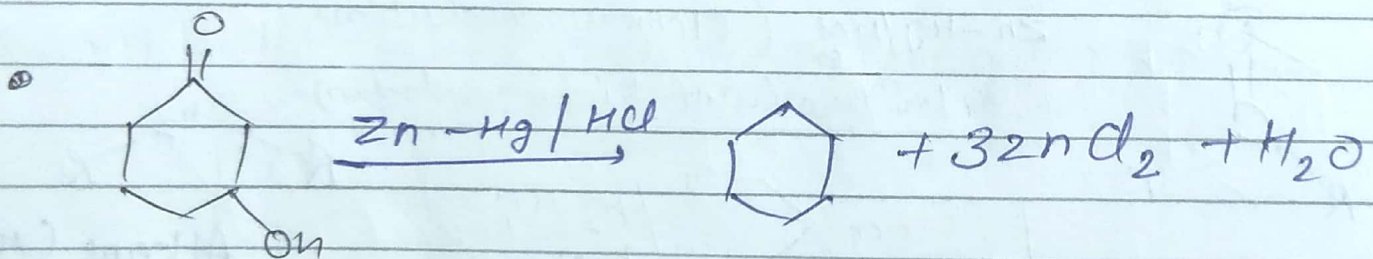
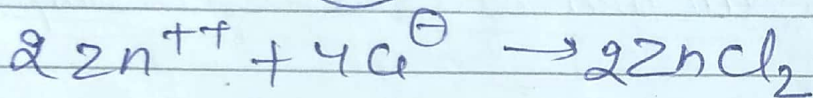
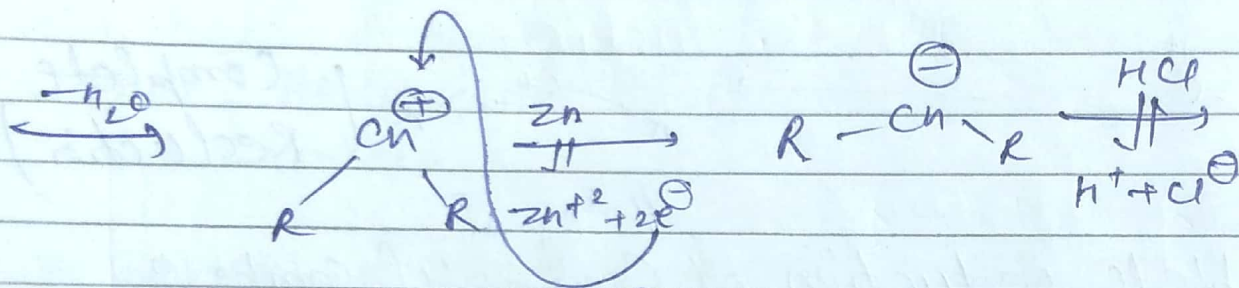
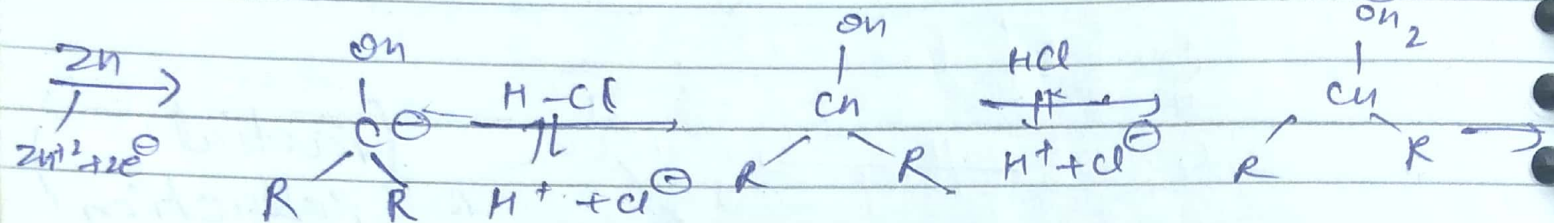
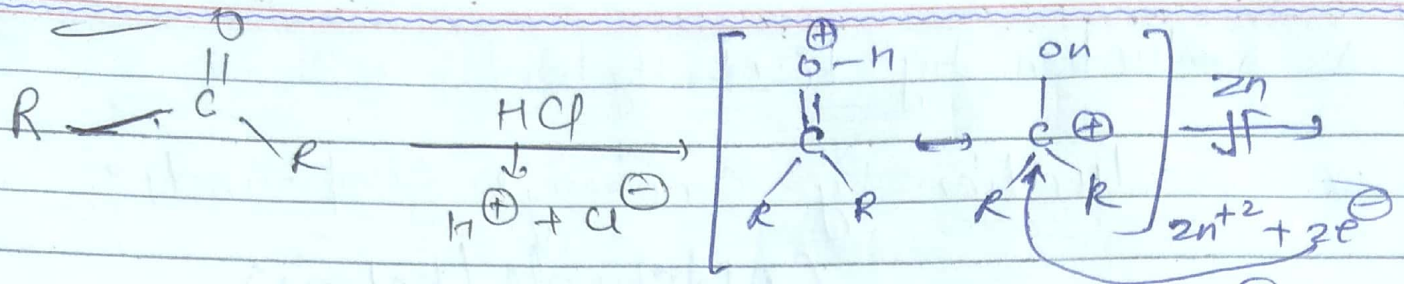
* Reduction by Carbonyl Compounds :
(Aldehyde / ketone)



* Complete Reduction of Carbonyl Comp. :

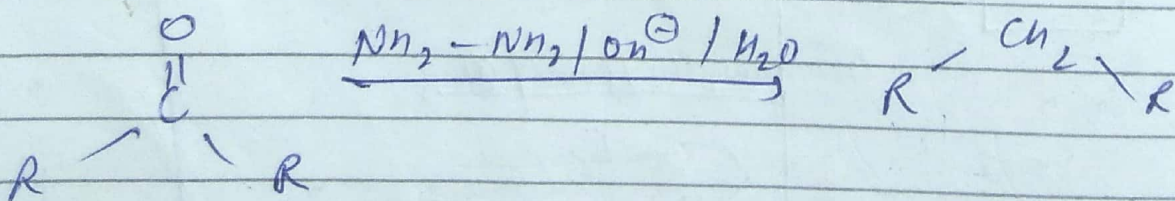


Mech!

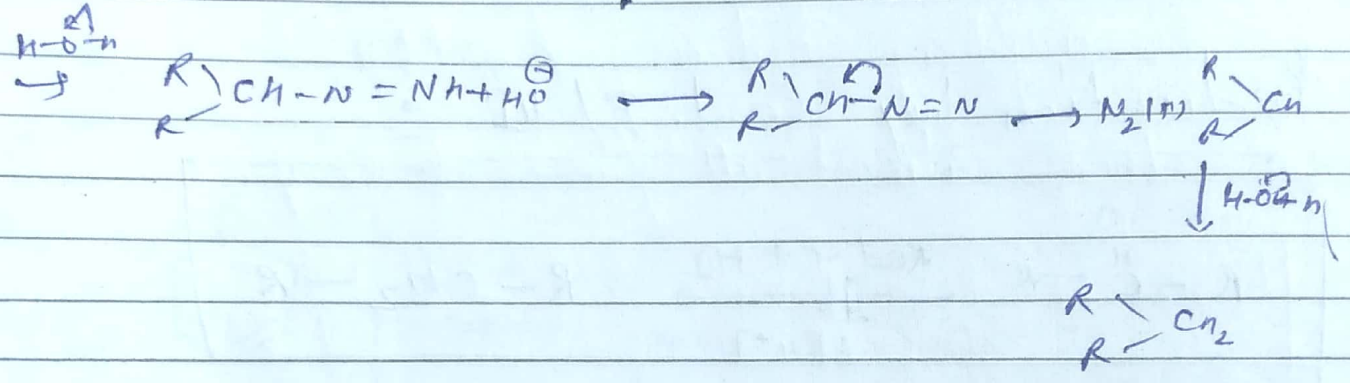
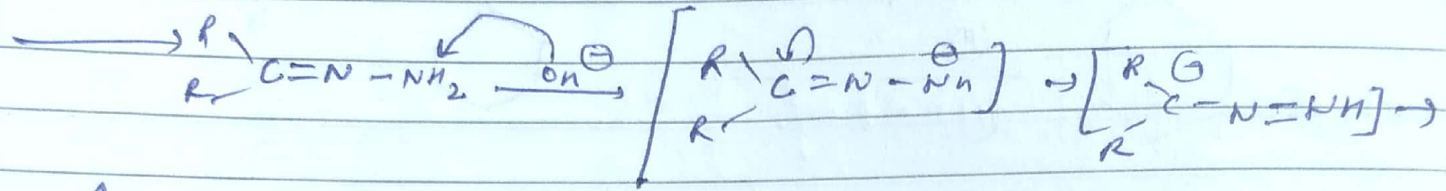
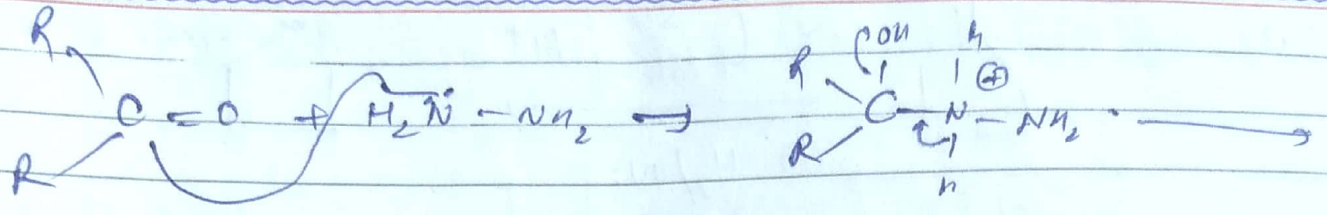


• In Clemmensen Reduction -OH, OR like also Reduces.

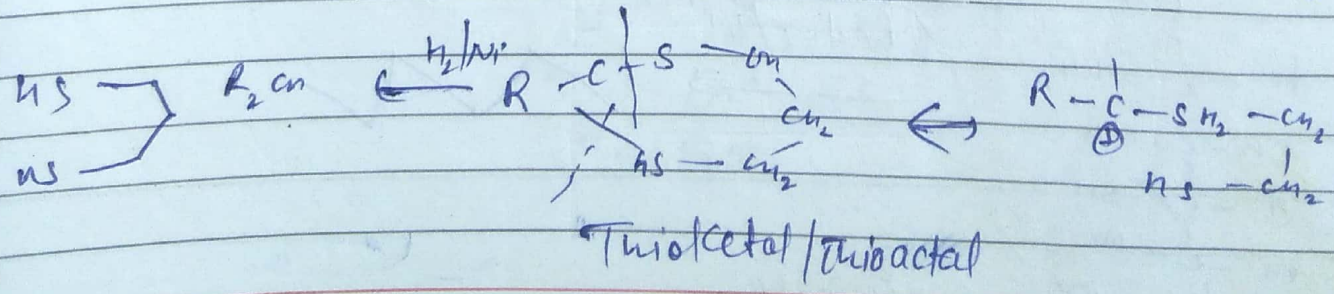
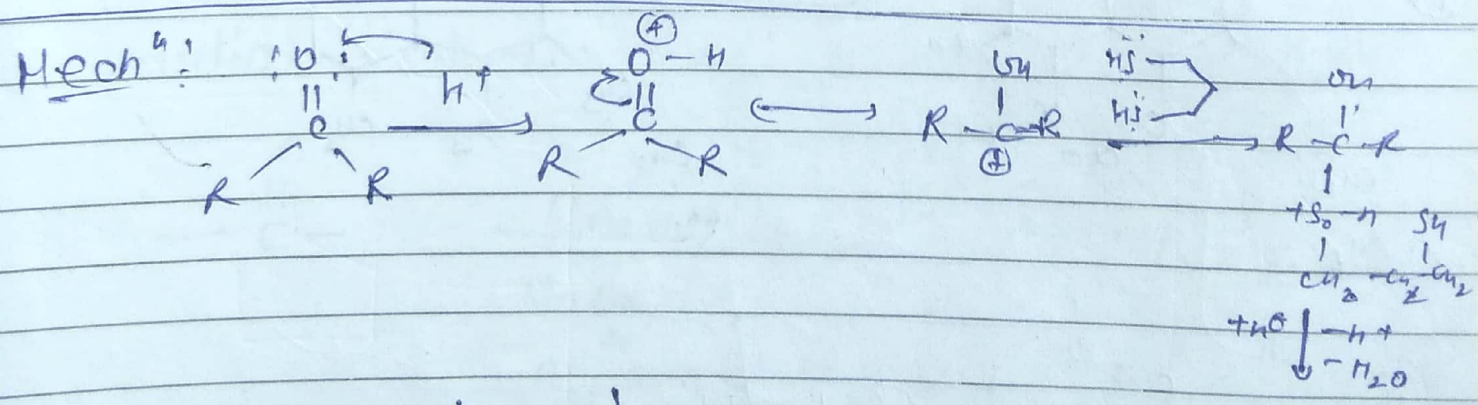
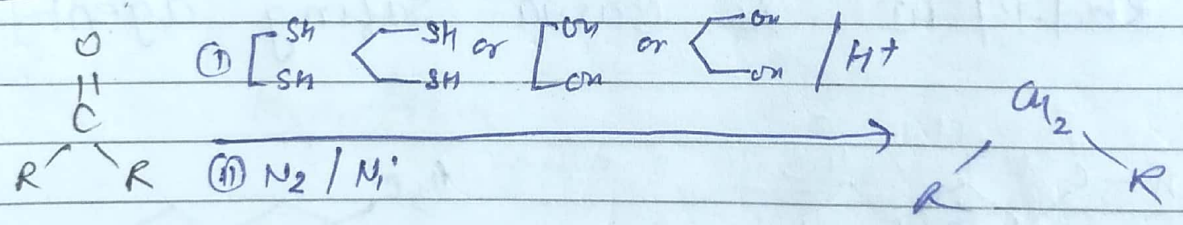
Mech! (WKR)

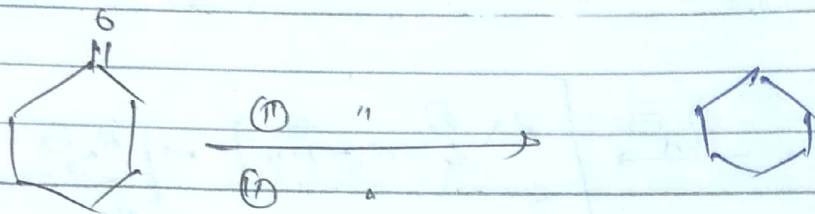
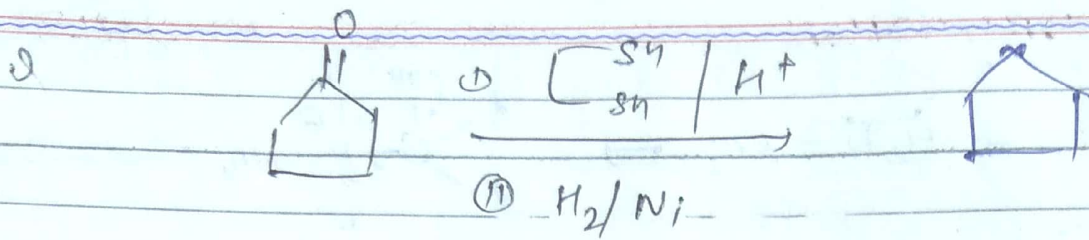


20/09/17

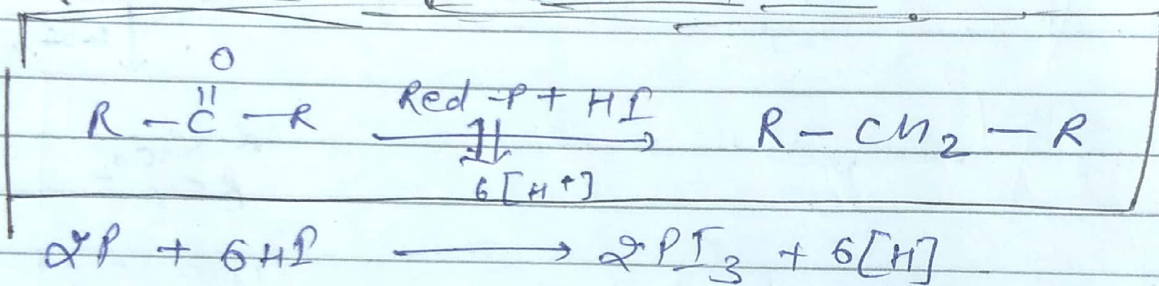


Mozingo Reduction:

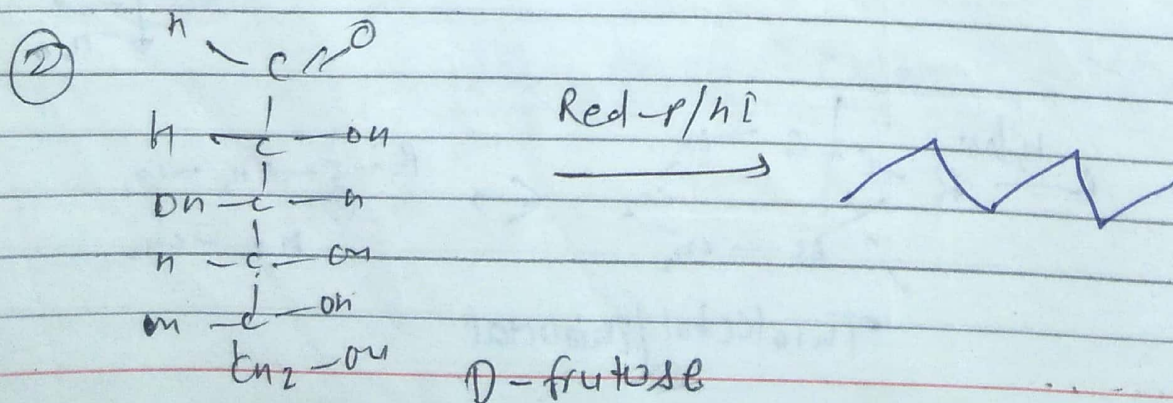
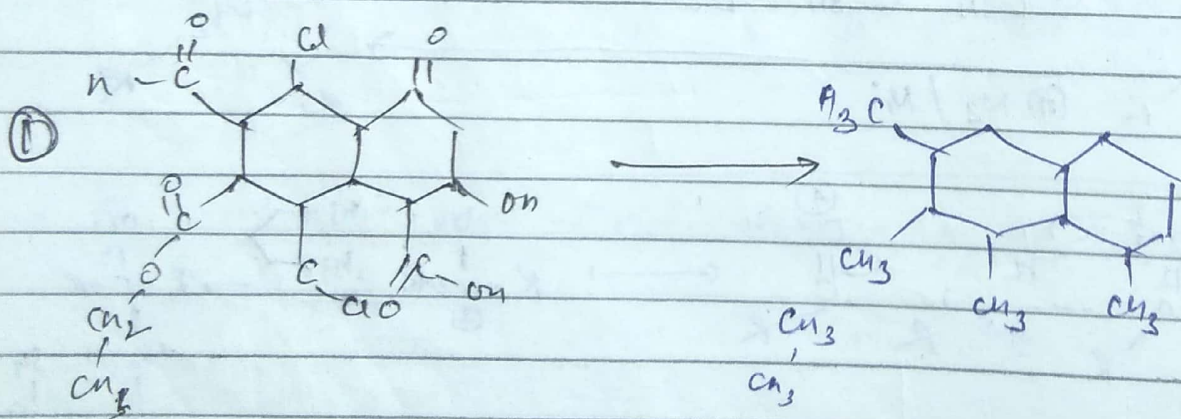




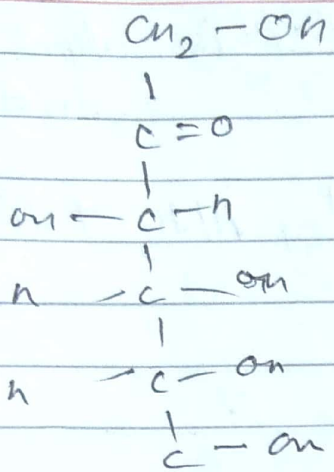
* Reduction by Red. P / HI :



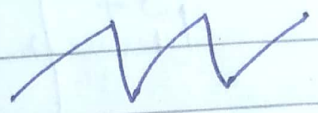
* Red-P/HI is a safe agent.



③



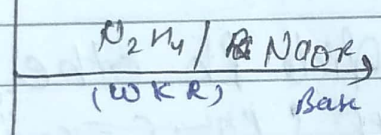
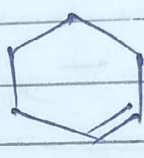
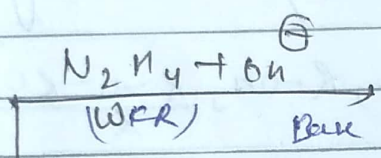
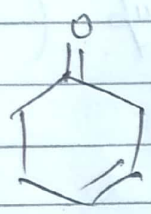
Red-P/HI



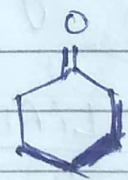
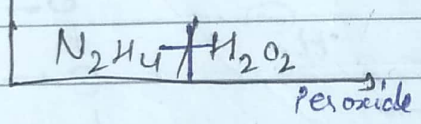
D-fructon

~~Wittig~~

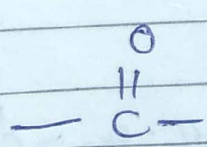
Q



"

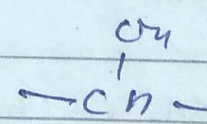


* Partial Reduction of aldehyde or ketone:



$\xrightarrow{\text{H}_2 / \text{cat} (\text{Ni or Pt or Pd})}$

$\xrightarrow[\text{or}]{\text{LiAlH}_4 / \text{H}_2\text{O}}$



$\xrightarrow[\text{or}]{\text{NaBH}_4 / \text{H}_2\text{O}}$

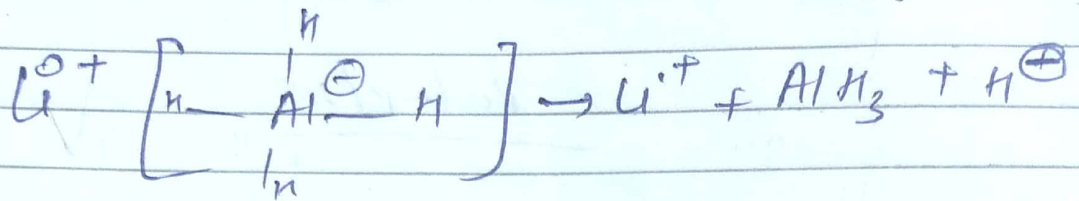
$\xrightarrow[\text{or}]{\text{B}_2\text{H}_6 \text{ or } \text{SnH}_4 / \text{H}_2\text{O}}$

$\xrightarrow[\text{or}]{\text{BH}_3 - \text{THF} / \text{H}^+}$

$\xrightarrow[\text{or}]{\text{B}_2\text{H}_6 / \text{H}^+}$

$\xrightarrow{\text{Na} / \text{EtOH}}$

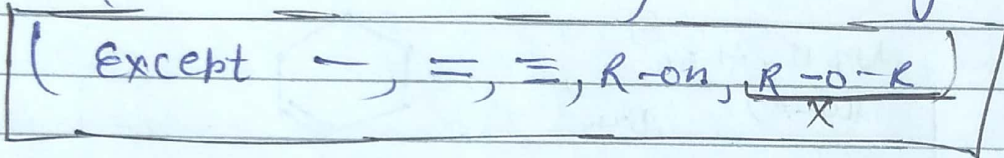
* Reduction by $\text{LiAlH}_4/\text{H}_2\text{O}$ (LAM) - Lithium aluminium hydride



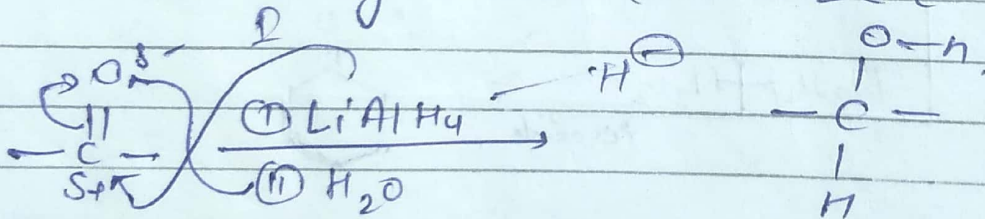
• LiAlH_4 is source of H^-

• It is a strong Reducing Agent (Work as RmgX)

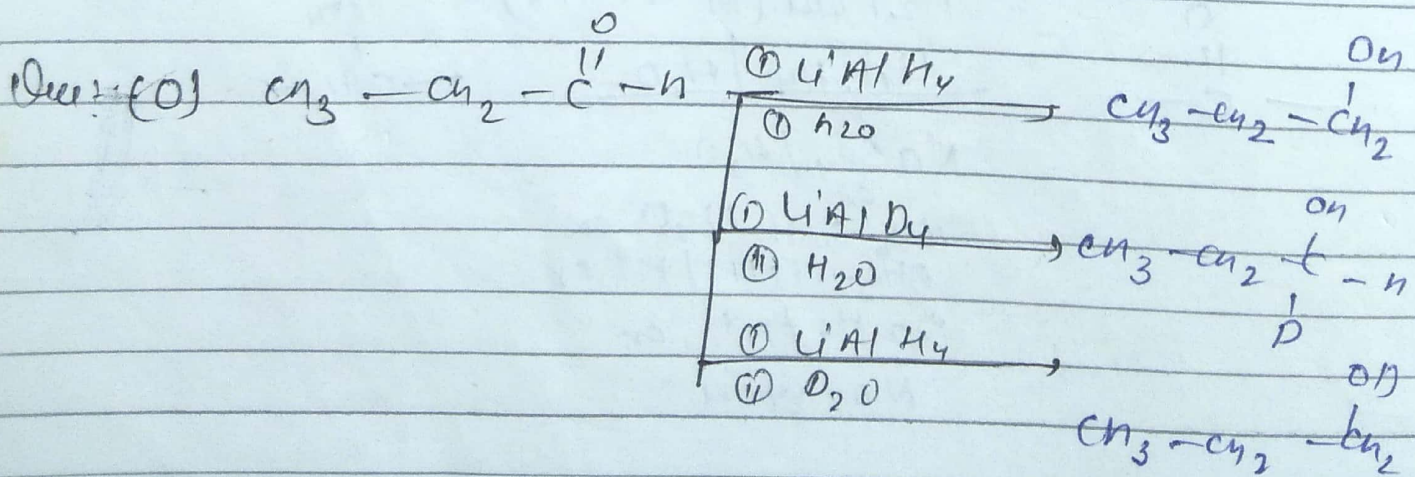
• It reduces almost all functional group (



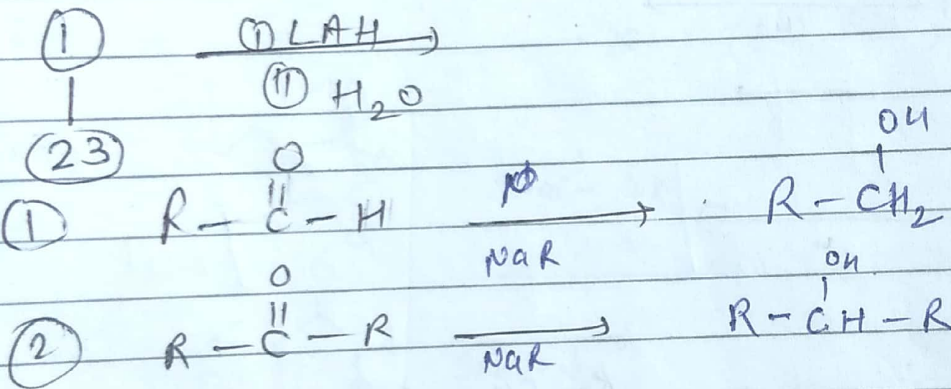
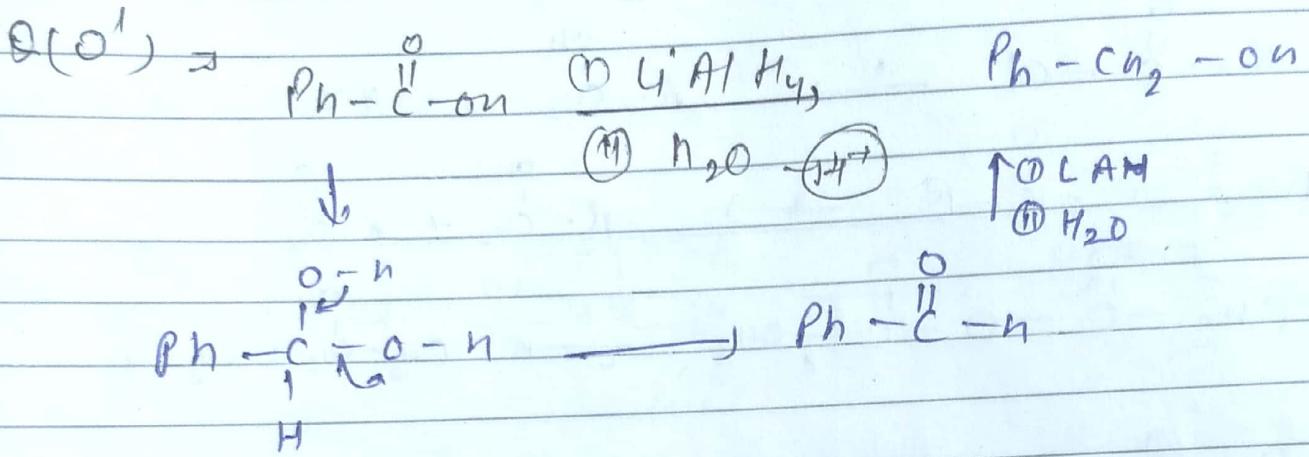
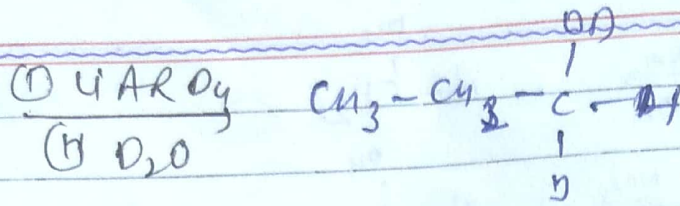
• db or α tb with one side ph other side -m gp also reduced by LAM ($\text{Ph-C}\equiv\text{C-C}^{\text{O}}\text{-H}$).

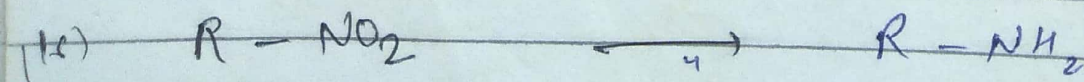
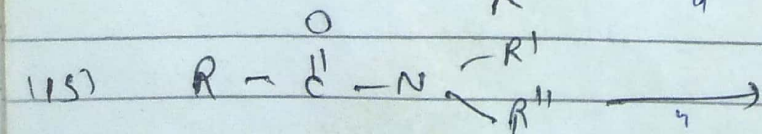
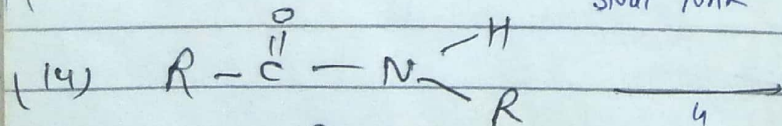
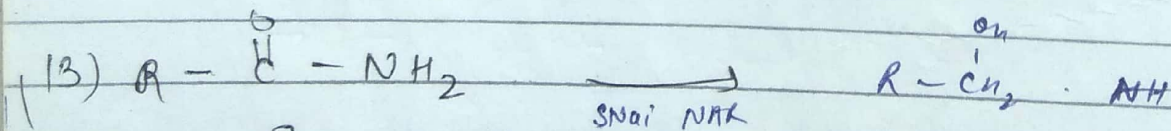
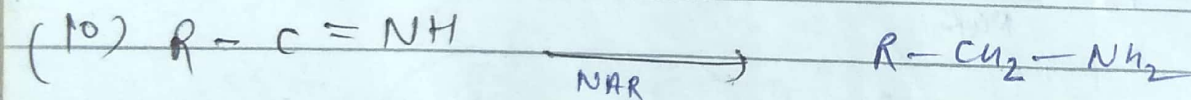
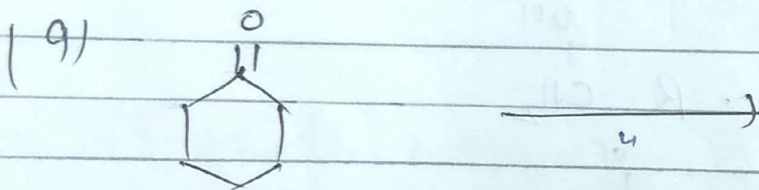
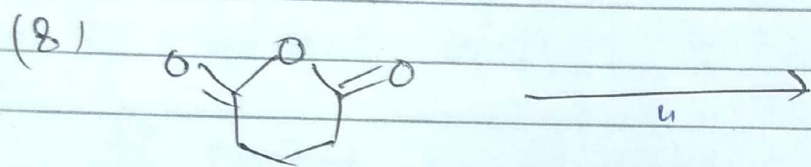
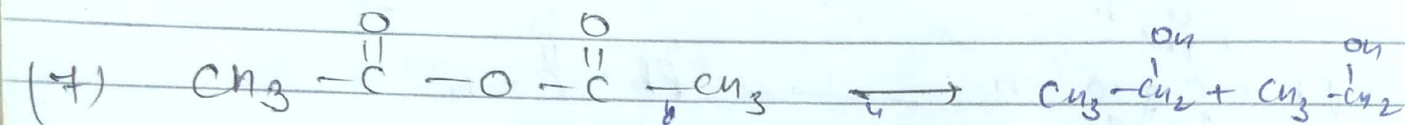
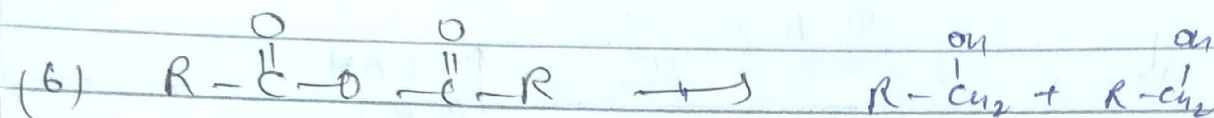
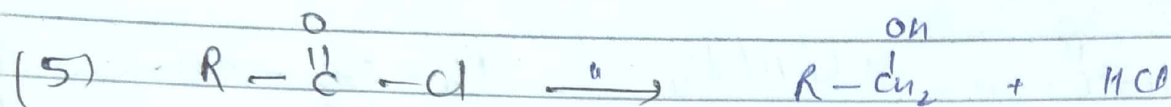
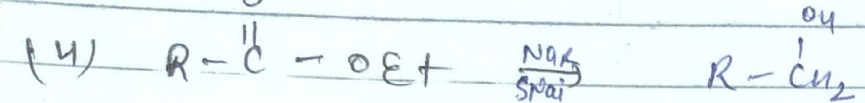
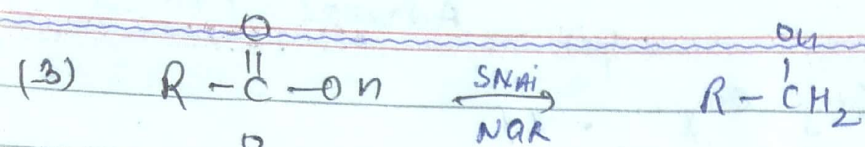


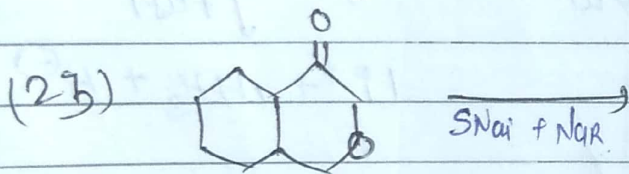
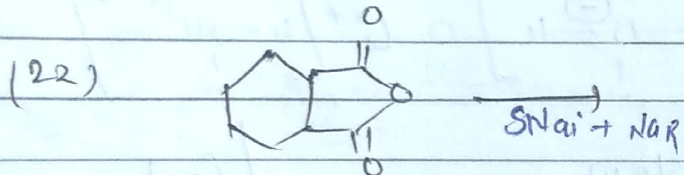
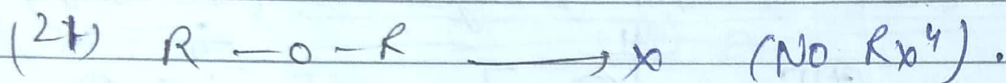
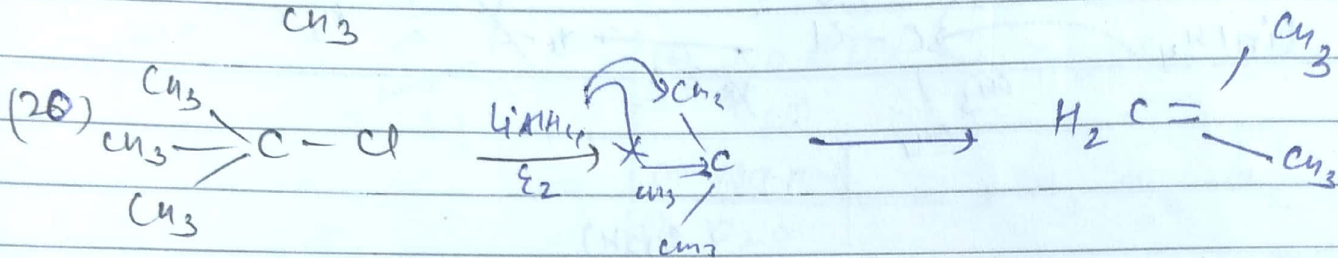
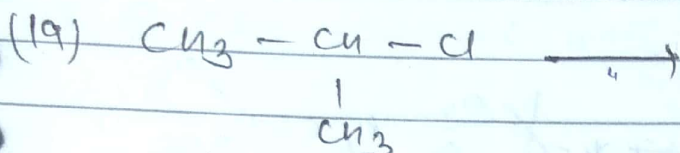
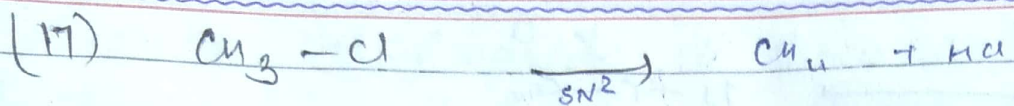
• This Rxn is also k/a NAR



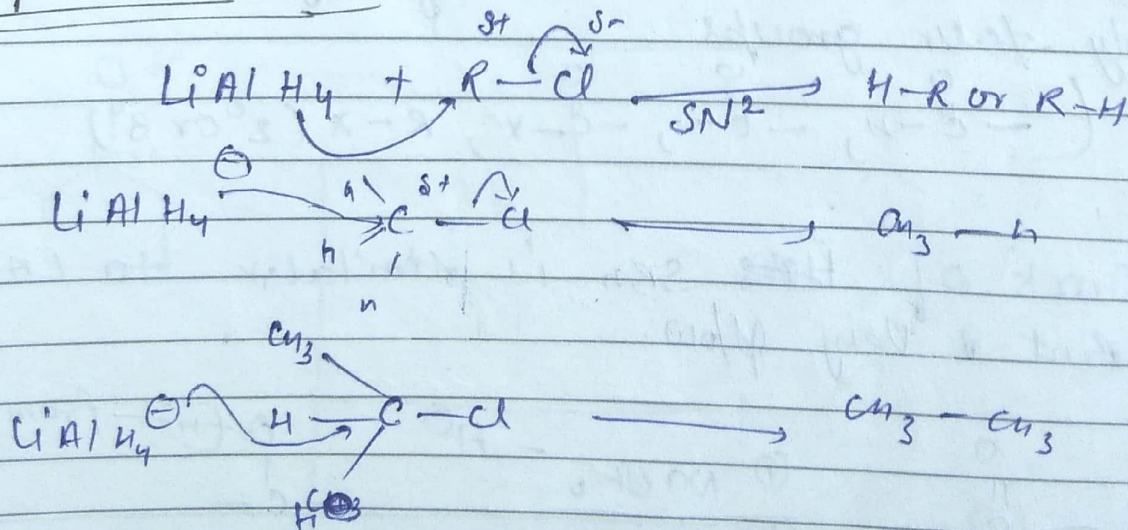
[Race: 19] X
 J.M. 1 to 14 ✓
 Advanced = 1 to 22 ✓

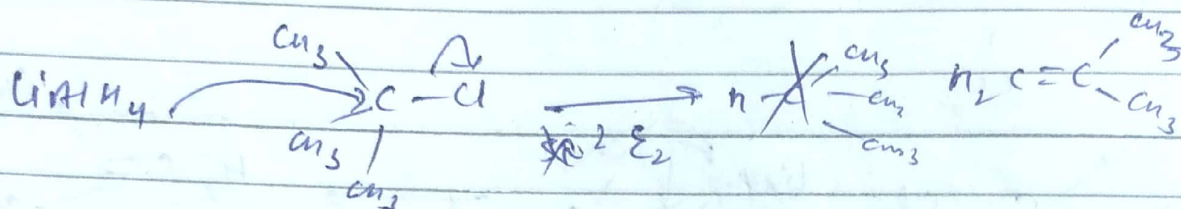
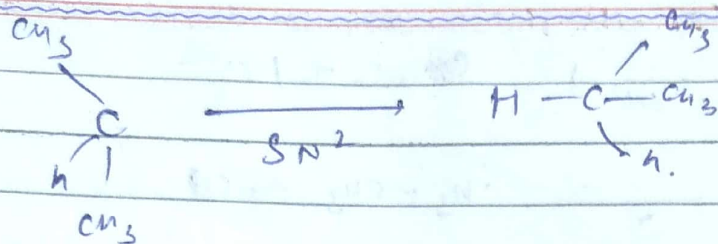




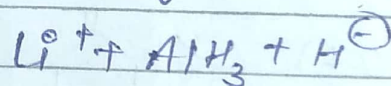
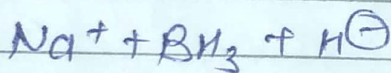
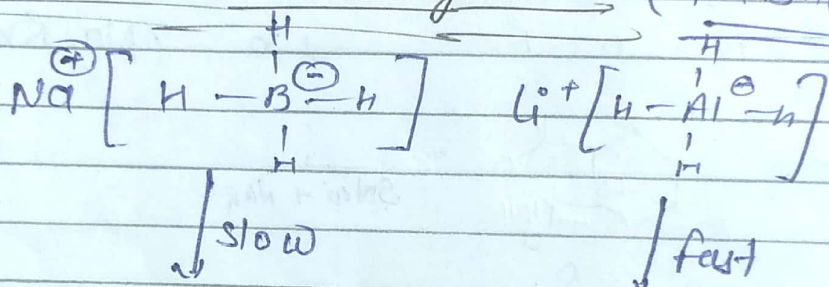


Important Note:





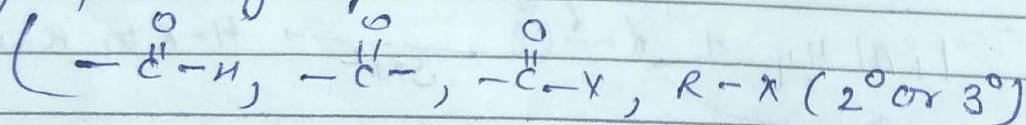
* Reduction with Sodium Borohydride (NaBH₄) (SBH)



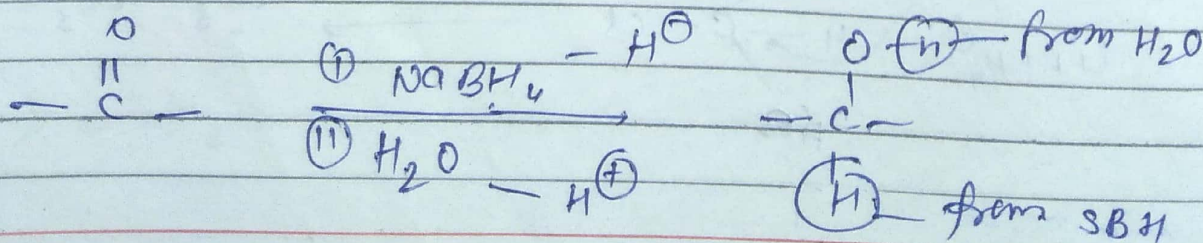
(1) SBH is a weak source of H[⊖]

(2) LAH is a strong source of H[⊖]

* SBH is a weak reducing Agent and reduces only four groups

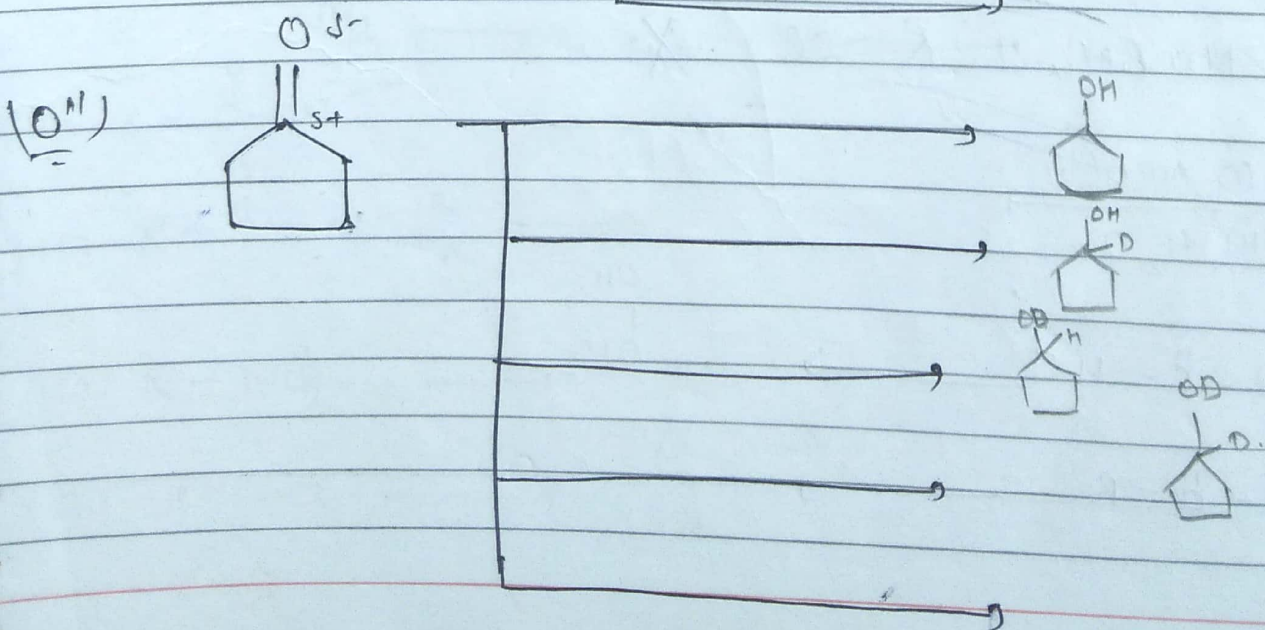
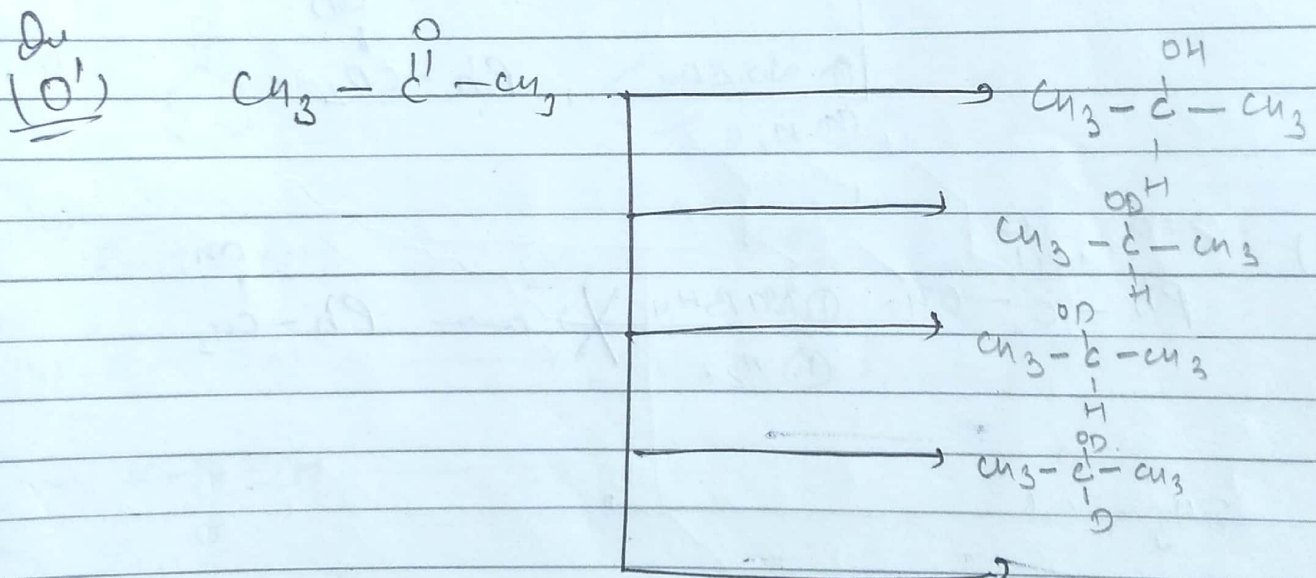
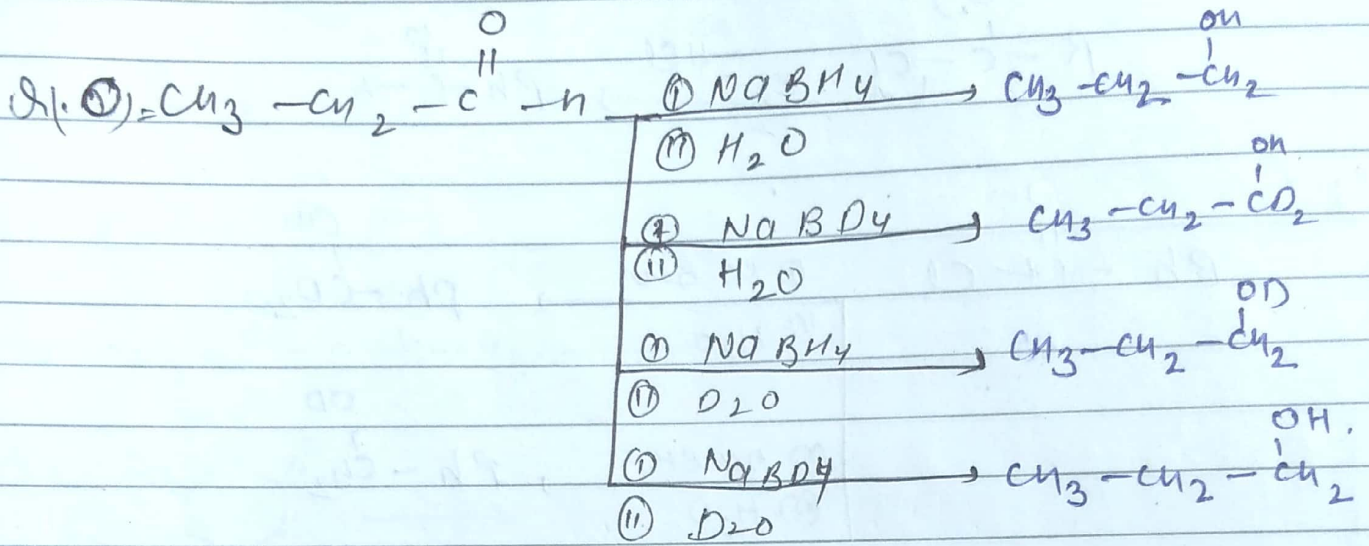


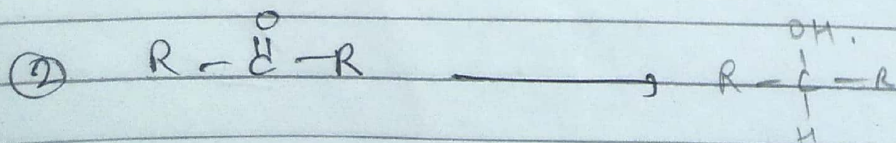
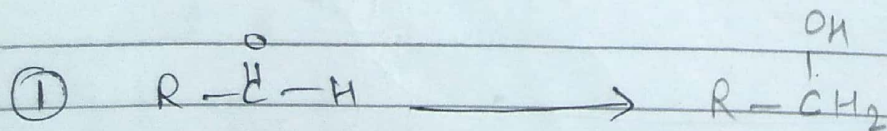
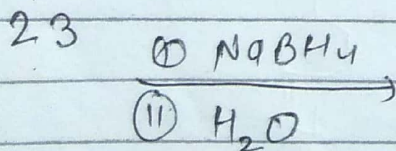
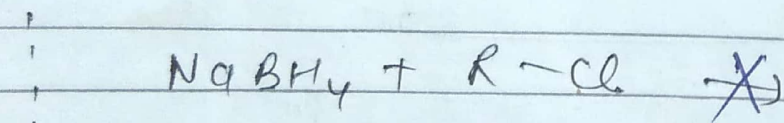
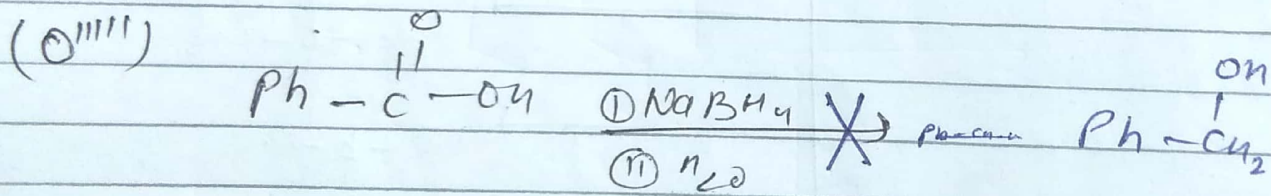
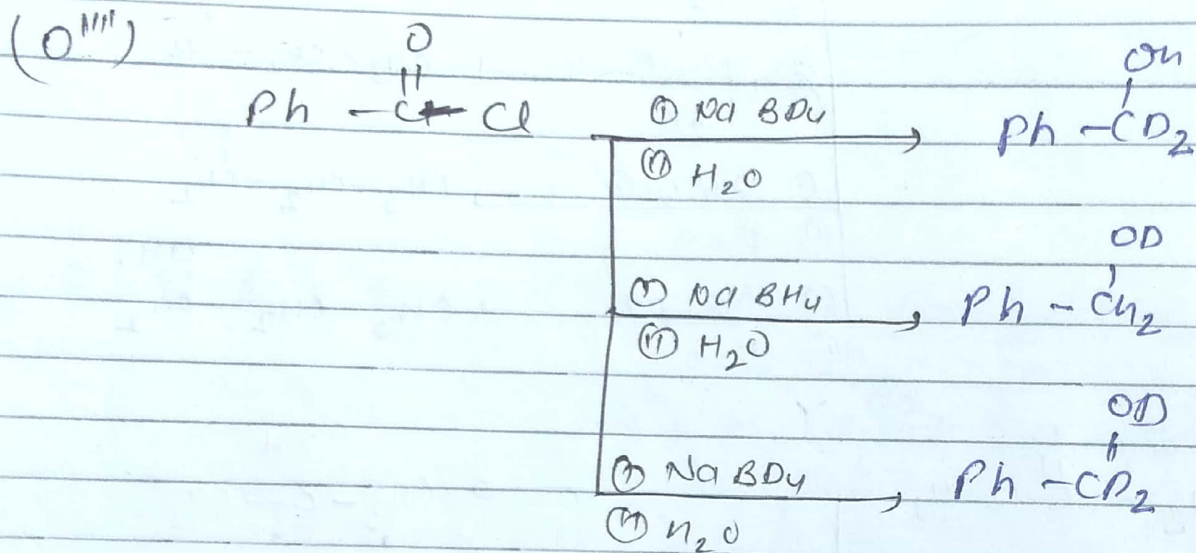
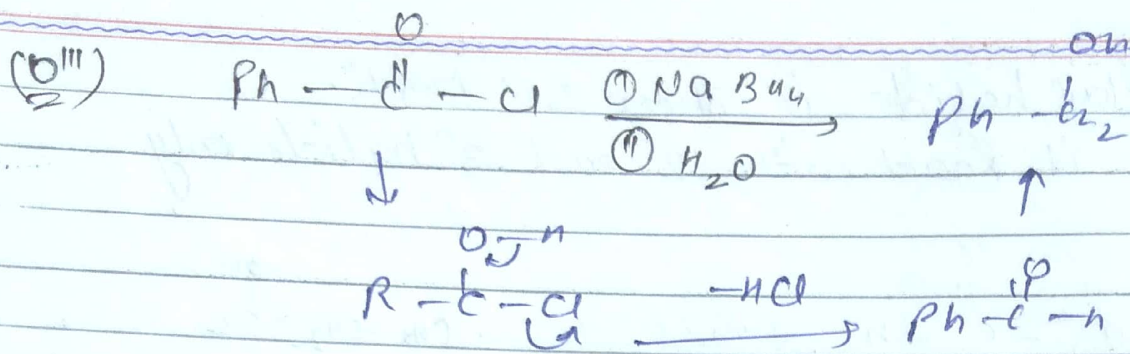
* Work of ~~SBH~~ SBH is similar to LAH but a very slow.

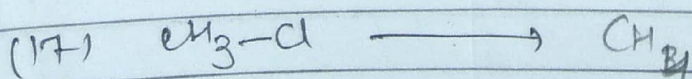
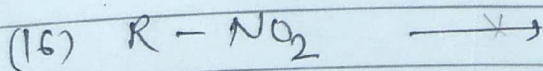
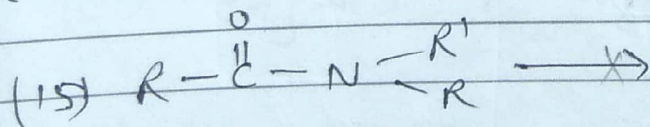
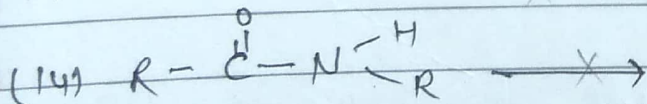
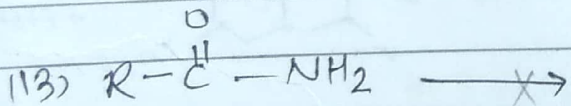
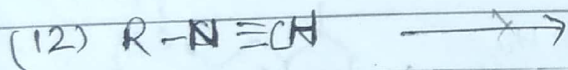
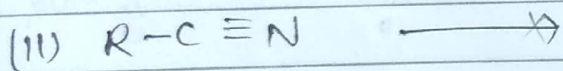
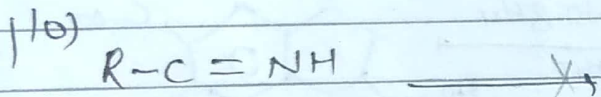
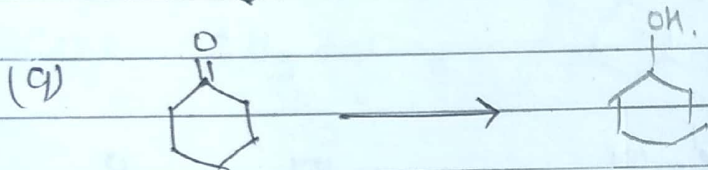
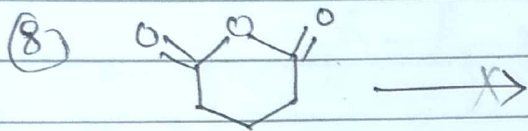
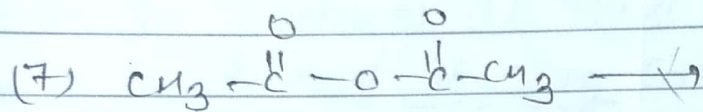
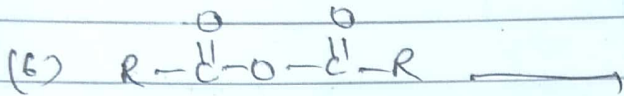
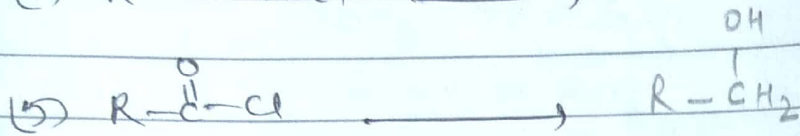
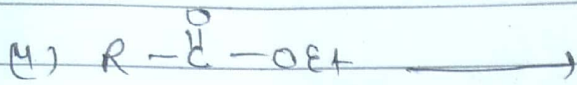
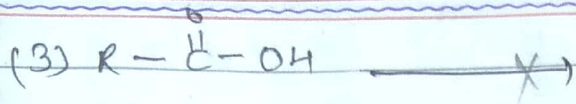


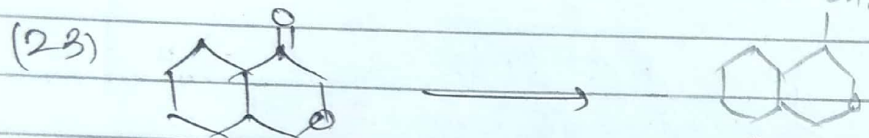
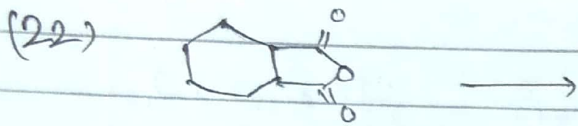
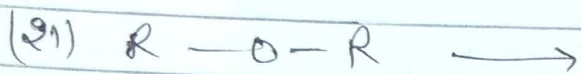
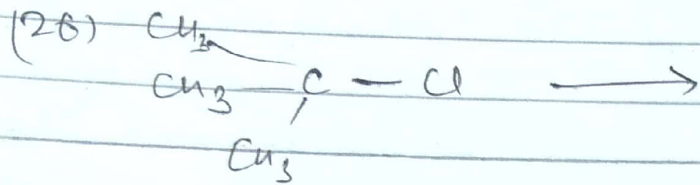
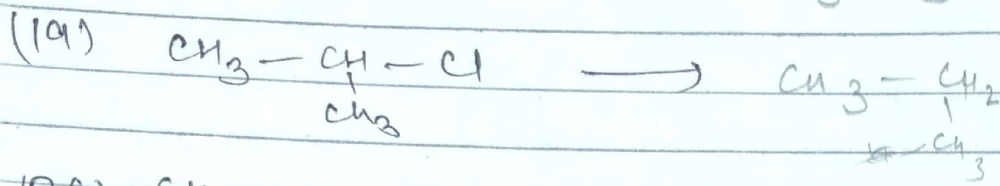
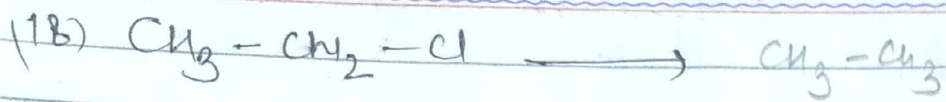
Alcohol ethers
Reduction complete

* with alkyl halide it show SN¹ Mechⁿ.
Therefore it react with 2° and 3° halide only

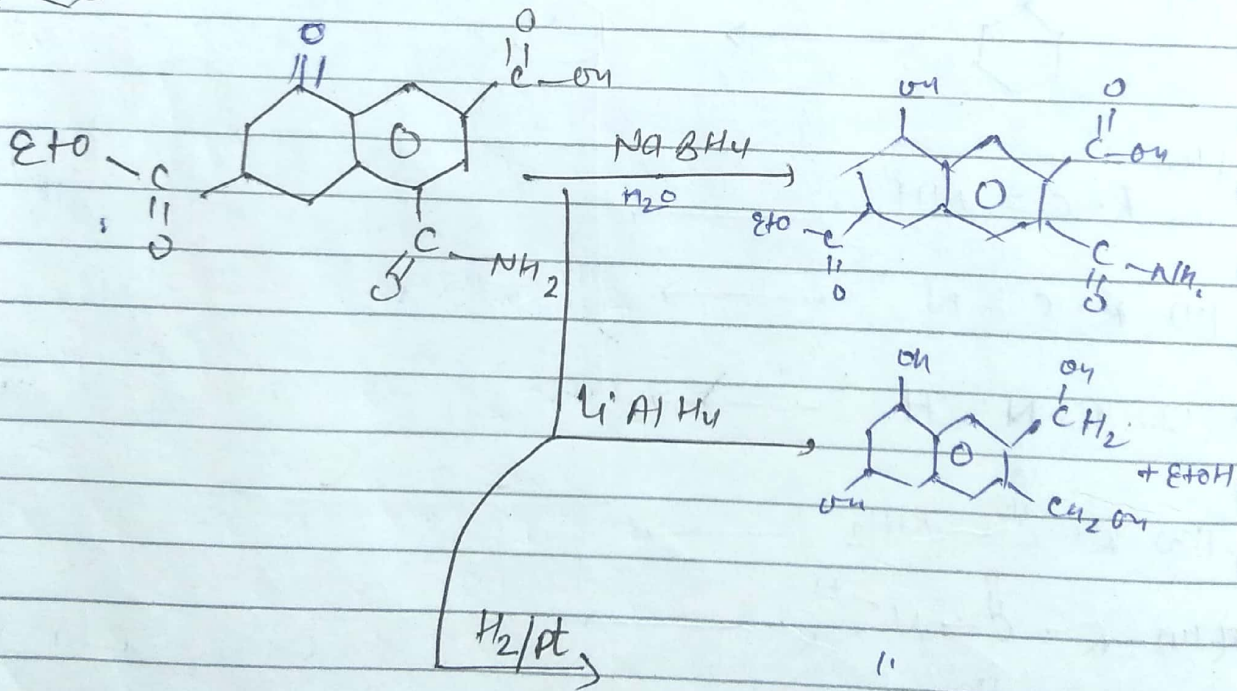




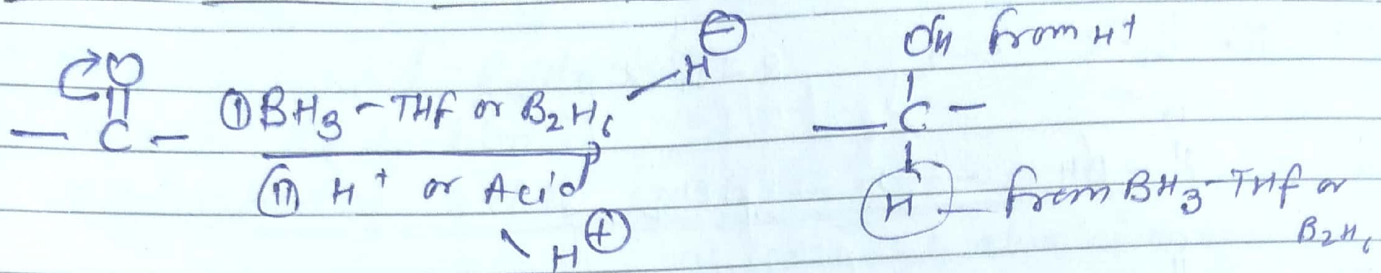




Q. 24

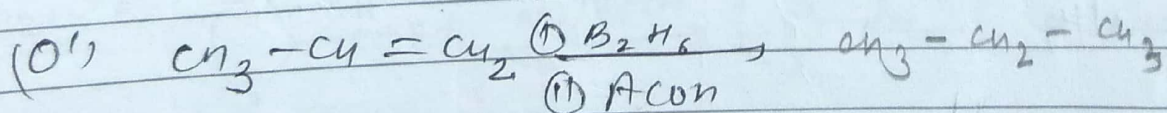
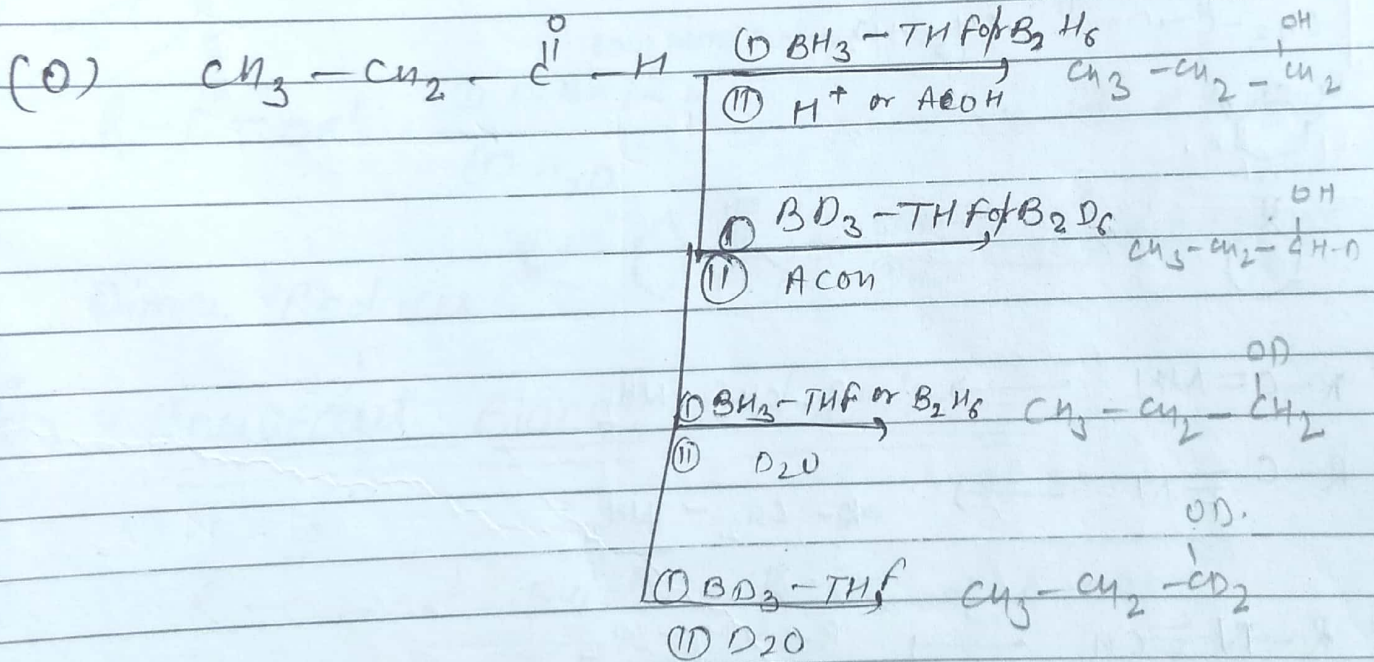


* Reduction by HBr (BH₃-THF / H⁺ or B₂H₆ / H⁺)



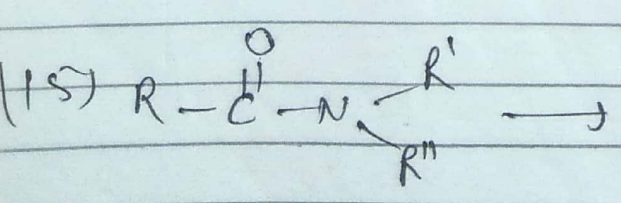
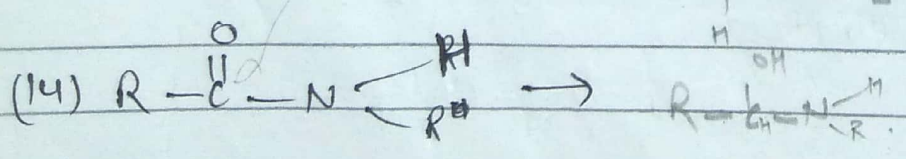
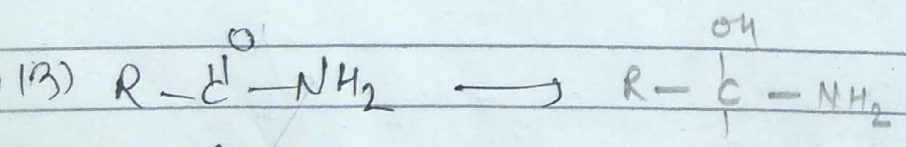
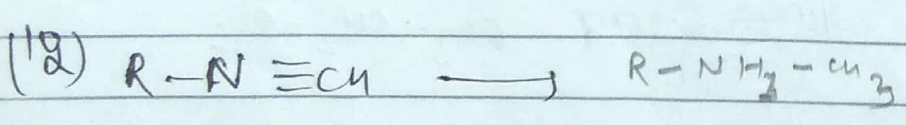
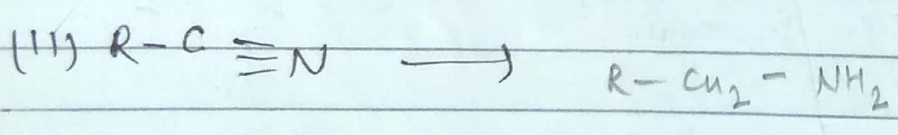
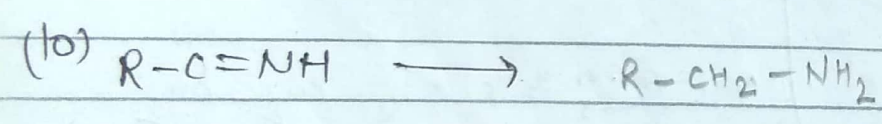
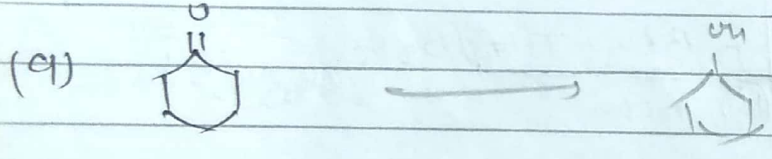
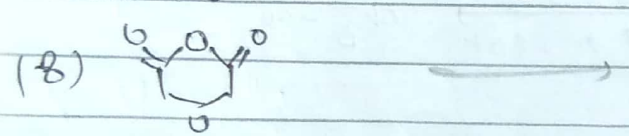
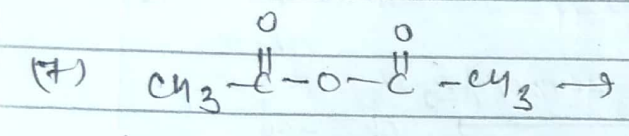
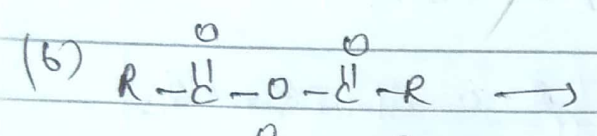
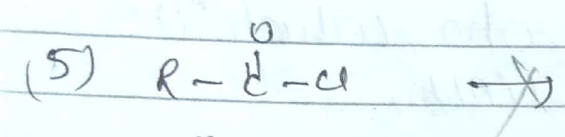
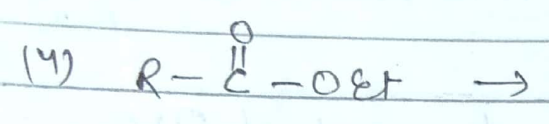
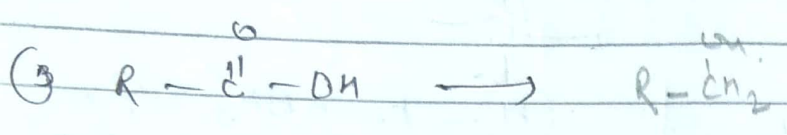
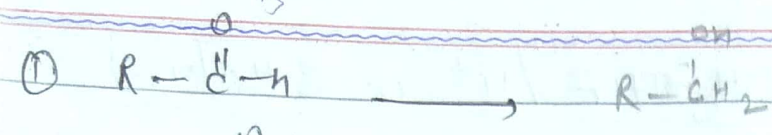
* It reduces all those comp. which are reduced by H₂ catalyst & LiAlH₄

Except $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$ or R-X, R-O-R, R-NO₂



1 5x

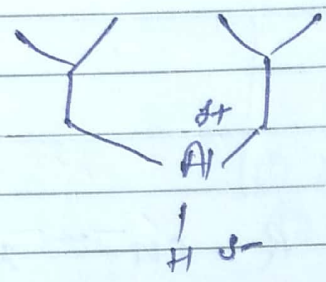
Elektro-
Hydrolyse



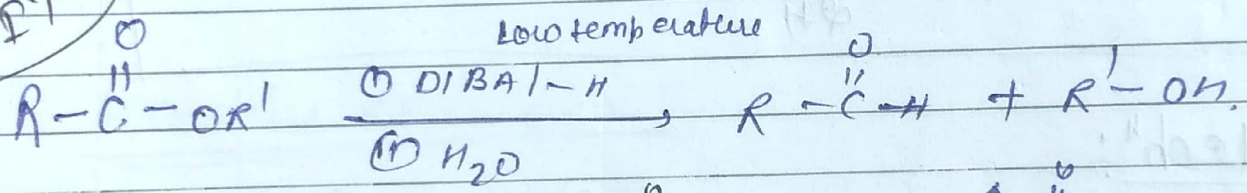
other

Some Important Reductions

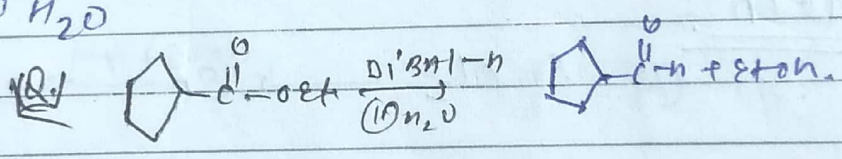
- ① Rosenmund Reduction
- ② Birch Reduction
- ③ Reduction of ester with DIBAL-H
Diisobutyl aluminium hydride



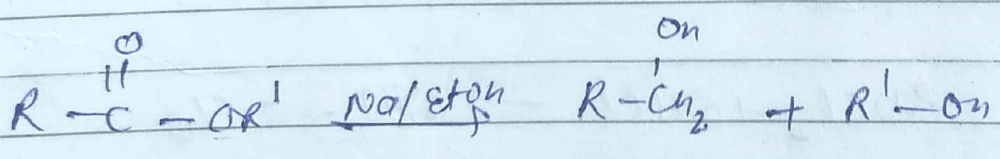
IPT



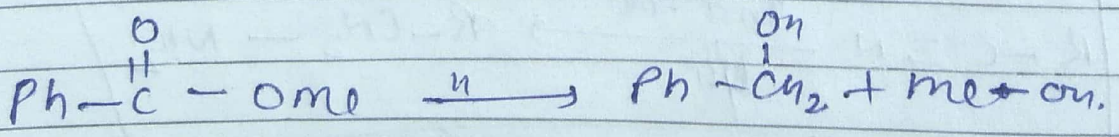
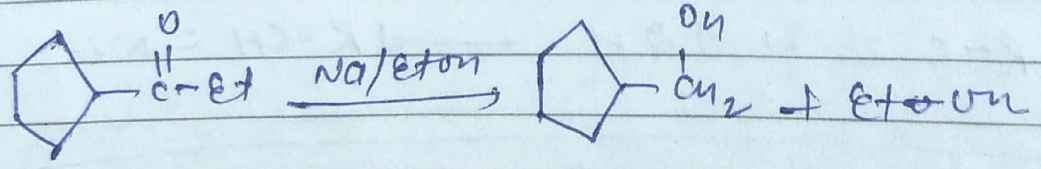
Dimer Reduces



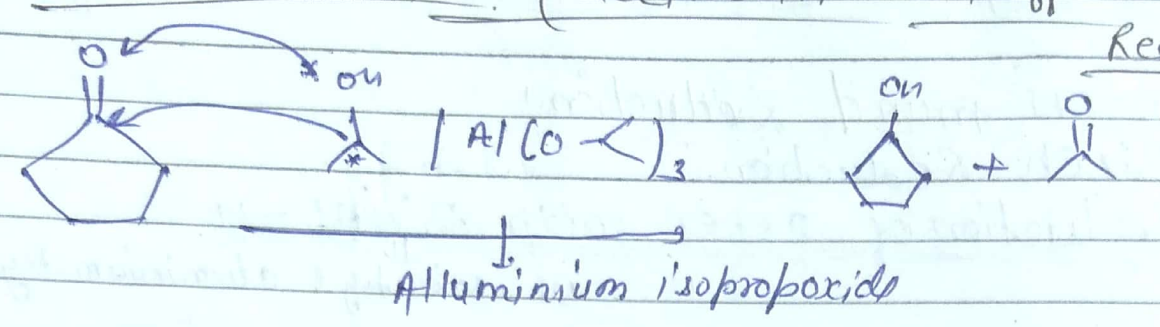
④ Bouveault Blanc Reduction



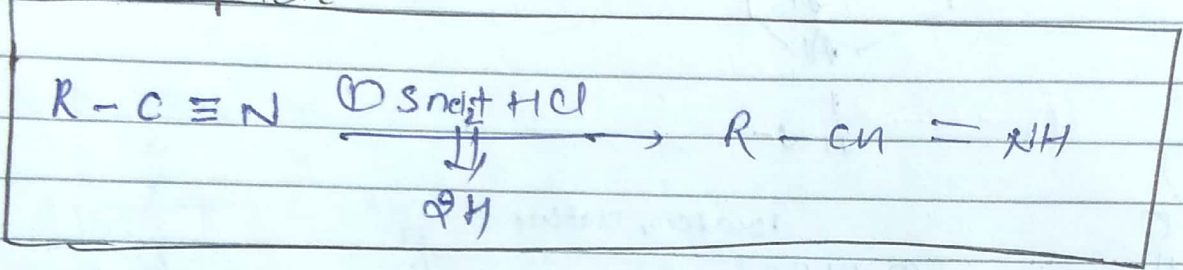
Mech:



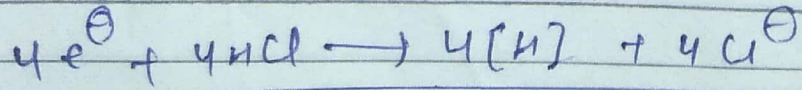
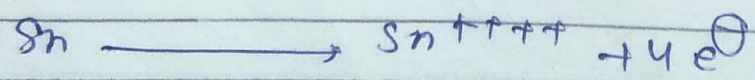
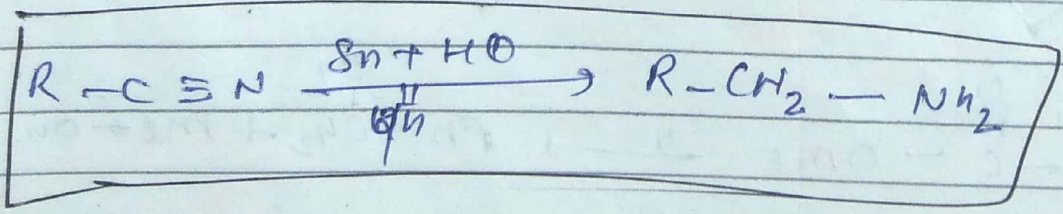
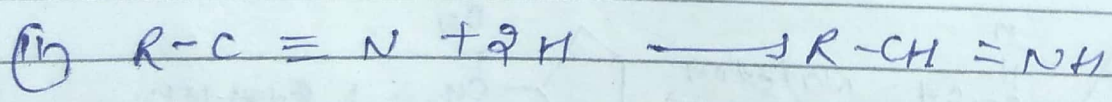
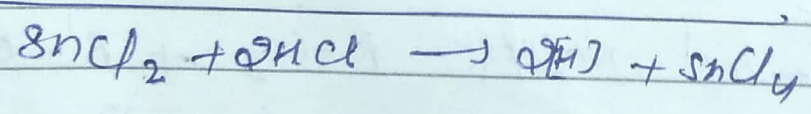
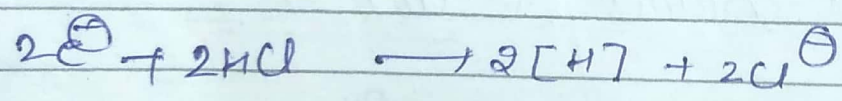
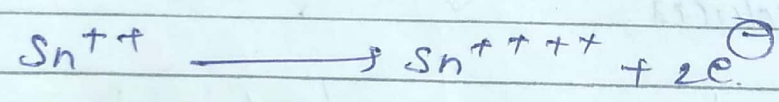
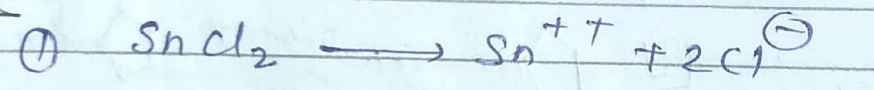
*
 (5) MPV - Reduction: (Meerwein-Ponndorf-Verley Reduction)

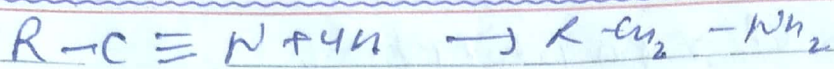


(6) Mendius Reduction:
 = Stephen

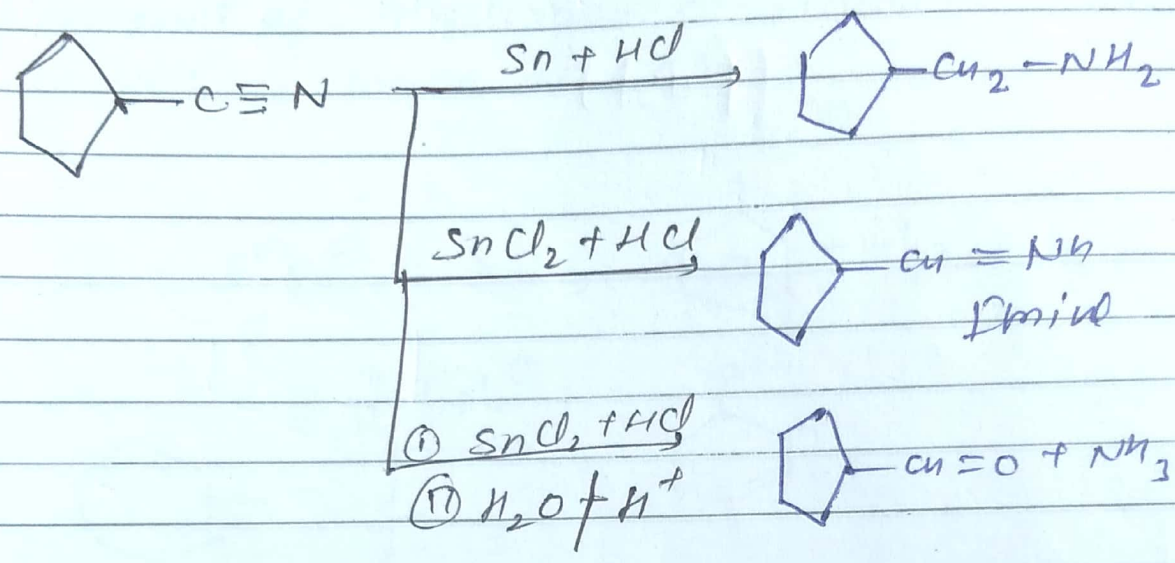


* Mechⁿ:

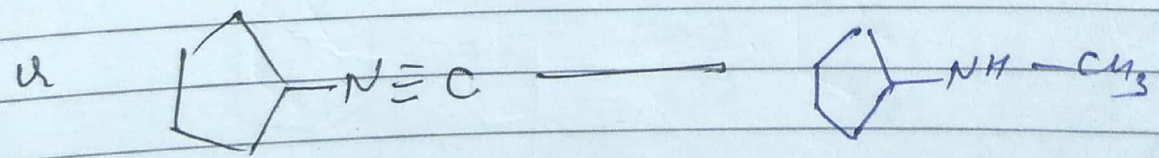
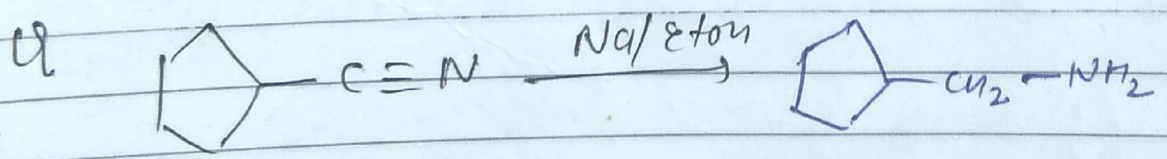
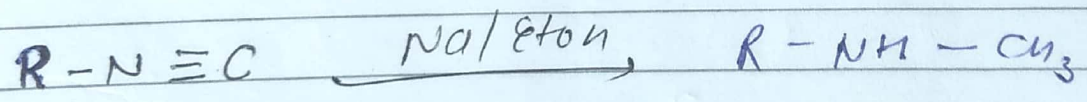
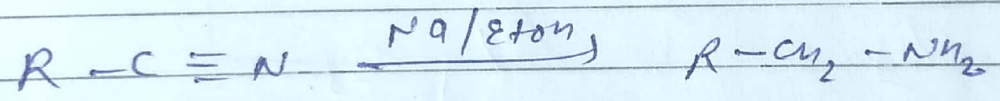




☆☆☆
AD☆



(7) Mendius reduction :-



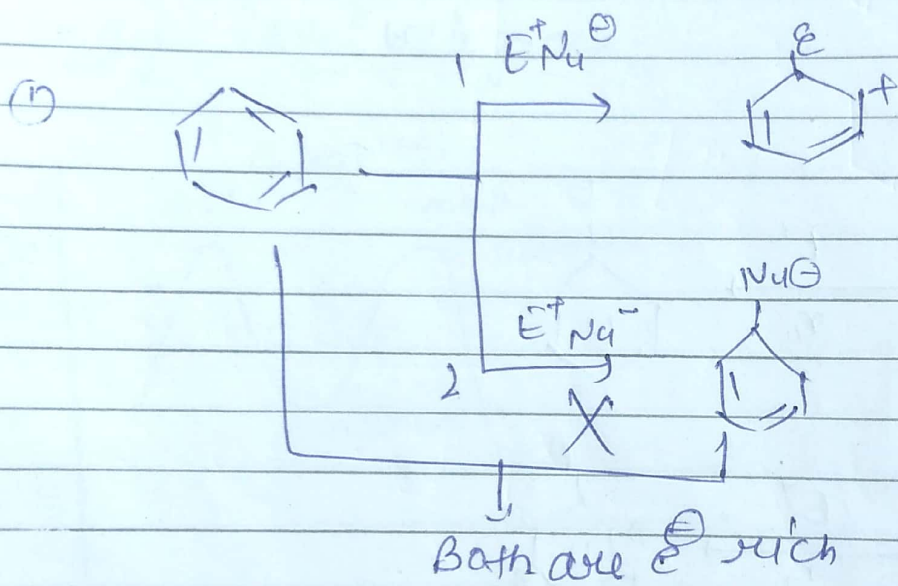
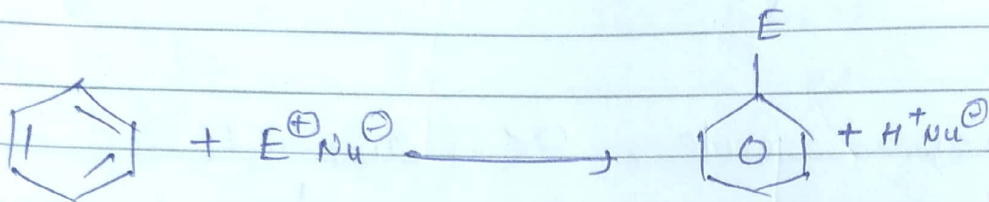
$R-F < R-Cl < R-Br < R-I$

$Ph-F > Ph-Cl > Ph-Br > Ph-I$

(EAS) Electrophilic Aromatic Substitution

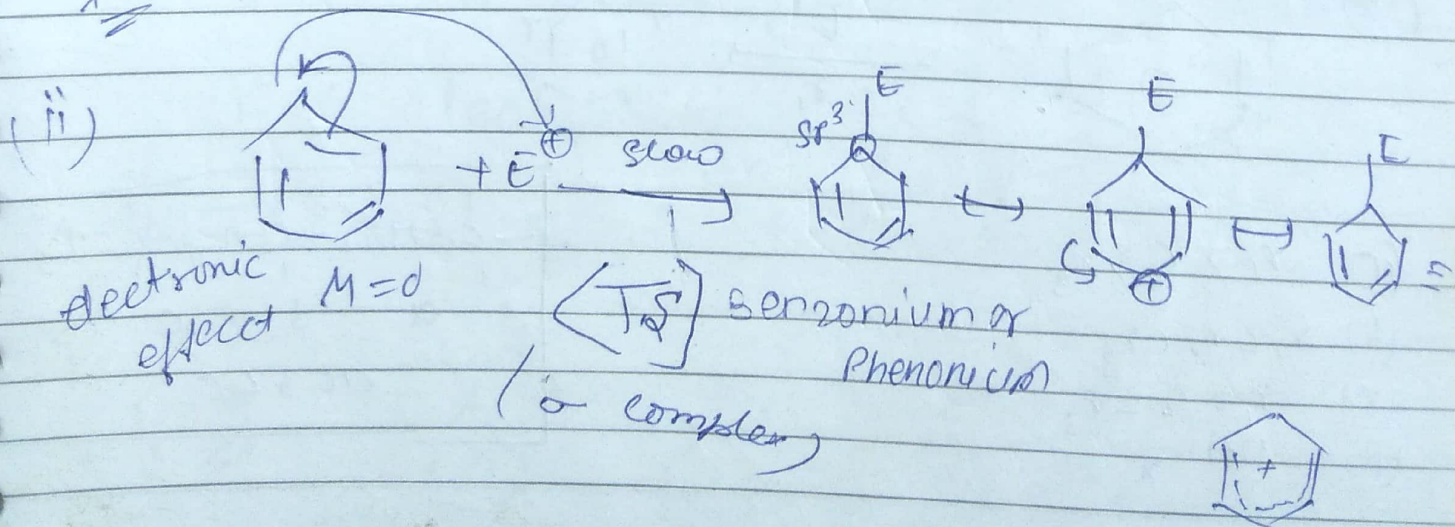
The replacement of Hydrogen of Aromatic Compound by electrophile is known as (EAS).

Ex:

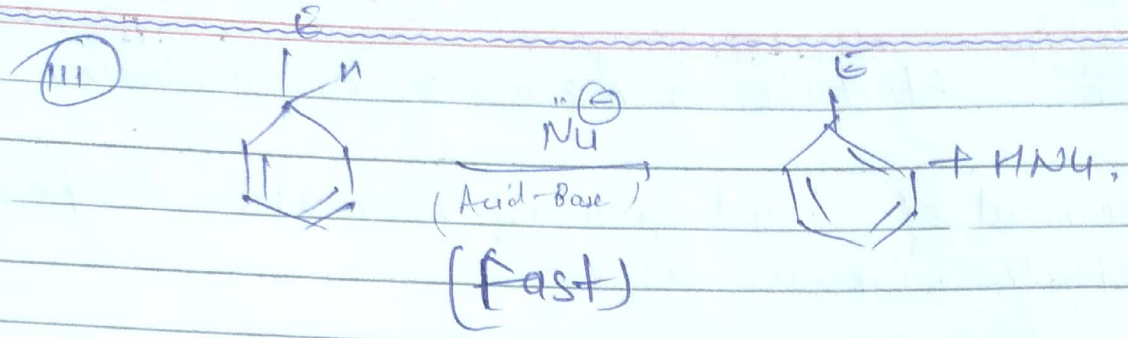


Mechⁿ

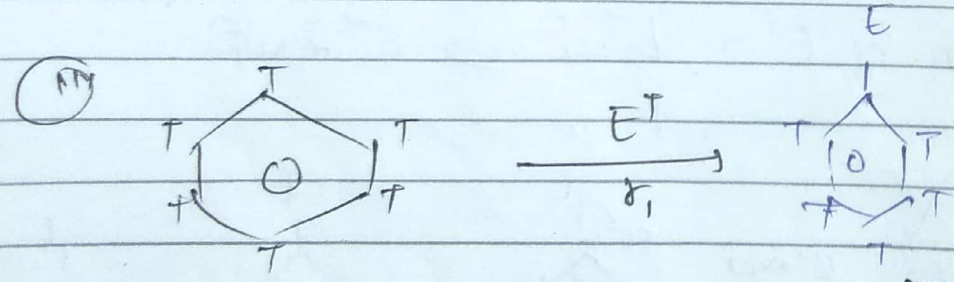
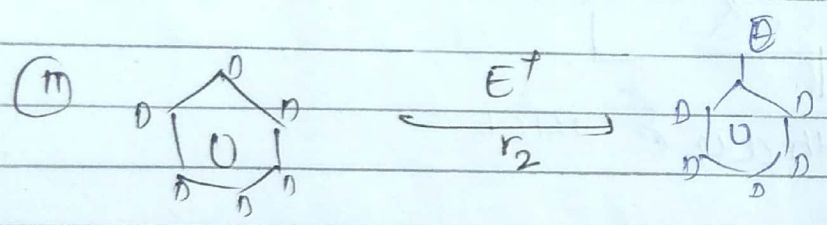
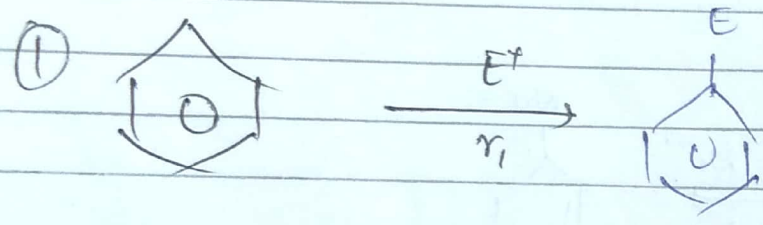
(i) Generation of $\text{E}^{\oplus} \Rightarrow \text{E}^{\oplus}\text{Nu}^{\ominus} \rightleftharpoons \text{E}^{\oplus} + \text{Nu}^{\ominus}$



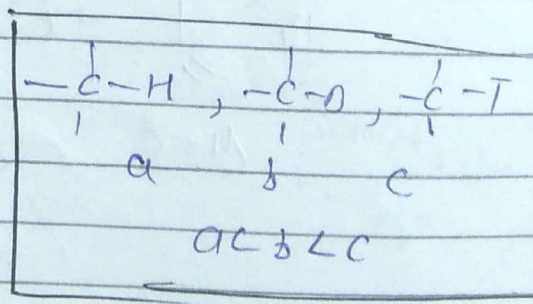
Behaviour



Kinetics: Rate \propto (Substrate) (E^\ddagger)
 \downarrow
 a)

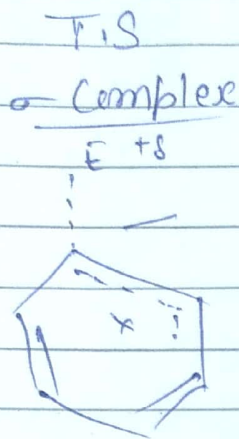


- (a) $r_1 > r_2 > r_3$
- (b) $r_1 < r_2 < r_3$
- (c) $r_1 = r_2 = r_3$
- (d) Not

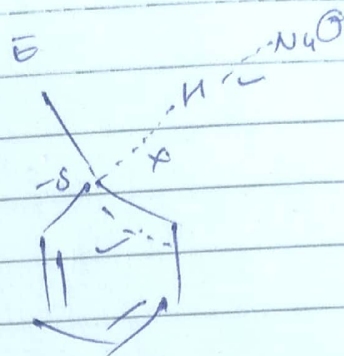


Comp.

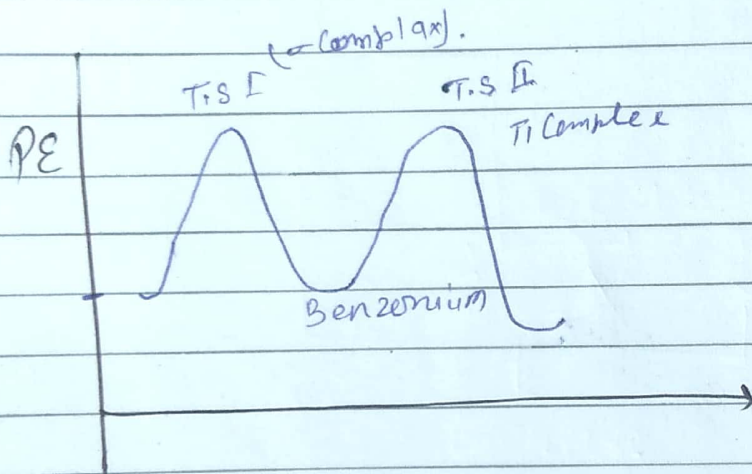
Slow step



π Complex



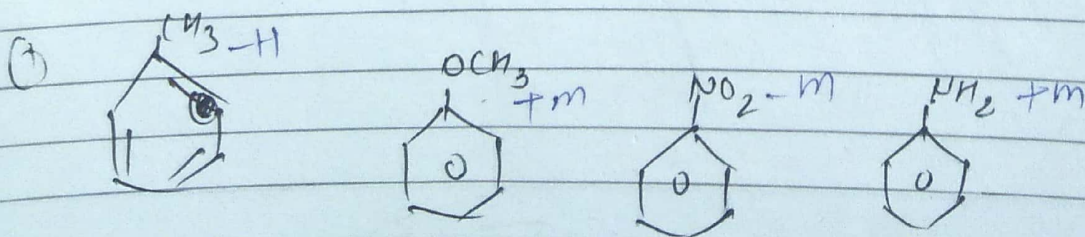
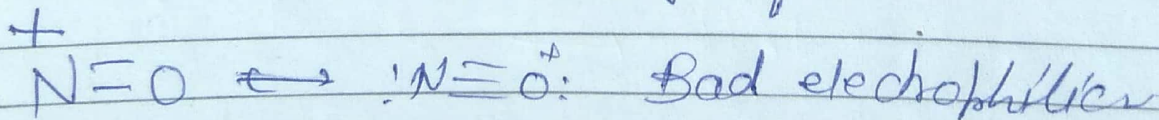
* Energy level diagram:



* Rate of R_N^+

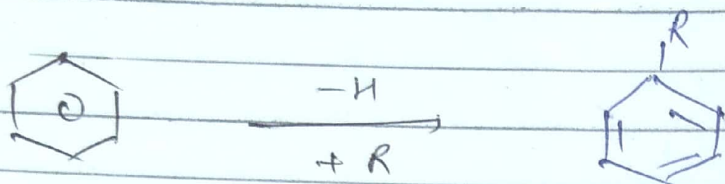
$r \propto$ nucleophilicity of Aromatic Compound

$r \propto$ electrophilicity of E^+



4 > 2 > 1 > 3

* Alkylation (Friedel-Craft Alkylation).



Attacking $E^+ \rightarrow R^+$

Reagent = $R-X + \text{Lewis Acid}$

Order of Lewis Acid $\Rightarrow \text{AlCl}_3 > \text{BF}_3 > \text{SnCl}_4 > \text{FeCl}_3 > \text{SnCl}_2$

Attack $E^+ = C^+$ (free)

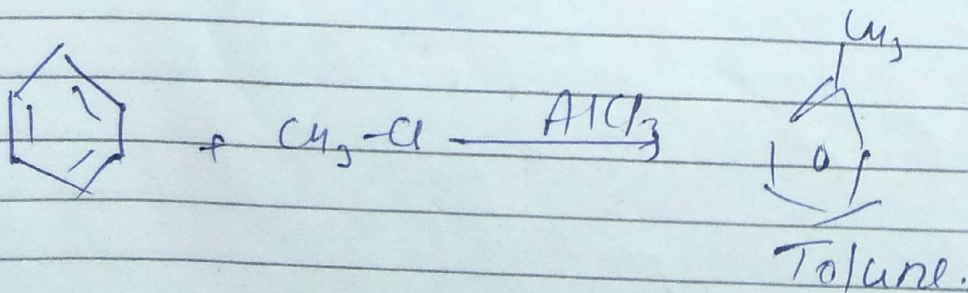
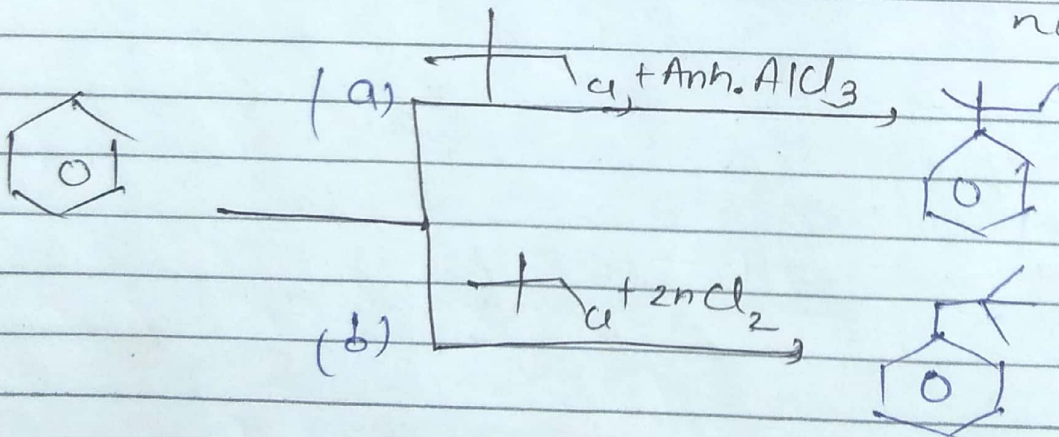
Rearrangement is possible

$2nd \text{ } Cl_2$

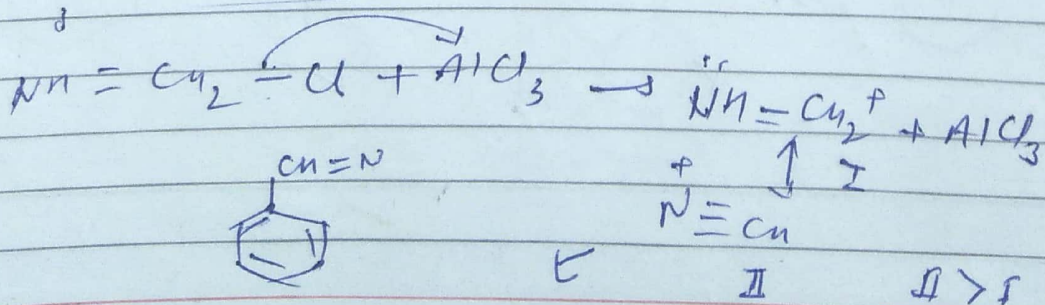
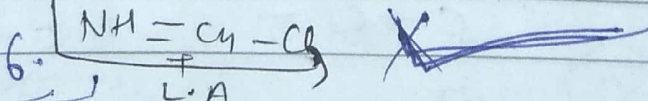
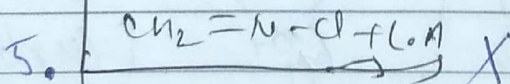
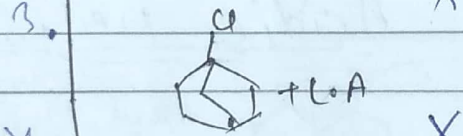
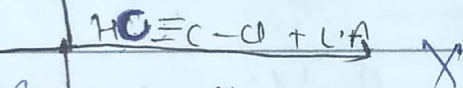
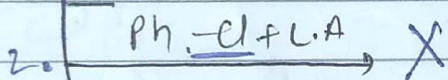
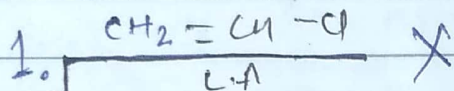
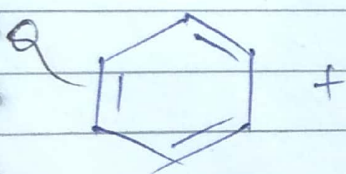
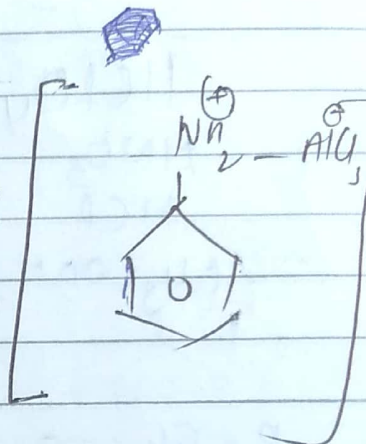
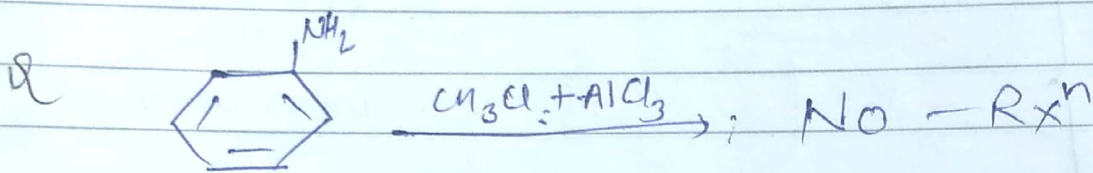
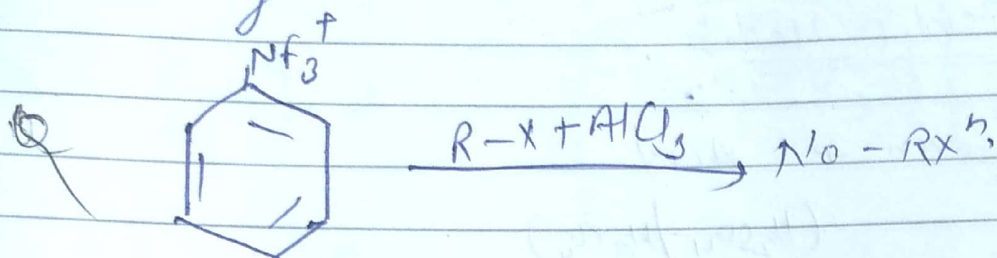
$A \cdot E^+ = \text{Complex}$

(Carbocation) Rearrangement is not possible

Ex:



* Highly deactivated B.R. does not give alkylates

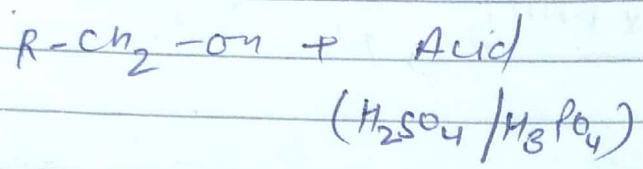


character

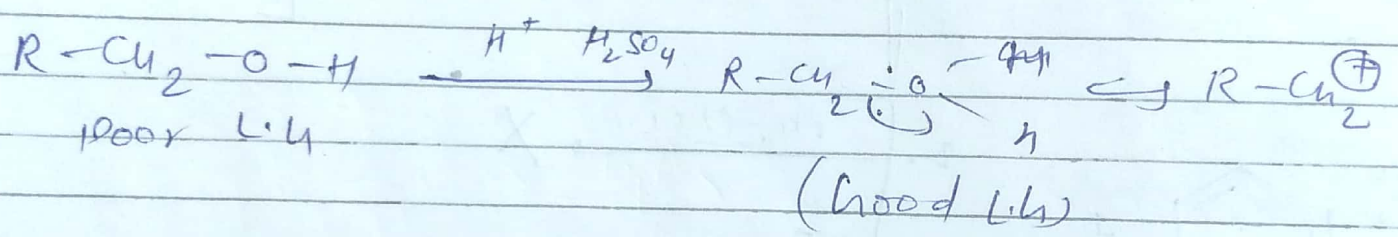
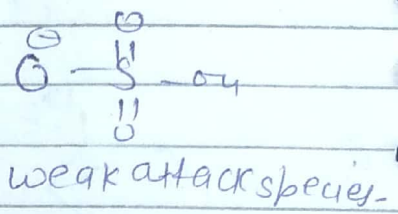
HClO₄

* Other sources of C⁺

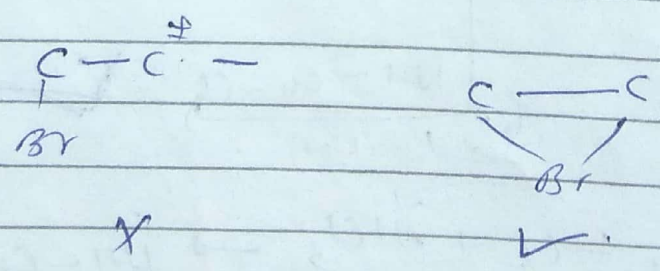
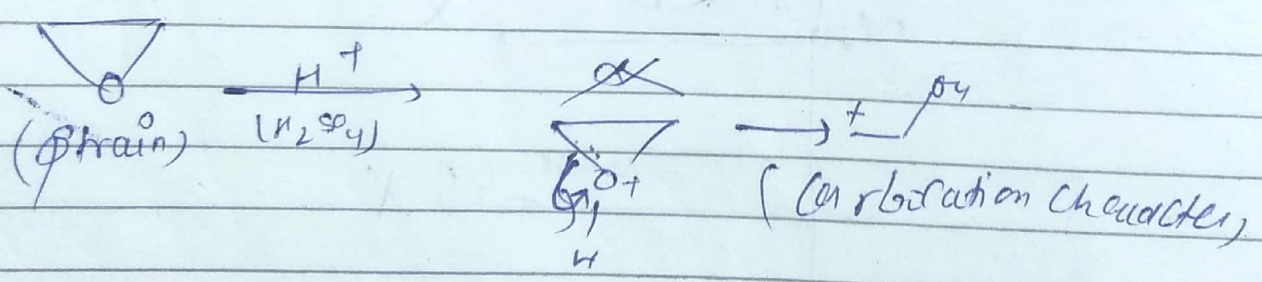
(a) Alcohol in Acidic Med.



- HClO₄
 - HNO₃
 - HCl
 - CH₃COOH
- } (1) H⁺



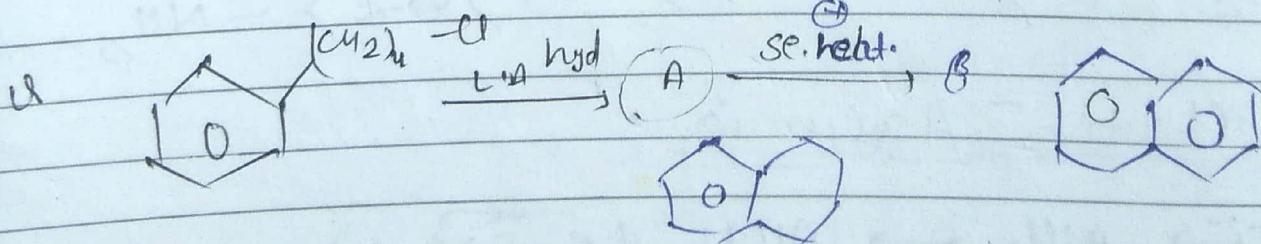
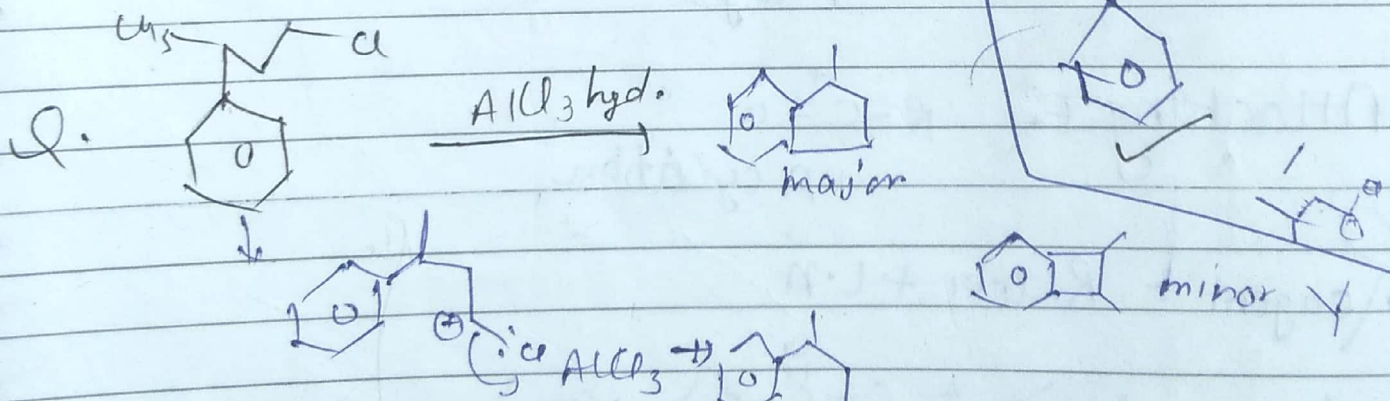
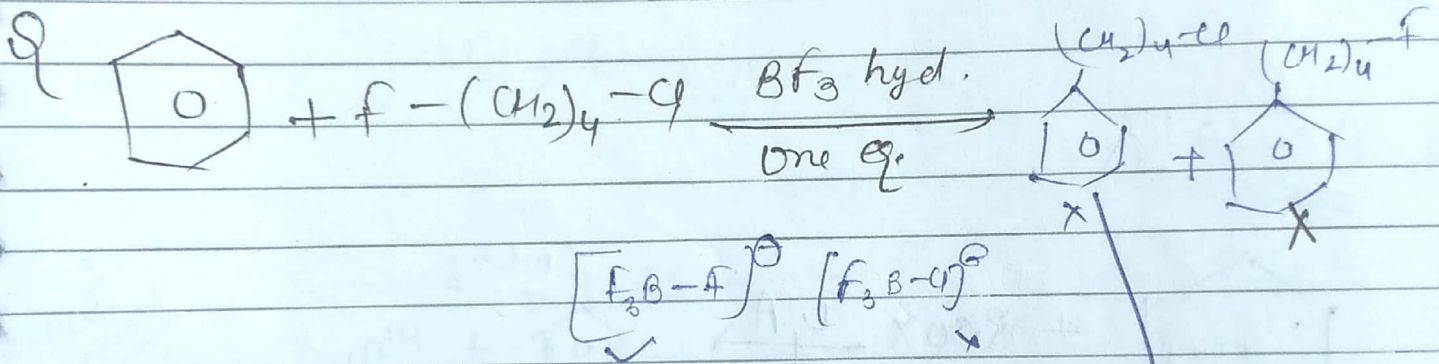
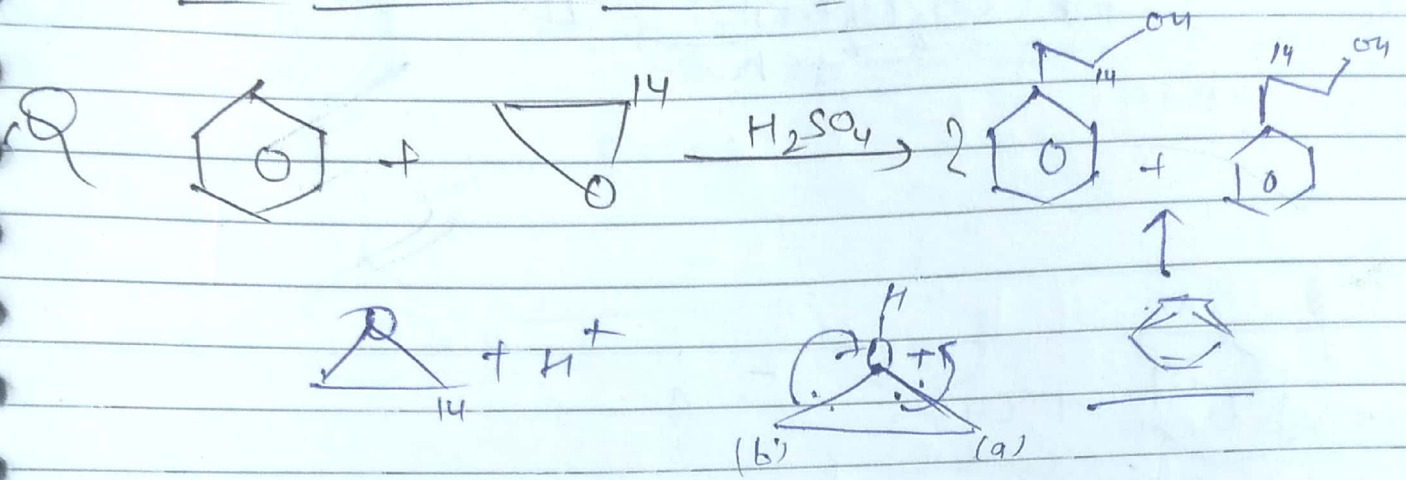
(b) Ethers in Acidic Med.

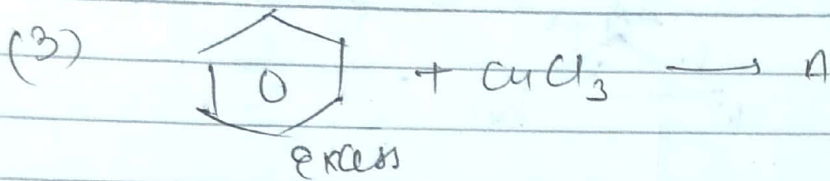
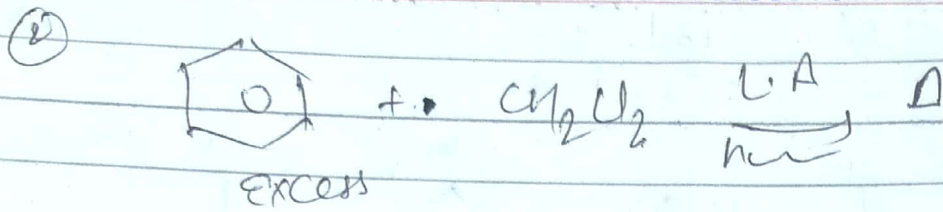


Size ↓ Bu ↓

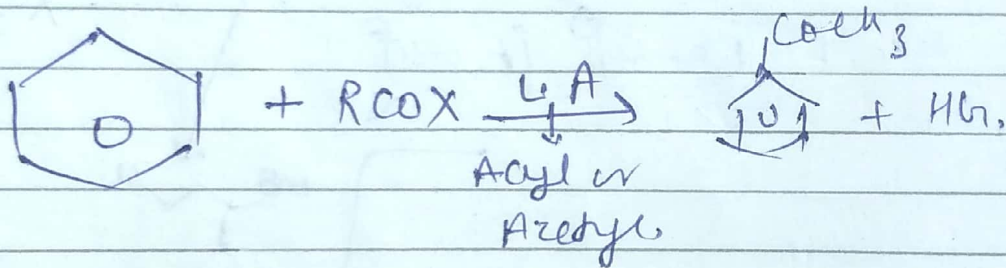
Concepts

(c) Alkenes In Acidic Med. :-





* Acylation:

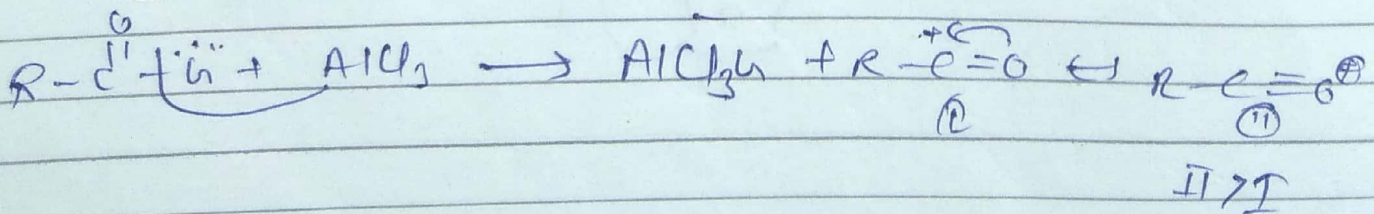


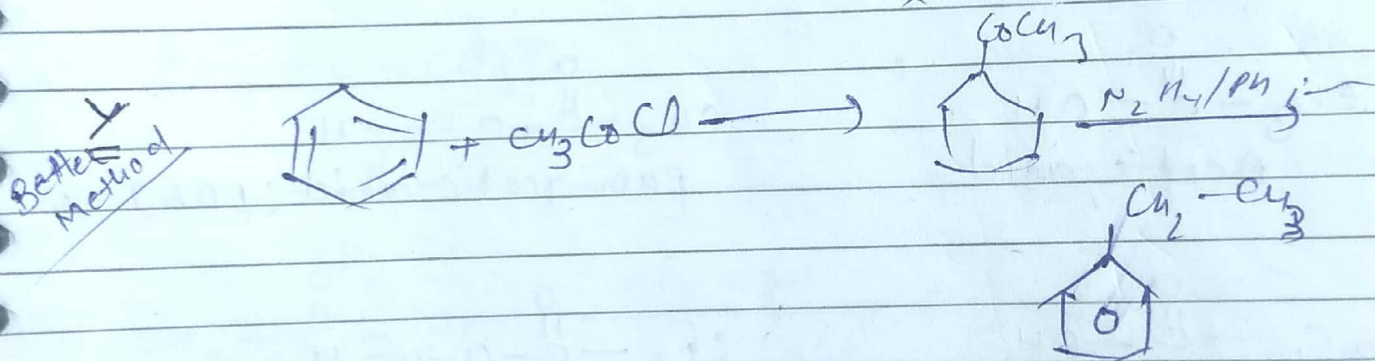
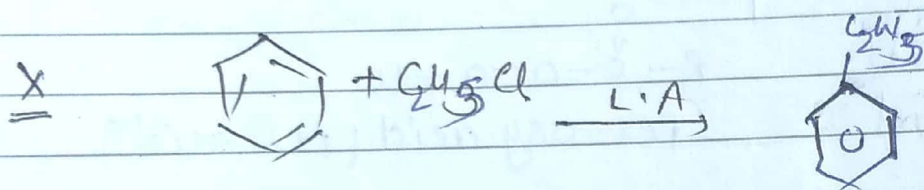
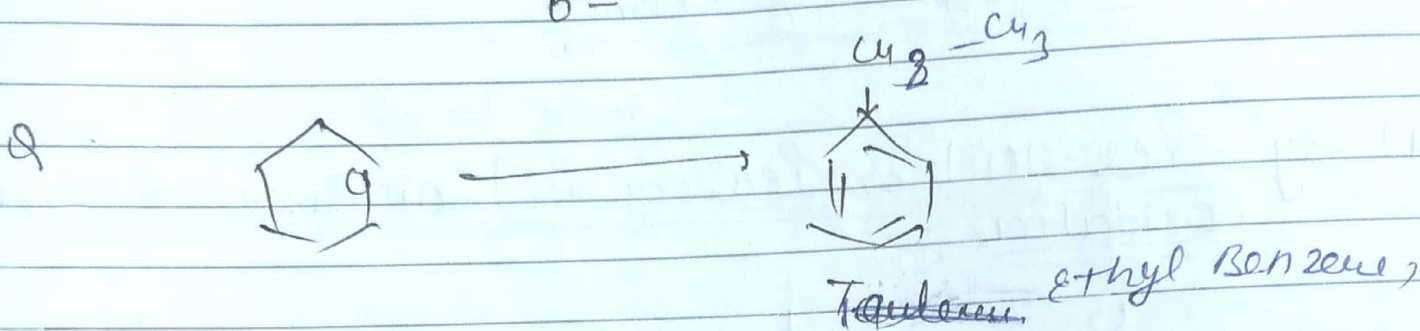
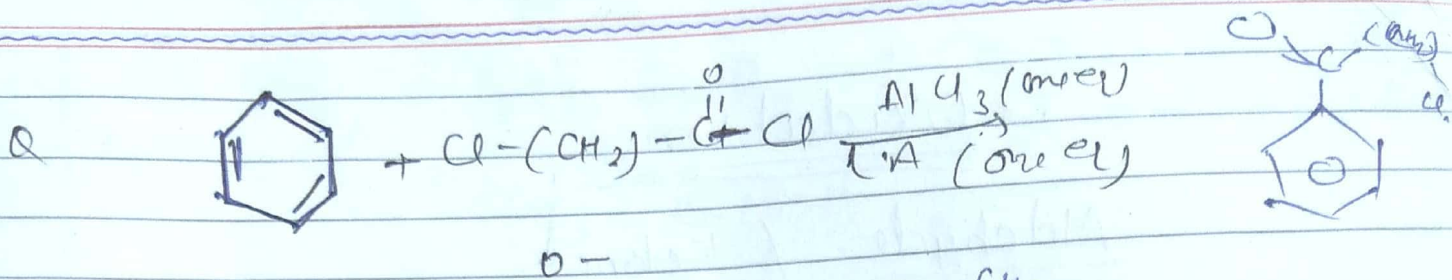
Attacking E^+ R-C^+=O
 Acylation

Reagent = RCO-Br + L.A

Br = X > -C(=O)-R > -OH > -OR > -NH2

* Generation Acylium ion:





SBG STUDY