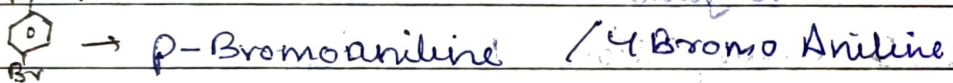
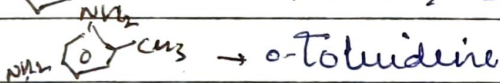
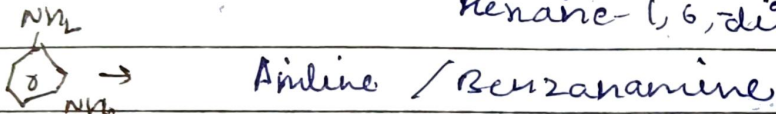
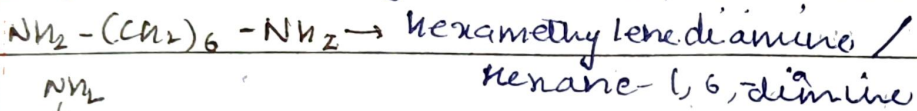
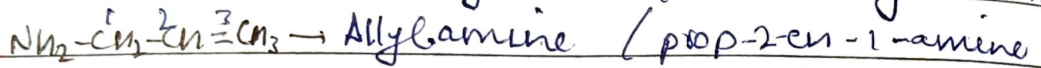
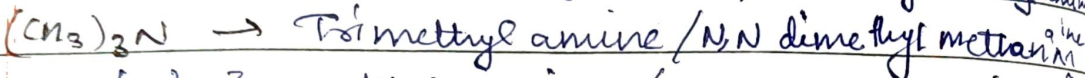
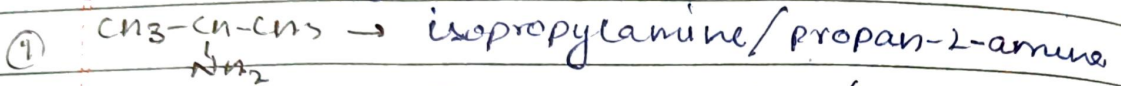
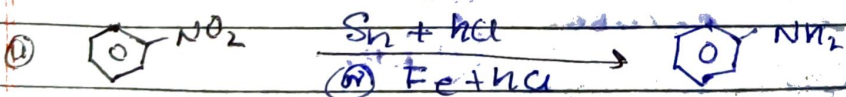
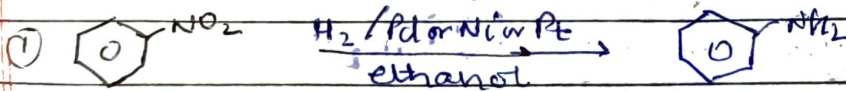


{alkanamines}



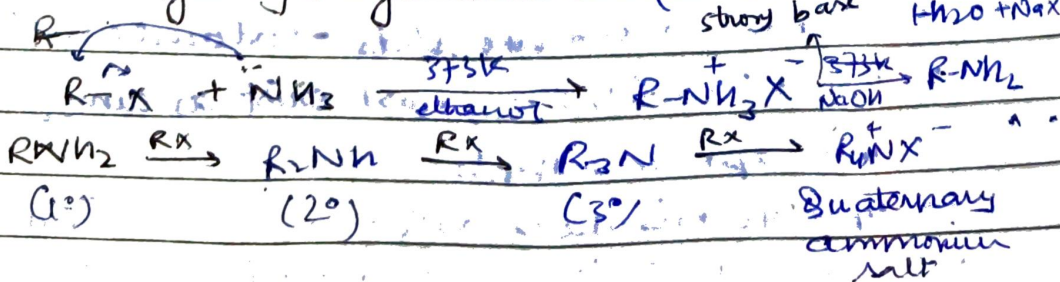
⑤ Preparation of Amines

① Reduction of Nitro compounds:



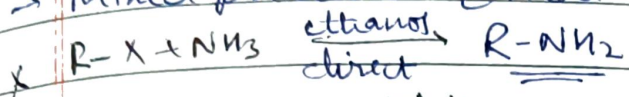
Preferred as Fe gets formed & hydrolysed \rightarrow release HCl \therefore less HCl req.

③ Ammonolysis of Alkyl halides: (Nucleophilic Subst)

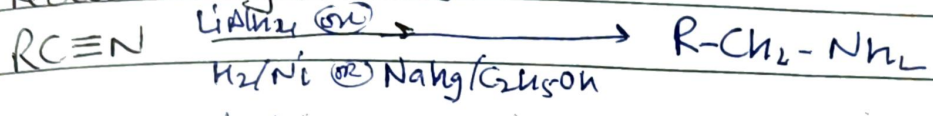


→ order of reactivity → $R-I > R-Br > R-Cl$

→ Mixed product [Yield of Amine ↑ ⇒ NH_3 ↑]

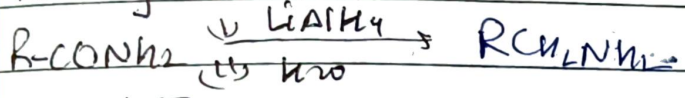


(c) Reduction of nitriles →



→ Acct of chain

(d) Red. of amides



(e) Named (31)

(f) Named (32)

Chemical Rxns -

(a) Basic character →



→ Salt → soluble in water, insoluble in ^{organic} solvent.

↳ Used for identification

→ Amines act as Lewis Base [L.P]

→ Aliphatic amines stronger bases than aromatic amines

(+I effect of alkyl groups) [pK_b (3-4.2)] ↳ EWG → aryl.

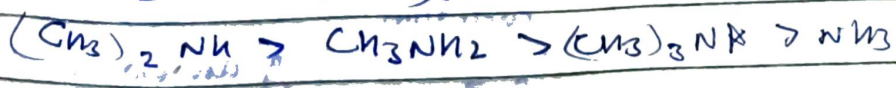
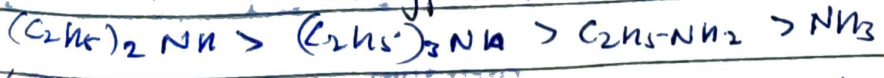
→ C^{\oplus} ↑ stable → Basic Amine ↑

→ Gaseous med. → $3^\circ \text{Amine} > 2^\circ \text{Amine} > 1^\circ \text{Amine} > NH_3$

→ Aqueous med. → $1^\circ \text{Amine} > 2^\circ \text{Amine} > 3^\circ \text{Amine}$
(+I + solvation by H₂O molecule) [solvation of $\frac{1}{\text{size of ion}}$ & stability of ion]


↳ [alkyl groups no. ↑ basicity ↑]

* Steric hindrance also affect basicity →



* Alkylamines vs Ammonia

↳ pK_b value high \Rightarrow l.p \rightarrow conjugation with benzene
 \Rightarrow Less available for protonation. [shyft R.S.]

1. Anilium ion () \rightarrow 2 R.S \rightarrow More available for protonation

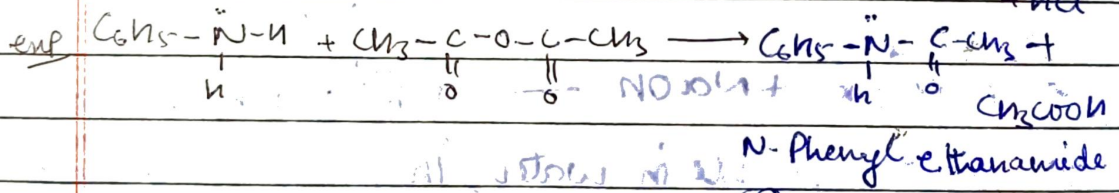
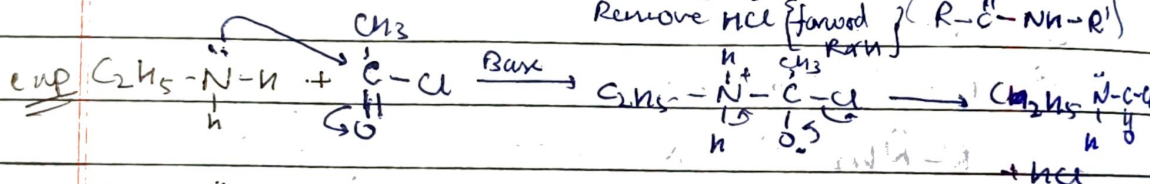
\Rightarrow Aromatic amines \leftarrow Ammonia
Basic

\Rightarrow E.A.G \rightarrow inc basicity

(2) Alkylation

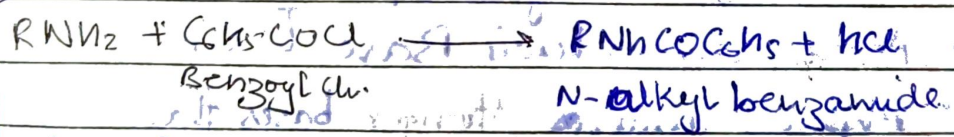
(3) Acylation \rightarrow formation of Amides [Aliphatic 1°/2° amine & Aromatic]

R/R₂ NH₂/N + acid Cl/esters/ anhydrides $\xrightarrow[\text{ie pyridine}]{\text{strong base}}$ Amide + HCl

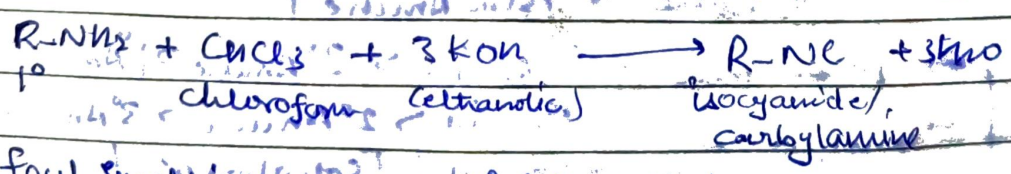


(4) Acetanilide

Benzoylation

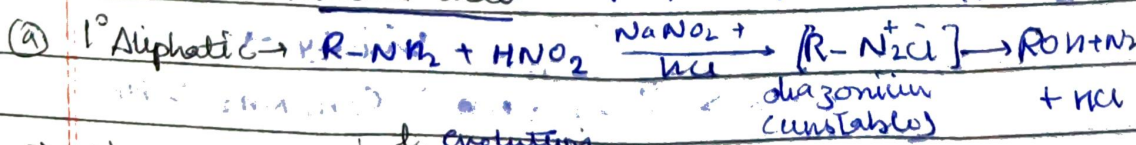


(4) Carbylamine R.NH₂ / Isocyanide test \rightarrow

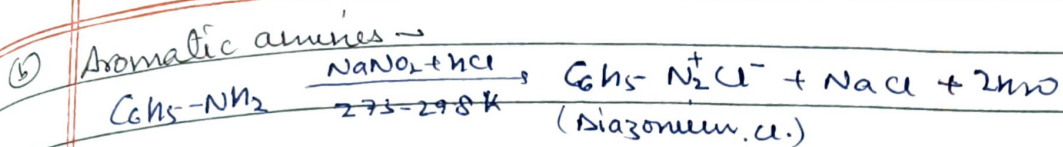


\rightarrow foul Smellery \rightarrow 2°/3° Not show

(5) Rxn with nitrous acid \rightarrow prep. in situ (from mineral acid + NaNO₂)

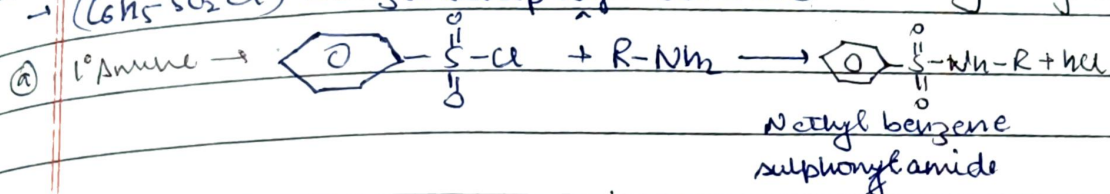


\rightarrow N₂ gas quantitative estimation of amino acids & proteins

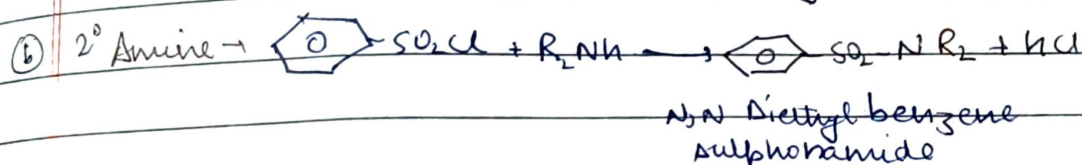


* 2°/3° react in diff. manner.

(c) Rxn with arylsulphonyl chloride \rightarrow
 \rightarrow ($\text{C}_6\text{H}_5\text{-SO}_2\text{Cl}$) Benzenesulphonyl chloride \rightarrow Hinsberg's Reagent



\rightarrow Soluble in alkali \rightarrow $\text{N} \rightarrow \text{N}^-$ acidic \therefore Presence of strong EWG (SO_2Cl)



\rightarrow NO NH \rightarrow Insoluble in alkali.

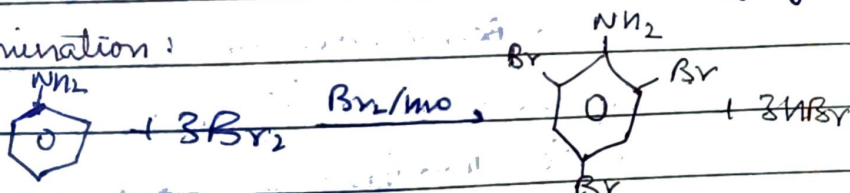
\rightarrow These days \rightarrow $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ $\xrightarrow{\text{instead}}$ p-toluenesulphonyl Cl.

\rightarrow 3° Amine NO Rxn.

\rightarrow Used for distinction of 1°/2°/3° Amine

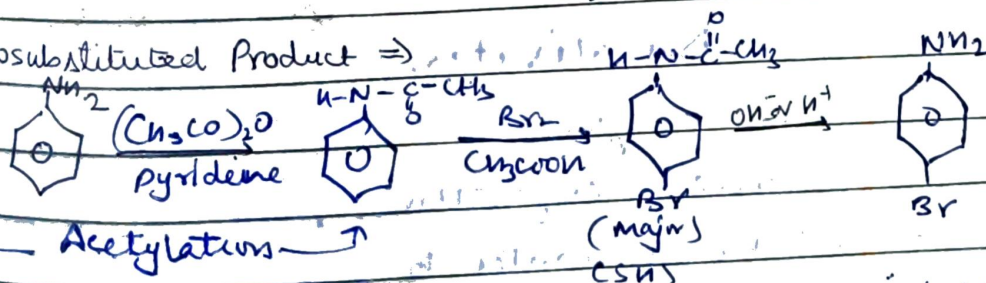
(a) E^+ Subs \rightarrow [$-\text{NH}_2$ grp \rightarrow o-p directing grp]

(a) Bromination:



2,4,6-Tribromoaniline

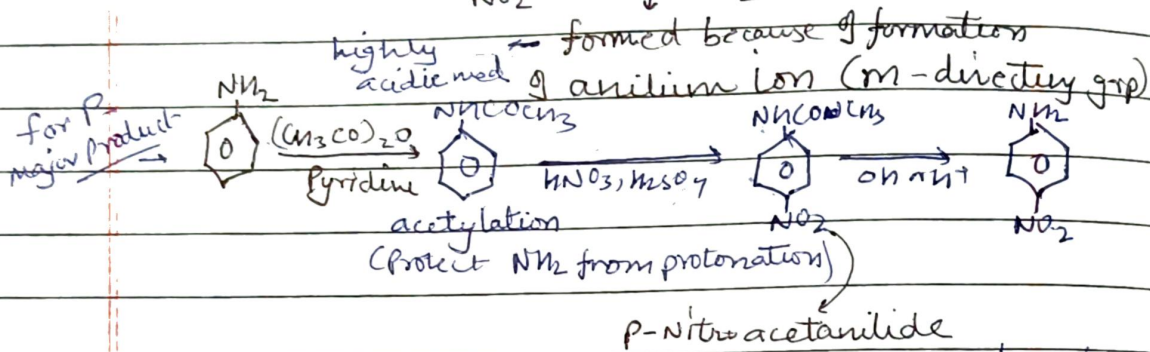
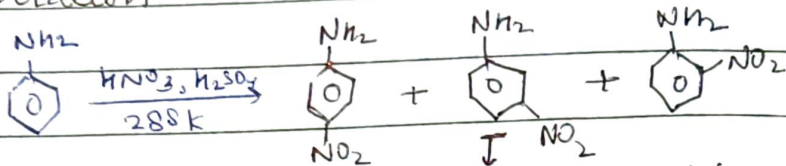
* Monosubstituted Product \Rightarrow



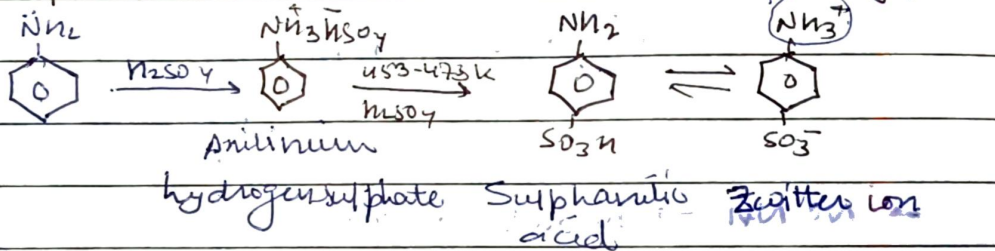
\leftarrow Acetylation \rightarrow

\rightarrow $\text{N}-\overset{\ominus}{\text{C}}-\text{CH}_3 \leftrightarrow \text{N}^+=\overset{\ominus}{\text{C}}-\text{CH}_3 \Rightarrow$ lp of e^- on N less available for donation to C_6H_6 by resonance \Rightarrow NHCOCH_3 less activating than amino grp.

(E) Nitration -



(C) Sulphonation -



Aniline

Not show/undergo friedel crafts rxn.

(D) Diazonium salt - (RN₂⁺X⁻)

benzyl grp
diazonium grp → Cl⁻, Br⁻, HSO₄⁻, BF₄⁻ etc

Naming → Parent hydrocarbon + diazonium + name of anion

ex: C₆H₅N₂⁺HSO₄⁻ → Benzenediazonium hydrogen sulphate

Primary aliphatic amines → highly unstable diaz. salts

" aromatic " → stable for short time in soln at low temp.

(1) Prep → Diazotisation

(a) Props → Physical → C₆H₅N₂⁺Cl⁻

→ colourless, crystalline solid

→ soluble in water & stable in cold / react with warm water.

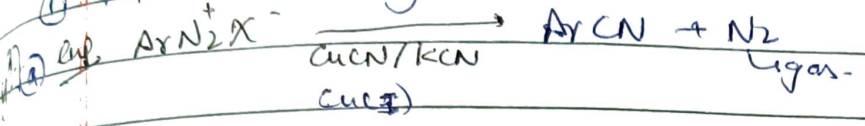
→ easily decompose in dry state.

→ C₆H₅N₂⁺BF₄⁻ → insoluble in water & stable at room temp.

① Chemical prop^s

① R₁N₂ → displacement of N. (Diazonium → Good L.G.)

② Replacement by halide e. / cyanide ion → Sandmeyer Rxn



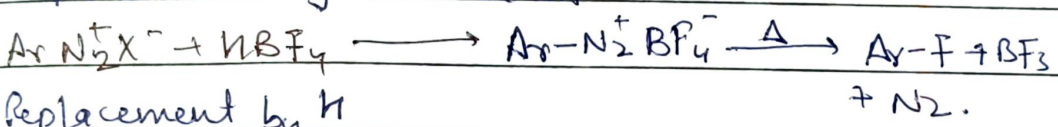
③ Gattermann Rxn

Yield in Sandmeyer better than Gattermann

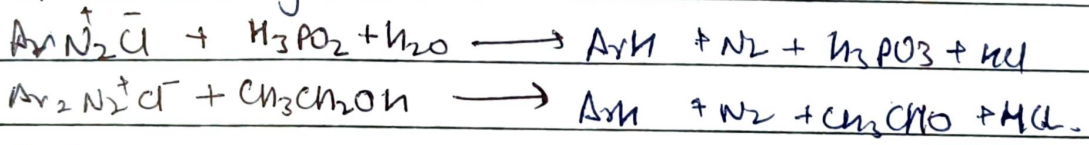
④ Replacement by Iodide ion



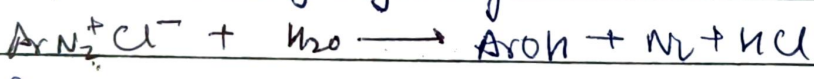
⑤ Replacement by fluoride ion



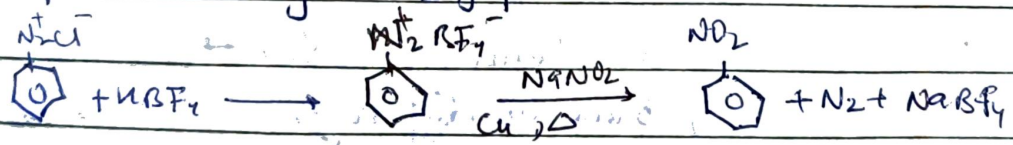
⑥ Replacement by H



⑦ Replacement by hydroxyl

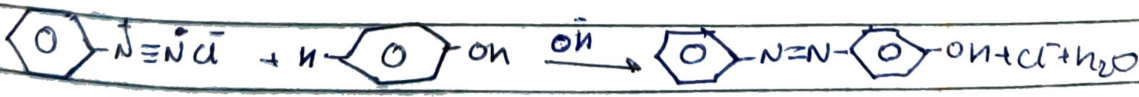


⑧ Replacement by -NO₂ grp

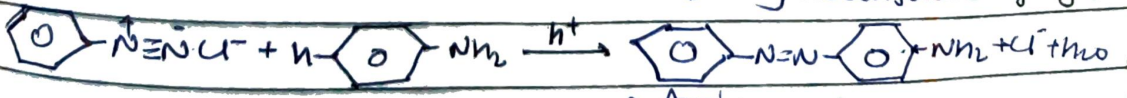


⑨ R₁N₂ → Retention of diazo grp →

① Coupling Rxn → (E⁺ subs) → often coloured rings.



p-hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)