

Amines

Preparation

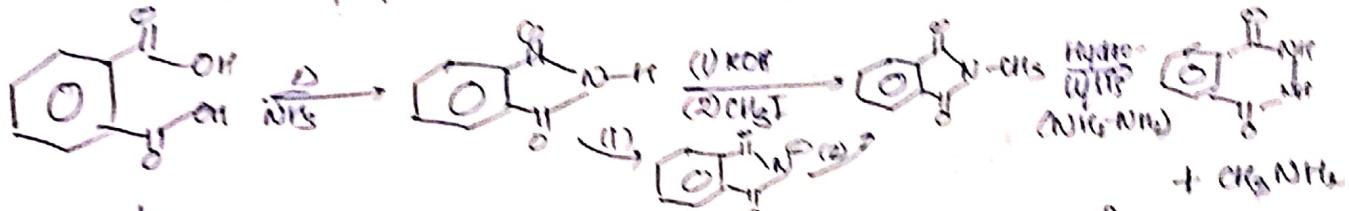


If Rx is excess,

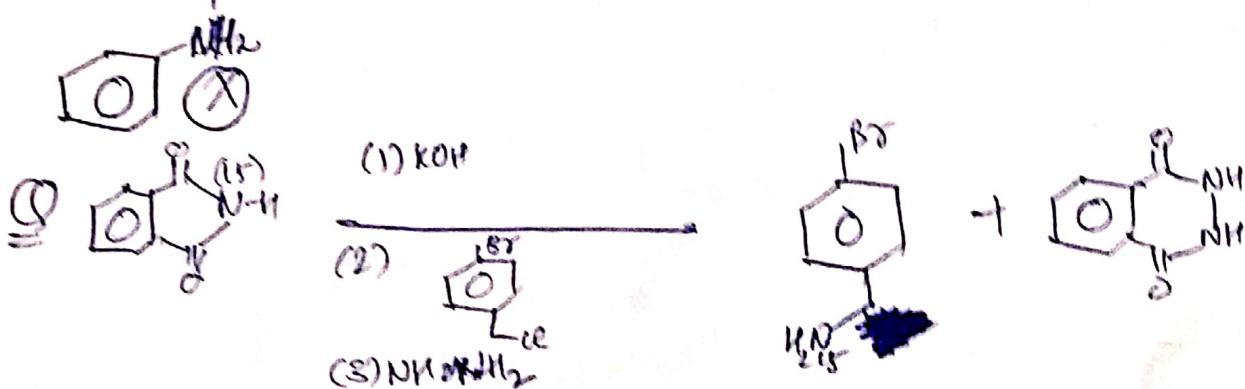
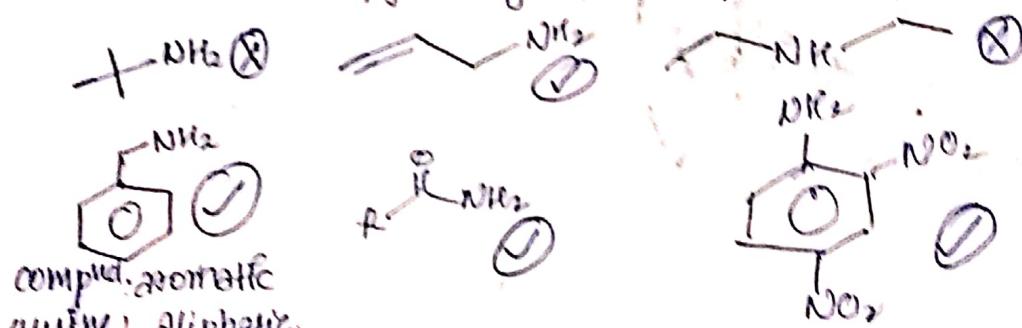


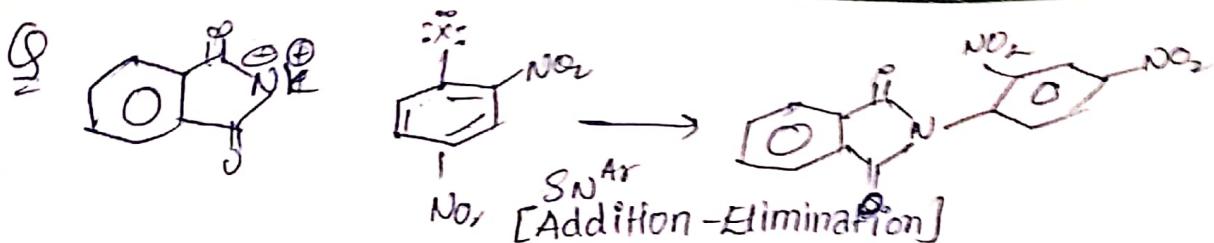
(2) Gabriel phthalimide synthesis.

→ Best method to prepare β -amine (not all)-

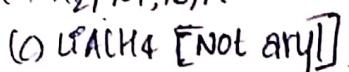
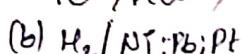
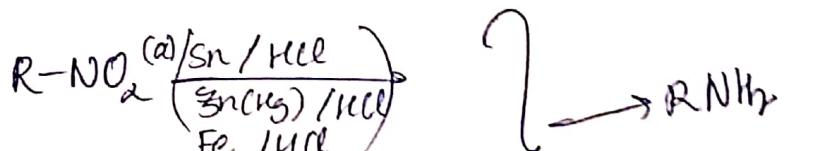
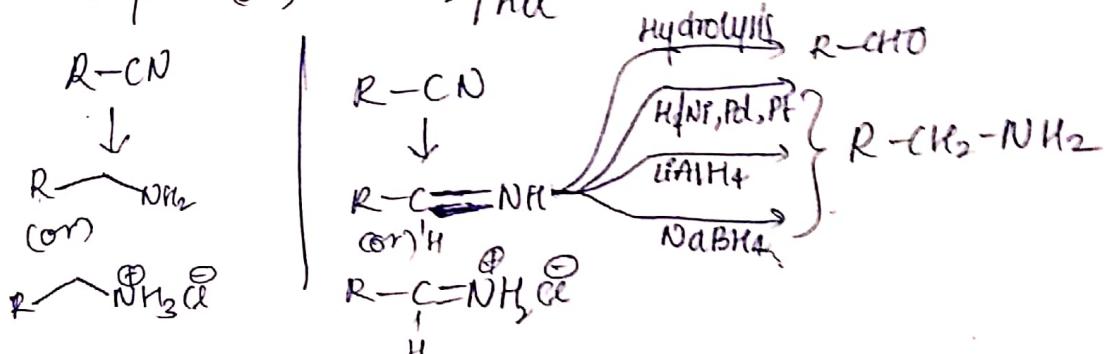


Example which of following can be synthesised by this method?

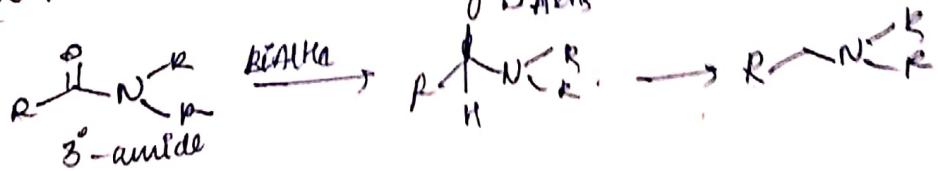
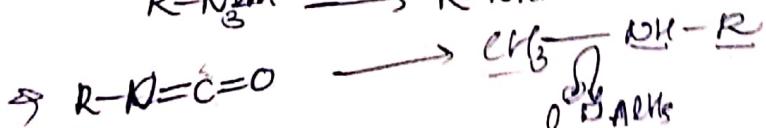


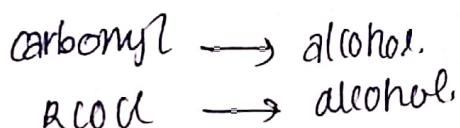
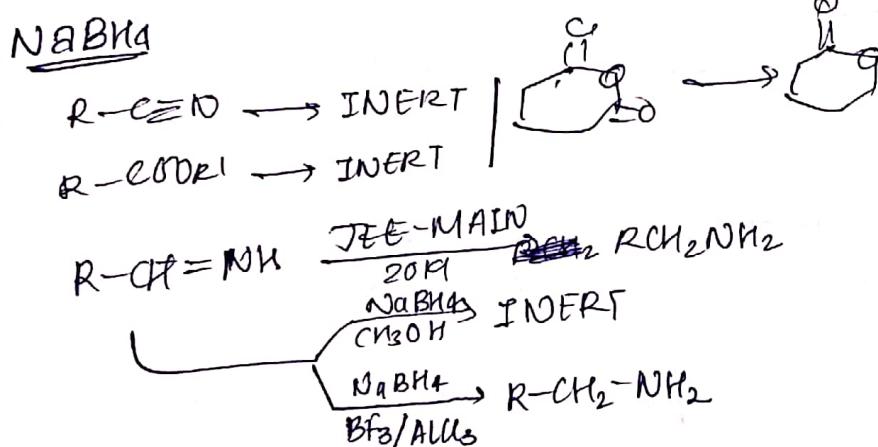
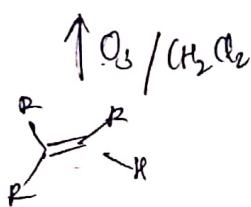
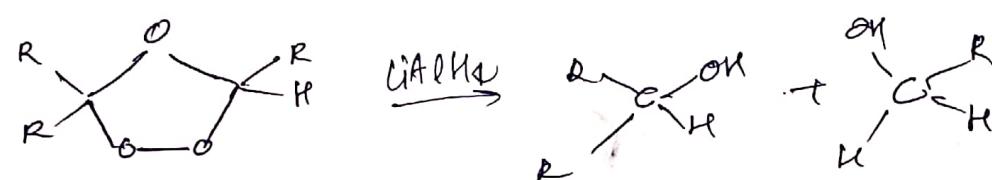
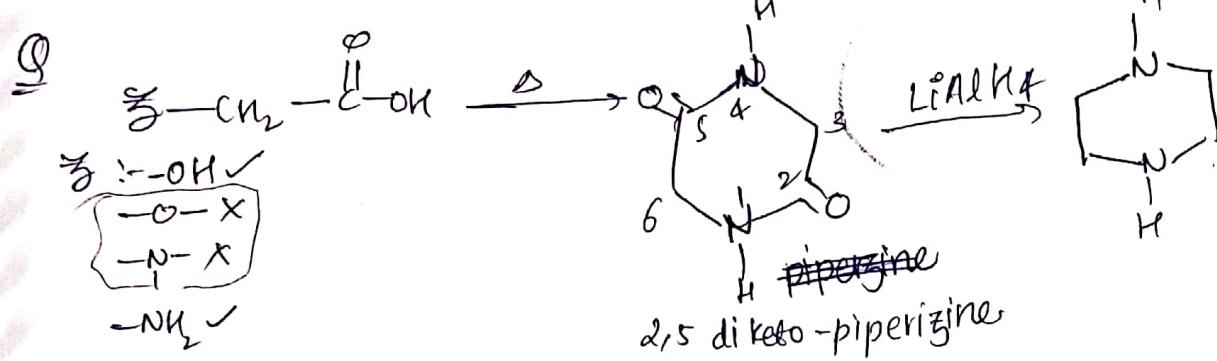
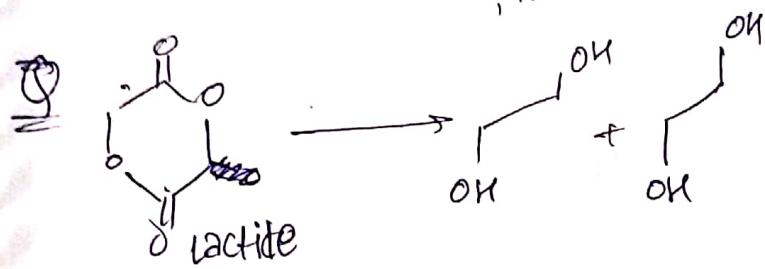
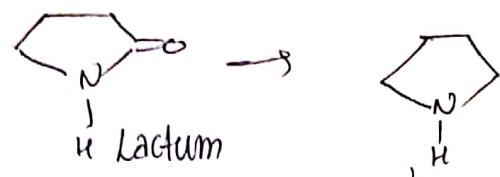


(3) Sn/HCl (or) SnCl_2/HCl

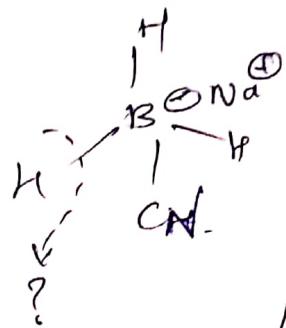
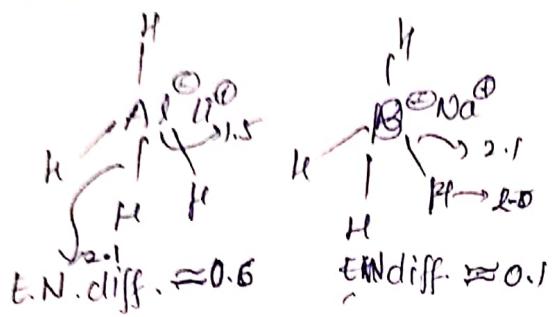


Function of LiAlH_4



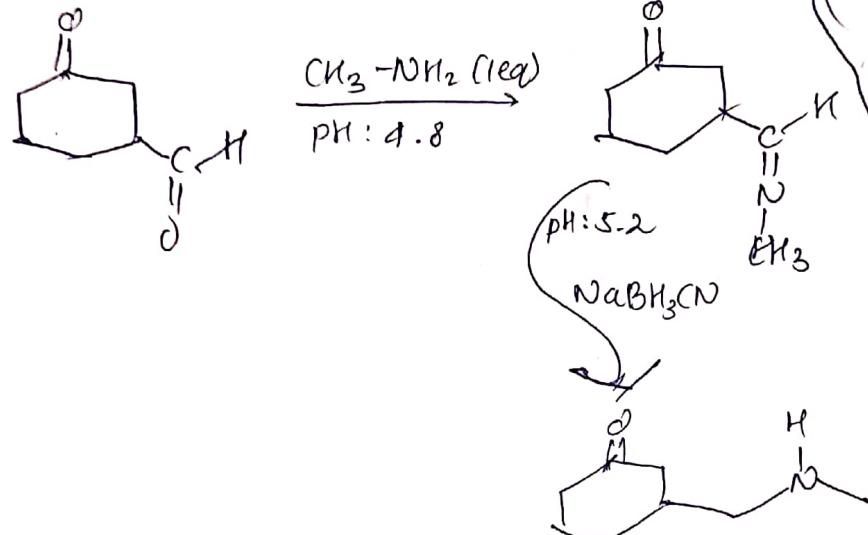
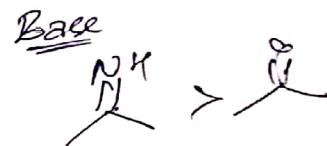


$\text{NaBH}_3(\text{CN})$

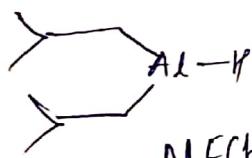


Electrophilic character

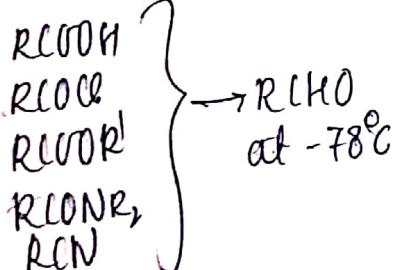
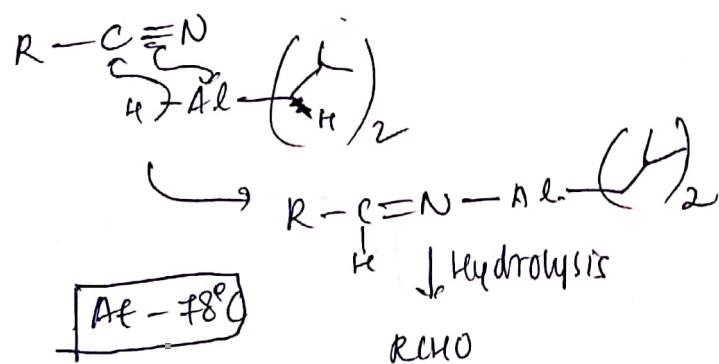
(i) carbonyl compound
 $>$ Imine.



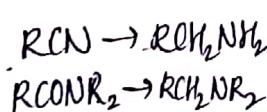
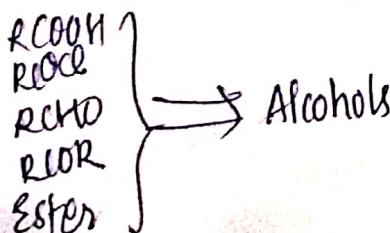
DIBALH and trialkoxy LiAl(OR'_3)



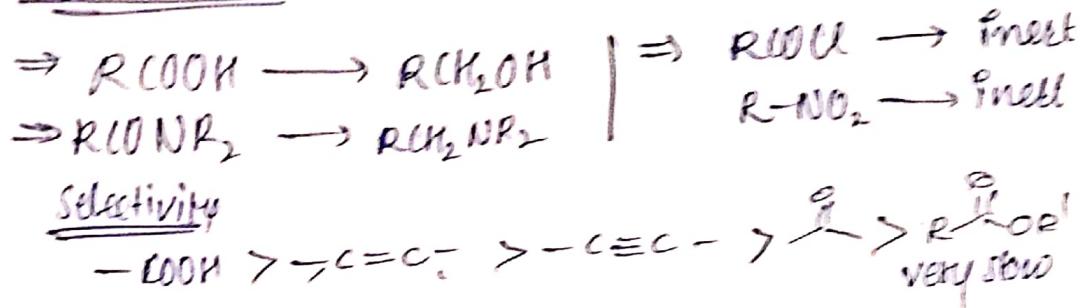
MECHANISM :-



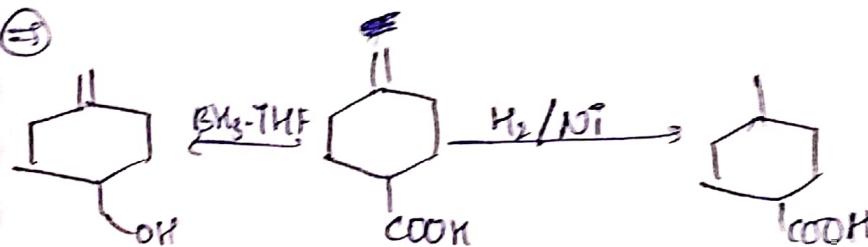
At room temp.



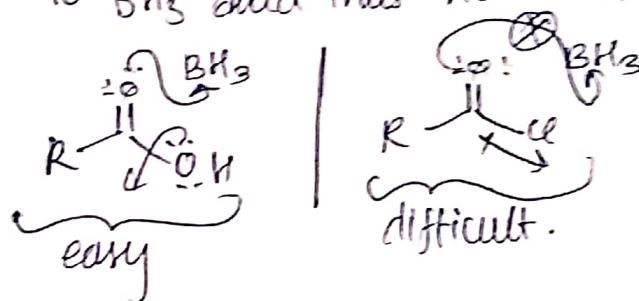
$\text{BH}_3 \cdot \text{THF}$ or B_2R_6



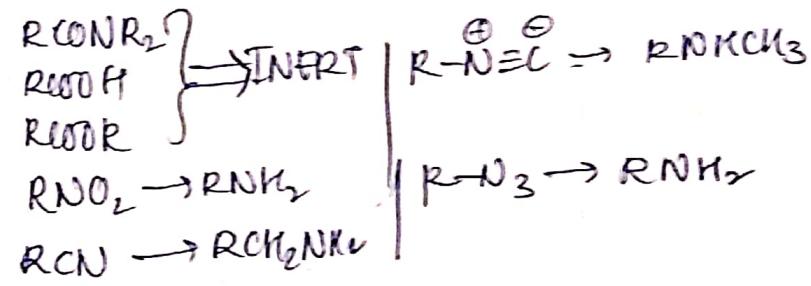
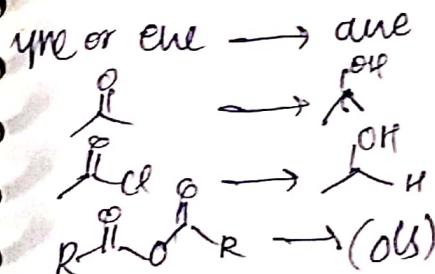
(i)



Due to deactivating ability of halogen, 'O' doesn't donate the LP to BH_3 and thus no donation of H^{\oplus} ion.

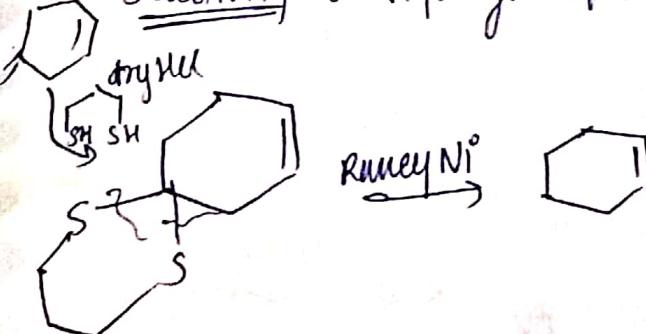


$\text{H}_2/\text{Ni} \text{ or } \text{Pt}(\text{OAc})_4 \text{ Pd}$



Raney Ni

Selectivity :- Hydrogenation \gg Hydrogenolysis.



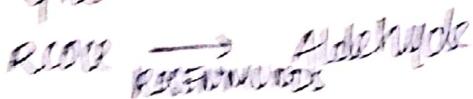
H₂/Ni-Cu mixed oxide

Function :- of H₂/Ni-Cu mixed oxide

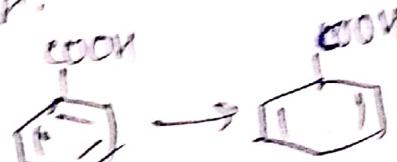


Amides → corresponding amines.

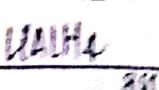
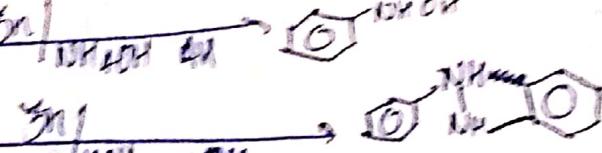
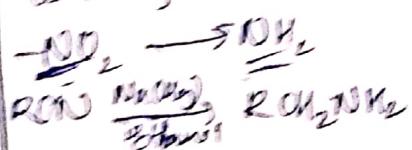
H₂/Pd-BaSO₄ (C) Cells : gasoline

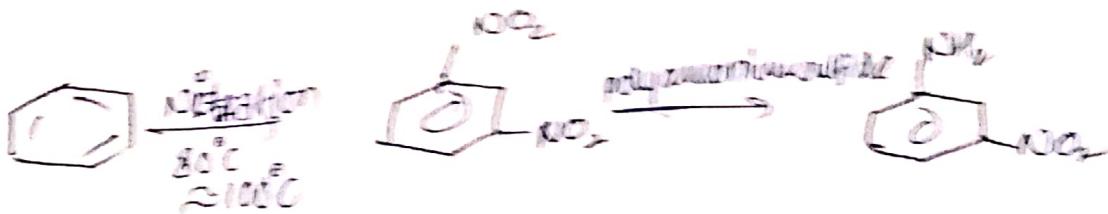


Na in Hg-Na₂(SO₄)₂ / Ethanol



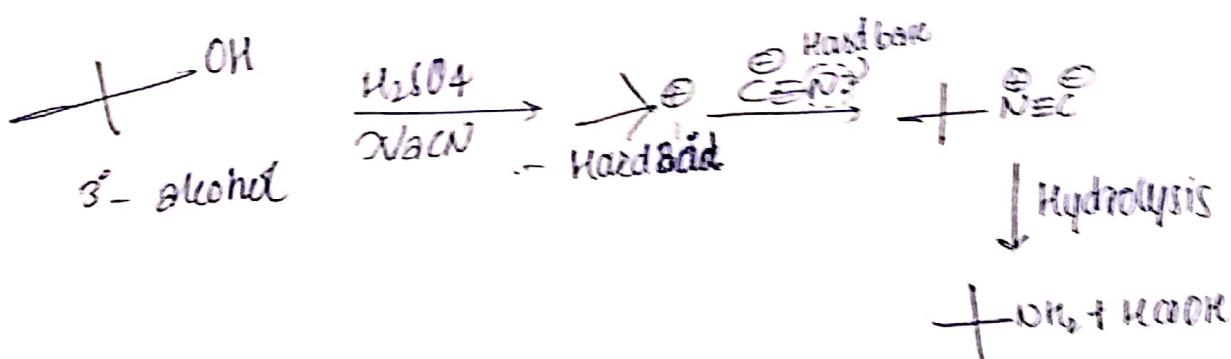
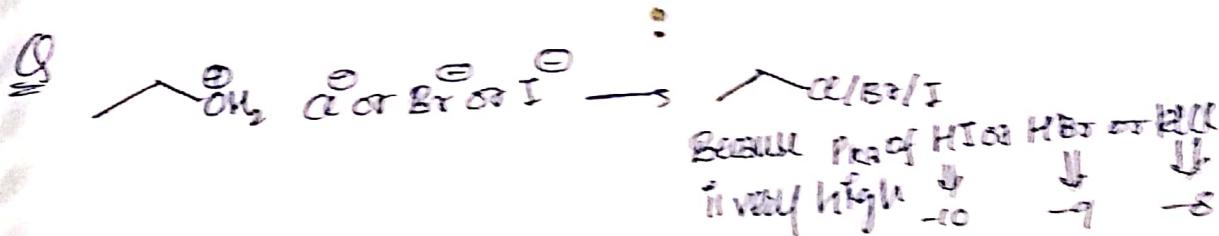
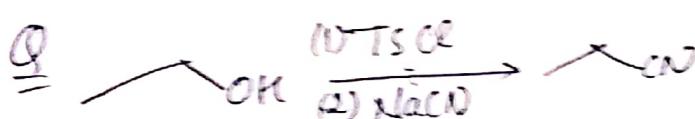
carboxylic → alcohol



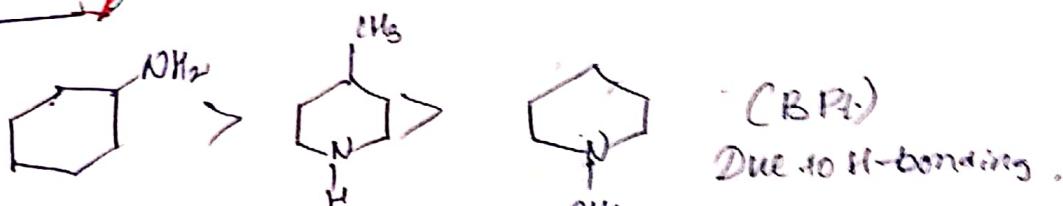


Ritter

Rxn

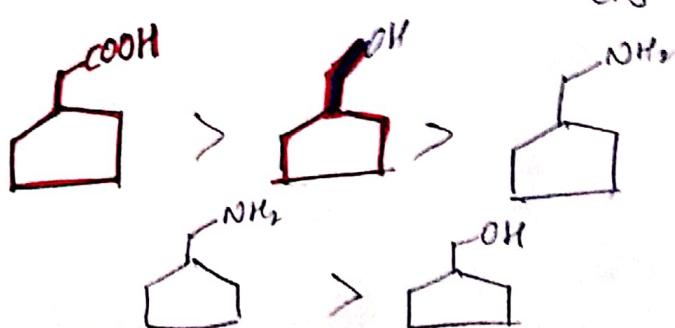


Properties of amines



CBP_4^-

Due to H-bonding.

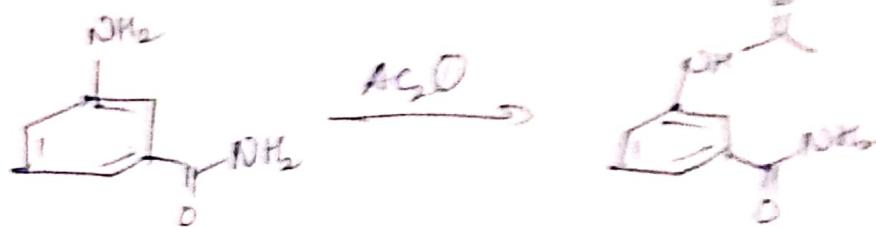


$\text{C}_6\text{H}_5\text{OH}$

Solubility

Chemical properties

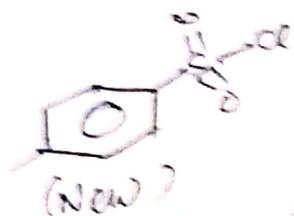
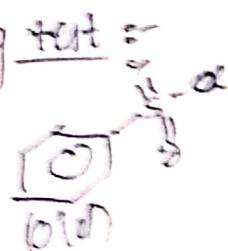
(i) Acylation rxn



(ii) Carbylamine rxn

(or) isocyanide test

(iii) Hinsberg test

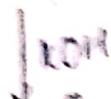


used to separate as well as distinguish mixture of $1,2^{\circ}$ and 3° amines.

(a) amine



N-alkyl sulfonamide (soluble)



(b) 2° amine

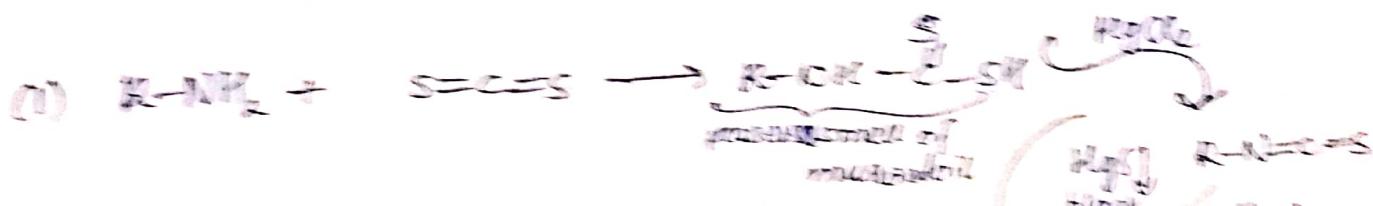
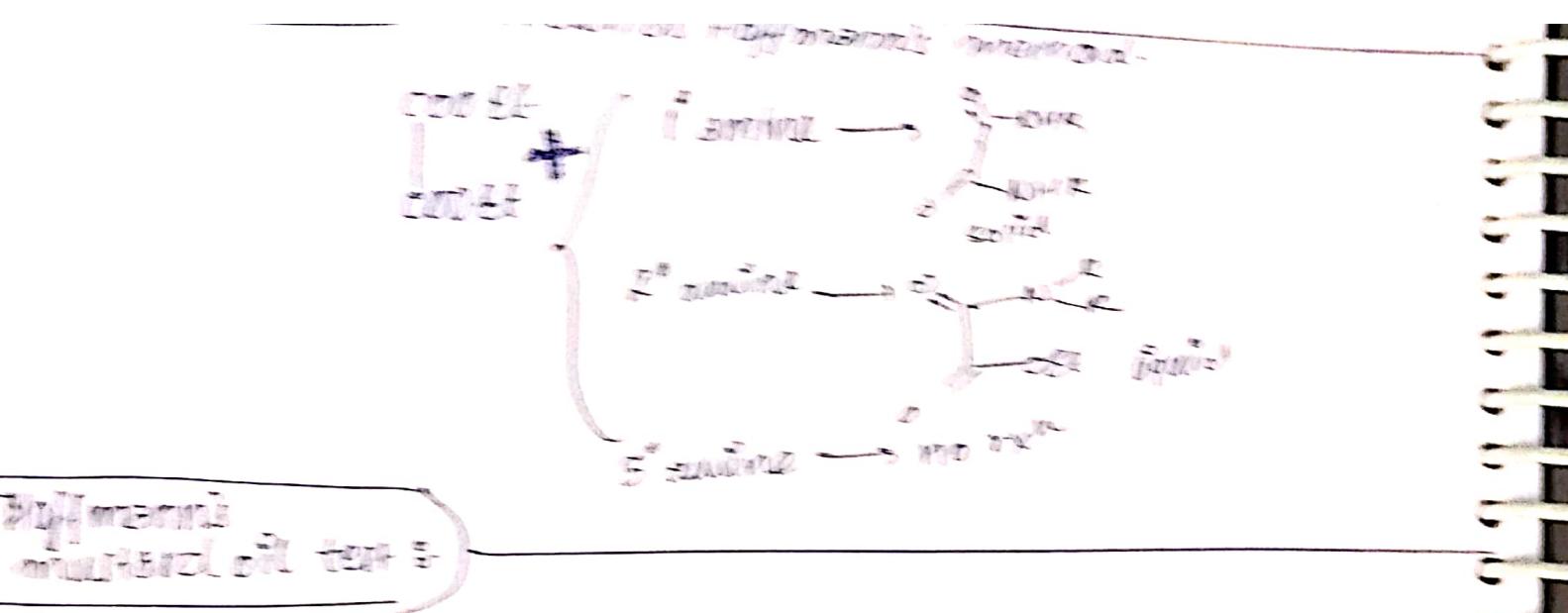


N,N-dialkyl sulfonamide (insoluble)

Not soluble
in KOH



In soluble



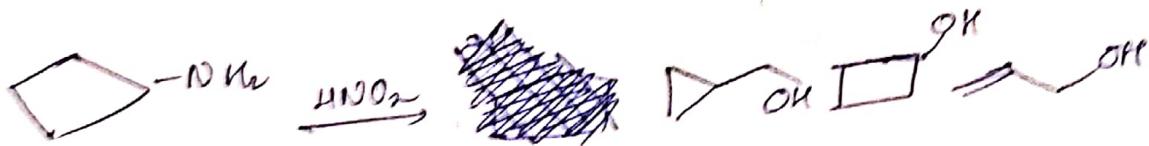
reactions with
nitric acid

Nitrate-famil

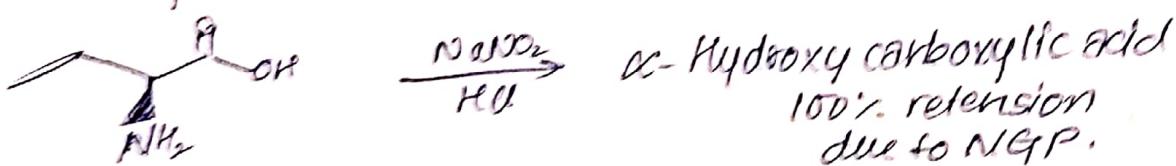


→ K_2O + NO_2 + O_2
 reaction by
 mixture.

(ii)

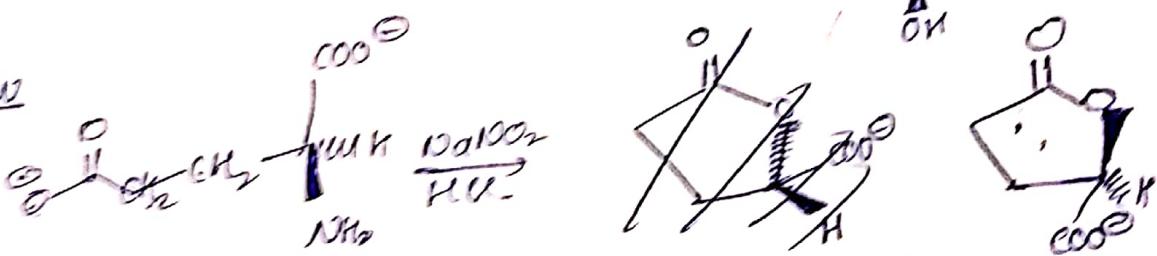


(iii) optically pure amino acid reacts with $\text{NaNO}_2 + \text{HCl}$.

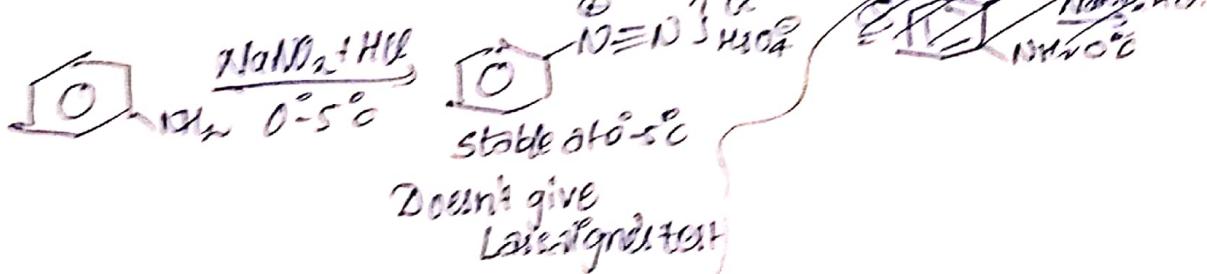


(iv)

2019-ADU



(B) Aromatic Amines



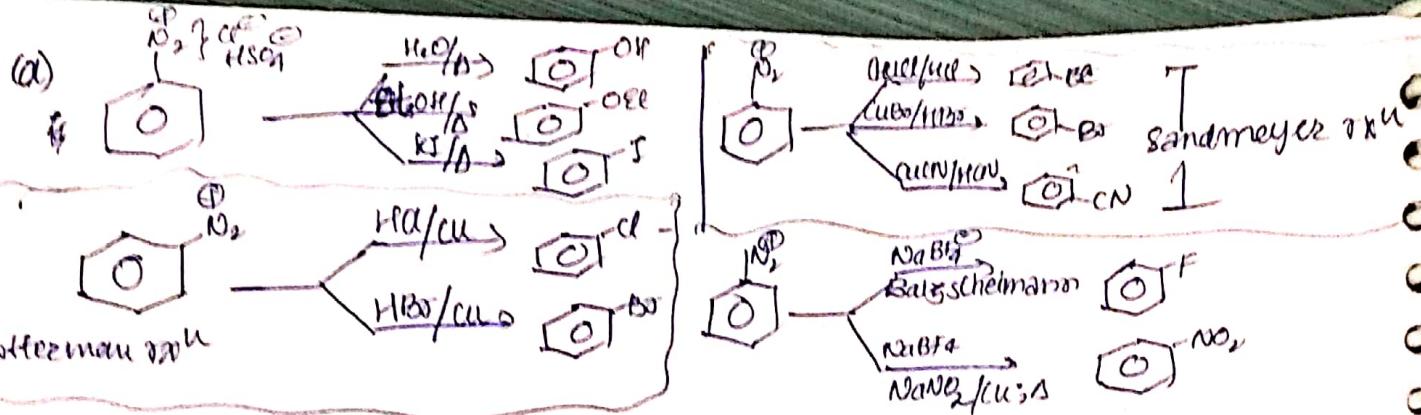
Mainly two ways are there,

- | | |
|--|---|
| (A)

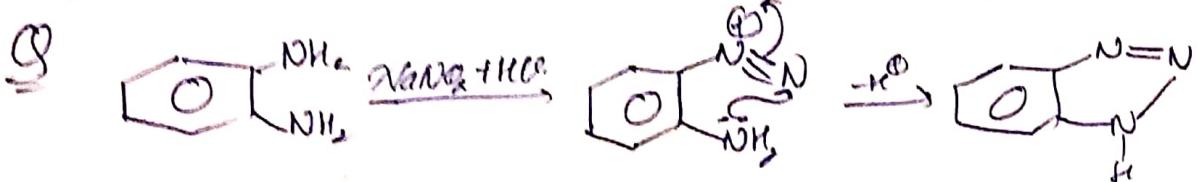
(i) N_2O_4 in $\text{H}_2\text{O}/\text{D}$
(ii) EtOAc/D
(iii) H_2/CuI
(iv) KtBu/CuBr
(v) $\text{KO}_{\text{tBu}}/\text{CuBr}$ | (i) H_2O_2 in $\text{H}_2\text{O}/\text{D}$
(ii) $\text{H}_2\text{O}_2/\text{CuI}$
(iii) $\text{H}_2\text{O}_2/\text{CuI}$
(iv) $\text{H}_2\text{O}_2/\text{CuI}$
(v) $\text{H}_2\text{O}_2/\text{CuI}$
(vi) $\text{H}_2\text{O}_2/\text{CuI}$
(vii) NaNO_2/D
(viii) $\text{NaNO}_2/\text{H}_2\text{O}_2/\text{CuI}$ |
|--|---|
- Gatterman reagent

(b) coupling ways, (resonance)

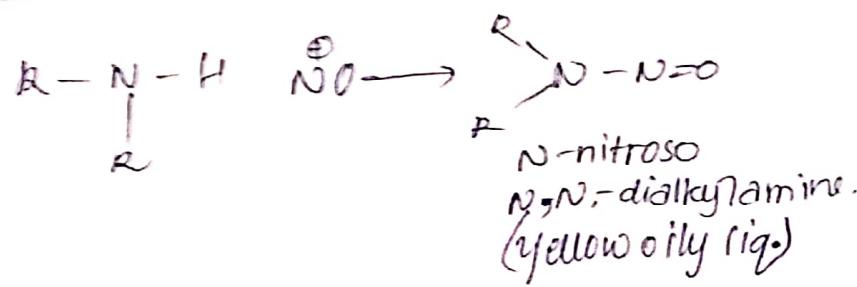
Retention of NO_2



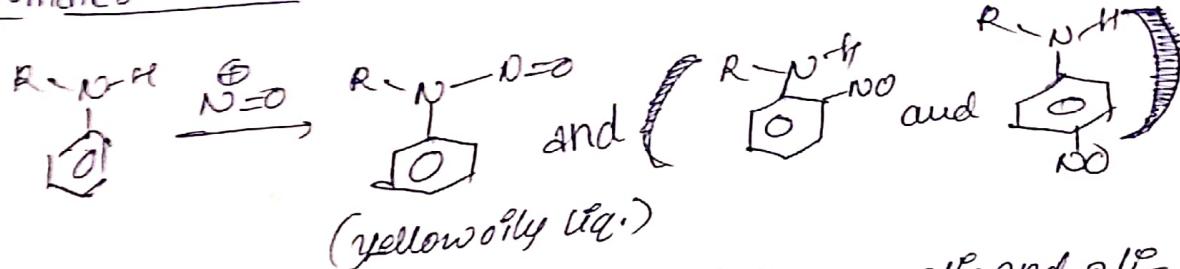
(b)



(C) Aliphatic 2°-amines



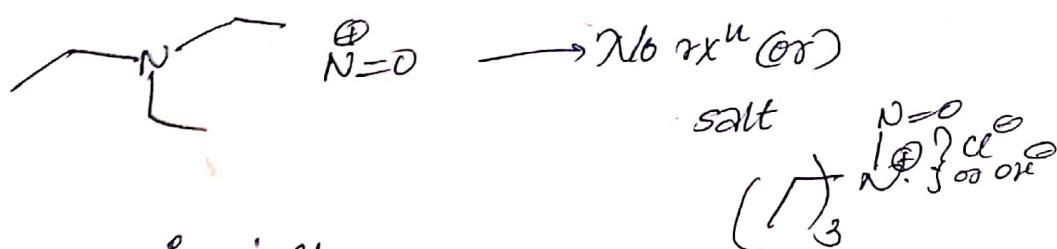
(D) Aromatic 2°-amines



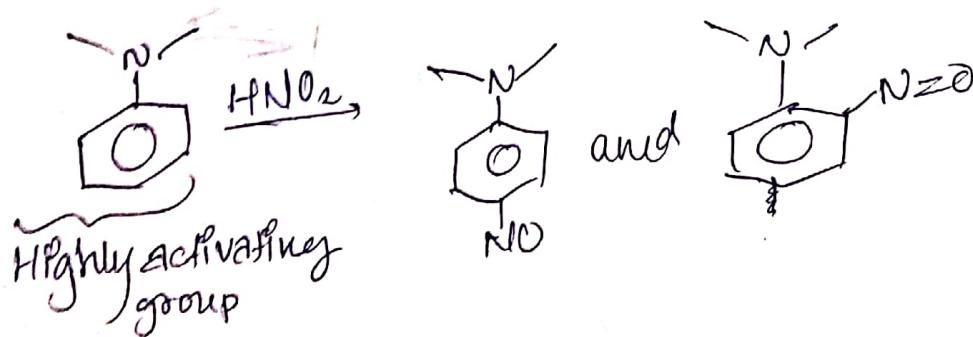
It is known as Libermann's nitroso oil test. Both aromatic and aliphatic 2° amines give this test.

→ phenols and para unsubstituted phenols also give Libermann's test.

(E) Aliphatic 3° amines



(F) Aromatic 3° amines

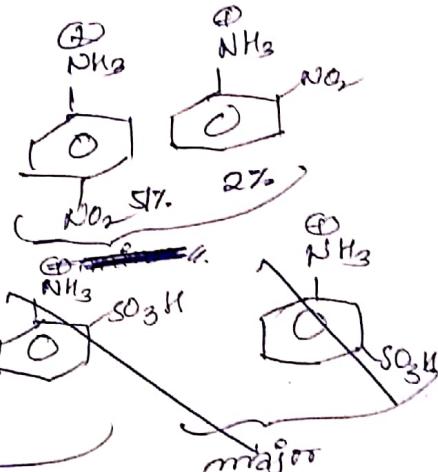
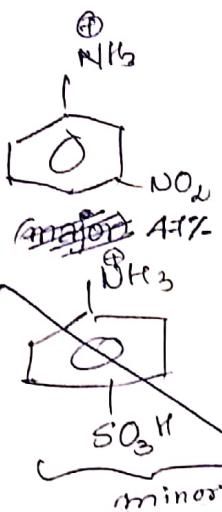
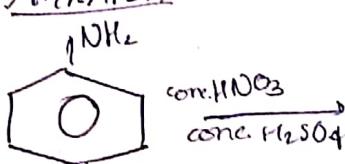


Dif⁺ types of EAr_2 subs. rxn's on Aniline

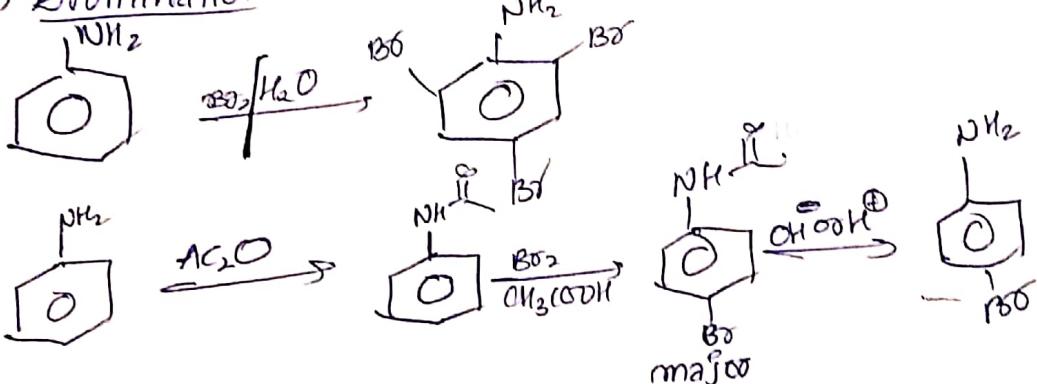
- (a) Nitration
- (b) Sulphonation
- (c) Bromination
- (d) Friedel-Crafts Ar^{\oplus}

(e) Aniline doesn't give Friedel-Crafts Ar^{\oplus} because -NH_2 gets involved into effective complex formation with Lewis acid and becomes thus a strongly deactivating group and hence no Friedel-Crafts Acylation or Alkylation takes place.

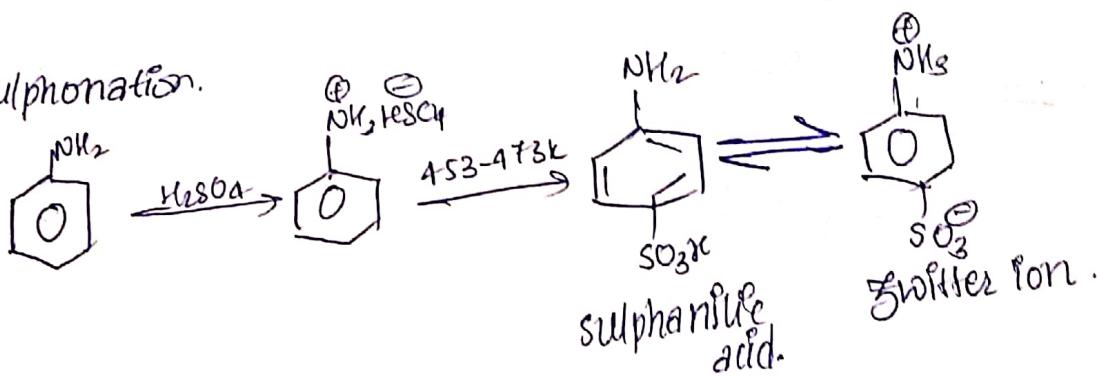
(a) Nitration



(c) Bromination

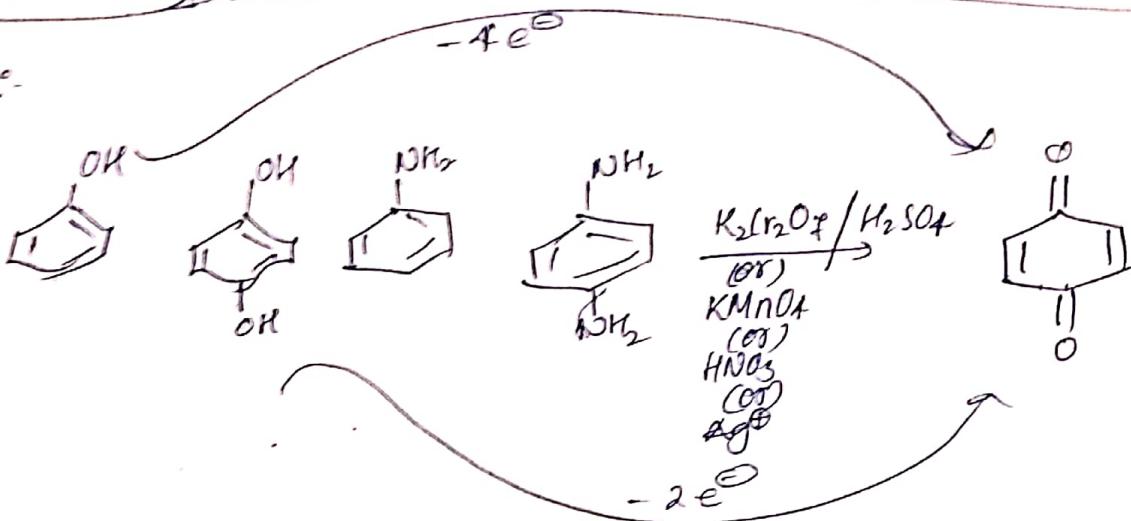


(b) Sulphonation

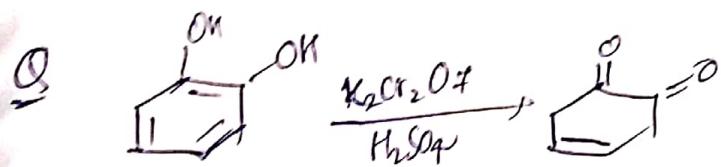
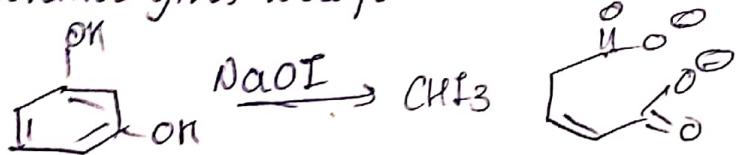


Oxidation rxn

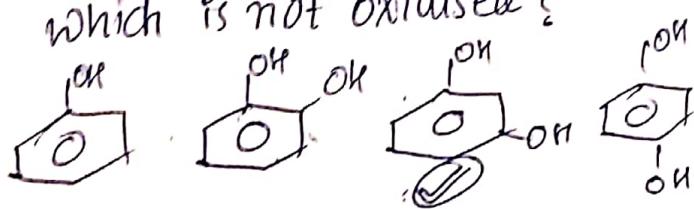
Hint:-



FACT :- Resorcinol gives Iodoform



Q which is not oxidised?

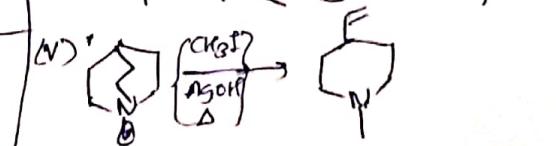
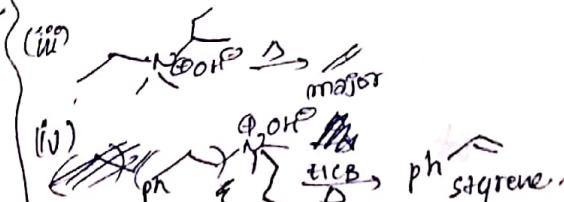
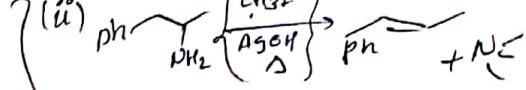
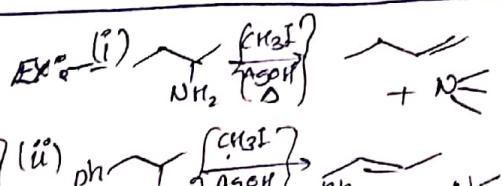
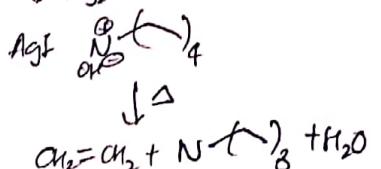
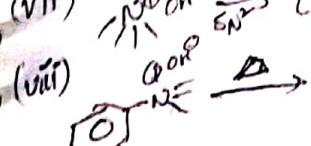
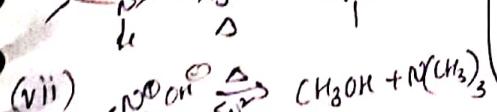
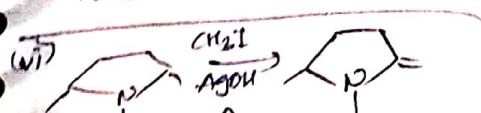
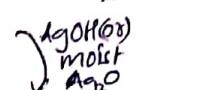
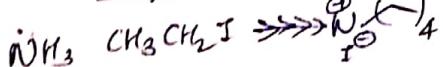


pyrolysis of quaternary ammonium hydroxides Hoffmann elimination / degradation

3° amine N-oxides

code elimination.

Hoffmann Degradation

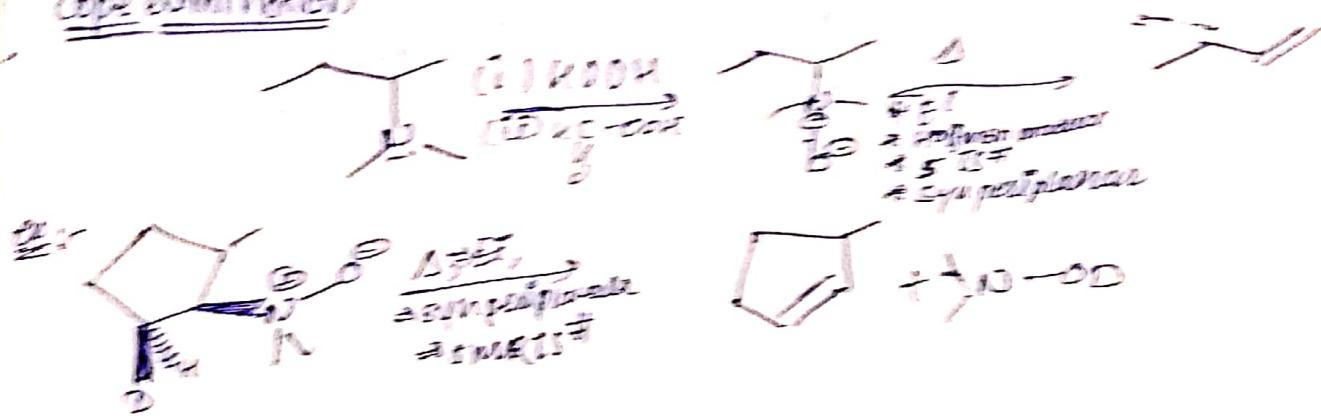




~~95% of~~

Due to hindrance, group CH_3 prevents through π path where CH_3 abstracts C^{\bullet} from CH_2 to give CH_2^{\bullet} and $\text{CH}_3\text{CH}_2\text{OH}$. Thus, transition state is formed.

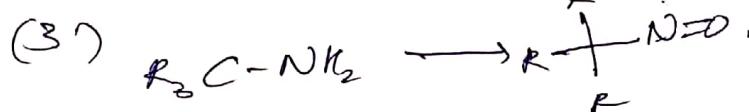
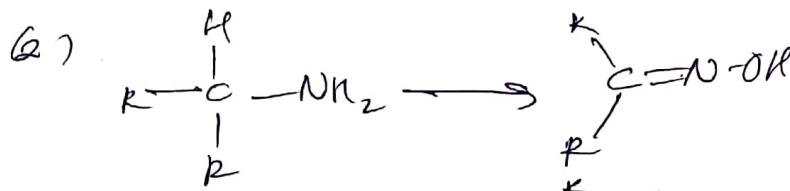
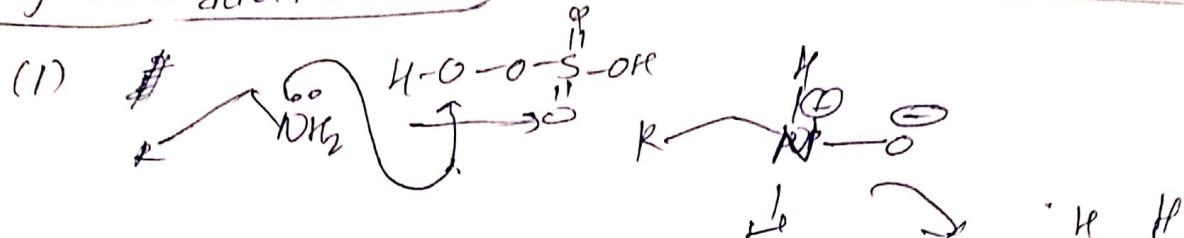
Cope elimination



Pf's of AmNO_2 :



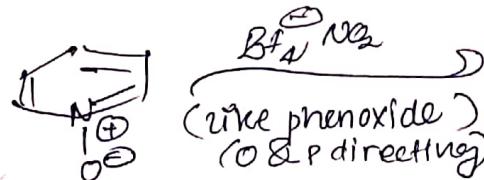
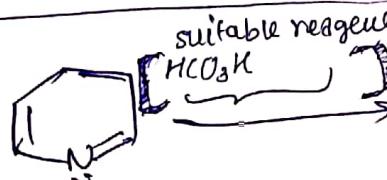
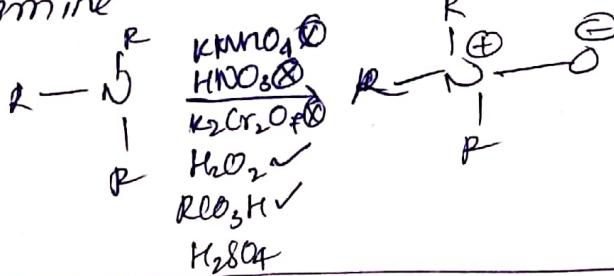
Rxns of azo's acid. (H_2SO_4)



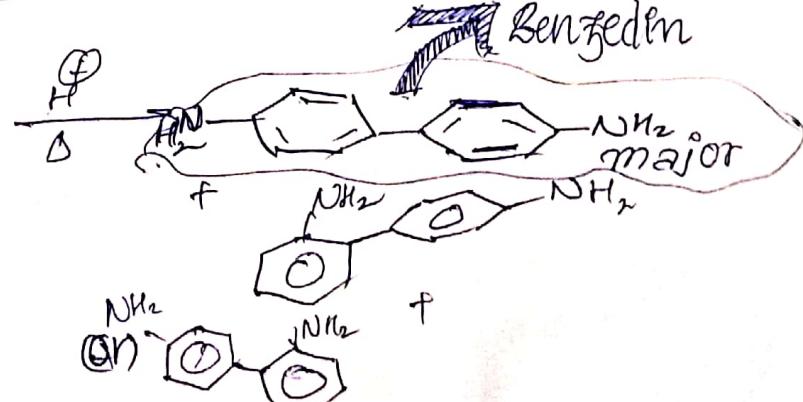
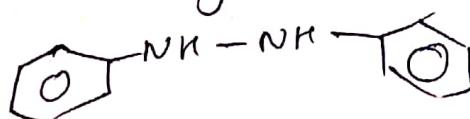
(4) α° amine.



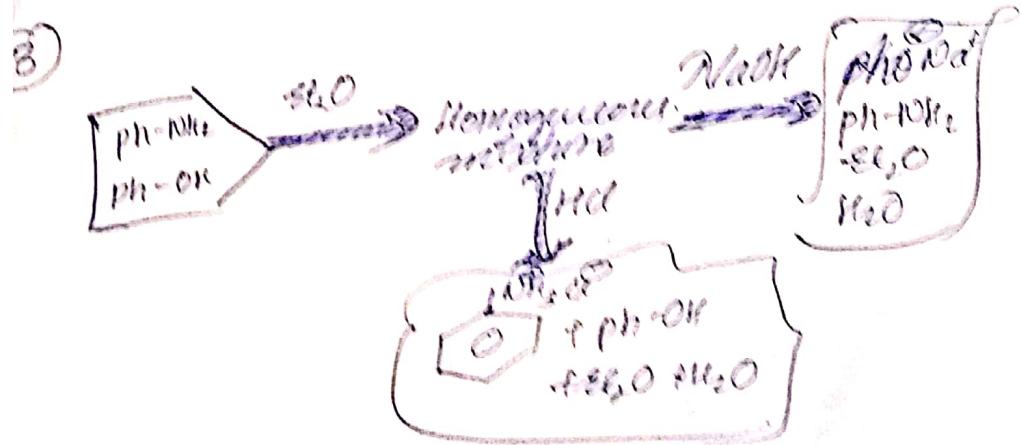
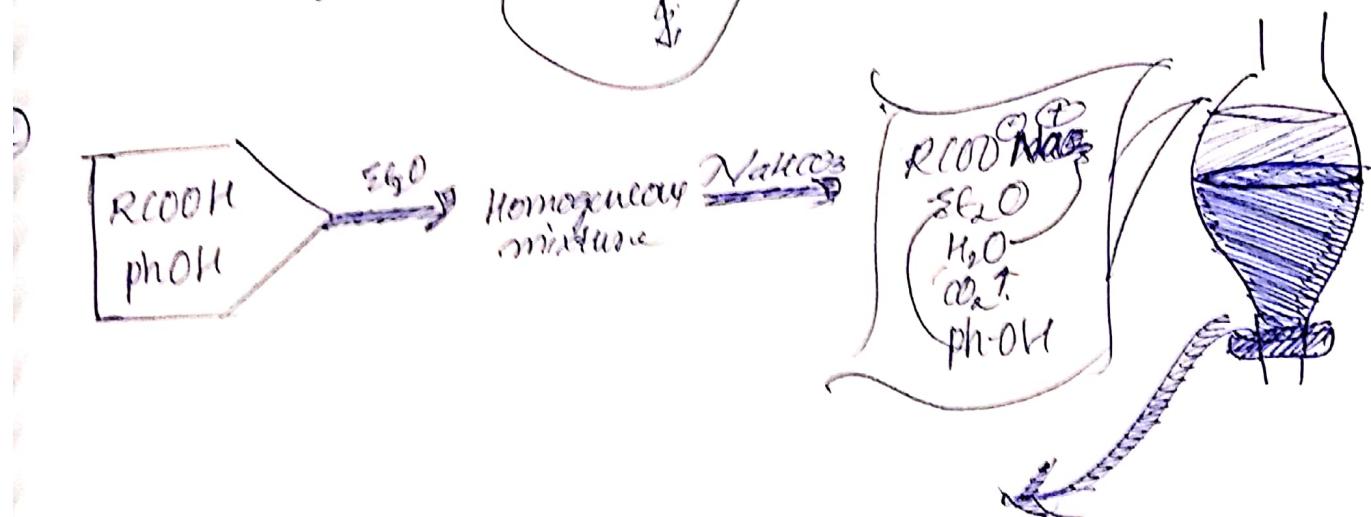
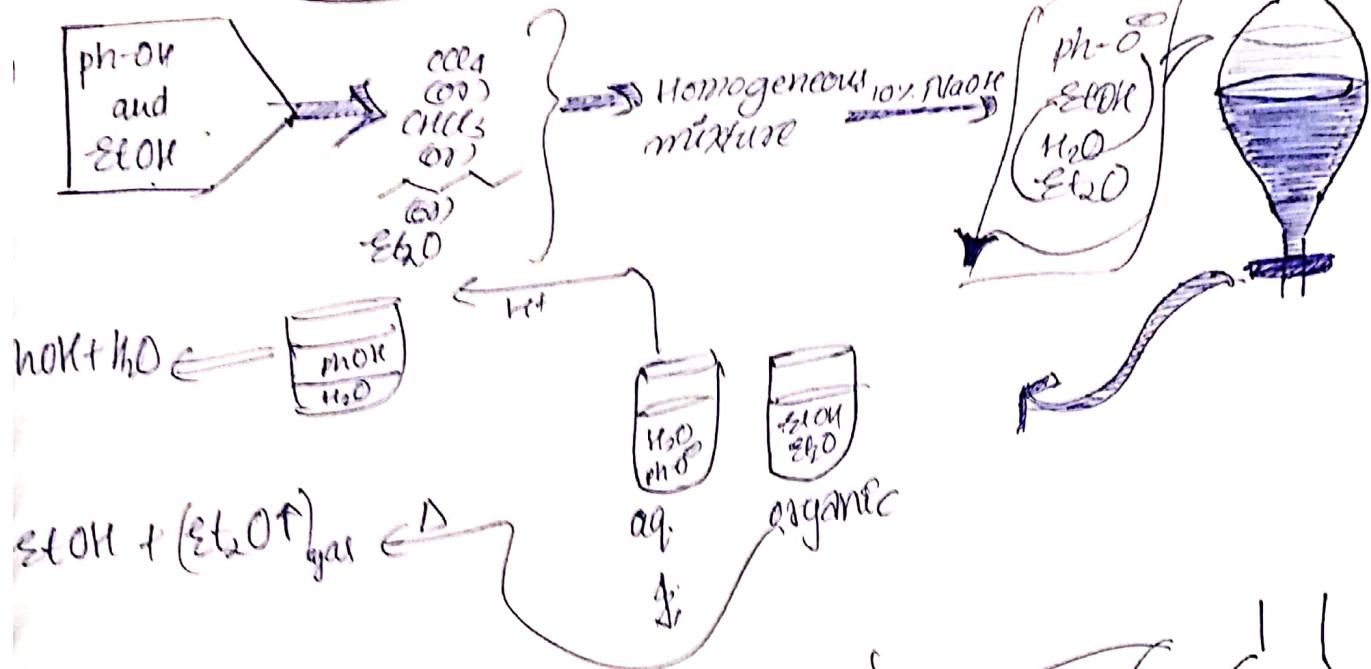
(5) β° amine



Benzidin Rearrange-ment



SEPARATION OF Binary mixture





CHCl₃ →

Homogeneously NaOH

