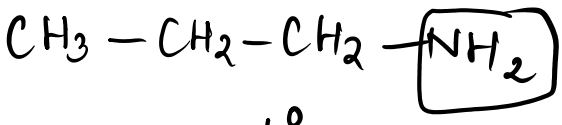
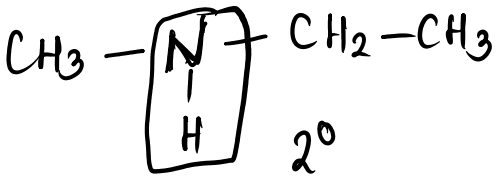
Nitrogen containing Compounds (Amines)

- ☑ Classify and name amines, nitro compounds, cyanides, and diazonium salts
- ☑ Understand the basicity trends of amines in different phases
- ☑ Learn key preparation methods and important named reactions
- ☑ Predict and apply reaction mechanisms for conversions
- ☑ Utilize shortcuts and tricks to solve JEE-level problems efficiently



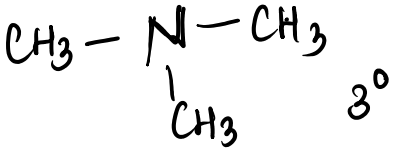
1°

Propan-1-amine.



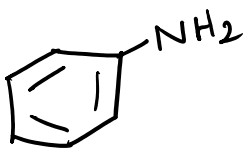
2°

N-methylethanamine.

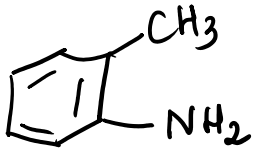


3°

N,N-dimethylmethamine.

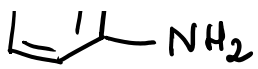


Aniline



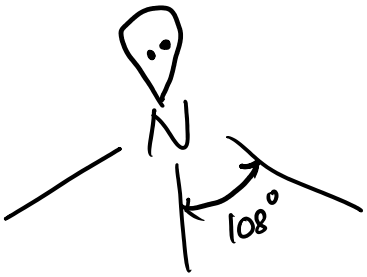
2-Aminotoluene

O-Toluidine.



O-Toluidine.

$NR_4^{\oplus}$ ⇒ Quaternary amine



∠RNR

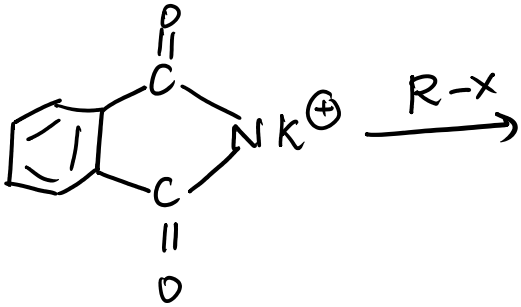
Preparation: Hoffmann Alkylation:

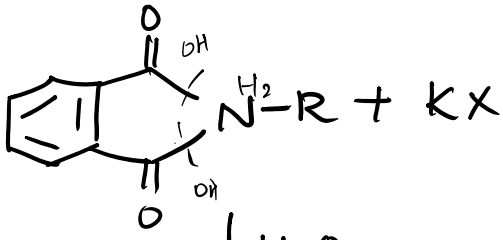
$$R\text{-}I + NH_3 \longrightarrow R\text{-}NH_2 + HI$$

$$R\text{-}NH_2 \xrightarrow{RI} R\text{-}\underset{\underset{H}{|}}{N}\text{-}R \xrightarrow{RI} R\text{-}\underset{\underset{R}{|}}{N}\text{-}R \xrightarrow{RI} R_4N^{\oplus}\,I^{\ominus}$$

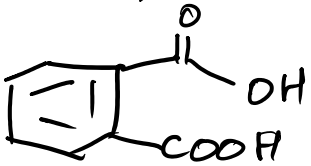
2° 3° 4°

2. Gabriel phthalimide Syn:





$\xrightarrow{H_2O}$

$R\text{-}NH_2 +$ 

Aromatic Amine ✗

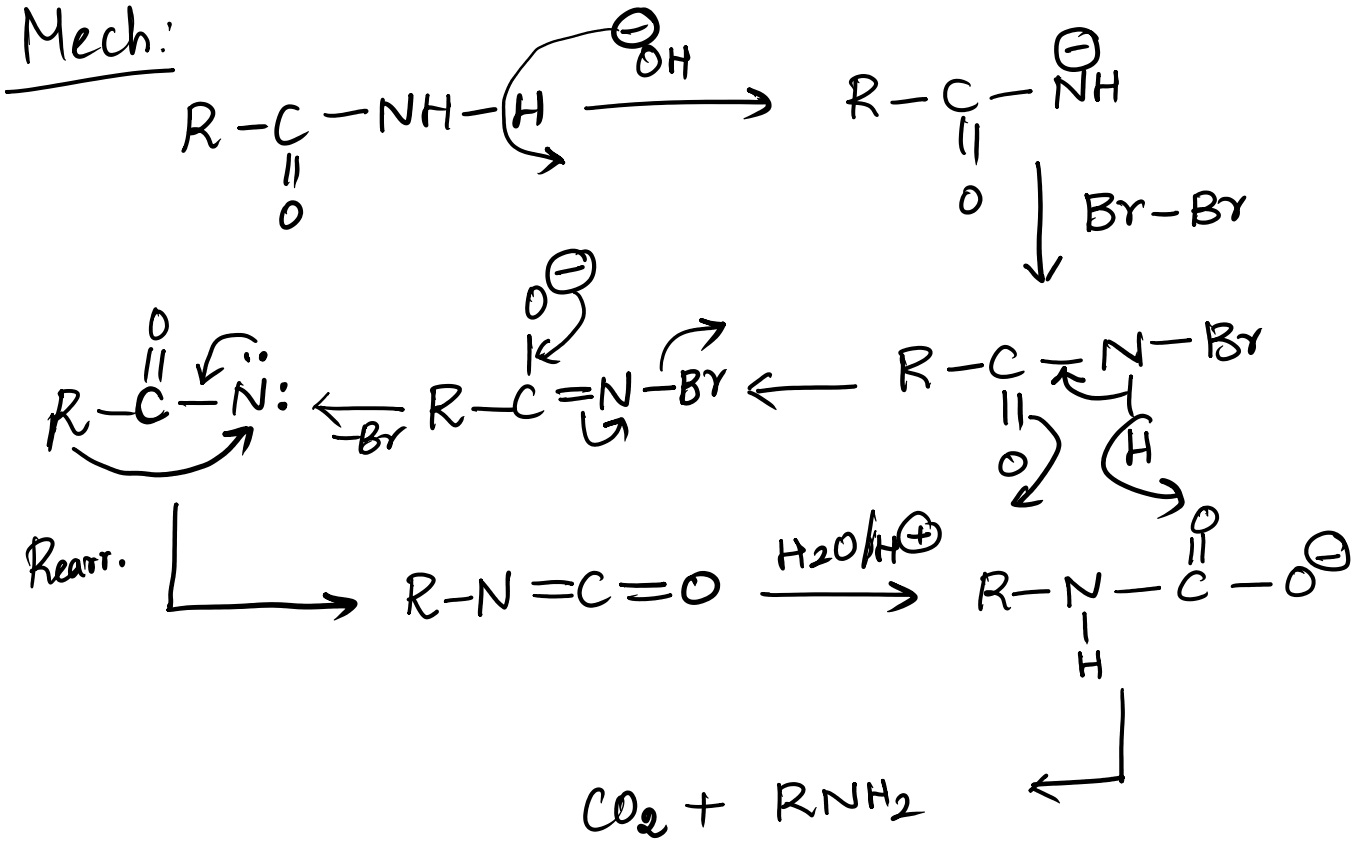
3. Hoffmann Bromamide

3. Hoffmann Bromamide

$$R-CONH_2 \xrightarrow{Br_2 + KOH} R-NH_2$$

Amide (1° amines only)

Mech:



Reduction:

i) $R-CH=NOH \xrightarrow{Et.\,|\,Na} R-CH_2-NH_2$ (1° only)

ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$.

iv) $R-CN \xrightarrow{Ni\,|\,H_2} \underset{1^\circ}{R-CH_2-NH_2}$

iv) $R-NC \xrightarrow{LiAlH_4} R-NH-CH_3$

2° (only)

2° (only)

v) $R-NO_2 \xrightarrow{Sn/HCl} R-NH_2$

vi) $C_6H_5NO_2 \xrightarrow{Redn} C_6H_5-NH_2$.

From Acid chloride (Curtius rxn)

$$R-COCl \xrightarrow{NaN_3/OH^-} R-NH_2$$

Schmidt rxn:

$$R-COOH \xrightarrow[H_2SO_4]{N_3H} R-NH_2$$

B.pt:

$1^0 > 2^0 > 3^0$

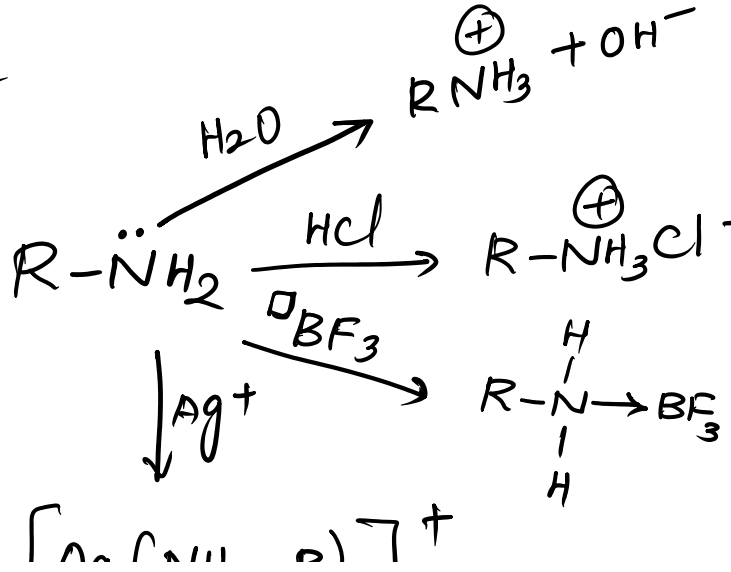
Basicity:

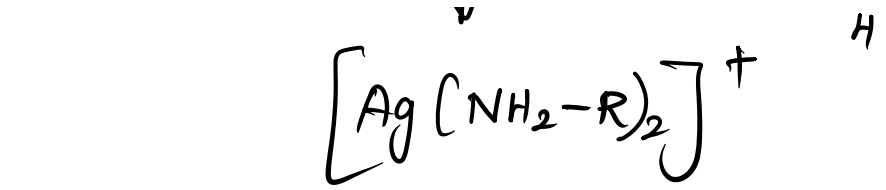
Aliphatic Amines are less basic.

↑ pK_b ↓ basic strength.

Properties:

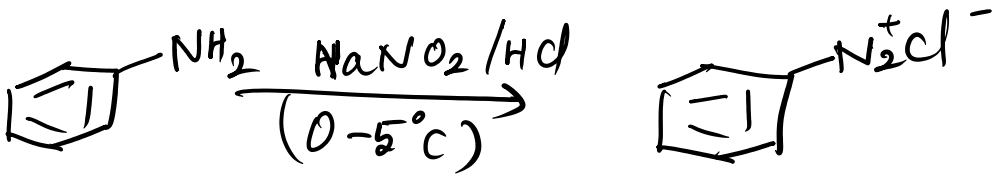
i) Basic Nature





Rxn with HNO_2 : (Nitrous Acid)

(Lack of resonance) $R-NH_2 \xrightarrow{HNO_2} ROH + N_2\uparrow$



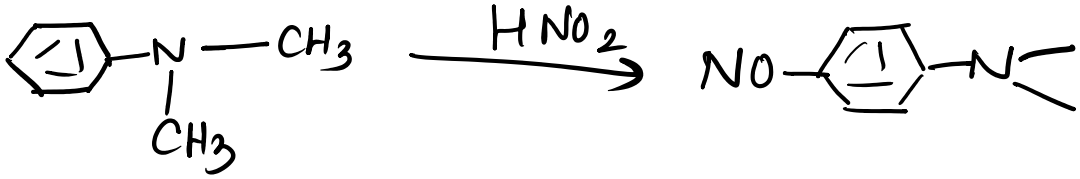
2° Amine.

$R_2NH \xrightarrow{HNO_2} R_2N{=}N{\rightarrow}O$

N-nitro soamine
(yellow oily liq)

3° Amine:

$R_3N \xrightarrow{HNO_2} [R_3NH]^+ NO_2^-$



(3) Acylation:

$RNH_2 + RCOCl \longrightarrow R-NH-COR$
1° Amide.

2° Amine $\longrightarrow$ 3° Amide.

④ Grignard Regent:

$$RMgX + RNH_2 \longrightarrow RH + R-NH-MgX$$

⑤ (X) Carbylamine Rxn. (1°) (Ali & Aro)

$$R-NH_2 + CHCl_3 + KOH \longrightarrow R-NC$$

1°

Mustard Oil rxn: 1°

$$RNH_2 + CS_2 \longrightarrow R-N=C=S$$

Isothiocyanate

$$\downarrow COCl_2$$

$$Ph-N=C=O$$

Distinguish Aro. 1°, 2°, 3°

$$R-NH_2 + HNO_2 \longrightarrow R-OH + N_2\uparrow$$

$$R_2NH + HNO_2 \longrightarrow \text{yellow oil.}$$

$$\text{red.} \leftarrow \text{deep blue} \xleftarrow{NaOH} \text{Green} \xleftarrow{} C_6H_5OH$$

Libermann's nitroso rxn.

$$R_3N + HNO_2 \longrightarrow 4^\circ \xrightarrow{C} \text{yellow oil}$$

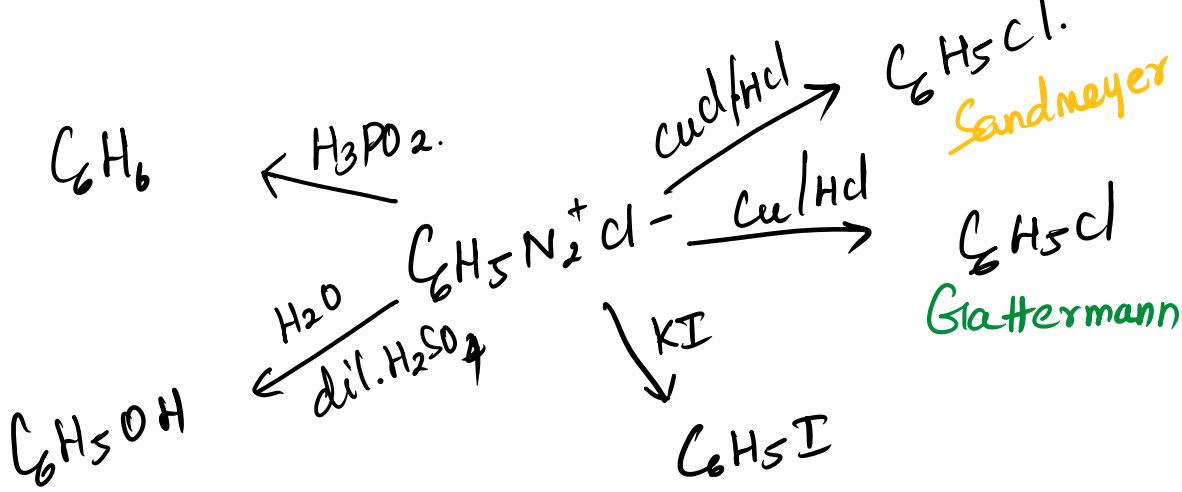
$R_3N + HNO_2 \longrightarrow 4^\circ \xrightarrow{C}$ yellow oil

↳ Cope rxn.

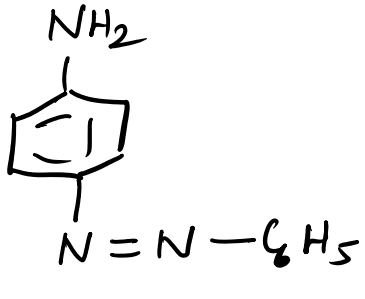
EAS :

$NH_2 \Rightarrow$ EDG $\Rightarrow$ "O, P"

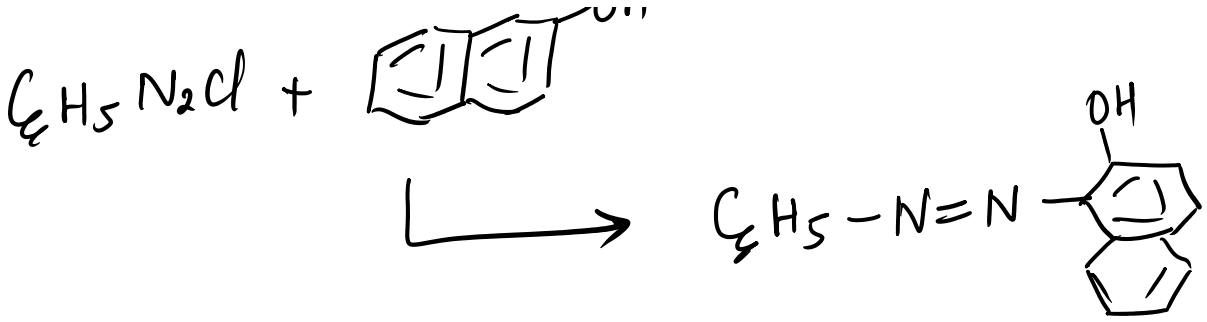
Benzene diazonium chloride:



$C_6H_5N_2Cl + C_6H_5NH_2 \longrightarrow C_6H_5N{=}N{-}C_6H_4NH_2$

$C_6H_5N_2Cl + C_6H_5OH \longrightarrow$ 

$C_6H_5N_2Cl +$ 

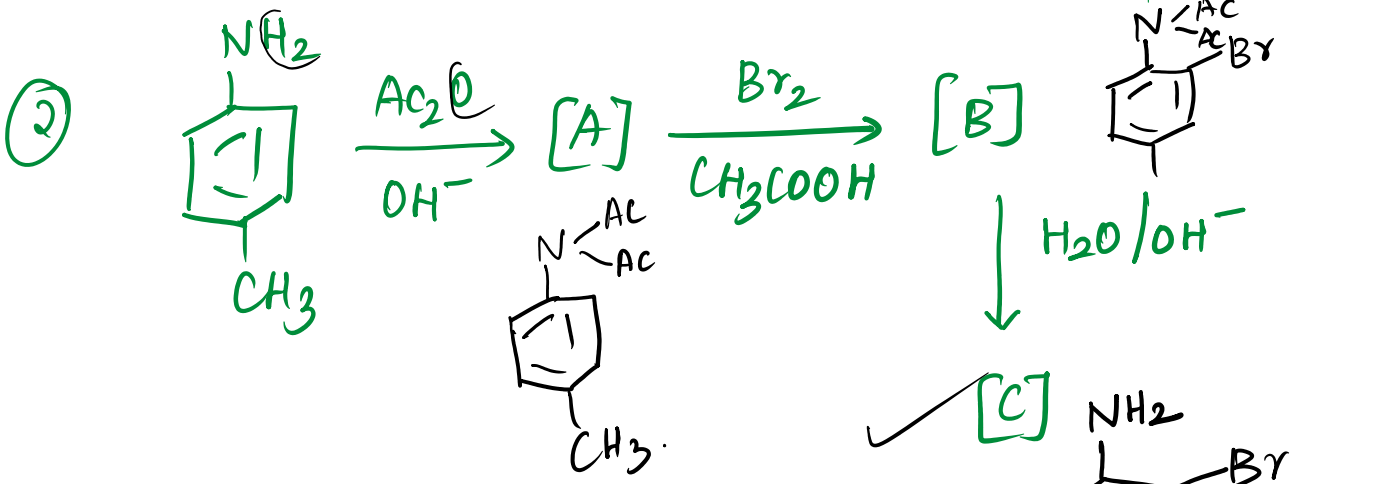


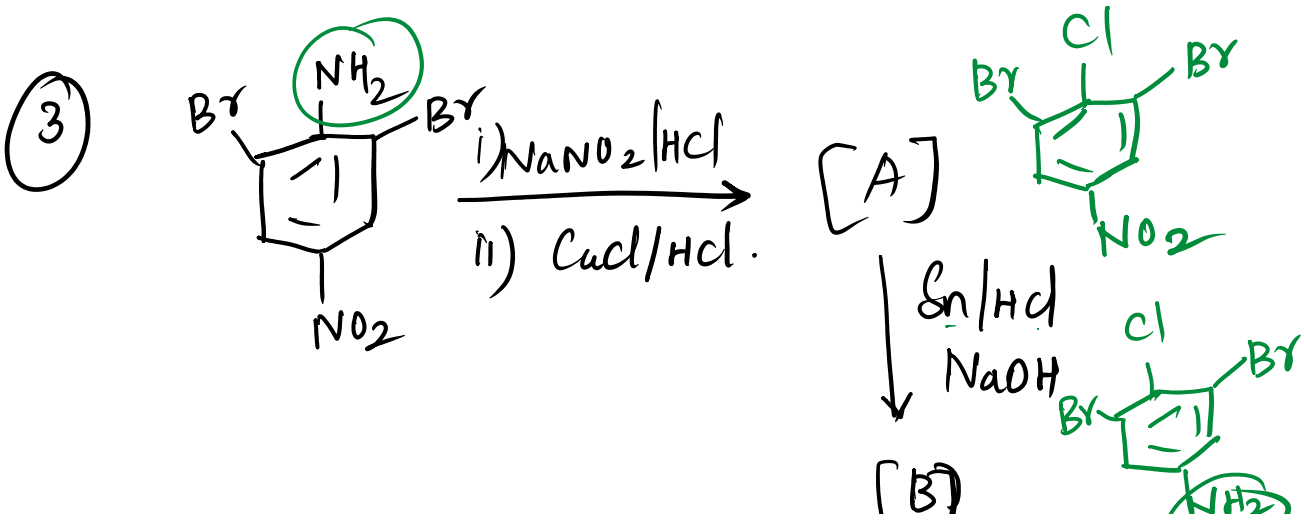
i) $C_6H_{13}COCl \xrightarrow[\text{Rosenmund'}]{H_2\ Pd/BaSO_4} [X] \xrightarrow{C_6H_{13}NH_2} [Y] \xrightarrow{Ni/H_2} [Z]$

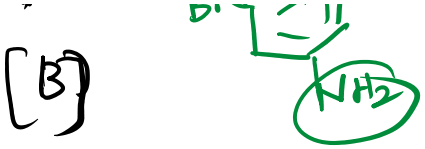
$C_6H_{13}CHO$

$C_6H_{13}CH_2-NHC_6H_{13}$

$C_6H_{13}CH=N-C_6H_{13}$

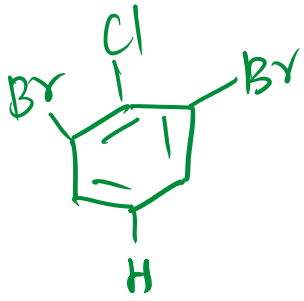




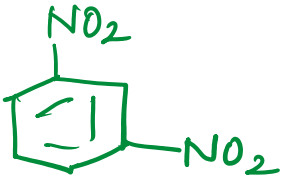


1. $NaNO_2 + HCl$

2. $H_3PO_2 + H_2O$



[C]



1,3-dinitro benzene

EAS → EWG. ⇒ m-position.

Acetamide CH_3CONH_2 ⟶ CH_3NH_2.

a) Caebylamine $R-NH_2 \rightarrow R-NC$

~~b)~~ Hoffmann bromamide $RCONH_2 \rightarrow CH_3NH_2$

c) Stephen's

d) Gabriel phthalimide.