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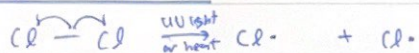
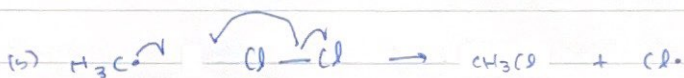
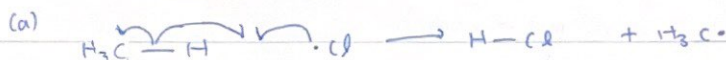
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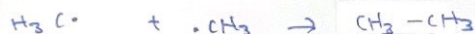
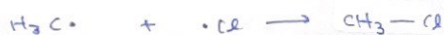
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AlkanesNOTHING IS TO  
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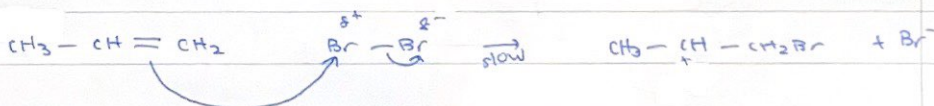
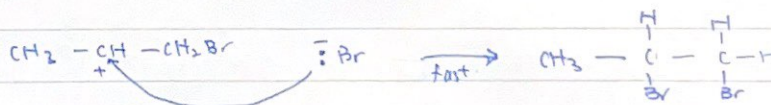
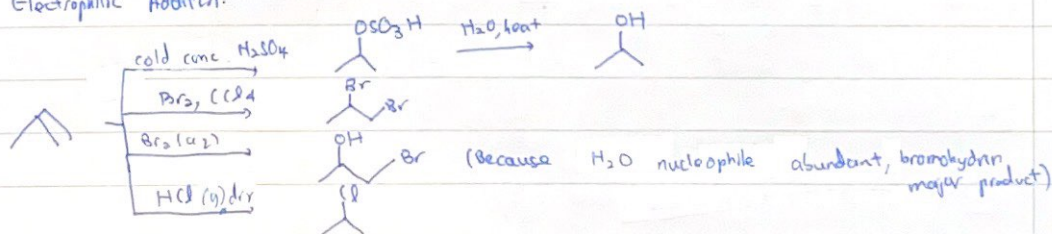
Mechanism: Free Radical Substitution.

Step 1: InitiationStep 2: Propagation

Then (a)(b)(a)(b)....

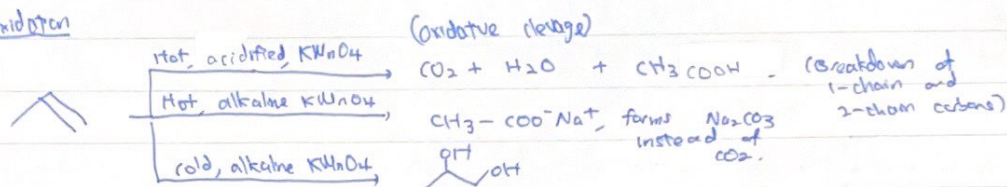
Step 3: TerminationAlkenes

Mechanism: Electrophilic Addition.

Step 1:Step 2:Electrophilic Addition:Reduction:  $\text{H}_2$ , Ni, heat to reduce alkene into alkane.

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## Oxidation



## Carbocation stability

→ Electron donating alkyl group, carbocation is more stable when catanic charge dispersed over more alkyl groups. Thus, formed faster in the rate determining step, major product formed.

Reduction: Cannot use  $\text{LiAlH}_4$  and  $\text{NaBH}_4$ .

→ Unlike a  $\text{C=O}$  bond, there is no partial positive charge in  $\text{C=C}$  alkene bond, hence not susceptible to nucleophilic attack of  $\text{H}^-$  nucleophile.

Adjacent species unreactive:

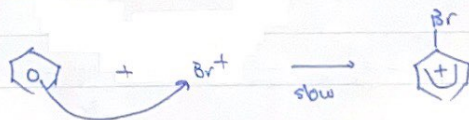
→ p-orbital of adjacent species overlaps with  $\pi$  electron cloud of adjacent  $\text{C=C}$  bond and lone pair delocalised onto  $\text{C=C}$  bond, resulting in partial double bond character.

## Arenes

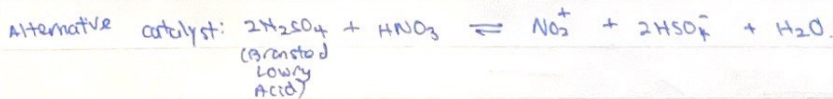
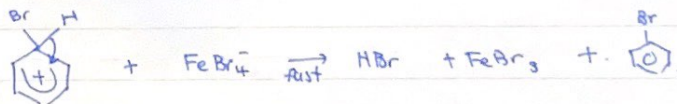
Mechanism: Electrophilic substitution:



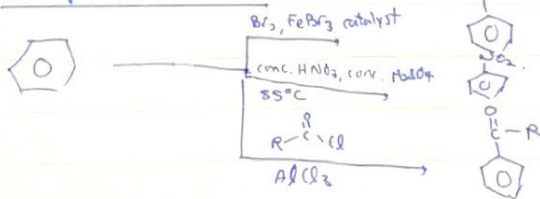
Step 1:



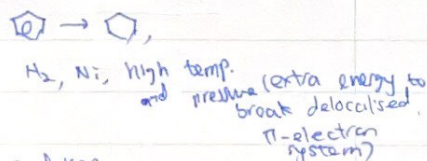
Step 2:



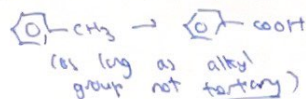
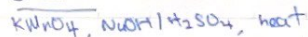
## Electrophilic substitution



## Reduction



## Oxidation







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### Band Breaking

→ Vertical double bond of  $\sigma$  bond due to overlap of p-orbitals of  $\text{C}$  and  $\pi$  electron cloud of benzene ring.

### Electrophilic attack

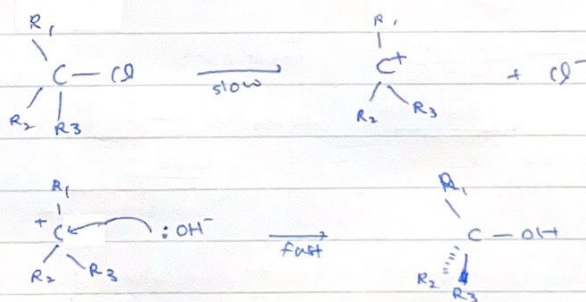
→ Increase/decrease electron density, more/less susceptible to electrophile attack. Additionally, disperses positive charge in carbocation, stabilising carbocation and reducing activation energy.

### Nucleophilic attack (substituent)

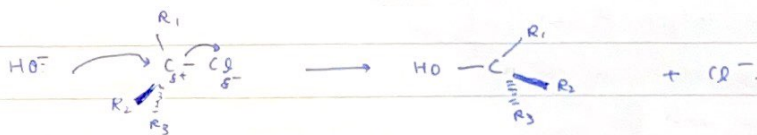
→ p-orbital of substituent interacts with  $\pi$  electron cloud of benzene ring and are delocalised, resulting in lone pair of electrons being less available for nucleophilic attack.

### Halogen

Mechanism:  $\text{S}_\text{N}1$  Nucleophilic Substitution



Mechanism:  $\text{S}_\text{N}2$  Nucleophilic Substitution.



### Racemisation

→  $\text{S}_\text{N}1$  Reaction process involves trigonal planar geometry about carbocation intermediate.

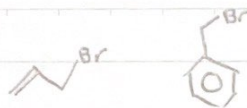
Nucleophile attacks from both sides of plane with equal likelihood, hence equal amounts of pair of enantiomers is formed. Hence racemic mixture that is optically inactive is formed.



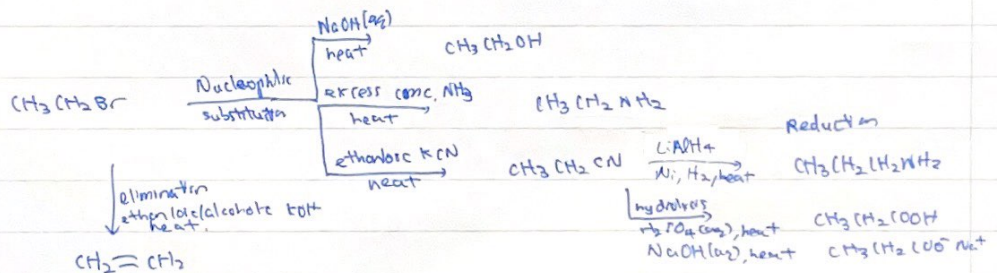
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## Mechanism Classification Rate & rxn

$1^\circ$  -  $S_N2$ ,  $3^\circ$  -  $S_N1$



- Exceptions: Benzyl bromide and  $CH_2=CHCH_2Br$ , where carbocation can be formed through  $S_N1$  reaction mechanism as  $\pi$  electrons of benzene ring / alkene bond delocalise over positive carbon atom, resulting in resonance stabilisation.
- $S_N2$ : Nucleophile approaches halogenoalkane from directly opposite halogen atom and approach hindered by alkyl substituents,  $S_N2$  reaction favored by less steric hindrance around carbon atom and occurs primarily in primary halogenoalkanes.
- $S_N1$ : Rate of  $S_N1$  reaction is dependent on rate of formation of carbocation in rate determining step through heterolytic fission of  $C-X$  bond, rate increases when stability of carbocation increases due to a lower activation energy, electron-donating alkyl groups stabilise carbocation by helping to disperse positive charge, hence primarily occurs in tertiary halogenoalkanes with 3 electron donating alkyl groups.
- Strength of  $C-X$  bond also affects rate of rxn (check periodic table II)



Halogenoarenes — PO not undergo nucleophilic substitution (steric hindrance of benzene ring and partial double bond character of  $CX$ )

### Distinguishing

Heat RX with  $NaOH(aq)$  in test tube ( $NaOH, X^-$ )  
 Cool mixture (prevents formation of  $AgNO_3$ )  
 Acidify with dilute  $HNO_3$  Removes excess  $OH^-$   
 $2Ag^+ + OH^- \rightarrow Ag_2O(s) + H_2O(l)$   
 prevents side reaction.  
 Add  $AgNO_3(aq)$   $AgX(s)$  precipitate  
 Cl — white Br — pale cream I — yellow

### CFCs

Only C, Cl, F. Stable due to strong  $C-Cl$  and  $C-F$ , can stay in atmosphere for long time.  
 $C-Cl$  bond enough to be split by UV and form  $Cl\cdot$ .  
 $CCl_2F_2 \xrightarrow{UV} \cdot CClF_2 + Cl\cdot$   
 $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$   
 $ClO\cdot + O_3 \rightarrow Cl\cdot + 2O_2$   
 Regenerates  $Cl$  radicals and destroys  $O_3$ .





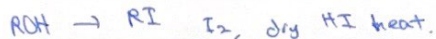
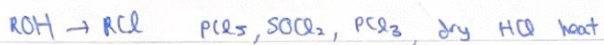
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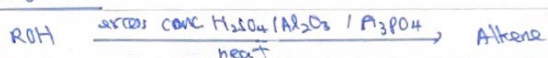
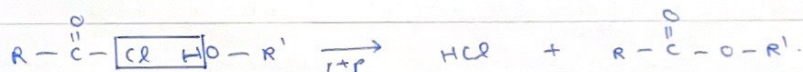
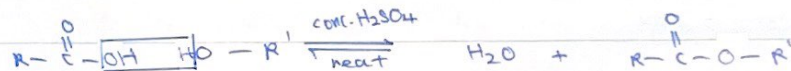
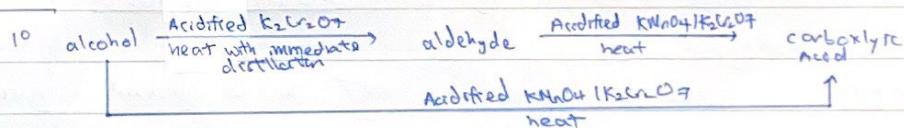
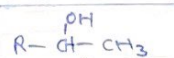
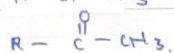
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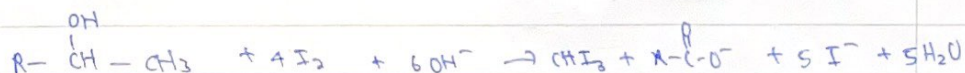
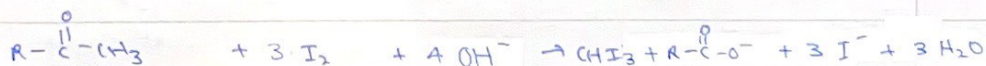
NOTHING IS TO  
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THIS MARGINHydroxyNucleophilic Substitution

Distinguishing test:

ROH +  $PCl_5$ .  
white fumes at HCl(g)  
turn damp blue  
litmus paper red.

DehydrationEsterification / AcylationOxidationIodoform test (oxidation) $I_2, NaOH, \text{ heat}$ yellow ppt. of  $CHI_3$  formed

3  $I_2$  to substitute onto  $CH_3$  can be  
1  $I_2$  to oxidise OH into ketone  
(naturally substituted)



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## Phenols

	<u>Metal Na</u>	<u>Base NaOH</u>	<u>Carbonate Na<sub>2</sub>CO<sub>3</sub></u>
Alcohol	✓	x	x
Phenol	✓	✓	x
Carboxylic Acid	✓	✓	✓

Phenols less reactive than alcohols due to partial double bond character of C-O bond and can only undergo reactions involving cleavage of off bond.

Phenols do not react with carboxylic acids as lone pair of electrons <sup>overlaps with  $\pi$ -electron cloud of benzene ring</sup> are delocalised into benzene ring, less available as a nucleophile.

Acidity: Carboxylic acid > phenol > water > alcohol

→ Acidity dependent on stability of conjugate base, more stable conjugate

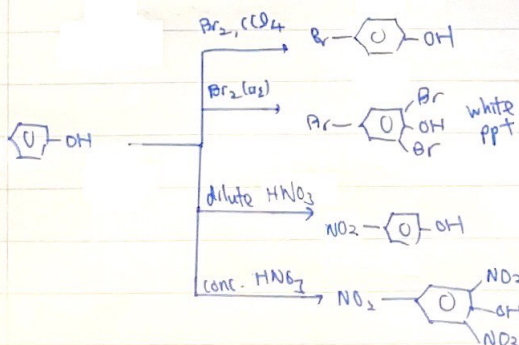
base will have greater extent of dissociation of H<sup>+</sup> and more acidic  
than alkoxide

→ hydroxide more stable, due to electron-donating alkyl group that intensifies negative charge

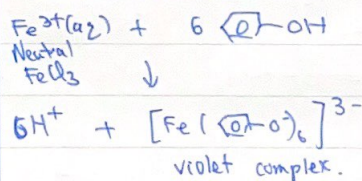
→ Phenoxide more stable than phenoxide as p-orbital of O overlaps with adjacent  $\pi$  electron cloud of benzene ring and is negative charge delocalised into ring, resulting in resonance stabilisation.

→ RCOO<sup>-</sup> more stable than phenoxide as RCOO<sup>-</sup> has 2 equivalent resonance structures with delocalisation of negative charge over 2 highly electronegative atoms. Carboxylate anion greater stabilised.

## Electrophilic Substitution (Benzene ring)



## Distinguishing test







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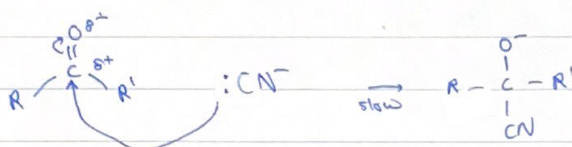
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## Carbonyl Compounds

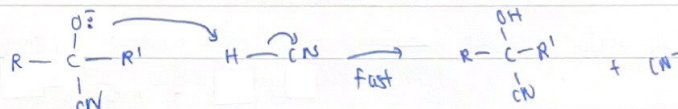
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Mechanism: Nucleophilic Addition.

Step 1:



Step 2:



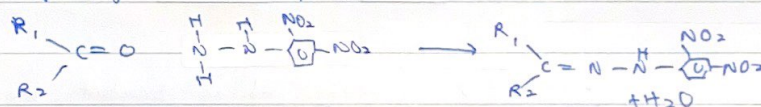
## Reactions

HCN, trace KOH (equilibrium)

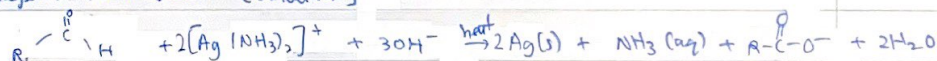
KCN in H<sub>2</sub>SO<sub>4</sub> (provides H<sup>+</sup>)

HCN, trace KCN (CN catalyst)

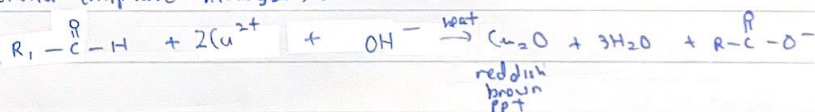
2,4-Dinitrophenylhydrazine (Carbonyl test) [Condensation]



Tollen's Reagent (Aldehydes) [Oxidation]



Fehling's Solution (Aliphatic Aldehydes) [Oxidation]



## Reduction Reagents

H<sub>2</sub>, Ni, heat

Aldehyde, ketone, nitrile, alkene

LiAlH<sub>4</sub>, dry ether

Aldehyde, ketone, nitrile, amide, carboxylic acid

NaBH<sub>4</sub>

Aldehyde, ketone

## Reactivity

→ sp<sup>2</sup> hybridised carbonyl carbon, partially positively charged due to more electronegative O. Electron-rich nucleophiles are attracted to electron deficient site.

→ Aromatic carbonyls less susceptible to nucleophilic attack due to interaction of π electron cloud of benzene ring and carbonyl group, resulting in carbonyl carbon less electron deficient and less susceptible to nucleophilic attack.

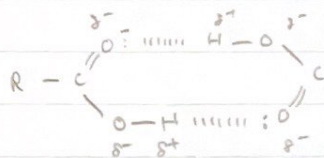


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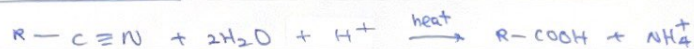
## Carboxylic Acids & Derivatives.

### Dimerise

Carboxylic acid dimerise in vapour state and nonpolar solvents, forming 2 intermolecular hydrogen bonds.



### Nitrile Hydrolysis



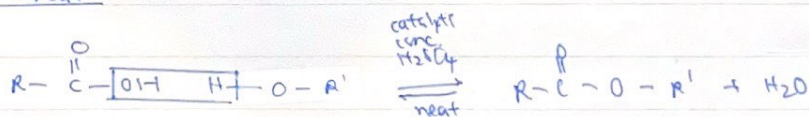
### Acidity (Substituents)

Greater number of electron-withdrawing substituent groups, greater extent of negative charge dispersal on  $RCOO^-$ . Conjugate base more stabilised and more acidic.

Greater number of electron-donating groups, more intensified negative charge on  $RCOO^-$ . Conjugate base destabilised and less acidic.

Inductive effects operate through  $\sigma$  bonds and are dependant on distance, effect of electron-withdrawing substituent decreases as substituent moves further from  $COOH$  group. Closer the electron-withdrawing substituent, more acidic.

### Condensation



Reversible, shift equilibrium position to the right by.

→ Removing water

→ Excess reactant.

conc.  $H_2SO_4$  catalyst to make carbonyl carbon more electrophilic.





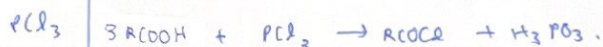
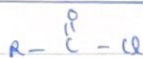
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'Acyl chlorides are volatile, low boiling points due to lack of electronegative H atom for intermolecular hydrogen bonding.

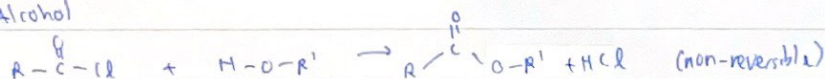
Acyl chlorides undergo hydrolysis easily

↳ Electronic factor: C=O carbon bonded to 2 highly electronegative atoms, resulting in a high partial positive charge and more susceptible to nucleophilic attack.

↳ Steric factor:  $sp^2$  hybridised C=O atom has less steric hindrance since nucleophile attacks trigonal planar geometry (rather than tetrahedral) and can approach without hindrance from either side of plane.

Esterification

Alcohol



Phenols — No reaction (as not strong nucleophile), but phenoxide reacts.



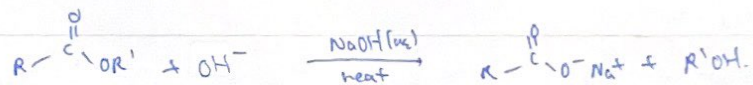
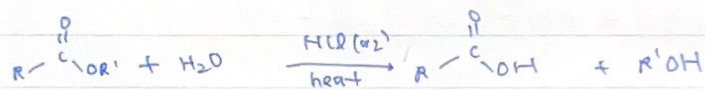
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### Formation of amides (0°, 1°, 2° amines)



### Ester

Hydrolysis through heating with acid/base.







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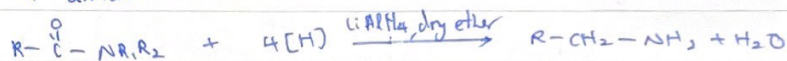
Nitrogen compounds.NOTHING IS TO  
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can be Lewis (lone pair) or Bronsted Lowry (donate bond with electron deficient species)  
Strength depends on electron density of N atom which affects availability

of lone pair of electrons to coordinate with lone pair.

→ Reduction of Nitriles ( $\text{LiAlH}_4$ ,  $\text{H}_2$ , Ni, heat)

→ Reduction of amides



→ Hydrolysis of amide

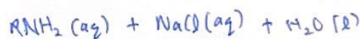
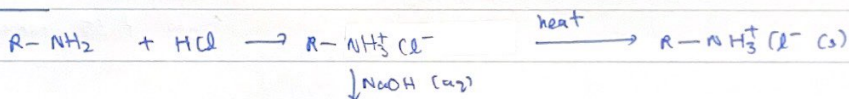


→ Aromatic amine: reduction of nitrobenzene.



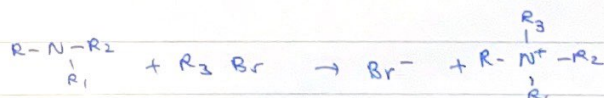
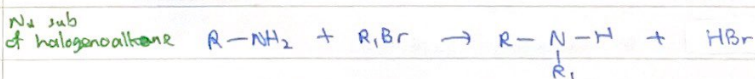
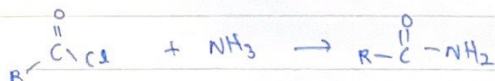
1.  $\text{Sn}$ , conc.  $\text{HCl}$ , heat under reflux

2.  $\text{NaOH}$  (aq) from  $\text{C}_6\text{H}_5-\text{NH}_2$  to  $\text{C}_6\text{H}_5-\text{NH}_2$ .

Amine reactionsAcid-base  
reaction

(Pungent  $\text{RNH}_2$  evolved on heating)

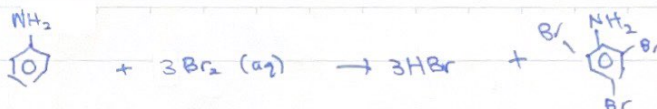
→ Separation of amines from neutral/lacidic compounds.

No sub  
of haloalkaneCondensation  
with acyl halide

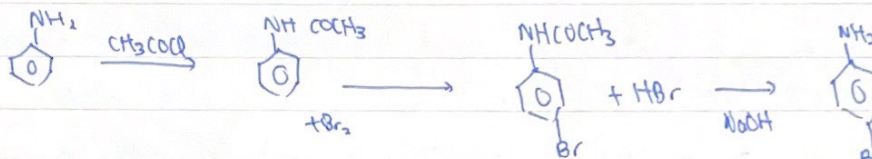
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RAFFLES INSTITUTION

Electrophilic substitution

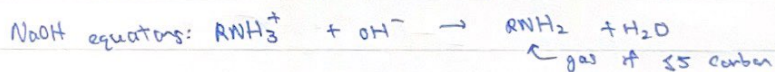


Mono bromination:



Distinguishing tests

	Amine ( $\leq 5\text{C}$ )	Amine ( $\geq 6\text{C}$ )	Phenylamine	Amide	Ammonium salt
solubility	Soluble.	Insoluble	Sparingly soluble	Soluble	Soluble
HCl	N/A	Water soluble salt Dissolves into homogeneous solution	N/A	N/A	N/A
NaOH	Pungent gas evolved (just from warming)	N/A (oily layer)	N/A (oily layer)	No gas. on strong heating, amine formed	Amine formed



Amides Neutral compound with N are nitriles or amides

Effectively neutral. Lone pair of electrons interacts with  $\pi$  electron cloud of adjacent  $\text{C=O}$  bond and is delocalised. Not available for coordination with a proton, neutral.

↳ prepared with acylation in anhydrous conditions

↳ Hydrolysis in acid/base — carboxylic acid and amine (or salts)





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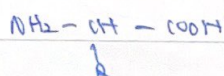
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BE WRITTEN IN  
THIS MARGIN

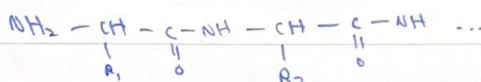
## Amino Acids

- Zwitterions in dry solid state. Dipole solid, electrically neutral molecule with oppositely charged ends. ( $-\text{COO}^-$ ,  $\text{NH}_3^+$ )
- Crystalline solids with high melting point as zwitterions held in place by strong ionic bonds. Soluble in water due to ion-dipole interactions.
- Can react with both acids and bases, titrated 2 equivalence points.

### Amino acid



### Peptide (N left, C right)



Undergoes condensation with acyl chloride and alcohol

## Proteins

- Complete hydrolysis obtains individual amino acids. Prolonged heating under reflux.
- Enzymatic hydrolysis: selectively hydrolyses specific peptide bonds.



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