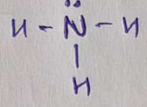
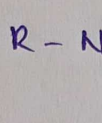
Amines

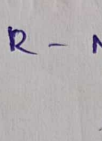
(Ammonia - NH_3)



$R-NH_2$ → 1° Amine



→ 2° Amine



→ 3° Amine.

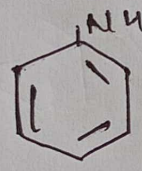
IUPAC

Q. $CH_3-CH_2-CH_2-NH_2$

Propan-1-amine.

Q. $CH_3-NH-CH_2-CH_2-CH_3$

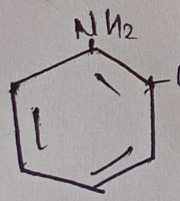
N-Methyl propan-1-amine.

Q. 

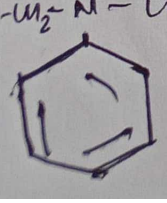
Aniline.

Q. $NH_2-CH_2-(CH_2)_4-CH_2-NH_2$

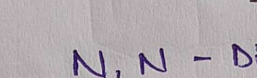
Hexan-1,6-Diamine.

Q 

2-Methyl Aniline.

Q 

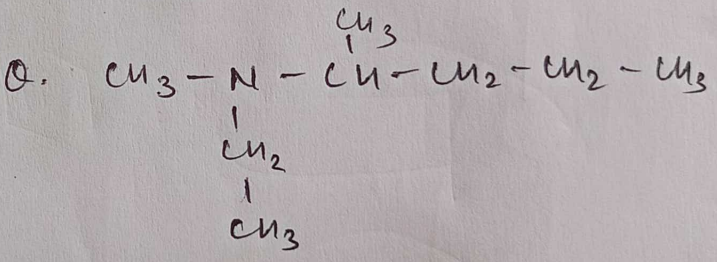
N-Ethyl-N Methyl Benzenamine.

Q. 

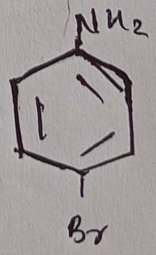
N,N-Dimethyl Propan-1-amine.

Q. $CH_2=CH-CH_2-NH_2$

Propan-2-en-1-amine

Q. 

N-Ethyl-N-Methyl pentan-2-amine.

Q. 

4-Bromo aniline.

4-Bromo benzenamine

METHODS OF PREPRATION ~

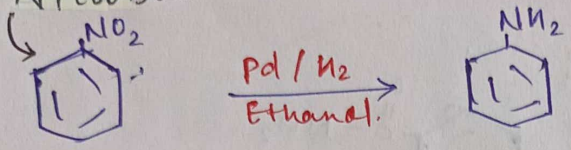
① Reduction of Nitro group. ($-NO_2$)

6 H - Need

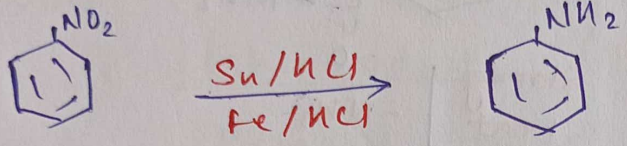
$\frac{Pd/H_2}{C_2H_5-OH}$, $\frac{Sn/HCl}{Fe/HCl}$

$-NO_2 \xleftarrow{4H} \rightarrow 2H_2O$ (2H)

a) Nitrobenzene.



b)



② From Nitriles.

$CH_3-\overset{H}{\underset{H}{C}}\equiv N \xrightarrow[Na/Hg/C_2H_5OH]{Ni/H_2} CH_3-CH_2-NH_2$

1° Amine

③ From Iso Nitriles.

$CH_3-\overset{H}{N}=\overset{\cdot\cdot}{C} \xrightarrow[Na/Hg/C_2H_5OH.]{Ni/H_2} CH_3-NH-CH_3.$

(3H.)

2° Amine.

④ From Amides

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O.]{LiAlH_4} CH_3-CH_2-NH_2.$

(2H) (2H)

⑤ Ammonolysis (SN-2)

$CH_3-Cl + NH_3 \longrightarrow CH_3-\overset{+}{N}H_3\,Cl^- \xrightarrow{-HCl} CH_3-NH_2$ 1° Amine

CH_3-Cl

$(CH_3)_4-\overset{+}{N}Cl^-$ ← CH_3Cl ← $(CH_3)_3-N$ (3°) ← CH_3Cl ← $(CH_3)_2-NH$ (2°)

quarnary Ammonium chloride

- If gives mixture of 1°/2°/3°/quarnary Ammonium salt

$CH_3-Cl + NH_2 \longrightarrow CH_3-NH_3Cl$

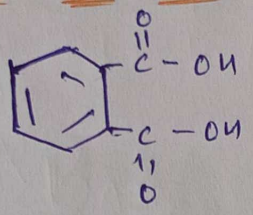
$1° > 2° > 3°$

$R-I > R-Br > R-Cl > R-F$

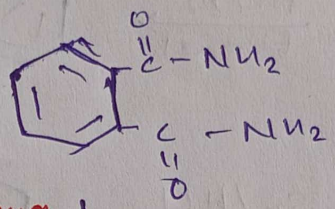
$CH_3-NH_3Cl^- + NaOH \longrightarrow CH_3-NH_2$ (1° Amine)

↑ strong Base supreses Reactivity

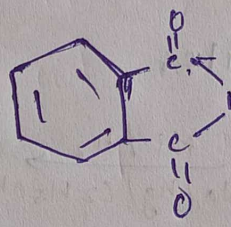
PREPRATION OF PTHALIMIDE :



+ $2NH_3$ ⟶



Strong heat ↓ $-NH_3$

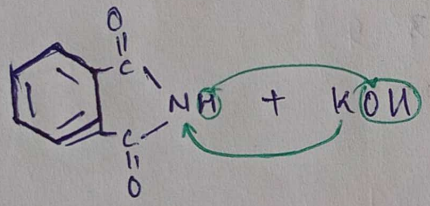


Phthalic Acid.

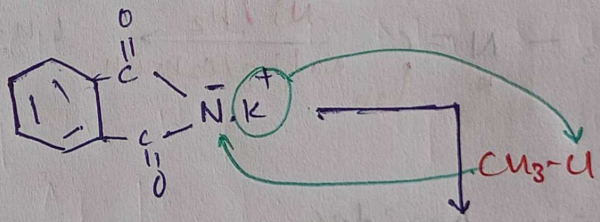
= Pthalimide

25☆

GABRIEL PHTHALIMIDE SYNTHESIS RXN :-

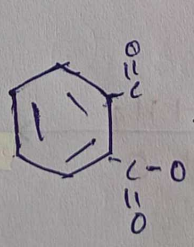


+ KOH ⟶

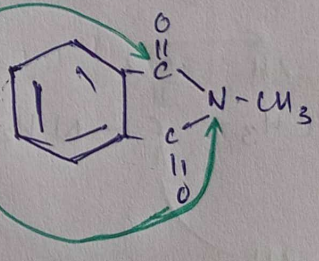


CH_3-Cl

Pthalimide



$2NaOH$

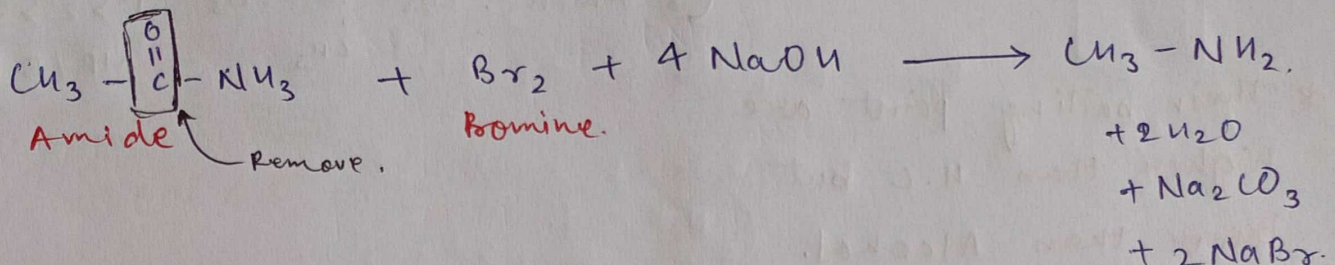


$+ CH_3-NH_2$

1° Amine

25☆

HOFFMAN BROMAMIDE DEGRADATION RXN. ~



$$CH_3-\underset{\underset{O}{\|}}{C}-NH_3 + Br_2 + 4NaOH \longrightarrow CH_3-NH_2 + 2H_2O + Na_2CO_3 + 2NaBr$$

PHYSICAL PROPERITES

(1) State : • Lower aliphatic amine are gas with fishy odour. • i gas < 2° liq < 3° solid.

• Primary Amine with 3 or more carbon are liq and higher are solid.

Aniline : • Tasteless - Poisonous

• Aniline are colourless liquid but coloured after some time due to the oxidation.

• Lower aliphatic amine are solube in water due to hydrogen bond with water.

• Solubility decreases when no. of C increases and no. of H-decreases.

$$\text{Solubility} \propto \frac{1}{\text{No. of C}} \propto \text{No. of H-Bond.}$$ (in H-Bond)

1° Amine have 2-H which can easily form Hydrogen bond with water. So, the order of solubility

$1° > 2° > 3°$ Density ∝ Mw.

• MP / BP also depend on the H-bond Amine which have more Hydrogen form more H-bond with each other. So, the order of boiling point for

Isomeric Amine. → 1° Amine $CH_3-CH_2-CH_2-NH_2$ · CH_3-NH_2
2° Amine $CH_3-NH-CH_2-CH_3$ · CH_3-NH_2
3° Amine. $CH_3-N(CH_3)-CH_3$

$1° > 2° > 3°$
MP / B.P.

✍ Their boiling point are higher than H.C but lower than Alcohol.
Amine > H.C , Alc > Amine.

CHEMICAL PROPERTY :-

1) BASIC EFFECTS :-

Amine shows Basic property in Aq. medium bcz they can give lone pair which can accepted by hydronium (H^+ ion) which can present in water. And form OH^- Ion.

$$R-\ddot{N}H_2 + H^+ + OH^- \longrightarrow R-NH_3^+ + OH^-$$

Basic property depens upon two properties in Aq. phase.

① L.P Giving
$\propto \frac{+I}{-I}$

② Solvation in H_2O.
$1° > 2° > 3°$

③ steric Effect.

So, In aq. phase both properties are anagonistic to each other.

CH_3-NH_2 < $(CH_3)_2NH$ < $(CH_3)_3N$ $\quad 1° < 2° < 3°$

CH_3-NH_2 : 1° +I
$(CH_3)_2NH$: 2 +I
$(CH_3)_3N$: 3 +I

* So It is very difficult to find basic properties in aq. medium but basic effect in gaseous state are clearly depends on I effects.

In gaseous state.

$1^\circ < 2^\circ < 3^\circ \propto \frac{+I}{-I}$

Experimentally some basic effect in aq. state are given below:

For 1 C : Methyl

$(CH_3)_2NH > (CH_3)NH_2 > (CH_3)_3N > NH_3$

2° 1° 3° Ammonium.

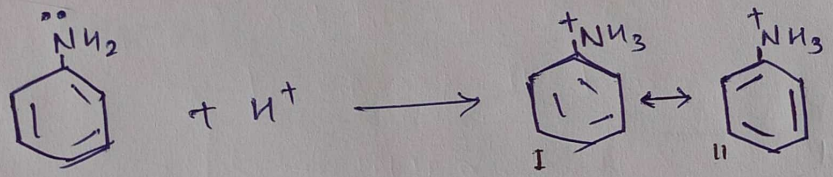
For 2 C: Ethyl.

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

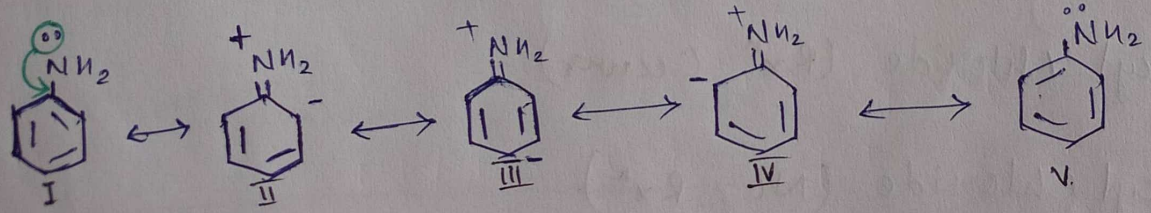
2° 3° 1° Amm.

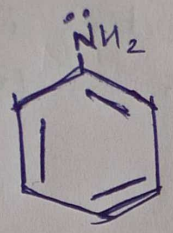
$P_{Kb} = 3$ $P_{Kb} = 6$ $P_{Kb} = 9$. *Basic Effect $\propto \frac{1}{P_{Kb}}$

Anilinium Ion have only Two Resonic structure But Aniline have 5 Resonic structure.



* It is clear that Aniline are more stable than Anilinium. So, L.P of Aniline are not available to anyone. So, it don't show basic property.





Aniline.

Do not have basic property due to Resonance.

Basic property in aq. sol.

$2^\circ > 3^\circ > 1^\circ > NH_3 > Aniline$

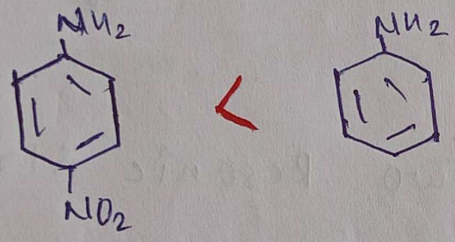
Not conf. it maybe $1^\circ > 3^\circ$ too,

Basic Property $\propto \frac{+M}{-M}$

$-OCH_3$, $-OH$, Cl . Basic property inc.

$-NO_2$, $-COOH$, $-CHO$ Basic property dec.
(-M)

Basic Effect.



2) Acylation.

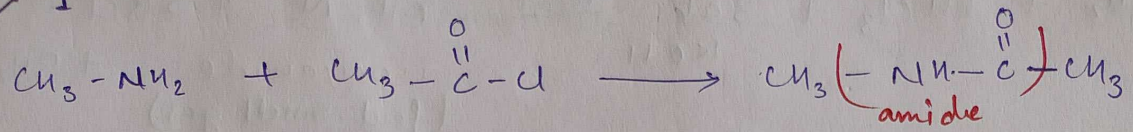
Amine + $CH_3-\underset{\underset{O}{\|}}{C}-Cl$

1° + Acyl Chloride (Rxn occurs)

2° + Acyl. Chloride (Rxn occurs)

3° + Acyl Chloride (No Rxn)

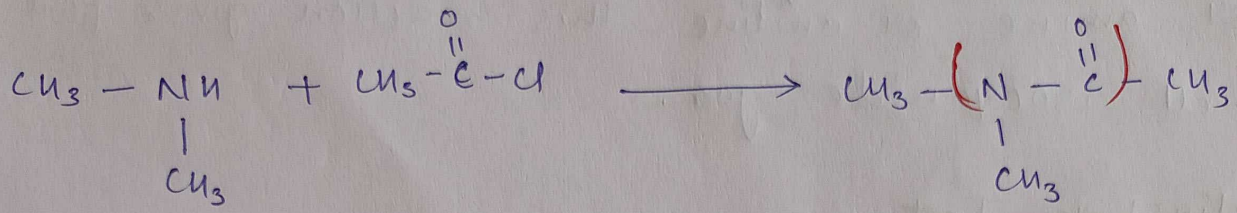
1) 1°



amide

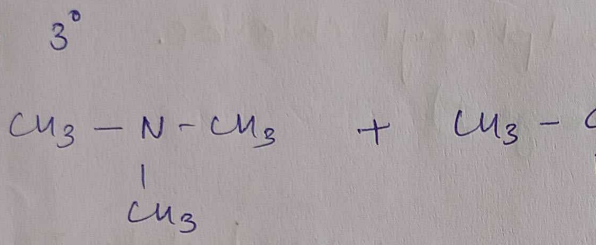
N- methyl ethanamide.

2) 2°



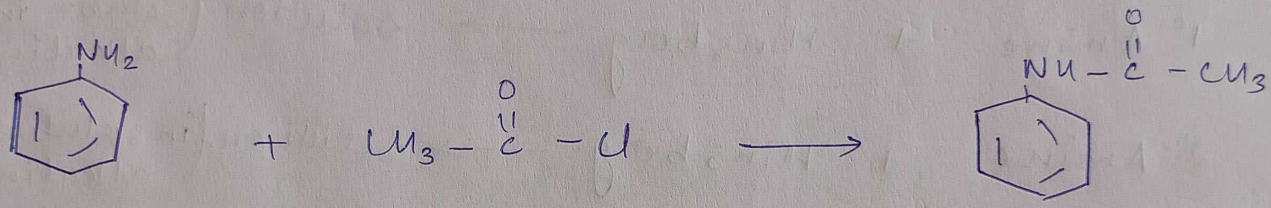
N,N-dimethyl ethanamide

3) 3°



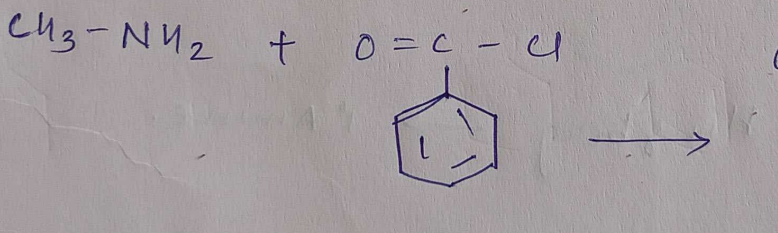
No Rxn.

4)



N-phenyl Ethanamide.

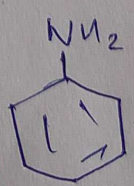
5)



N- Methyl benzanamide.

> Carbyl Amine Test / Isocyanide Test / Test Of 1° Amine

1° Amine → R-NH_2 ,



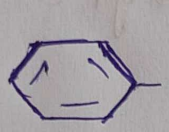
1° Amine	→ Rxn occurs
2° Amine.	→ Rxn occurs
3° Amine	→ No Rxn.

$CH_3-NH_2 + CHCl_3 + 3\,alc.\,KOH \xrightarrow{heat} CH_3-NC + 3KCl + 3H_2O$

isocyanide (foul smell gas)

* This is also isocynaide test this test is only for amine or aniline. This reaction gives foul smell isocyanide gas.

→ Hinsberg Test.



Benzene sulphonyl chloride.

(Hinsberg Reagent)

1° Amine + Hinsberg → Solution. (Solube in alkaline)

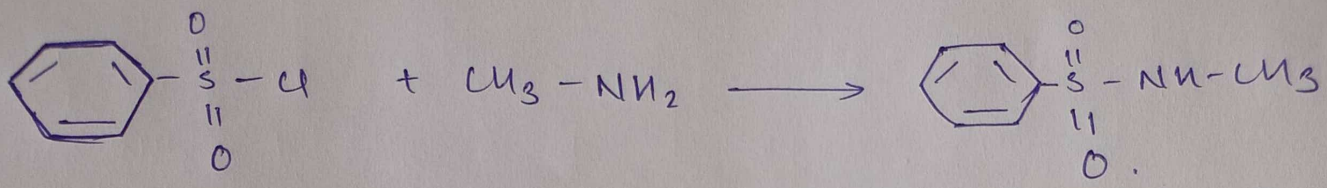
2° Amine + Hinsberg → Solution. (insolube in alkaline)

3° Amine + Hinsberg → No Reaction.

Carbyl + Hinsberg → 1° Amine.

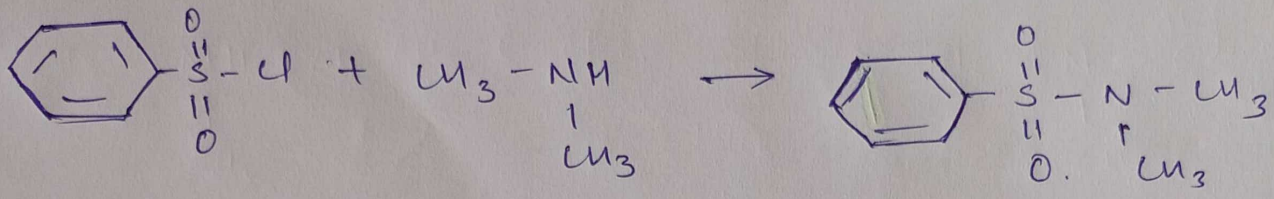
Carbyl (X) + Hinsberg → 2° Amine.

Carbyl (X) + Hinsberg (X) → 3° Amine.



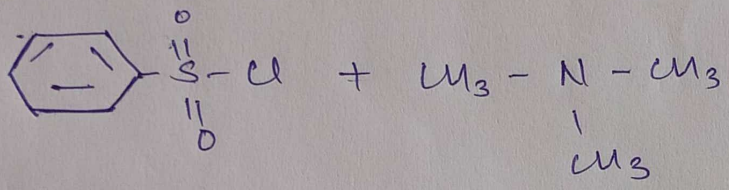
N-methyl benzene sulphonamide

(Soluble in Alkaline)



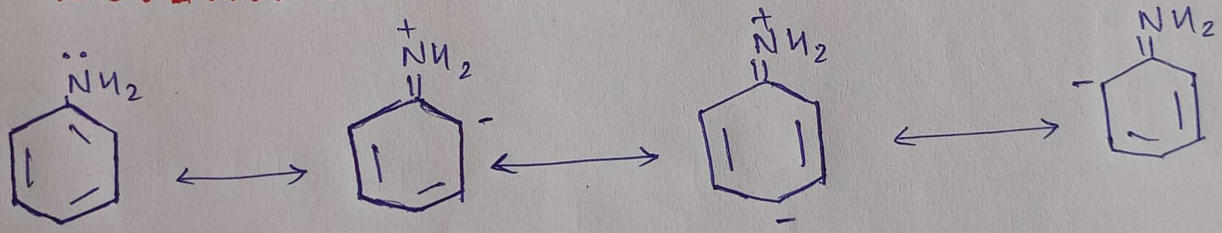
N, N- Dimethyl benzene sulphonamide.

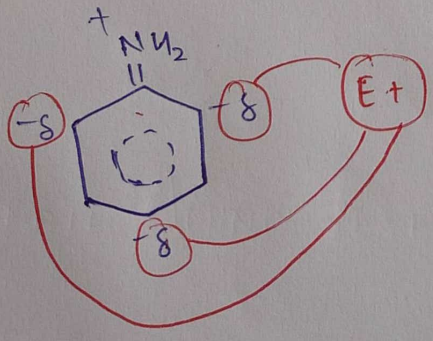
(Insoluble in Alkaline)



No Reaction.

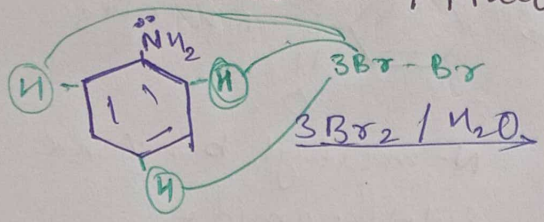
3) Electrophilic Substitution Rxn.

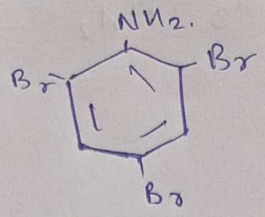




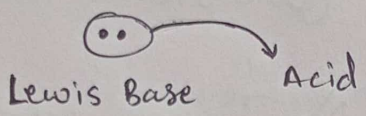
→ NH_2 group are ortho/para derivative groups.

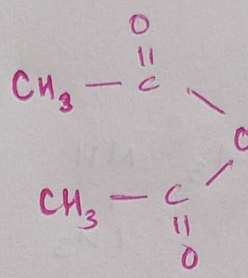
(a) Bromination / Halogenation.



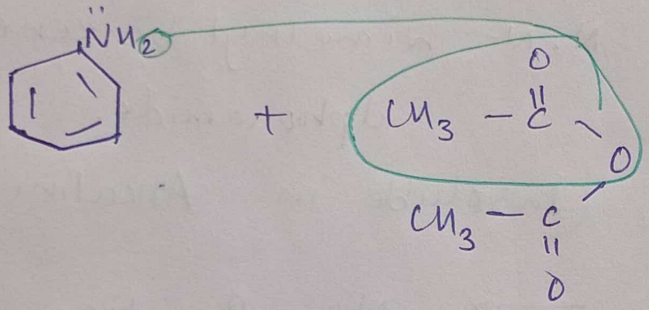


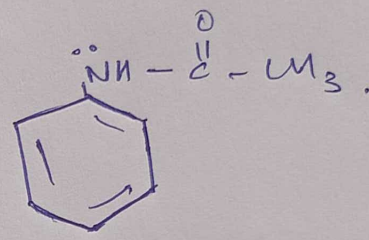
2, 4, 6 Tribromo Aniline.

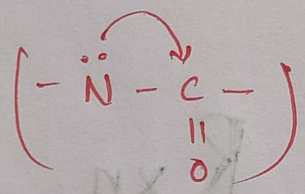




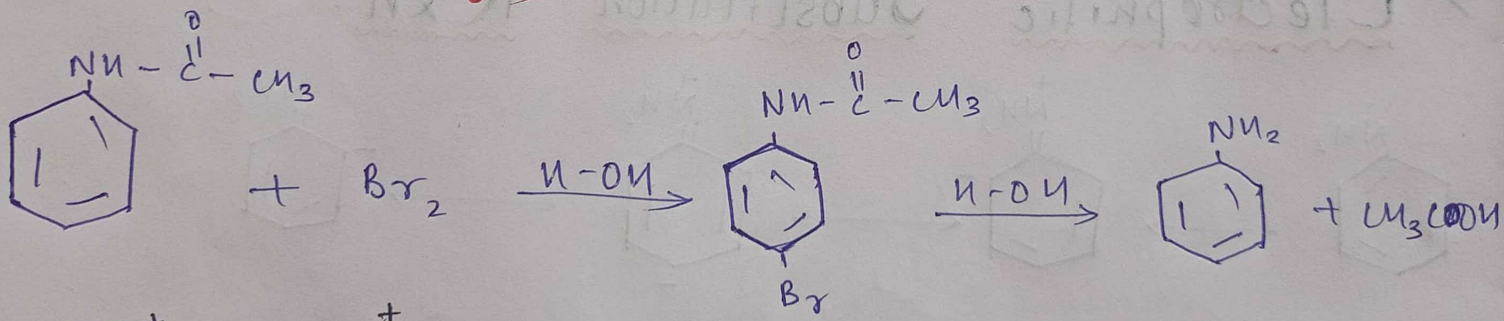
Acid Anhydride.







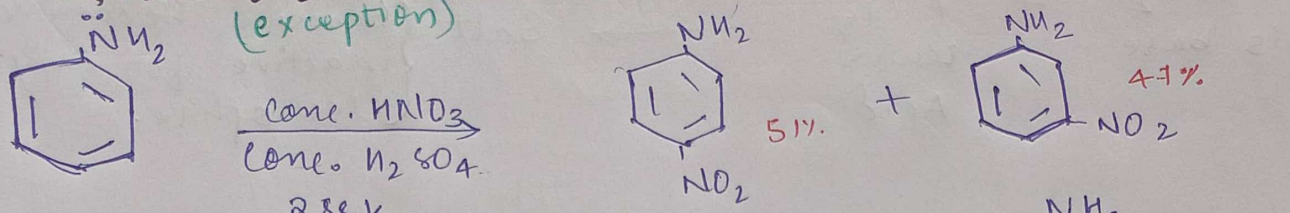
Resonance.



$E^+ \longrightarrow Br^+$

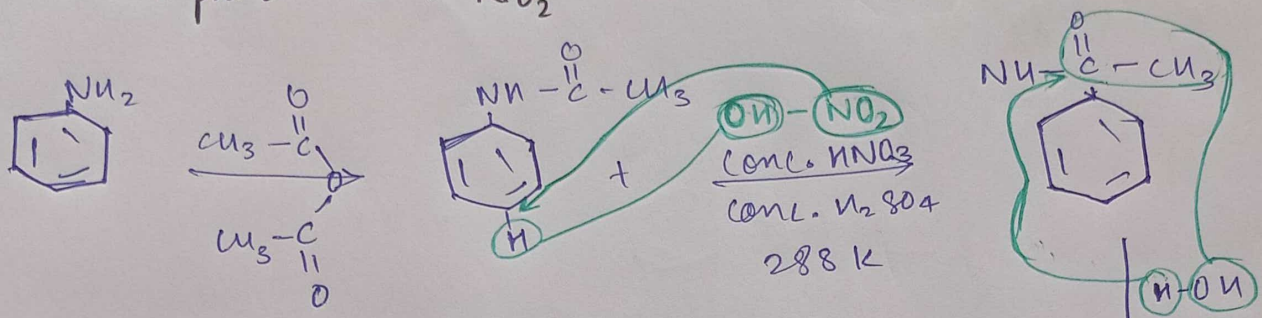
Major $\longrightarrow$ Para.

(b) Nitration. meta formed.



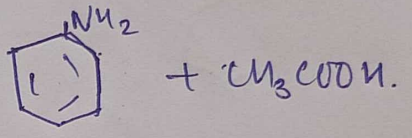
Major → Para.

Electrophile → NO_2^+

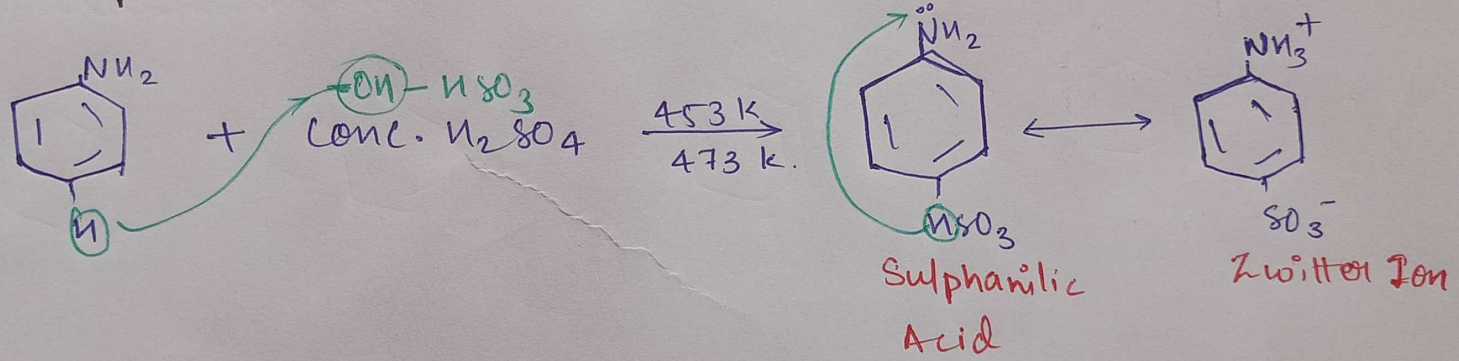


Electrophile → NO_2^+.

Major → Para.



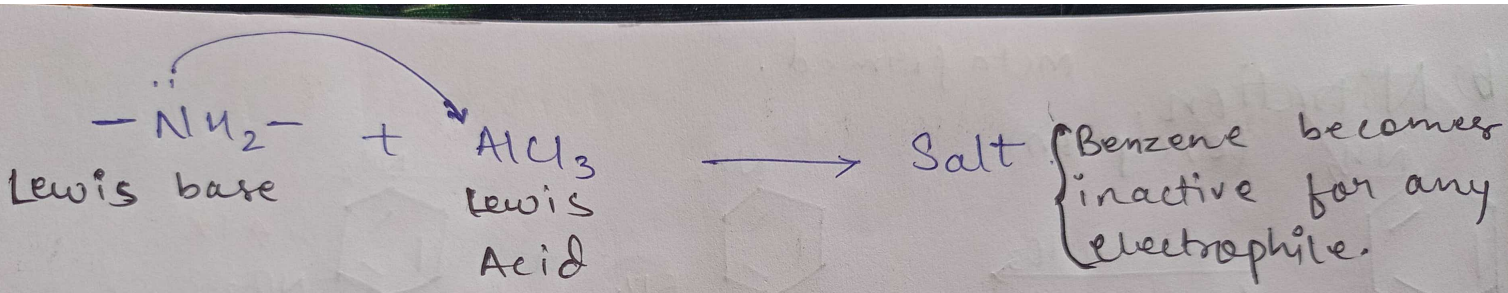
(c) Sulphonation.



Sulphanilic Acid

Zwitter Ion

Aniline does not participate in friedel craft acylation or friedel craft alkylation because NH_2 group (lewis base) gives lone pair to $AlCl_3$ (lewis Acid) and form stable salt which do not break easily so the lone pair of 'N' are not available for resonance. So, does not participate in friedel craft reaction.


$-NH_2-$
Lewis base
+
$AlCl_3$
Lewis
Acid
Salt
Benzene becomes inactive for any electrophile.

DIAZONIUM SALT

$(-N=N-)$

$$C_2H_5-NH_2 + NaNO_2 + HX \xrightarrow[0-5^\circ C]{273-278\,K} C_2H_5-N_2^+X^-$$

Aliphatic Diazonium Salt Halide.

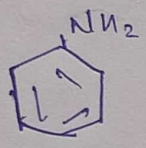
$-H_2O$
$-NaOH$

NaOH + HNO_2

Nitrous Acid.
(weak acid)

• Highly Unstable

Aliphatic Diazonium Salt are highly Unstable bcz the energy b/w N≡N are very very high.



+ $NaNO_2$ + HX ⟶

+ $NaOH$ + H_2O.

Benzene Diazonium Salt.

Benzene Diazonium salt are stable bcz their positive charges are stable by resonance and benzene are inactive for electrophilic substitution Rxn.

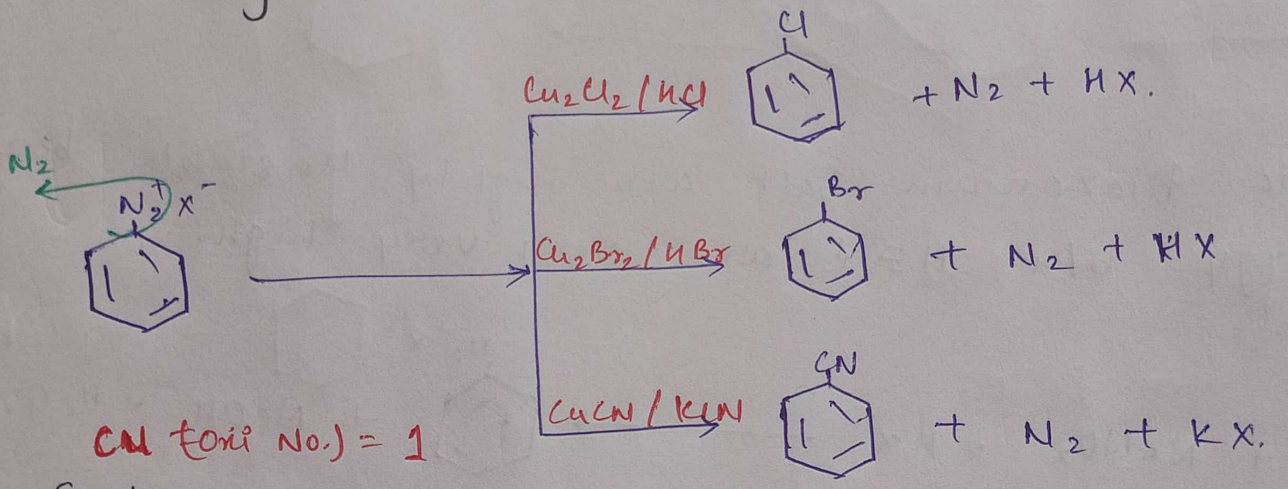
Benzene Diazonium salt are stable at cold temp. When temp increases they breaks into N_2 and phenyl. So, it is very compulsory to form Diazo immediately and they do not stored in bottle. This process is called Diazotisation.

Physical Properties

- It is colourless crystalines solid.
- It is raidly soluble in water.
- It is stable in cold water / temp but react with water at normal temp.
- It decompose easily in dry state.

Chemical Properties.

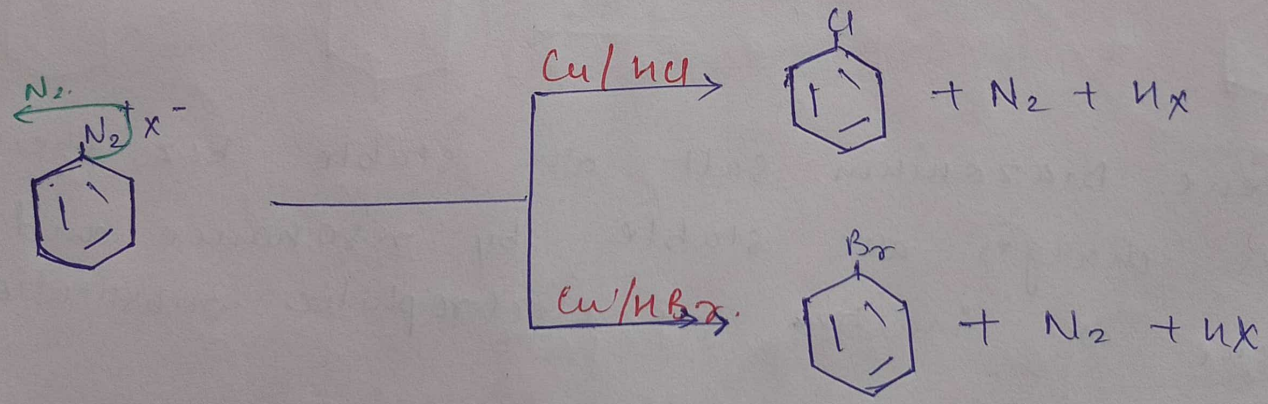
① Sandmeyers Reaction:



Cu (oxi No.) = 1

Sign. Sandmeyer's Rxn.

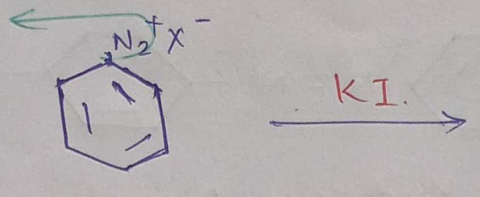
② Gatterman Reaction



Cu = (Oxi No.) = 0

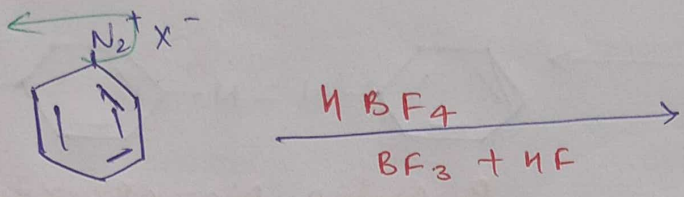
Sign of Gatterman Rxn.

(3) Reaction with KI.



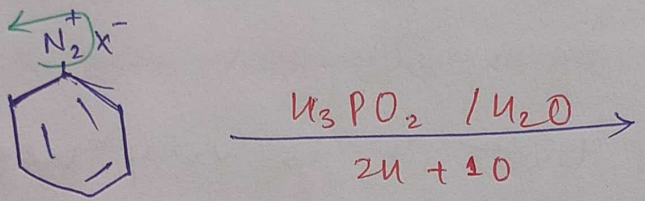
$+ N_2 + KX.$

(4) Reaction with HBF_4. (Balz Schizmann Rxn.)



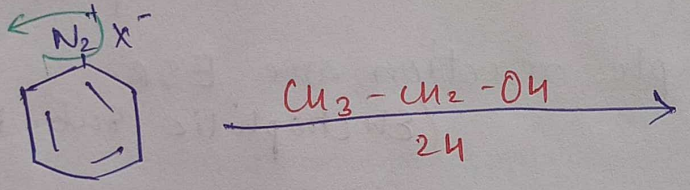
$+ N_2 + BF_3 + HX.$

(5) Reaction with Phosphinic Acid (H_3PO_2)



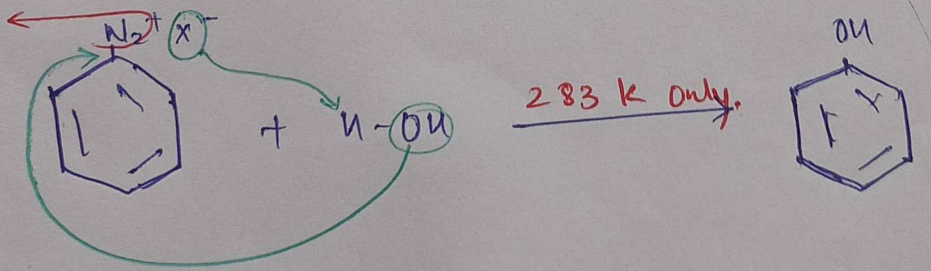
$+ H_3PO_3 + HX.$
$+ N_2.$

(6) Reaction with CH_3-CH_2-OH (Alc.)



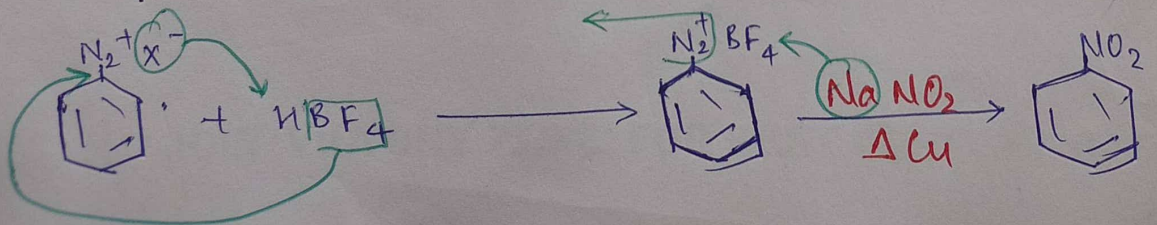
$+ CH_3-CHO + N_2 + HX.$

(7) Replacement of OH.



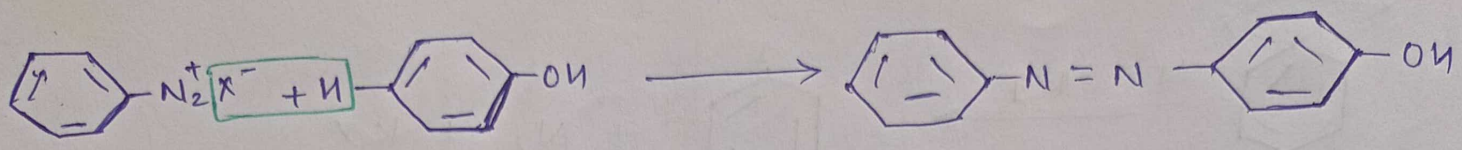
$+ N_2 + HX$

(8) Replacement of NO_2.

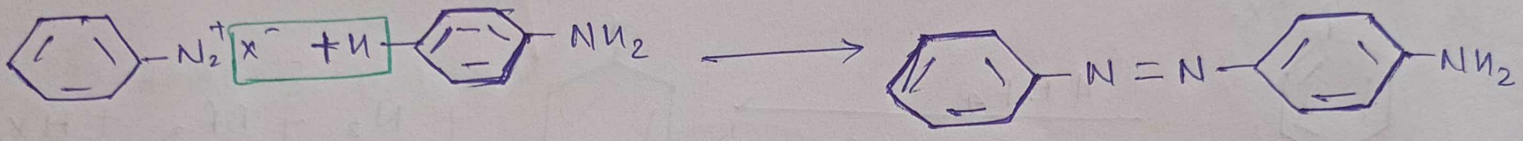


$+ NaBF_4$
$+ N_2.$

(9) Couple Rxn.



P - Hydroxy Diazobenze Orange Dye.



P-Amino DiazoBenzene. Yellow Dye.

USES

It is clearly mention that it is very useful reagent for replacement of F, Cl, Br, I, CN NO_2, OH, H in any aromatic ring. Some products can't be formed when diaxo are not present.

Eg: Flouro, Cyano, both couple reaction are ESR (Electrophilic Sub. Rxn.)

VICTORY ZONE CHEMISTRY CLASSES

ADDRESS – 1ST FLOOR PRADEEP PLAZA, IN FRONT OF CHOPRA PALACE , ADARSH NAGAR DURG

MO 9424168056,8269055301

Amines

Topic:- Reasoning Questions.

Give Reasons

1. It is difficult to prepare pure amines by ammonolysis of alkylhalides.
2. Amines have higher boiling points than hydrocarbons of similar molecular mass.
3. Aniline is weaker base than cyclohexylamine.
4. Methylamine is a stronger base than aniline.
5. Before nitration, aniline is converted to acetanilide.
6. It is easier to brominate aniline as compared to benzene.
7. Reduction of nitro compound to aniline using iron scrap and HCl is preferred.
8. Aromatic amines cannot be prepared by Gabriel Phthalimide synthesis.
9. During acylation of amines, pyridine is added.
10. Aniline does not undergo Friedel – Craft's reaction.

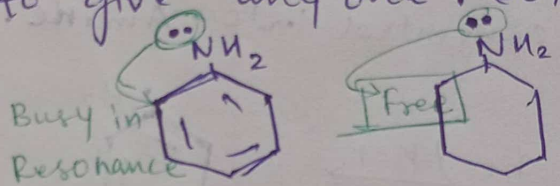
Topic - Reasoning Quest.

(1) Ammonalysis of haloalkane form mixture of 1°, 2°, 3° Amine. So, it is not considered.

$$R-X \xrightarrow{NH_3} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

(2) Amines are polar in nature so they can easily form H-bond with each other. But H.C do not have this type of H-Bond (Non-polar Nature).

(3) Aniline lone pair's are busy with resonance so it is not available for anyone but cyclohexyamines lone pair's are free to give anyone. So, it is more basic in nature.



(4) Lone pair of Aniline are busy with resonance but methylamide have 1+I grup & basic effect of aniline is (directly prop) ∝ +I.

(5) During Nitration of Aniline it ~~form~~ Anilium Ion which ~~form~~ is meta directing grup ~~form~~ so aniline form ortho, para, meta (multiple products) but after acylation of Aniline actanilide so the lone pair of anilines is busy with other due to less reactive ring of acetanalide

(8) Gabriel Phthalimide Rxn. form 1° Amines by NSR. & Halo Arenes are not easily ~~for~~ available for NSR.

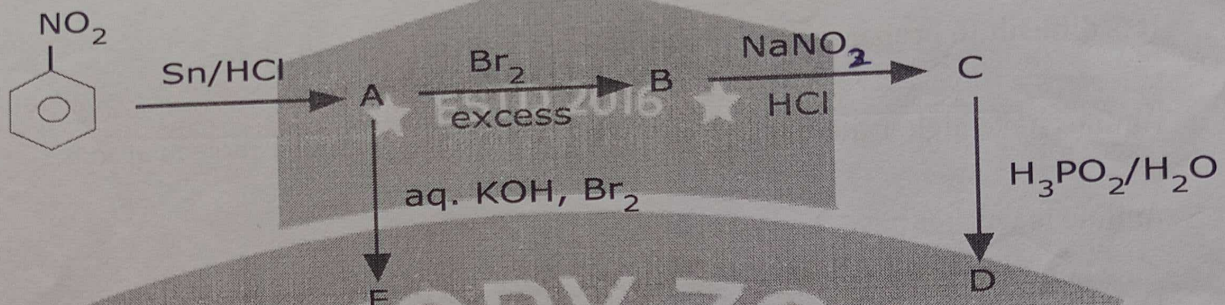
(9) During Acylation the biproduct are HCL. Acc. to Le Chatler's principle it is removed by Pyrinide (C_5H_5N).

(10) Aniline don't undergo acylation bcz NH_2 are

Amines

Topic:- Identification Question.

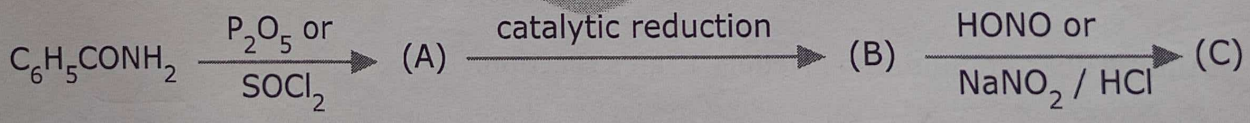
1.



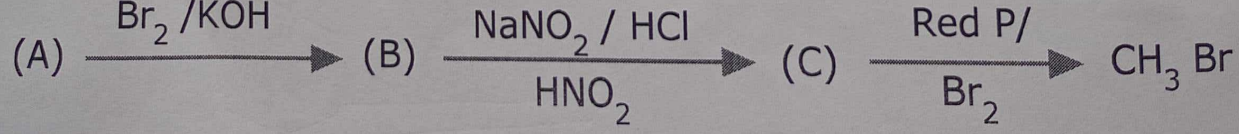
2. A compound (X) having formula C_3H_7NO reacts with Br_2 in the presence of NaOH to give another compound (Y). Compound (Y) reacts with HNO_2 to form ethanol and N_2 gas . Identify (X) and (Y) . Write the reaction involved.

3. An organic compound A (C_3H_5N) on boiling with alkali gives NH_3 and sodium salt of an acid B ($C_3H_6O_2$). The compound A on reduction gives C (C_3H_9N) which on treatment with nitrous acid gives an alcohol D (C_3H_8O). Identify A to D

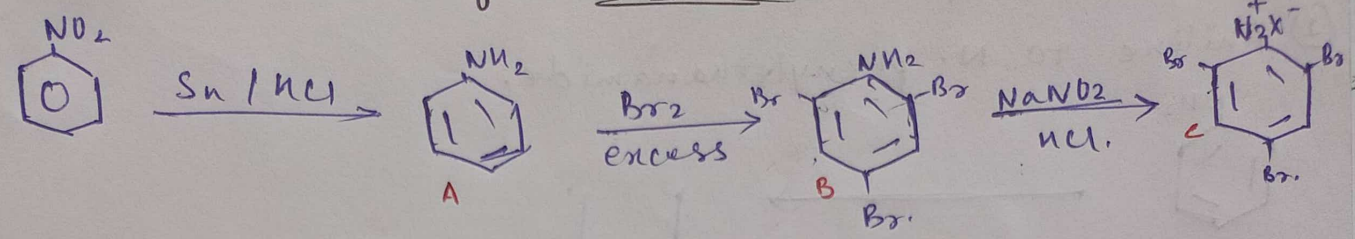
4.



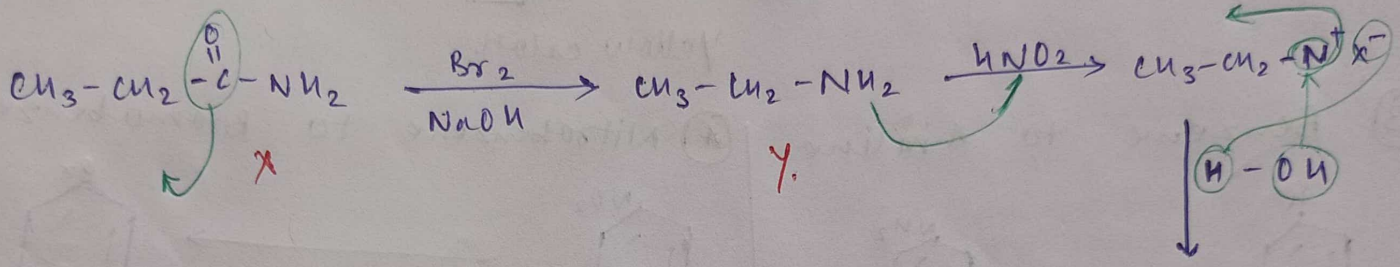
5.



Topic - Identification. Quest.

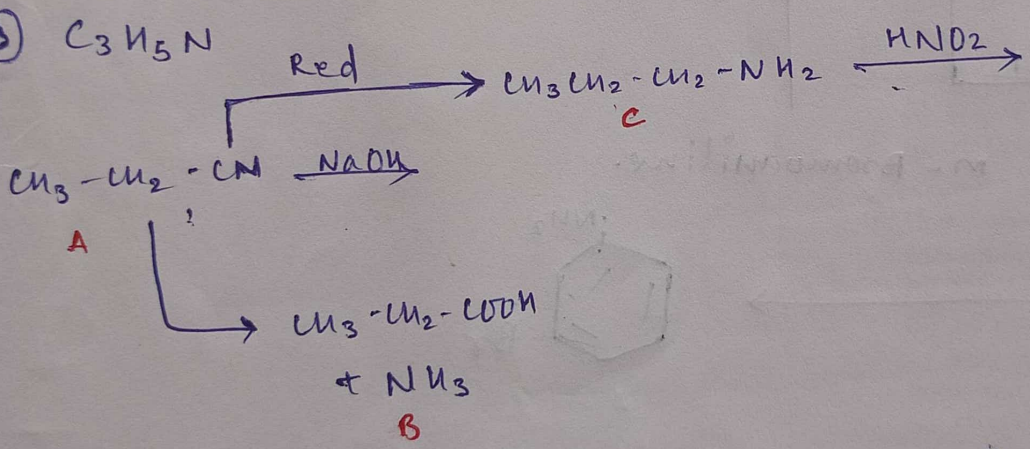
(1) 

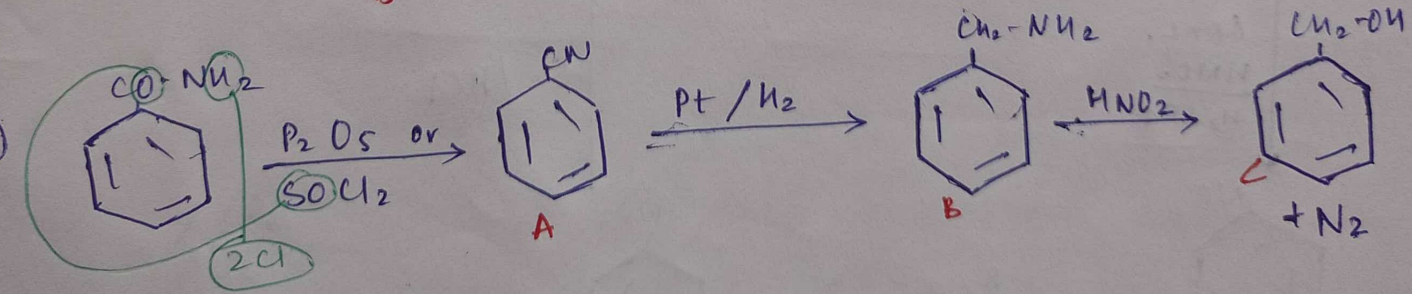
(2) C_3H_7NO.

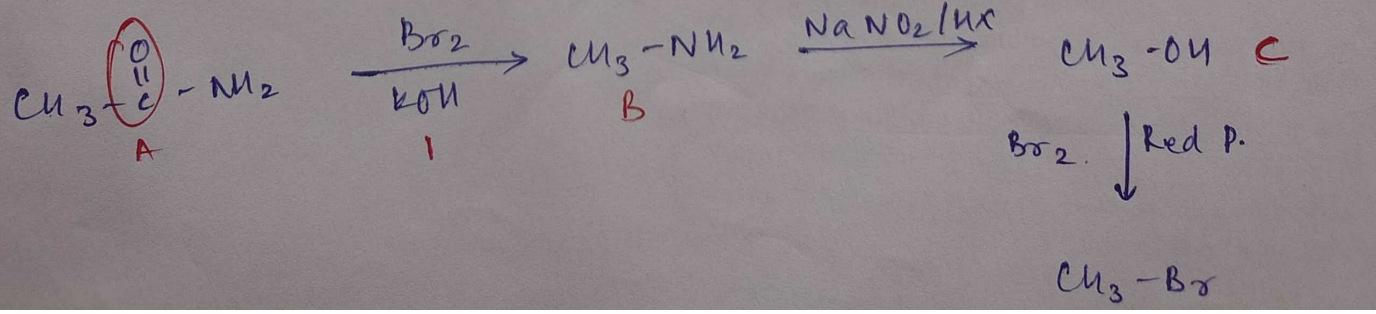


$N_2 + CH_3 - CH_2 - OH$.

(3) C_3H_5N



(4) 

(5) 

VICTORY ZONE CHEMISTRY CLA

DDRESS – 1ST FLOOR PRADEEP PLAZA, IN FRONT OF CHOPRA PALACE , ADARS

MO 9424168056,8269055301

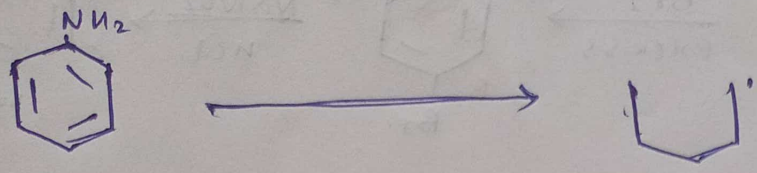
Amines

Topic:- Conversions

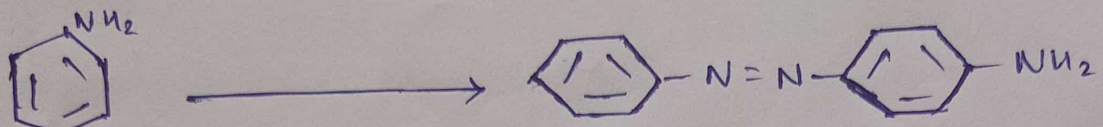
1. Aniline to N- phenylethanamide
2. Aniline to P- aminoazobenzene
3. Benzene to Aniline
4. Nitrobenzene to bromobenzene
5. Benzene to m- bromoaniline
6. Aniline to benzoic acid
7. Aniline to p- nitro aniline
8. Methylamine to ethylamine
9. Nitroethane to Nitro methane
10. Benzene to 1,3,5 – tribromobenzene

Topic - Conversions!

① Aniline to N-phenylethanamide.

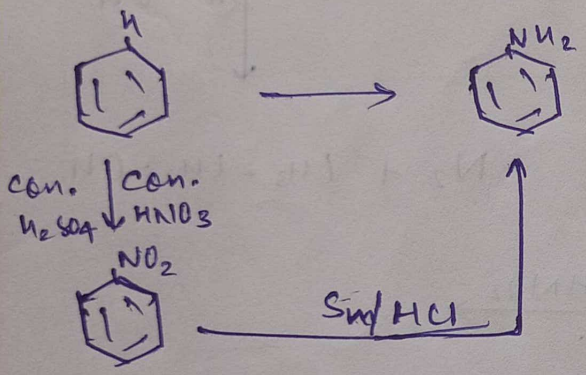


② Aniline to P-Aminoazobenzene.

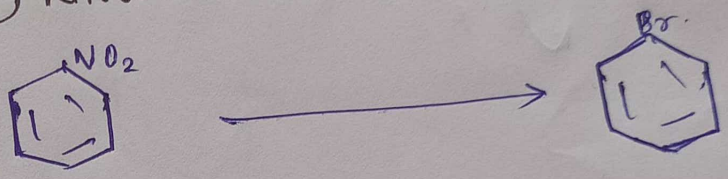


Yellow color.

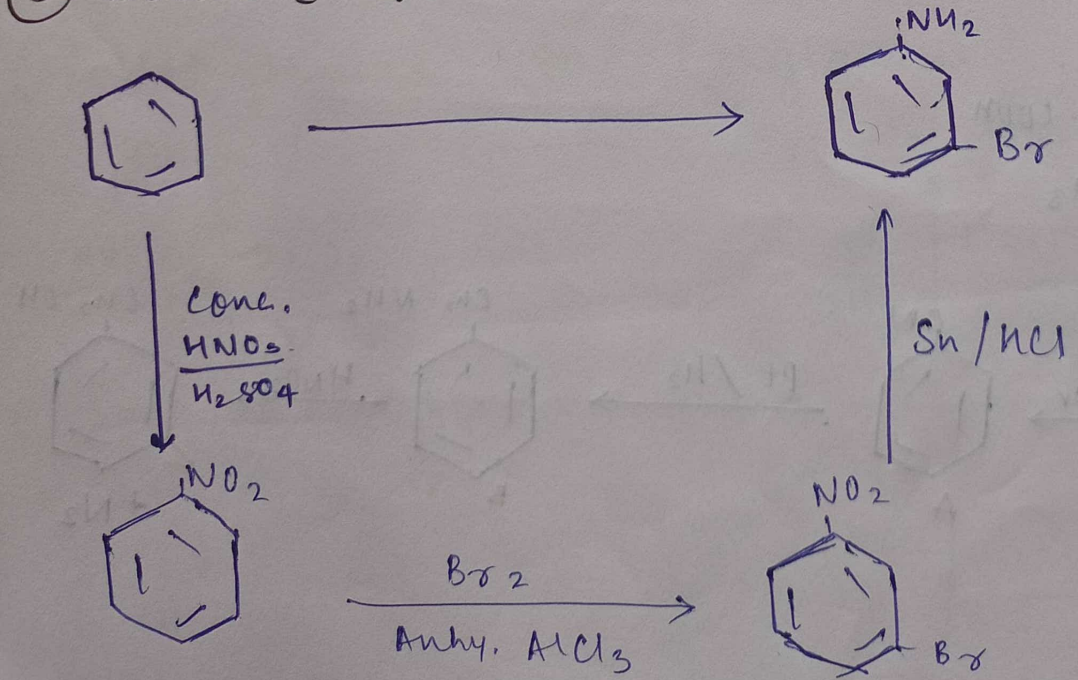
③ Benzene to Aniline.



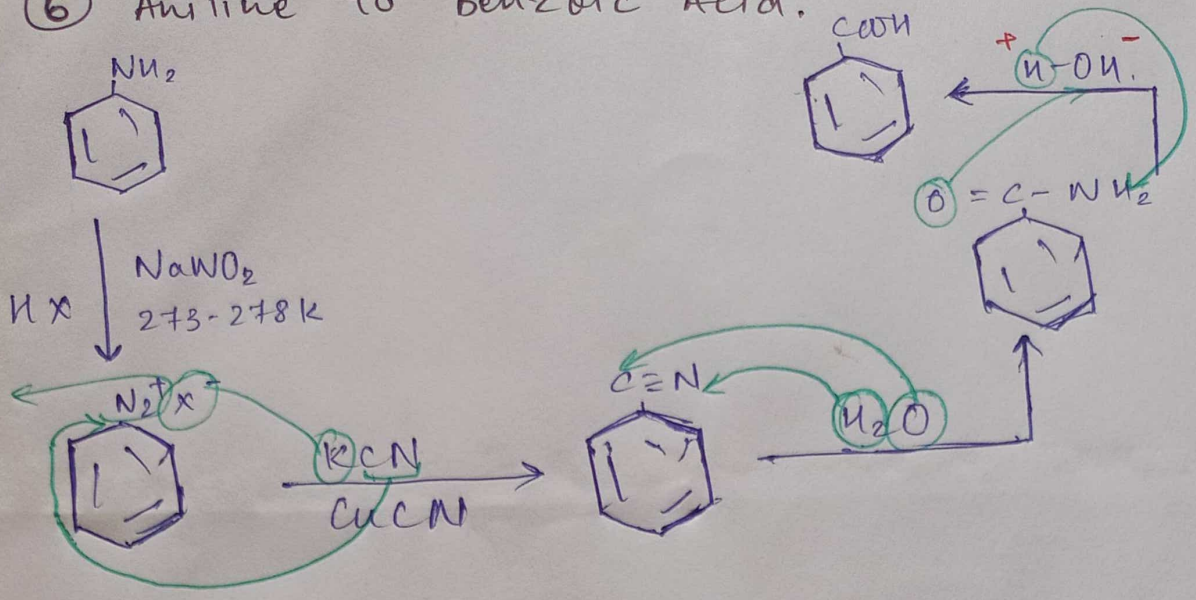
④ Nitrobenzene to Bromobenzene.



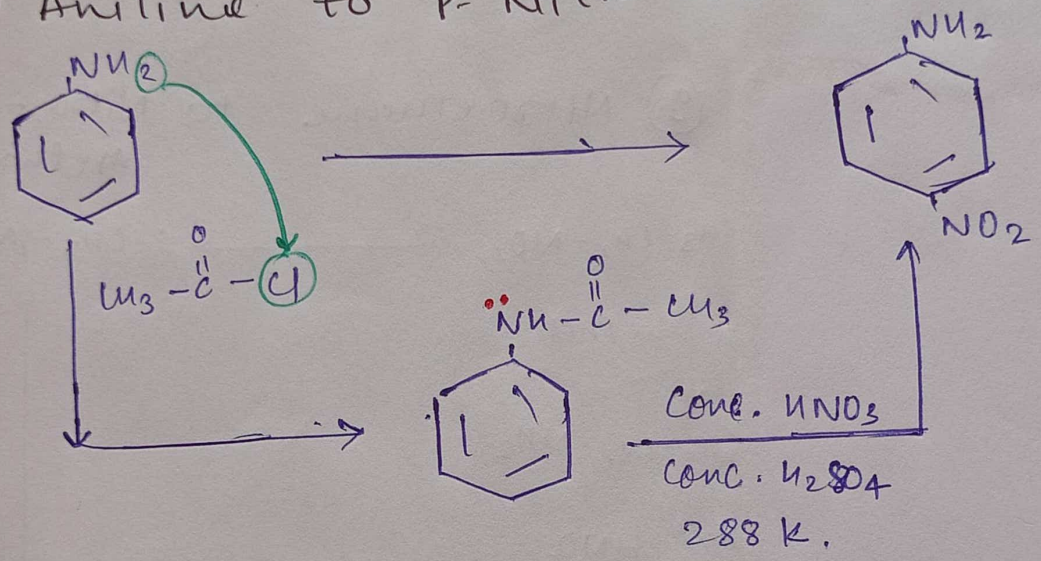
⑤ Benzene to m-Bromoaniline.



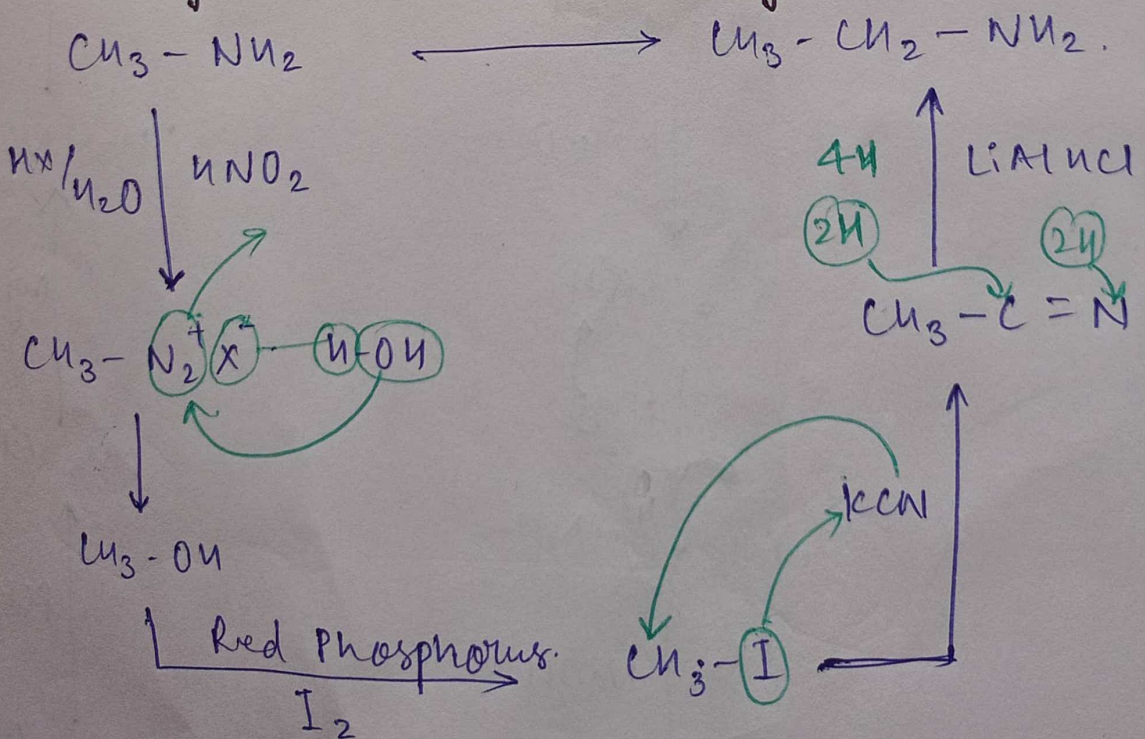
(6) Aniline to Benzoic Acid.



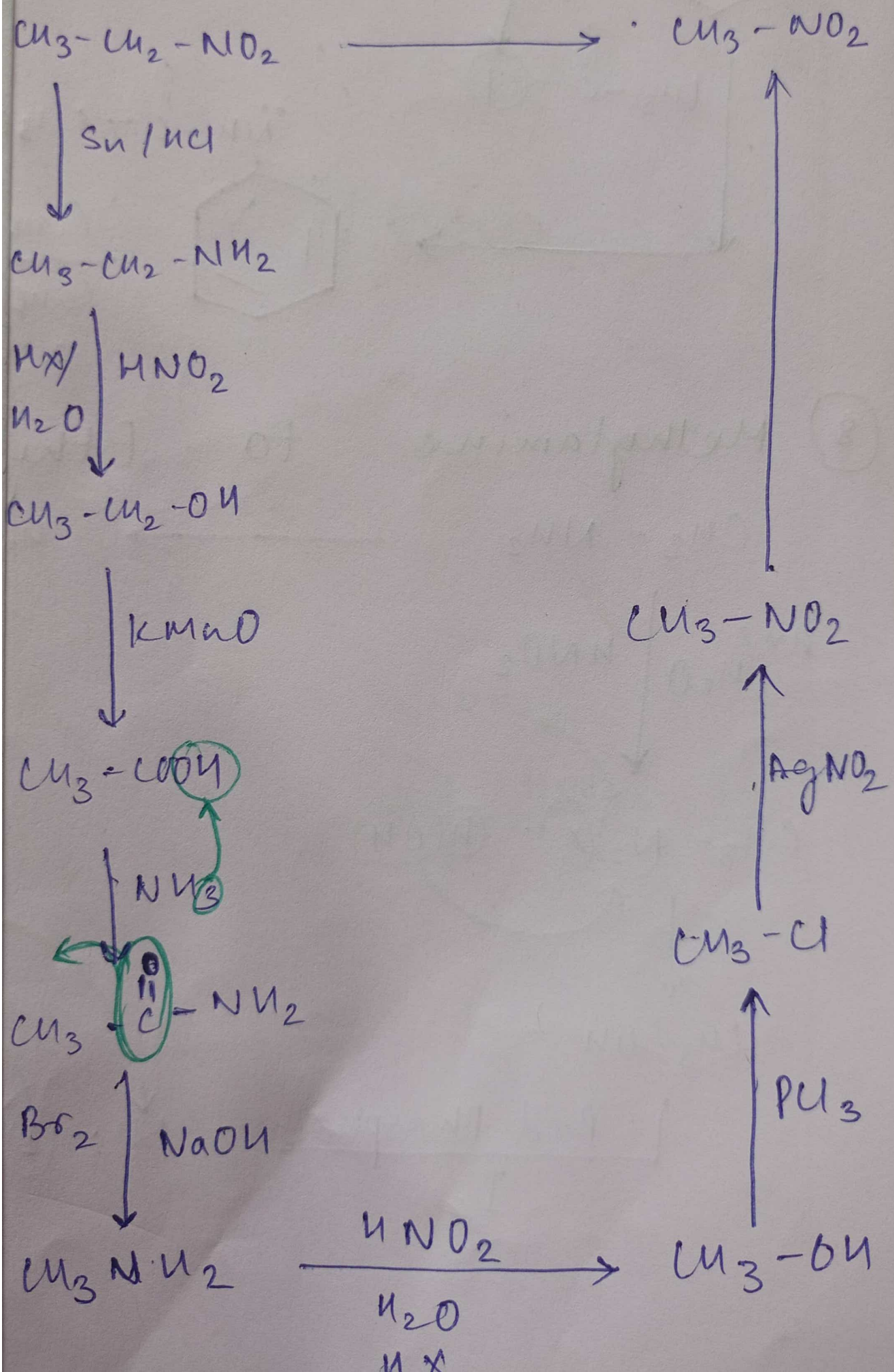
(7) Aniline to P-Nitro Aniline.



(8) Methylamine to Ethylamine.



(9) Nitroethane to Nitro-methane



(10) Benzene to 1,3,5 tribromobenzene