UNIT - V

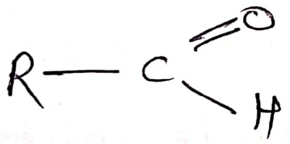
CARBOXYLIC ACID

→ The Carboxyllic functional group represented as $-COOH$.

→ It can be said that carbonyl group is attached to hydroxyl group.

→ A large no. of natural products are either carboxylic acid derivative or are derived from them.

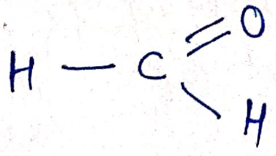
→ **Structure**



1) sp^2 hybridized 'c'
2) one π bond
3) $3 \cdot \sigma$ bond.
4) shape → planner.

Ex.

$HCOOH$



PHYSICAL PROPERTY OF CARBOXYLIC ACID

1. ACIDITY OF CARBOXYLIC ACID

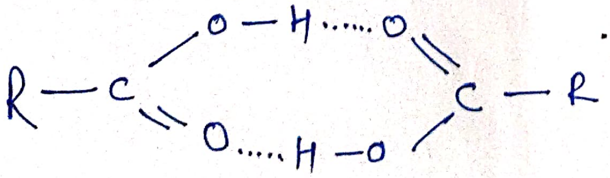
→ Carboxylic acid act as both Hydrogen bond acceptor, due to Carbonyl group & Hydrogen bond donor due to hydroxyl group.

→ They often participate in H- bonding.

→ They usally exist as dimeric pairs in non. polar media b/c of their tendancy to self associate.

→ Carboxylic acid is polar molecule but as alkyl group increases it's solubility get decreases.

→ Carboxylic acid are characterized as weak acid.



{Dimeric form of acid}

CHEMICAL REACTION OF CARBOXYLIC ACID

→ Reaction involving the cleavage of O-H bond.

Acidity of Carboxylic Acid

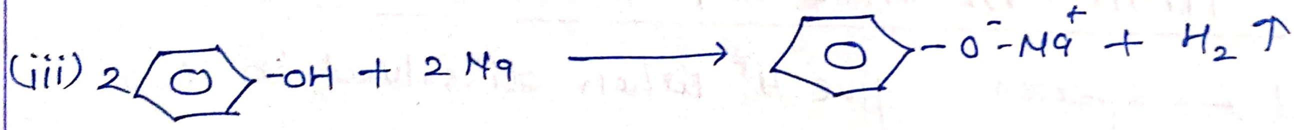
Acidity = which donate H^+ ion.

① Reaction c̄ Na^+ Active metal

When Carboxyllic acid reacts c̄ Na metal, it produces Hydrogen gas, like alcohol & phenol do.
(Removal of H_2 gas shows Acidity of Acid)

(i) $2R-COOH + 2Na \longrightarrow 2R-COO^-Na^+ + H_2\uparrow$
(Carboxyllic acid)

(ii) $2R-O-H + 2Na \longrightarrow 2R-O^-Na^+ + H_2\uparrow$
(aliphatic alcohol)

(iii)


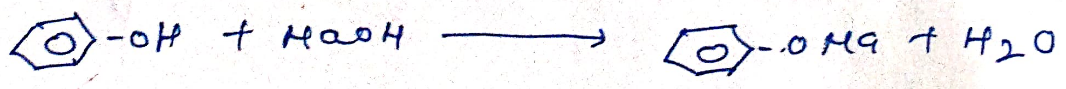
(aromatic Alc) (Sod. phenoxide)

② Reaction c̄ aq. NaOH

Phenol & Carboxylic acid react c̄ NaOH but Alcohol do not.

→ $R-COOH + NaOH \longrightarrow R-COONa + H_2O$

→ $R-O-H + NaOH \longrightarrow$ X or Very unstable.

→


③ Reaction c̄ weaker base like carbonates .. ($NaHCO_3$, Na_2CO_3).
phenol & alcohol do not react, so this also shows presence of R-COOH group.

(i) $R-COOH + NaHCO_3 \longrightarrow R-COO^-Na^+ + H_2O + \underline{CO_{2(g)}}\uparrow$

(ii) $R-COOH + Na_2CO_3 \longrightarrow R-COONa + H_2O + \underline{CO_{2(g)}}\uparrow$

(if CO_2 is releasing then it shows that compound having ~~at~~ carboxylic acid.)

ORDER OF ACIDIC NATURE

carboxylic acid > phenol > Alcohol

WHY CARBOXYLIC ACID IS MORE ACIDIC THAN ALCOHOL & PHENOL

Acid → species c̄ give H^+ when dissolved in H_2O.

$$HA + H_2O \longrightarrow H^+ + \enclose{circle}{A^-}$$

for being stronger acid this A^- must be stable. b/c if this counter ion is unstable then reaction will be backwarded (again can react c̄ H^+).

⇒ So acid c̄ have stable A^- will be strong acid.

Alcohol

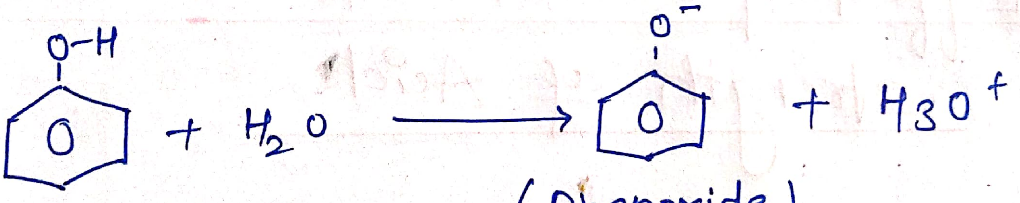
$$R-O-H + H_2O \longrightarrow \underbrace{R-O^-}_{\text{Alkoxide}} + H_3O^+ \text{ (Hydronium ion)}$$

here $R \to O^-$ → R^+ shows +I effect means it direct electron to oxygen atom. so, more electron accomodate on O_2 which make it more unstable. hence $\overset{+}{R}-O^-$ is not stable

(More accomodation/concentration of charge ∝ unstability of ion)

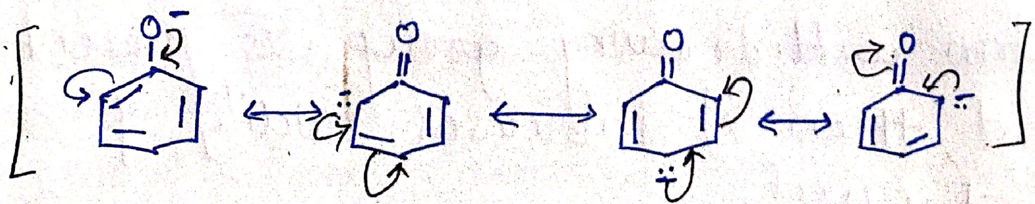
* Alcohols are not much acidic.

PHENOL



(Phenoxide)

phenoxide ion is stable due to resonating structure so more stable than alcohol, but lower than carboxylic acid

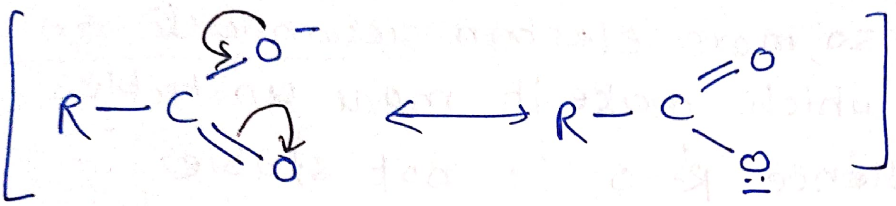


so here Negative ion stays on 'c' in resonance & Carbon is less electro negative. so -ve ion is unstable.

Carboxylic Acid

$$R-COOH + H_2O \longrightarrow \underset{\text{(Carboxylate ion)}}{R-COO^-} + H_3O^+$$

Resonating structure of carboxylate ion.



⇒ Negative charge/ion lies on more electro-negative species rather than 'c' in phenols. hence carboxylate ion is more stable.

Effect of Substituents on the strength of Acids

→ The acidity of carboxylic acids depends on the acidic strength of substituents attached to the carboxyl group.

→ when electron withdrawing group is present in compound, then it increases acidity of acid, due to −I effect.

→ when electron donating group is present it ↓ acidity of carboxylic acid due to +I effect.

① Inductive Effect

example

F = electron withdrawing group.

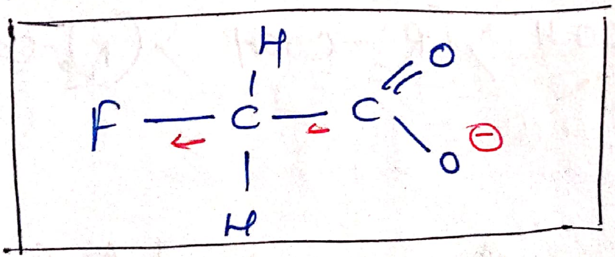
ex. Cl, Br, f, OH, CN

$CH_3COOH < CH_2FCOOH < CHF_2COOH < CF_3COOH$

* Electronegativity of substituent ∝ Acidity of COOH

(a) Withdrawing Inductive effect (–I)

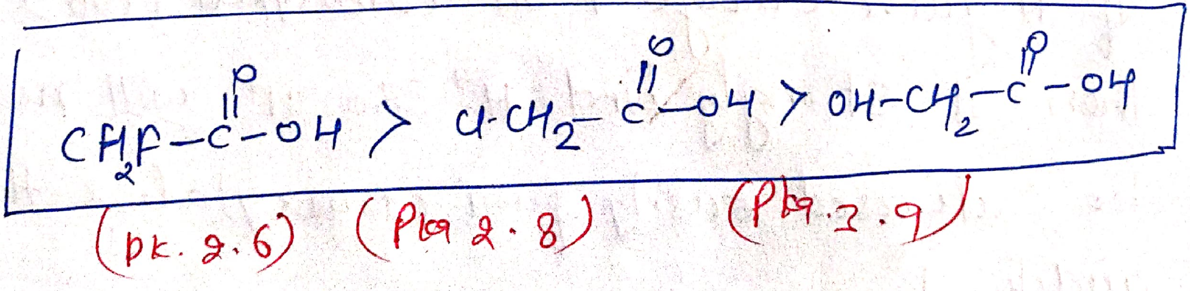
→ Flourine atom is more electronegative than H-atom, so it pull electron density toward itself. so making carboxylate ion stable, hence ↑ acidity.



f > Br > i > Cl

f' > Cl > Br > I

ex.



$CH_2F-\overset{O}{\overset{\|}{C}}-OH > Cl\text{-}CH_2-\overset{O}{\overset{\|}{C}}-OH > OH-CH_2-\overset{O}{\overset{\|}{C}}-OH$

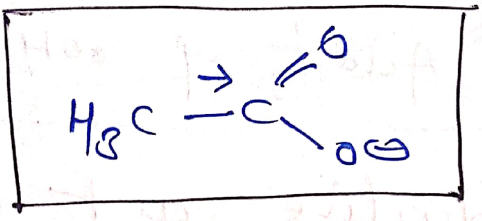
(pK. 2.6) (Pka 2.8) (Pka 3.9)

concept: here Carboxylate ion (COO^-) having less Negative charge so it can release H^+ easily hence acidity will ↑.

(B) Donating Inductive Effect (+I)

→ Alkyl group (-R) is electron donating.

→ In this it pushes electron to carboxylate anion, making it destabilized, so ↓ acidity.



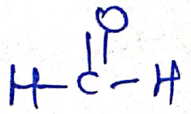
→ Lengthening the alkyl chain of -COOH can ↑ inductive effect but no longer ↓ acidity after three 'C' long.

$$HCOOH > R\text{-}COOH > (R)_2\text{-}COOH > (R)_3\text{-}COOH$$

concept:

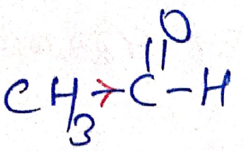
If negative charge ↑ on carboxylate (COO^-) ion then it strongly bind H^+ so H^+ will not be released easily from carboxylate & thus acidity ↓.

Ex.



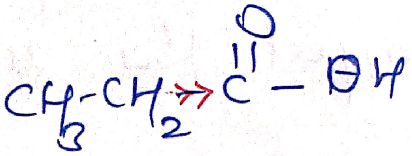
$H-\overset{O}{\overset{\|}{C}}-H$

formic acid >



$CH_3 \rightarrow \overset{O}{\overset{\|}{C}}-H$

Acetic Acid >

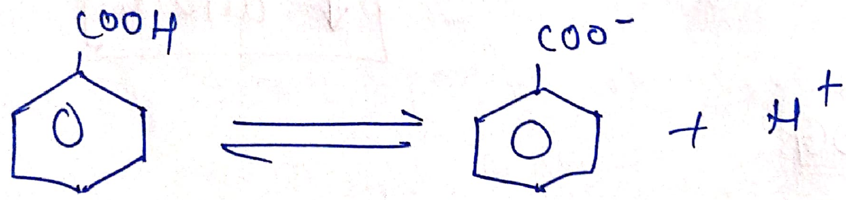


$CH_3-CH_2 \rightarrow \overset{O}{\overset{\|}{C}}-OH$

Proponoic acid.

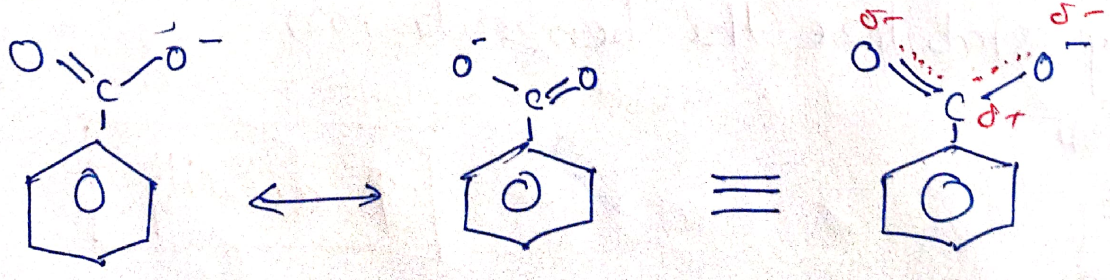
(II) Effect of substituent on aromatic Acid.

Benzoic acid undergoes dissociation & gives benzoate & proton.



(Benzoic acid) (Benzoate ion)

These ions are resonance stable.



(1) (2) Resonance hybrid

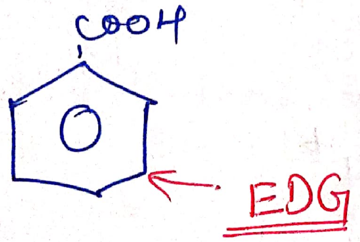
⇒ Nature and position of substituent both affect the acidity of aromatic acid.

ⓐ Electron releasing group

($-CH_3$, $-OH$, $-NH_2$) ⟶ (↓ acidity)

⇒ These group destabilize the benzoate ion & ↓ acidity.

⇒ But this effect work in some case at only p- position ($-OH$, $-OCH_3$)

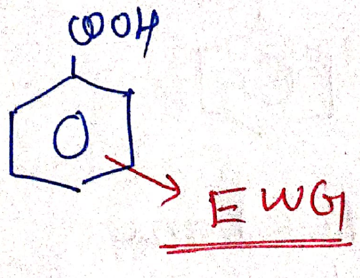


↓ acidity

ⓑ Electron withdrawing group

($-CN$, $-NO_2$, $-CHO$ etc.) → ↑ acidity.

→ They stabilize the benzoate ion



↑ acidity

(ii) position of groups

→ Some groups like −OH, −OCH_3 at para position, shows mesomeric effect c dominate over Inductive effect so ↓ acidity.

⇒ At meta position these groups shows e⁻ withdrawing or −I effect only. so they stabilized the ion & ↑ acidity

⇒ These group at ortho-position ↑ acidity due to stabilization of carboxylate ion (due to intermolecular H-bonding)

(iii) Effect of hallogen

→ Halogen shows −I effect hence they ↑ acidity of aromatic acid.

(IV) Ortho effect:

⇒ All ortho substituent shows acid strength effect wether they are e⁻ releasing or e⁻ withdrawing group.

→ This is called "Ortho effect"

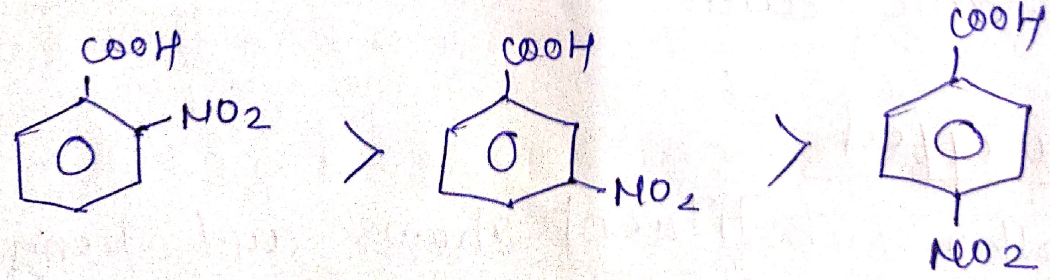
→ This is some how explained by steric hindrance but the exact reason is not k/n.

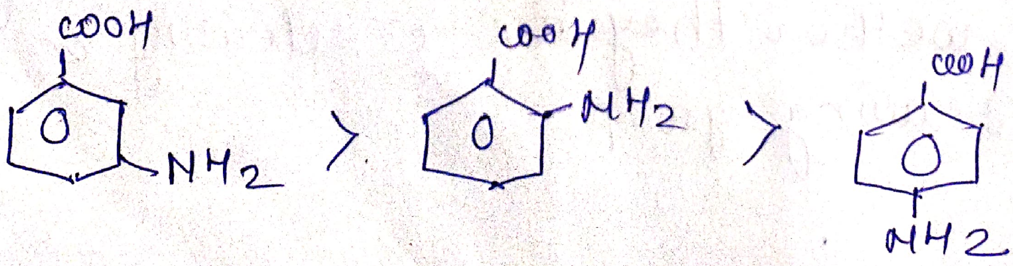
Acidity constant (K_a) of different groups on Benzoic acid.

$$\boxed{K_a \propto \text{Acidity of B.A.}}$$

Subst. Name	Ka of 'p' substituted	Ka of M-substituted	Ka of 'O' substituted acid
$-NO_2$ (nitro)	30×10^{-5}	32×10^{-5}	670×10^{-5}
$-Cl^-$	10.3×10^{-5}	15.1×10^{-5}	120×10^{-5}
$-CH_3$	4.2×10^{-5}	5.4×10^{-5}	12.4×10^{-5}
$-OH$	2.6×10^{-5}	8.3×10^{-5}	105×10^{-5}
$-NH_2$	1.4×10^{-5}	1.9×10^{-5}	1.6×10^{-5}

Ex. ($-NO_2$)

(I)


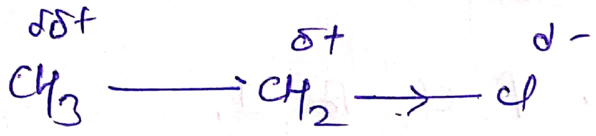
(II)


Inductive Effect

Definition

It refers to the polarization of electron density along a chain of atom in a molecule due to electronegativity of substituent.

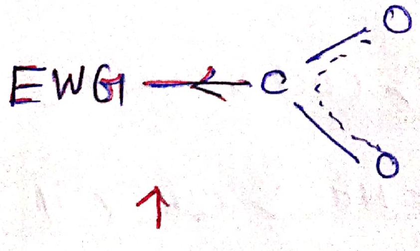
→ It is permanent effect and occurs through sigma bonds.

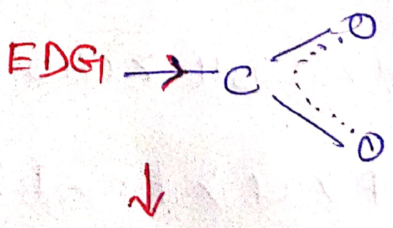


$$\overset{\delta\delta+}{CH_3} \longrightarrow \overset{\delta+}{CH_2} \rightarrow \overset{\delta-}{Cl}$$

Effect on Acidity and basicity

→ As said Electron withdrawing group (EWG) ↑ acidity & electron donating group ↓ acidity of molecule.





Types of Inductive Effect

(I) Negative I effect (-I)

(II) Possitive I effect (+I)

① Negative Inductive Effect

⇒ Group or atom that withdraw the electron from rest of molecule.

Ex. Halogen → F, Cl, Br, I,

Nitro group → $-NO_2$

Carboxyl group → $-COOH$

cyanide group → CN

* These group increase the possitive charge on 'C' atom

Order of reactivity of EWG

$NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2$

$CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

(2) Possitive Inductive Effect (+I)

→ It Include the groups or atom c̄ donate electron to rest of molecule.

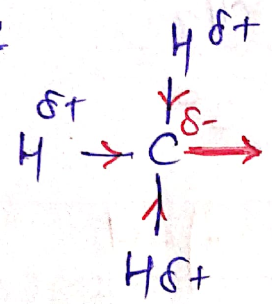
~~ex~~.

→ These group ↓ the possitive charge on 'c'.

Order of reactivity

$C(CH_3)_3 > CH(CH_3)_2 > CH_2(CH_3) > CH_3 > H$

Ex.



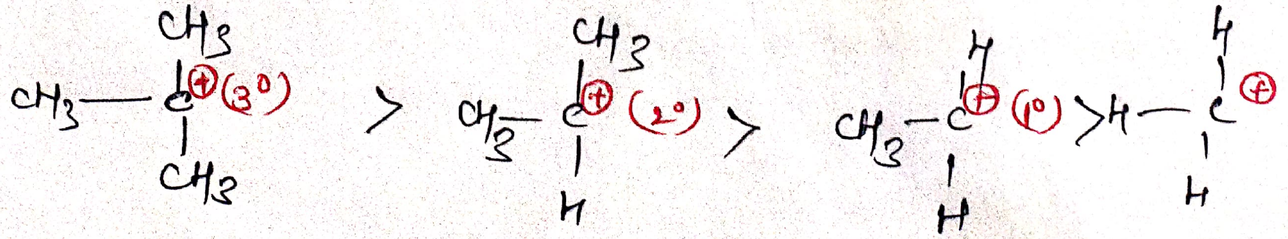
here H act as e⁻ donating atom towards carbon Now the overall donation turn ~~a~~ the alkyle moitey into Electron donating group.

APPLICATION OF INDUCTIVE EFFECT

① stability of Carbanion & Carbocations.

(i) Stability of Carbocation ↑ c̄ +I effect as alkyle group decrease +ve charge on 'c' by donating -ve charge density, so causes greater stability of Carbocation.

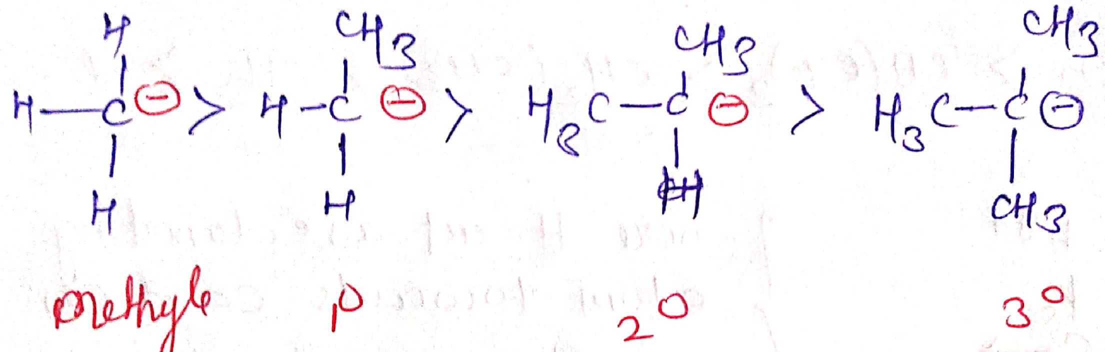
ex.



→ where as -I group destabilize the Carbocation.

⇒ Stability of carbanions

-I group ↑ stability, while +I group ↓ stability of carbanions.



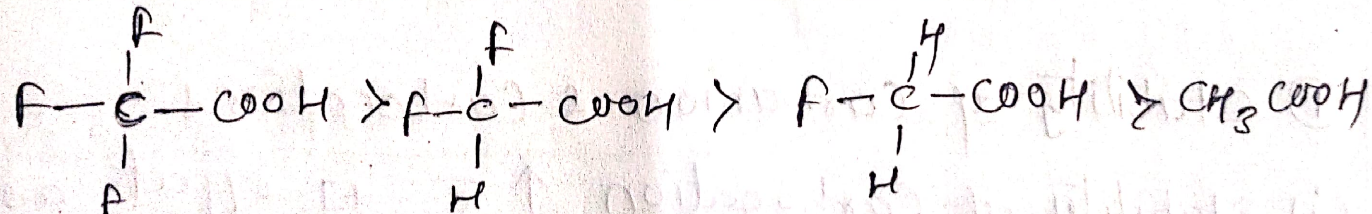
$$H-\overset{H}{\underset{H}{C}}{}^{\ominus} > H-\overset{CH_3}{\underset{H}{C}}{}^{\ominus} > H_3C-\overset{CH_3}{\underset{H}{C}}{}^{\ominus} > H_3C-\overset{CH_3}{\underset{CH_3}{C}}{}^{\ominus}$$

methyle 1° 2° 3°

② Acidic strength of Carboxylic Acid

EWG ↑ acidity of Carboxylic acid.

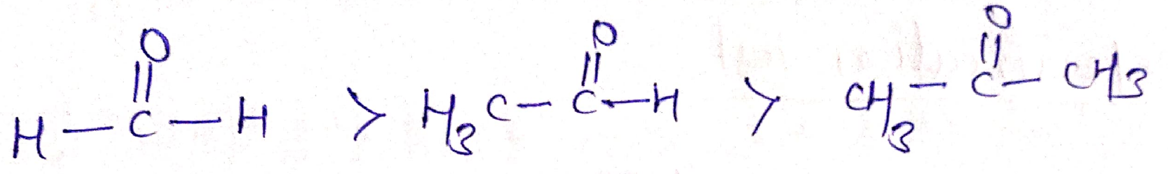
EDG ↓ acidity of Carboxylic acid.



$$F-\overset{F}{\underset{F}{C}}-COOH > F-\overset{F}{\underset{H}{C}}-COOH > F-\overset{H}{\underset{H}{C}}-COOH > CH_3COOH$$

③ Reactivity of Carbonyl Compound

+I effect shows electron density at carbonyl carbon. hence their reactivity towards nucleophiles decreases.



$$H-\overset{\overset{O}{\|}}{C}-H > H_3C-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

(formaldehyde) (Acetaldehyde) (Acetone)

Qualitative Test for Carboxylic Acid

① Limit test

⇒ Procedure :→ Dip blue litmus paper in sample.

⇒ Observation → litmus paper turn red.

⇒ explaination → Carboxylic acid donate H^+ causing colour change.

② Sodium Bicarbonate test

$$R-COOH + NaHCO_3 \longrightarrow R-COONa + CO_2 + H_2O$$

Observation: Effervescence is observed due to production of CO_2 gas.

(3) Sodium Hydroxide test (NaOH)

$R-COOH + NaOH \longrightarrow R-COONa + H_2O$

observation : form a clear solution of salt.

(4) Esterification test

$R-COOH + R'-OH \xrightarrow{H_2SO_4} R-COOR' + H_2O$

(Ester)

observation : odour is pleasant.

(5) Silver Nitrate test

$R-COOH + AgNO_3 \longrightarrow R-COOAg + HNO_3$

(Silver Carboxylate)

TEST FOR AMIDE

① Litmus test

→ Dip Red & blue litmus to sample solution.

obse → Amide generally show no colour change.

Exp → Amide is neutral compound, do not exhibit acidic / basic behaviour in aq. solution.

(2) Hydrolysis test

$$R-COONH_2 + H_2O + HCl \rightarrow R-COOH + NH_4Cl$$

$$R-CONH_2 + NaOH \rightarrow R-COONa + NH_3$$

$\boxed{\text{observation}}$ ⇒ Amide undergoes hydrolysis to form carboxylic acid & NH_3.

③ sodium Hypochlorite test (Hinsberg test)

Amides are oxidized by sod. hypochlorite & release ammonia

$$\boxed{R-CONH_2 + NaOCl \rightarrow R-COOH + NH_3 + NaCl}$$

④ Bromine water test

~~Procedure. i) Add Hydroxylamine hydrochloride fix"~~
~~ii) then add $FeCl_3$~~
~~observation: formation of colour complex. c̄~~
~~feric ion.~~

Procedure → Add Br to sample,
→ disappearance of colour shows the presence of Amide.

TEST FOR ESTER

(1) Hydroxylamine - fecl3 test

($NH_2OH \cdot HCl$)
Hydroxylamine hydrochloride

1) $R-COO-R' + NH_2OH \xrightarrow{HCl} R-CONHOH + R'-OH$

2) $R-CONHOH + FeCl_3 \longrightarrow [Fe(RCONHOH)_3] + 3HCl$

Observation : coloured product formed.

(II) Ester hydrolysis test

$R-COOR' + H_2O + HCl \longrightarrow \underset{(Acid)}{R-COOH} + R'-OH$

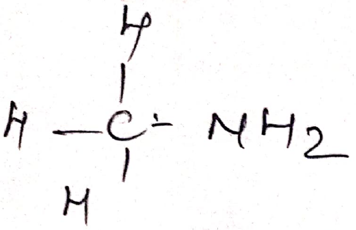
$R-COOR' + NaOH \longrightarrow \underset{(salt)}{RCOONa} + R'-OH$

(III) Odor test

- → Smell the sample
- → sweet, fruity smell.
- → may be ester.

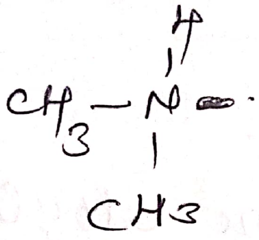
ALIPHATIC AMINES

Amines are derivative of ammonia in c̄ one or more hydrogen atom have been replaced by alkyl group.



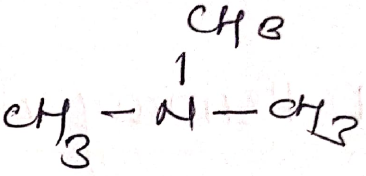
$H-\overset{H}{\underset{H}{C}}-NH_2$

(Methyl amine)



$CH_3-\overset{H}{\underset{CH_3}{N}}$

(Dimethyl amine)



$CH_3-\overset{CH_3}{N}-CH_3$

{Trimethyl amine}

Physical Property of Amines

1) Nature = Lower amin liquid in nature

2) solubility => water insoluble b/c of N-H bond, they do not form H-bond c̄ H_2O.
→ soluble in Organic solvent.

3) Spectroscopy => IR spectra shows N-H $= 3300-3500\ cm^{-1}$

NMR → $0.5-5.0\ \delta$

CLASSIFICATION OF AMINE

- Primary
- Secondary
- Tertiary

(1) Primary Amine

→ In this only one alkyl group is present, attached to nitrogen.

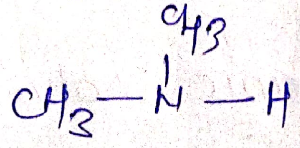
Ex.

CH_3-NH_2 (methyl amine)

② Secondary Amine

→ Two alkyl group is attached to the nitrogen of Amine.

e.g.



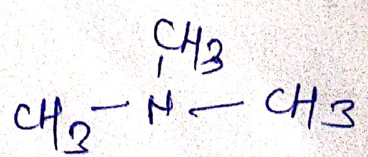
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-H$$

(dimethyl amine)

③ Tertiary Amine

→ Three methyl group is attached to N.

e.g.



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_3$$

Basicity of Amine

→ Amines acts as lewis base b/c it donate lone pair of electron to form a new bond to a hydrogen.

$$\boxed{R-NH_2 + H_2O \rightleftharpoons R-NH_3 + OH^-}$$

Preparation of Amines and Reaction

① **Alkylation**

Industrial amines are prepared from alcohol & Ammonia

$$R-OH + NH_3 \longrightarrow R-NH_2 + H_2O$$

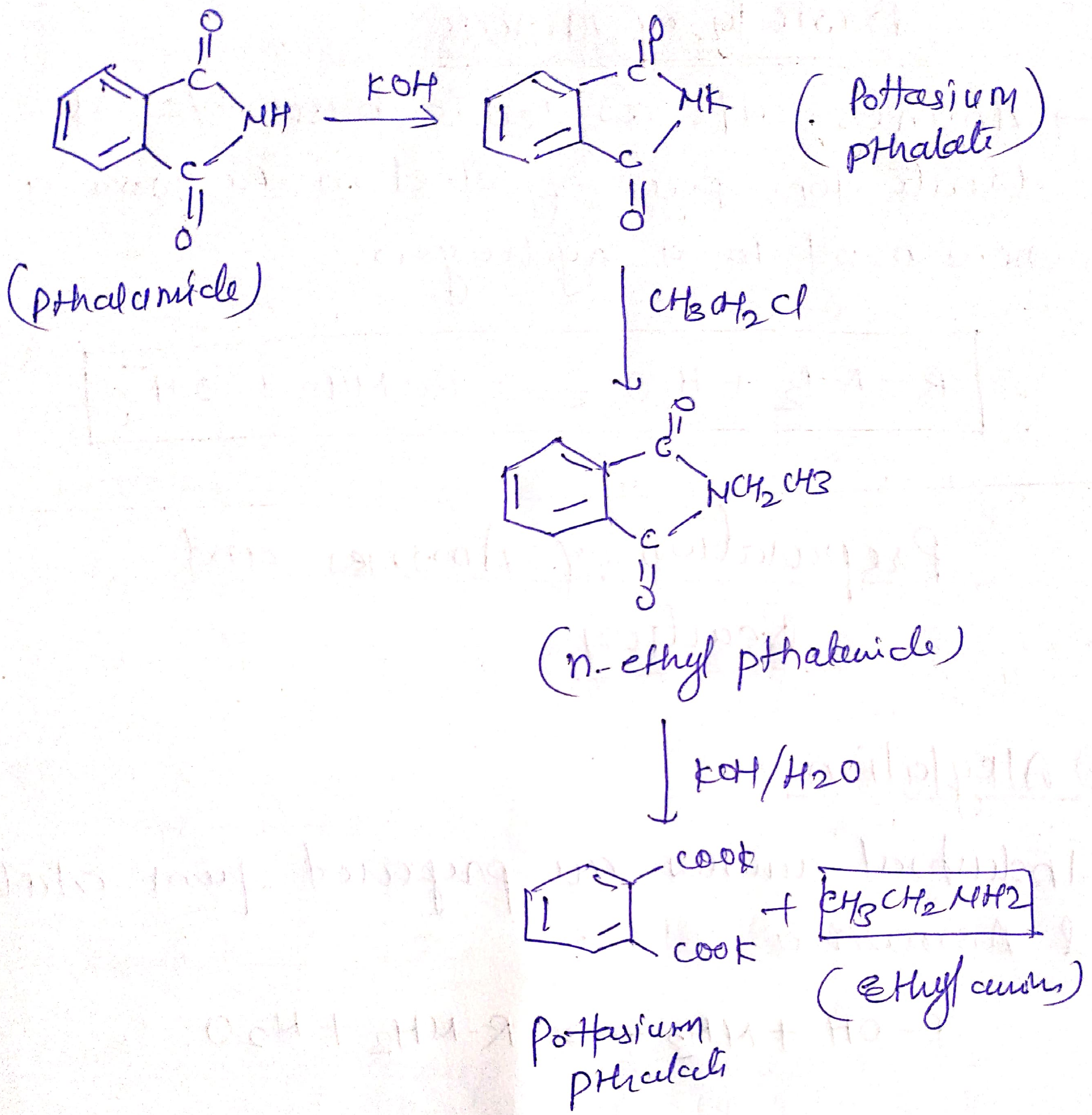
② Reaction of alkyl halide c̄ Ammonia

$$CH_3-CH_2-Br + NH_3 \longrightarrow CH_3-CH_2-NH_2 + HBr$$

(Ethyl amine)

③ Gabrial PHthalamide Reaction

It involve the reaction of pHthalamide c̄ KOH to form pottasium salt.



④ Reaction of nitro alkane

Primary amine can be obtained by reduction of nitro-alkane c̄ Ni/Pt

$$CH_3-CH_2-NO_2 + 3H_2 \xrightarrow{Pt} CH_3-CH_2-NH_2 + H_2O$$

(Ethylamine)

⑤ Reaction of nitril in presence of Ni/Pt.

$$H_3C-CH_2-C\equiv N + 2H_2 \xrightarrow[\text{(Reduction)}]{Ni} CH_3-CH_2-CH_2-NH_2$$

(n-propyl amine)

⑥ Reduction of Isonitrile

2° amine can be obtained from isonitrile.

$$H_3C-CH_2-\overset{+}{N}\equiv\overset{-}{C} + 2H_2 \xrightarrow{Pt} CH_3-CH_2-NH-CH_3$$

(Ethyl Isocyanide) (N-methyl amine)

REACTION OF AMINES

① Salt formation
② Reactic c̄ Alkyl halide
③ —"— c̄ Acid chloride
④ —"— c̄ benzene sulfonyl chloride
⑤ Carbylamine reaction.

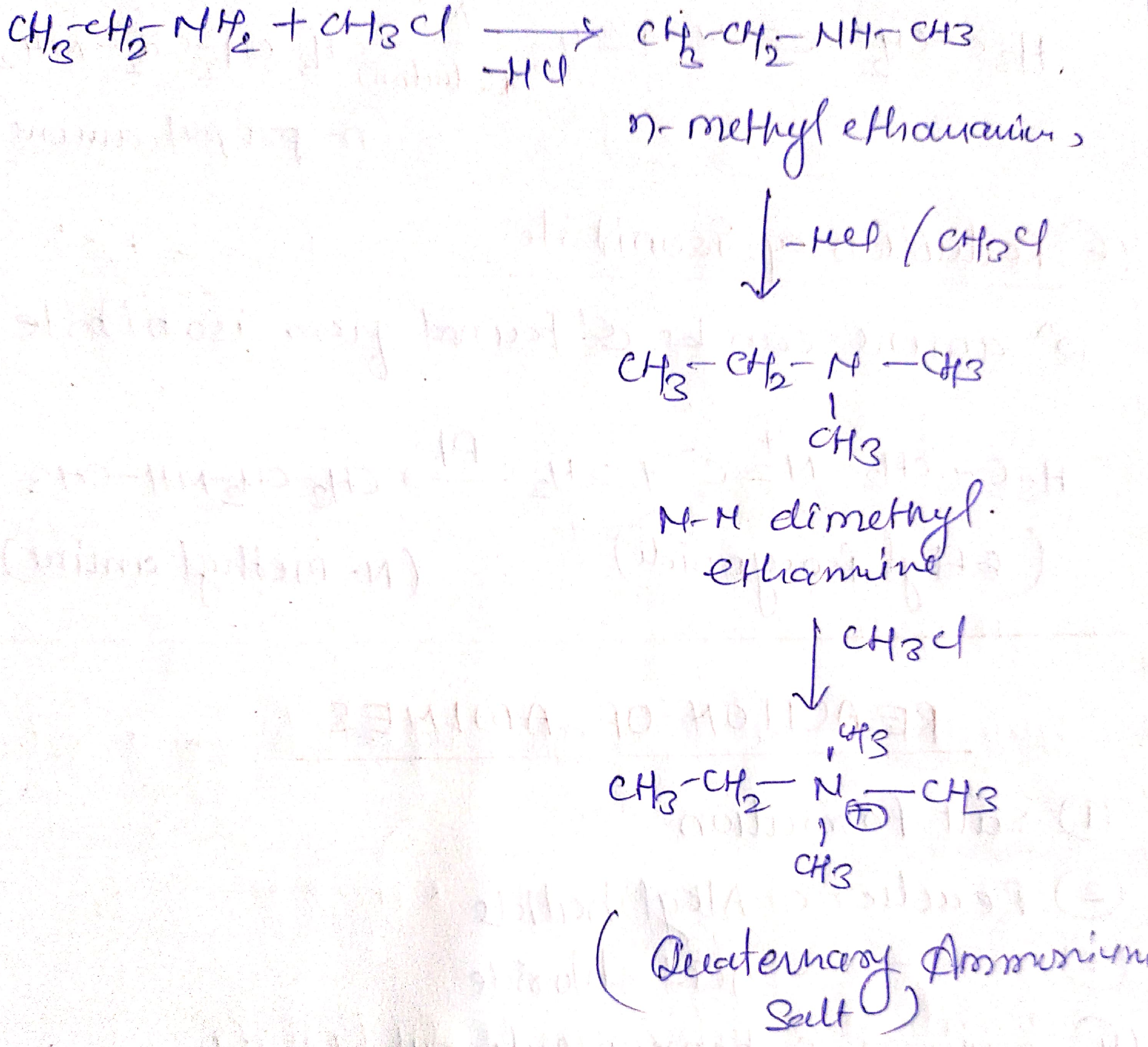
① Salt formation

Amine react c̄ mineral acid to form ammonia salt.

$$CH_3-CH_2-NH_2 + HCl \longrightarrow CH_3-CH_2-NH_3\,Cl$$

(Ethyl amine) (Ethyl ammonium chloride)

② Reaction c̄ Alkyl halide



$CH_3-CH_2-NH_2 + CH_3Cl \xrightarrow[-HCl]{} CH_3-CH_2-NH-CH_3$

n-methyl ethanamine,

$\downarrow$ $-HCl$ / CH_3Cl

$CH_3-CH_2-\underset{\substack{|\\ CH_3}}{N}-CH_3$

N-N dimethyl ethamine

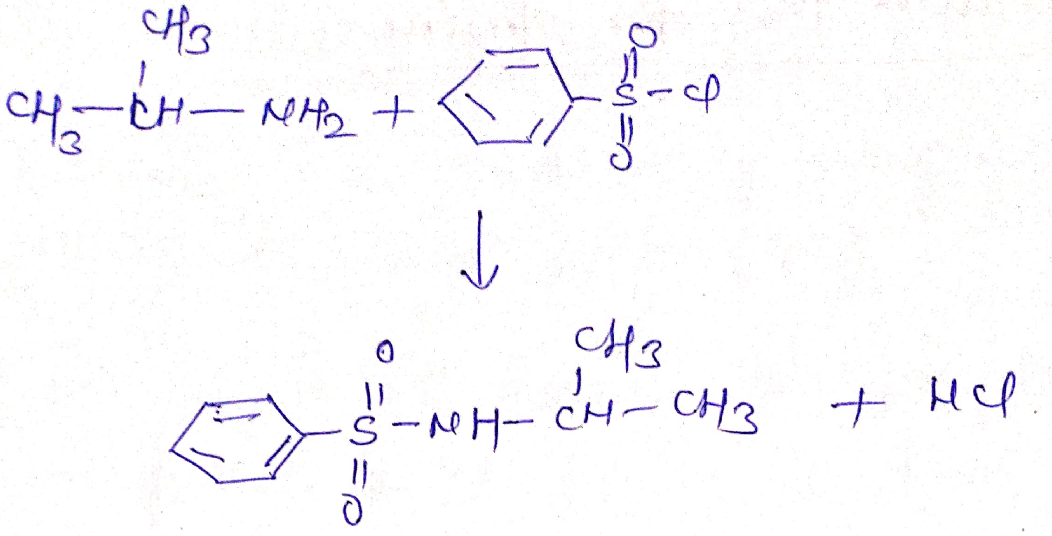
$\downarrow$ CH_3Cl

$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3$

(Quaternary Ammonium Salt)

③ Reaction c̄ benzene sulfonyl chloride

Primary amine react c̄ benzene Sulfonyl chloride to form n- alkyl benzene sulfonamide.



(n- isopropyl benzene sulfonamide)

Carbilamine Reaction

1° amine react $\bar{c}$ $CHCl_3$ & KOH (ethanolic) to form isocyanide.

(Methyl isocyanide)

$$CH_3-NH_2 + CHCl_3 + KOH \xrightarrow{C_2H_5OH} CH_3-\underset{+}{N}\equiv C + 3KCl + 3H_2O$$

Basicity of Amine

- Basicity is a measure of compound's ability to accept proton (H^+).

→ for aliphatic amine, this property due to presence of l.p. of electron on the nitrogen atom, enabling the formation of positively charged ammonium ion upon protonation.

→ Basicity can also be measured by pKb value.

$$\boxed{pKb \propto \frac{1}{basicity}}$$

Effect of Substituent

The basicity of amine can be influenced by the nature, position or closeness from nitrogen atom.

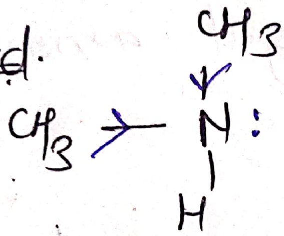
① Alkyl Groups

(a) Electron donating effect

⇒ alkyl group shows +I effect, pushing electron density towards N-atom.

⇒ This enhance the ability to donate it's l.p. of electron, ↑ basicity.

~~(b) Eed~~.



(b) order of Basicity

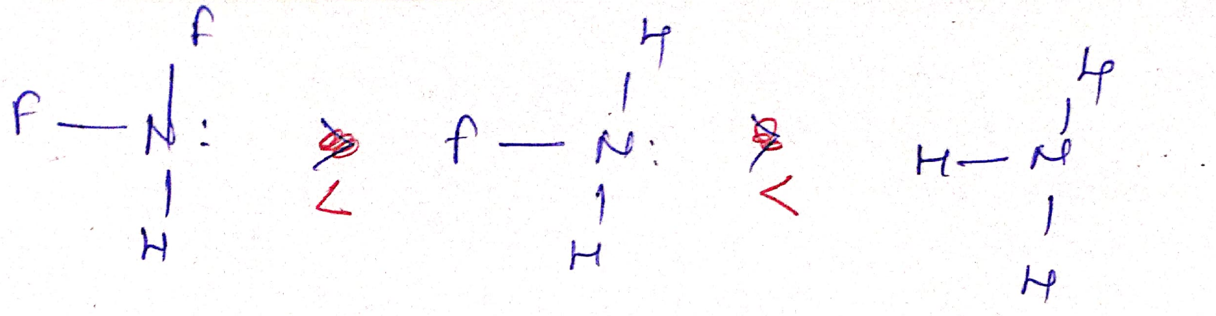
Basicity ↑ c̄ increase in number of Alkyl group.

3° amine > 2° amine > 1° amine.

② Eelectron withdrawing group.

→ These group pull the electron density from nitrogen atom.

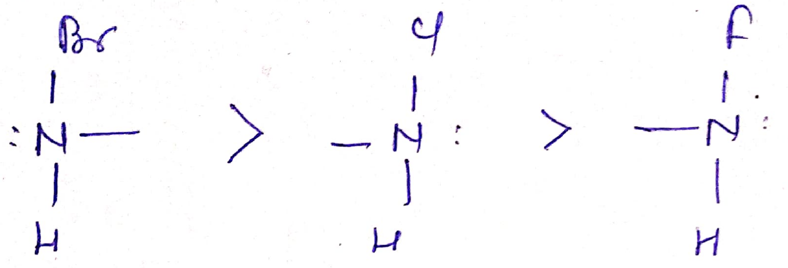
→ This ↓ e⁻ density for protonation hence ↓ basicity.



(less basic)

(more basic)

②



(more basic)

(less basic)

Qualitative test