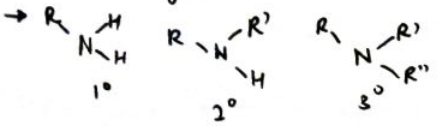
organic nitrogen compounds (amines) 10.3

AMINES

→ derivatives of NH_3 ∴ react same way.



→ eg. $C_2H_5NH_2$ ethylamine

$C_6H_5NH_2$ phenylamine * benzene= prefix.

PROPERTIES OF AMINES

→ due to lp on N:
- → Lewis base (lp donor)
- → Brønsted-Lowry base (H^+ acceptor)
- → Nucleophile

→ Bp → mr↑, Bp↑
- → Bp↑ than alkanes due to H-bonding.
- → Bp↓ than alcohols ∵ H-bonds weaker
  - ↳ (NH bond less polar than O-H)

→ Solubility → soluble in H_2O (H-bonds)
- → C chain ↑ solubility ↓

→ Basic properties → lp allows amines to accept protons via dative covalent bond formation

→ ∴ amines are weak alkalis in H_2O

$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

→ e^- withdrawing substituents → basicity↓ ∵ e^- density on N↓ ∴ less susceptible to accept H^+

→ e^- releasing substituents → basicity↑ ∵ e^- density↑, more susceptible to accept H^+

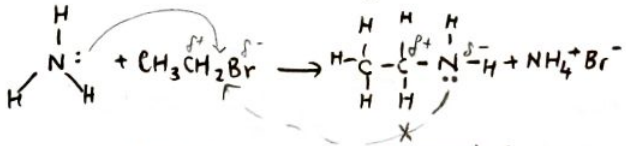
$CH_3CH_2 \rightarrow NH_2$

→ delocalisation of lp e^- of N (overlaps ring)

FORMATION OF AMINES

① Aliphatic amines from halogenoalkanes

→ Reagent: ammonia (excess)
Condition: alcoholic medium, heat in closed vessel under pressure.



* excess ammonia to prevent further substitution. (use up all CH_3CH_2Br)
* the product acts as a nucleophile.

② Reduction of nitrile

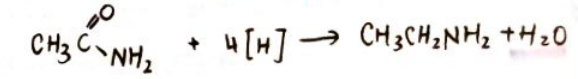
→ Reagent: $LiAlH_4$ (lithium aluminium hydride)

→ Condition: dry ether

$$CH_3CH_2CN + H[H] \xrightarrow[\text{in ether}]{LiAlH_4} CH_3CH_2CH_2NH_2$$

propylamine

③ Reduction of amide



→ Reagent: $LiAlH_4$

→ condition: dry ether

AROMATIC AMINES

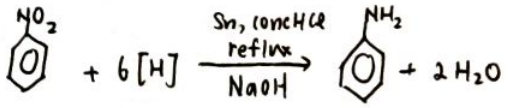
→ Reduction of nitrobenzene

→ mix nitrobenzene with tin & conc HCl → $C_6H_5NH_3^+Cl^-$

→ Add NaOH to salt to release phenylamine

→ Reagent: tin + conc HCl, then NaOH

→ Conditions: reflux



REACTIONS OF AMINES (ACID BASE)

→ Amines dissolve in H_2O to produce weak alkaline solutions.

→ Amines react w/ acids → salts

$$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$$

↑ more soluble

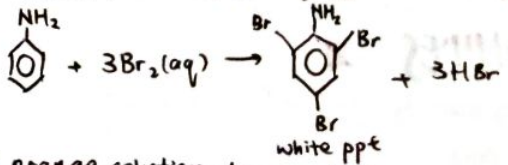
→ $SaH + NaOH \rightarrow$ amine

$$CH_3CH_2NH_3^+ + OH^- \rightarrow CH_3CH_2NH_2 + H_2O$$

REACTION w/ Br (aq)

→ aliphatic amine no reaction

→ phenylamine goes through electrophilic substitution w/ Br(aq) @ room temp



→ orange solution decolourised.

→ NH_2 group has lp e^- that delocalises into benzene ring. e^- density↑ ∴ more susceptible to attack.

organic nitrogen (amines / amides) compounds

REACTION W/ HNO_2 (nitrous acid)

→ HNO_2 = unstable. Produced 'in situ' using $NaNO_2$ & HCl at <10°C

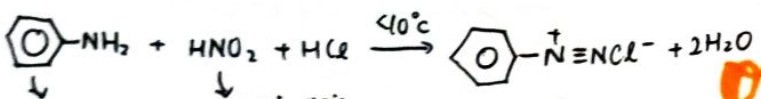
$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

→ @ room temp, HNO_2 decomposes. ∴ put in ice.

→ Amines + HNO_2 → diazonium ions

$$RNH_2 + NNO_2 + H^+ \longrightarrow R-\overset{+}{N}\equiv N + 2H_2O$$

↳ aliphatic amines' diazonium ions decompose <10°C
∴ aromatic amine used.

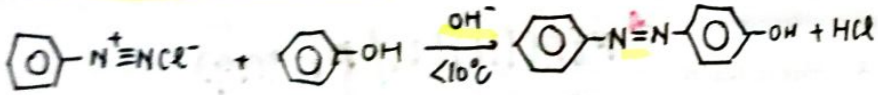
→ 

↓ this used cuz stable <10°C

↓ must <10°C

COUPLING REACTION

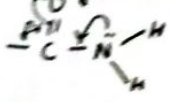
→ dissolve phenol in NaOH (aq), <10°C
→ add benzenediazonium little by little
→ electrophilic substitution



→ delocalised π bonding system between 2 benzene rings acts as a bridge & makes dye stable.

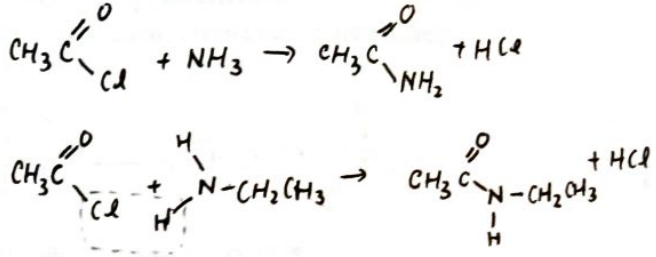
AMIDES

→ ↑mp due to H-bonds, soluble in H_2O
→ neutral
↳ e^- withdrawing character of carbonyl group ↓ e^- density on N ∴ less effective proton acceptor



FORMATION OF AMIDES

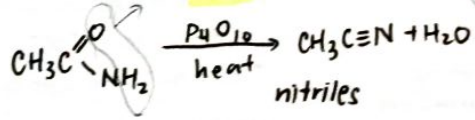
→ acyl chloride + amonia / amines
→ eg.



→ cannot use c. acid (acid base occurs.)

DEHYDRATION OF AMIDES

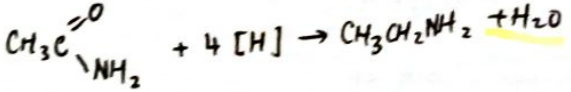
→ Reagent : P_4O_{10}
→ Condition : heat



nitriles

REDUCTION OF AMIDES

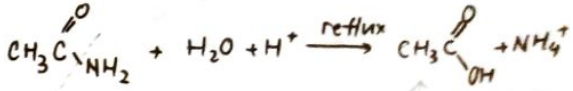
→ Reagent : $LiAlH_4$, dry ether
OR sodium + ethanol
OR H_2, Ni catalyst 140°C



1° amines.

HYDROLYSIS OF AMIDES

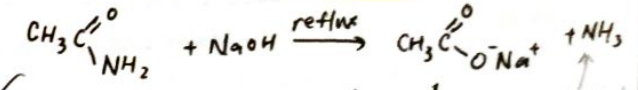
① Acid hydrolysis (like amino acid)
→ Reagent : dilute H_2SO_4 / HCl
Conditions : reflux



c. acid

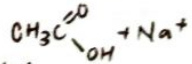
w/ acid, c. acid forms

② Alkaline hydrolysis
→ Reagent : NaOH (aq)
→ conditions : Reflux.



∴ → NaOH (aq) can distinguish amide from ammonium salt
→ amide liberate NH_3 when heated
→ NH_4^+ salt liberate NH_3 WITHOUT heating

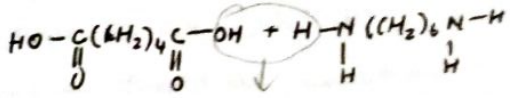
+ H^+ to liberate c.acid



w/ alkali, alkali forms

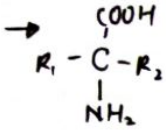
FORMATION OF POLYAMIDES

→ Condensation polymerisation
→ amide linkage

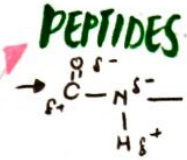


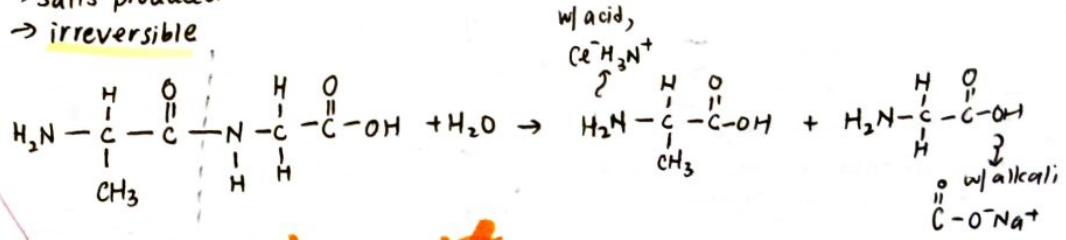
organic nitrogen (amino acids) compounds

STRUCTURE

- 2 functional groups
  - ↳ amine, NH_2
  - ↳ carboxyl, COOH
-  if R_1 & R_2 diff, then have optical isomers.
- glycine doesn't have optical isomers.

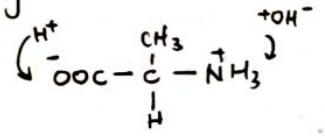
PEPTIDES

-  , by condensation reaction
- Hydrolysis
  - → w/ just H_2O not feasible ∴ use acid / alkali
  - → salts produced
  - → irreversible

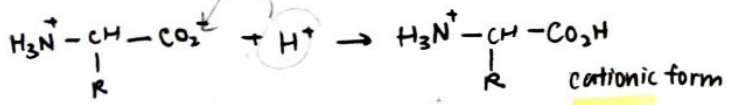


ZWITTERIONS

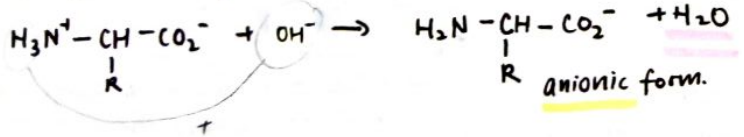
- ↳ dipolar ion that have both acidic & basic properties
- → resist changes in pH when small amount of acid / alkali added → buffer.
- → exist at certain pH → isoelectric point (least soluble in H_2O) => pH @ which amino acid has net charge 0
- → nature of zwitterions gives amino acids strong intermolecular forces of attraction.
  - ↳ crystalline solid soluble in water
  - ↳ mp, bp↑

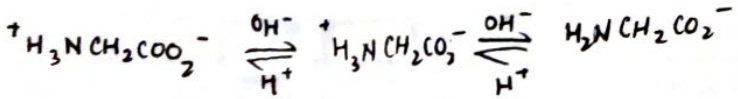


- → As buffers,
  - → When add acid,



  - → When add alkali,

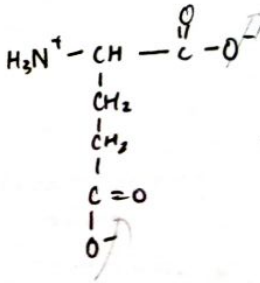




ELECTROPHORESIS

- → used to separate amino acids from hydrolysis.
- → procedure:
  - → soak strip of filter paper w/ pH 7 buffer & clip to microscope slide w/ crocodile clips

  - → place drop of solution in middle
  - → apply voltage for 1 hr
  - → disconnect, develop spots w/ ninhydrin spray.
- → where amino acids move depend on overall charge

eg 

→ moves towards -ve.