03 Practical Organic Chemistry

Identification of Functional groups :

(i) All organic compound are grouped into smaller number, each group exhibits similar chemical properties.

(ii) This means that all the compounds of the group must have something common, this common feature is known as functional group or reactive functional group.

(iii) It is defined as the group which largely determine the properties of a compound e.g., CH_3OH C_2H_5OH, C_3H_7OH are all collectively called alcohol as the common reactive group in all is – OH.

Characteristic of functional group :

(i) The physical and chemical properties of compound containing different functional groups are different.

(ii) There exists a homologous series of compound containing each type of functional group. For example, homologous series of alcohol like CH_3OH, CH_3CH_2OH, CH_3CH_2OH etc.

(iii) The chemical properties of compound containing same functional group are similar. For example methyl alcohol [CH_3OH] & ethyl alcohol (C_2H_5OH) have similar chemical properties. Therefore,

(iv) Chemical identification of a class of compounds involues the same type of tests.

Practical Organic Chemistry (POC) :

While looking for the information regarding the functional nature of the compound, we go for the following lab tests.

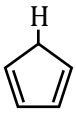
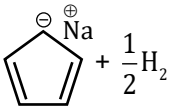
Test for acidic/active hydrogen

When any compound release H_2 gas after reaction with sodium or potassium or alkali metals or sodamide then this reflects the presence of acidic hydrogen.

Active H : The H atoms which are attached with more electronegative atoms like O,N,S,X, C_{sp}.

General reaction : $Z—\textcircled{H} + Na \longrightarrow \overset{\ominus}{Z}\ \overset{\oplus}{Na} + \frac{1}{2}H_2\uparrow$

S.No	Reactant	Reagent (Na metal)	Product
1	$R–NH_2$	$\xrightarrow{Na}$	$R-NHNa + \frac{1}{2}H_2 \leftarrow$
2	R–SH	$\xrightarrow{Na}$	$RSNa + \frac{1}{2}H_2 \leftarrow$
3	R–COOH	$\xrightarrow{Na}$	$R-COONa + \frac{1}{2}H_2 \uparrow$
4	PhOH	$\xrightarrow{Na}$	$PhONa + \frac{1}{2}H_2 \uparrow$
5	R—OH	$\xrightarrow{Na}$	$R— O^-Na^{\oplus} + \frac{1}{2}H_2\uparrow$

6	$R—SO_3H$	$\xrightarrow{Na}$	$R—SO_3^{\ominus}Na^{\oplus} + \frac{1}{2}H_2\uparrow$
7	$R—C\equiv CH$	$\xrightarrow{Na}$	$R—C\equiv C^{\ominus}Na^{\oplus} + \frac{1}{2}H_2\uparrow$
8	$R—CH=CH_2$	$\xrightarrow{Na}$	No reaction.
9	$R—CH_2—O—CH_3$	$\xrightarrow{Na}$	No reaction.
10	HCl	$\xrightarrow{Na}$	$NaCl + \frac{1}{2}H_2\uparrow$
11		$\xrightarrow{Na}$	

Test for unsaturation

(a) $(Br_2 + CCl_4)$

This is used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) hydrocarbon.

S.No	Reactant	Reagent	Product	Observation
1	$R–CH_2–CH_3$	$(Br_2 + CCl_4)$	–	No reaction
2	$R–CH=CH_2$	$(Br_2 + CCl_4)$	$R–\underset{Br}{CH}–\underset{Br}{CH_2}$	Red-brown colour disappears
3	$R–C\equiv CR$	$(Br_2 + CCl_4)$	$R—\underset{Br}{\overset{Br}{C}}—\underset{Br}{\overset{Br}{C}}—R$	Red-brown colour disappears

Note : Benzene does not give this test, whereas phenol and aniline give this test.

(b) Baeyer reagent (Cold dil. alkaline $KMnO_4$ Pink/purple solution)

This is also used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) compounds.

S.No	Reactant	Reagent	Product	Observation
1	$R–CH_2–CH_3$	Cold dil. alkaline $KMnO_4$	–	No reaction
2	$R–CH=CH_2$	Cold dil. alkaline $KMnO_4$	$R–\underset{OH}{CH}–\underset{OH}{CH_2}$	Purple colour disappears
3	$R–C\equiv CR$	Cold dil. alkaline $KMnO_4$	$R–\underset{O}{\overset{O}{C}}–\underset{O}{\overset{O}{C}}–R$	Purple colour disappears

$$2KMnO_4 \longrightarrow K_2O + 2MnO_2 + 3[O]$$
$$\uparrow$$
Brown solution

Test for terminal alkyne

S.No	Reactant	Reagent	Product	Observation
1	RC≡CH	Tollen's Reagent [$AgNO_3 + NH_4OH$ or $\{Ag(NH_3)_2\}^{\oplus} OH^{\ominus}$]	$R-C\equiv CAg + NH_4NO_3$	White precipitate
2	RC≡CH	Ammonical cuprous chloride ($Cu_2Cl_2 + NH_4OH$)	$R-C\equiv CCu\downarrow + 2NH_4Cl$	Red precipitate

Test for alcohols

(a) Lucas reagent test (Conc. HCl + anhydrous $ZnCl_2$)

It gives white turbidity or cloudiness with alcohols (OH groups attached with sp^3 hybridised carbon).

Lucas reagent is also used to distinguish between 1°, 2°, 3° alcohol because 1°, 2°, 3° alcohols react with different rates.

(i) 1° alcohol $R-CH_2-OH \xrightarrow{Conc.HCl + anhydrous\ ZnCl_2} RCH_2-Cl$

(does not give appreciable reaction or gives white turbidity in 30 min.)

(ii) 2° alcohol $R_2CH-OH \xrightarrow{Conc.HCl + anhydrous\ ZnCl_2} R_2CH-Cl$ (gives white turbidity in 5 min.

(iii) 3° alcohol $R_3C-OH \xrightarrow{Conc.HCl + anhydrous\ ZnCl_2} R_3C-Cl$ (gives white turbidity immediately)

Phenols and enols do not give Lucas test.

(b) Victor Mayer test

1° Alcohol :

$$RCH_2-OH \xrightarrow{P+I_2} RCH_2-I \xrightarrow{AgNO_2} RCH_2-NO_2 \xrightarrow{HNO_2} R-\overset{NO_2}{\overset{|}{C}}=N-OH \xrightarrow{base} \text{Blood Red colour}$$

2° Alcohol : $R_2CH-OH \xrightarrow{P+I_2} R_2CH-I \xrightarrow{AgNO_2} R_2CH-NO_2 \xrightarrow{HNO_2} R_2\overset{N=O}{\overset{|}{C}}-NO_2 \xrightarrow{base}$ Blue colour

3° Alcohol : $R_3C-OH \xrightarrow{P+I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2}$ no reaction $\xrightarrow{base}$ no colour

(c) Cerric Ammonium Nitrate test

Alcohols(1°,2°,3°) give characteristic red colour with cerric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ solution. It is group reagent for alcohols.

Test for phenol or enol

Neutral $FeCl_3$ test :

It forms violet purple complex with phenol or enol (OH groups attached with sp^2 carbon).

$$6\ PhOH + FeCl_3 \longrightarrow \left[(PhO)_6Fe\right]^{3\ominus} + 3HCl + 3H^{\oplus}$$

(Coloured complex)

$$6\ PhOH + FeCl_3 \longrightarrow \left[(PhO)_6Fe\right]^{3\ominus} + 3HCl + 3H^{\oplus}$$

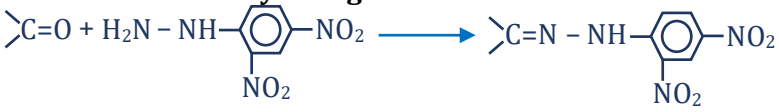
(Coloured complex)

It does not give positive test with alcohols.

Test for carbonyl compounds

2, 4-DNP … 2,4-Dinitrophenyl hydrazine+½Test :

Carbonyl compounds (all aldehydes and ketones) give yellow–orange precipitate with 2,4–DNP. It is also known as **Brady's reagent**.

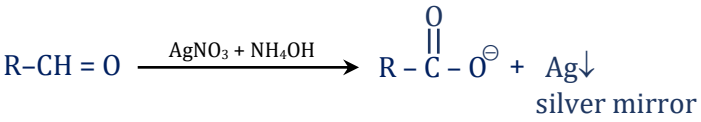


2,4–DNP (yellow-orange precipitate of Hydrazone)

Test for aldehydes

(a) Tollen's reagent [$AgNO_3 + NH_4OH$ or $\{Ag(NH_3)_2\}^+ OH^-$] :

Tollen's reagent gives silver mirror or Black precipitate with aldehydes.



silver mirror

Note : HCOOH also gives this test.

(b) Fehling's solution

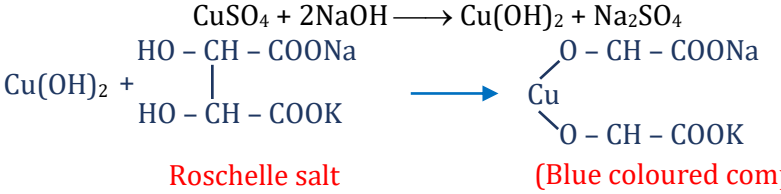
It is an alkaline solution of cupric ion complexed with sodium potassium tartrate.

There are two solutions in Fehling solution

Solution (A) : $CuSO_4$ solution

Solution (B) : Alkaline solution of sodium potassiumtartrate.

When these two solutions are mixed we get deep blue coloured solution.



Roschelle salt (Blue coloured compound)

Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

Blue Red ppt

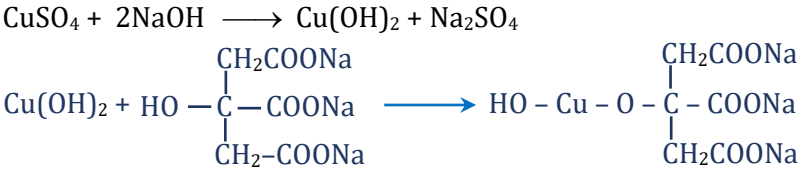
Red ppt

(c) Benedict solution

It also consists of two solutions.

Solution (A) : $CuSO_4$ solution

Solution (B) : Alkaline solution of sodium citrate.



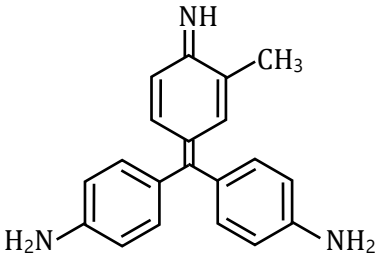
(Blue colour)

Aldehyde gives positive test with Benedict solution.

(blue) (Red ppt.)

(d) Schiff's reagent

It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2. Aldehyde restores pink colour when treated with Schiff's reagent (Magenta solution in H_2SO_3). **Aromatic aldehydes (**Benzaldehyde**) do not give** Fehling and Benedict **tests.**

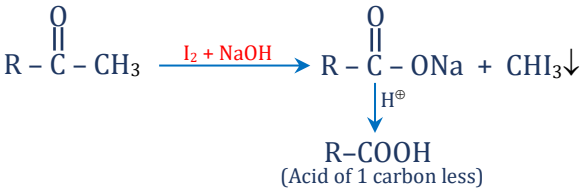


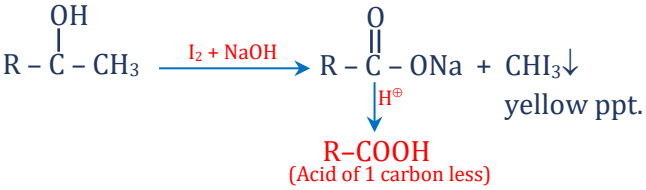
Schiff reagent

Iodoform Test

Reagents : I_2 + NaOH or NaOI … Where R = H, alkyl, aryl group½

Acetaldehyde, all methyl ketones & ethyl alcohol give Iodoform test.





Test for acids/esters/amides

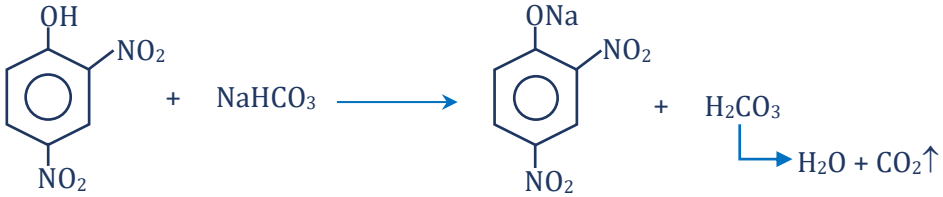
(a) Sodium bicarbonate test ($NaHCO_3$)

All the acids which are stronger than H_2CO_3 give CO_2 gas with $NaHCO_3$.

$HCl + NaHCO_3 \longrightarrow NaCl + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$

$RCOOH + NaHCO_3 \longrightarrow RCO_2Na + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$

$RSO_3H + NaHCO_3 \longrightarrow RSO_3Na + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$

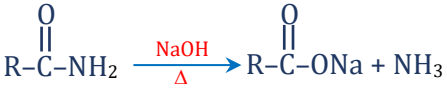


Note:

If electron withdrawing group (NO_2) is present at ortho or para position of phenol then it gives positive test with sodium bicarbonate.

(b) Litmus test % Acid converts blue litmus into red litmus while base converts red litmus into blue.

(c) Acid amide gives smell of ammonia when heated with alkali.



(d) Esters are sweet (fruity) smelling liquids.

Esters when react with NaOH & phenolphthalein, pink colour disappears on heating.

RCOOR' + NaOH + Phenolphthalein (Pink) $\xrightarrow{\Delta}$ R COOH + R' OH (Colourless solution)

Test for amines

(i) $NaNO_2$ + aqueous HCl test : it is used to distinguish between 1°, 2° and 3° amines and also distinguish between aliphatic and aromatic primary amines.

1° Aliphatic amine : $R-CH_2-NH_2 \xrightarrow{NaNO_2 + aq.\ HCl} R-CH_2-OH + N_2\uparrow$

1° Aromatic amine : $Ph-NH_2 \xrightarrow[(0-5°C)]{NaNO_2 + aq.\ HCl} Ph-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$ …diazonium salt)

2° Amine : $R-NH-R \xrightarrow{NaNO_2 + aq.\ HCl} R-\underset{\displaystyle N=O}{\underset{|}{N}}-R$ (N -Nitroso amine) yellow oily liquid

3° Amine : $R_3N \xrightarrow{NaNO_2 + aq.\ HCl}$ unstable nitrite

(ii) Carbyl amine test ($CHCl_3$ + KOH)

1° Amine (Aliphatic and Aromatic)

$R-CH_2-NH_2 \xrightarrow{CHCl_3 + KOH} R-CH_2-N\equiv C + 3KCl + 3H_2O$

(unpleasent smell of isocyanide)

$Ph-NH_2 \xrightarrow{CHCl_3 + KOH} Ph-N\equiv C$

*** 2° Amines and 3° Amines do not give this test.**

(iii) Hofmann mustard oil test

It is a test for 1º amine and aniline. Primary amine reacts with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride ($HgCl_2$) to give alkyl isothiocyanate having smell like mustard oil.

(a) $R-NH_2 + S=C=S \longrightarrow R-NH-\underset{\displaystyle S}{\overset{\displaystyle SH}{\overset{/}{\underset{\backslash\!\!\|}{C}}}} \xrightarrow[\Delta\alpha]{HgCl_2} R-N=C=S + HgS + 2HCl$

Dithioethylcarbamic acid — Alkylisothiocyanate

(b) $CH_3CH_2NH_2 + S=C=S \xrightarrow{\Delta} CH_3CH_2NH_2-\underset{\displaystyle S}{\underset{\|}{C}}-SH \xrightarrow[\Delta]{HgCl_2} CH_3CH_2-N=C=S + HgS + 2HCl$

(1° amine) — Ethyl isothiocyanate

Similarly aniline gives phenylisothiocyanate.

(c) $C_6H_5NH_2 \xrightarrow[(ii)\ HgCl_2]{(i)\ S=C=S} C_6H_5N=C=S$

Phenylisothiocyanate

*** 2° Amines and 3° Amines do not give this test.**

(iv) Hinsberg reagent ($C_6H_5SO_2Cl$)

This is used to distinguish between 1°,2° & 3° amines.

1° Amine : $R-NH_2 + PhSO_2Cl \xrightarrow{Pyridine} R-NH-SO_2-Ph \xrightarrow{Base}$ Compound is **soluble** in base.

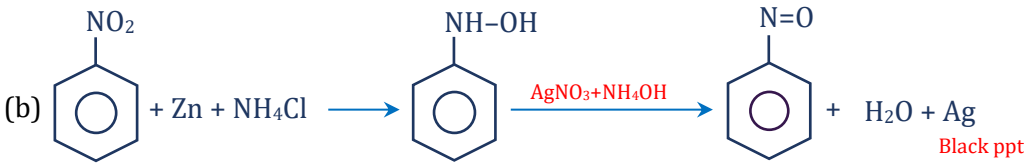
2° Amine : $R_2NH + PhSO_2Cl \xrightarrow{Pyridine} R_2N-SO_2-Ph \xrightarrow{Base}$ Compound is **insoluble** in base.

3° Amine : $R_3N + PhSO_2Cl \xrightarrow{Pyridine}$ No reaction.

Test of nitro group (Mulliken- Barker Test)

Nitroalkane & nitrobenzene gives black ppt on reduction with Zn and ammonium chloride followed by treating with Tollen's reagent. **This is also called Mulliken's test.**

(a) $R-NO_2 \xrightarrow[\Delta]{Zn\text{-}NH_4Cl} R-NHOH \xrightarrow[\Delta]{AgNO_3+NH_4OH} Ag(\text{black ppt})\downarrow$

(b) 

Elements detection:

Detection of carbon and hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

$2H + CuO \xrightarrow{\Delta} Cu + H_2O$

$CO_2 + Ca(OH)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O$

$5H_2O + CuSO_4 \xrightarrow{\Delta} CuSO_4.5H_2O$

White Blue

Detection of other elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from their covalent form to their ionic form by fusing the organic compound with sodium metal.

Following reactions take place: C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium formed by sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne solution.

$Na + C + N \xrightarrow{\Delta} NaCN$; $2Na + S \xrightarrow{\Delta} Na_2S$

$Na + X \xrightarrow{\Delta} NaX$; $Na + C + N + S \xrightarrow{\Delta} NaSCN$

(i) Test for nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with dilute sulphuric acid. The formation of Prussian blue or green colour confirms the presence of nitrogen.

Alternatively $FeCl_3$ and dil. HCl may be added.

$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]$

$Na_4[Fe(CN)_6] + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$

Ferric ferrocyanide (Prussian blue)

(ii) Test for sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS$ (Black)

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour indicates the presence of sulphur.

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$

Sodium nitroprusside — Sodium thionitroprusside (Violet/Purple)

(c) In case, nitrogen and sulphur both are present in an organic compound, then sodium thiocyanate is formed. It gives blood red colour with neutral $FeCl_3$.

$Na + C + N + S \longrightarrow NaSCN$; Neutral $FeCl_3 + NaSCN \longrightarrow Fe(SCN)_3$(Blood red)

(iii) Test for halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

Note :

The sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

$NaX + AgNO_3 \longrightarrow AgX\downarrow$

(iv) Test for phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\ HNO_3 \longrightarrow (NH_4)_3PO_4.\ 12\ MoO_3 + 21\ NH_4NO_3 + 12H_2O$

Ammonium Molybdate — Ammonium Phosphomolybdate

Summary

1. Unsaturation : Alkenes & alkynes:

(a) Bayers test : Cold dil alk. $KMnO_4$ decolourisation test

Purple colour $\rightarrow$ Colourless + MnO_2 (Brown ppt)

(b) Br_2 water decolourisation test

Violet colourless of $Br_2 \rightarrow$ Colourless

2. Terminal alkynes:

Confirmed by ppt of Acetylide ion with $NaNH_2$ or $AgNO_3$ or $Cu_2Cl_2NH_4OH$

3. Alkyl halides:

(a) If they are capable of carbocation formation then they will give ppt with $AgNO_3$.

(b) Beilstein's test : A green colour is imported to the flame if small amount of organic compound is taken on copper wire.

4. Alcohol:

(a) Cerric ammonium nitrate → Give red colour

(b) Boil with acetic acid & conc. H_2SO_4 → fruity smell

(c) 2-alkanol & ethanol also give Iodoform test → Yellow ppt. of CH_3I on reaction with $I_2 + \overset{\ominus}{O}H$

5. Aldehyde & Ketones:

2,4- Dinitrophenyl hydrazize (or) Braddy's reagent give yellow, orange or red color with ald. & Ketones (2,4-DNP)

6. Aldehydes:

(a) Tollen's test → Silver mirror

(b) Fehling's test {except benzaldehyde}→ Red colour

(c) Benedicts test → Red colour

(d) Schiff's dye colour regeneration test → Pink colour

(e) Gly ppt with $HgCl_2$.

7. Ketones:

(a) Methyl Ketones give haloform test

(b) α-hydroxy Ketones give Tollen's & Fehling test's too.

8. Carboxylic acids:

(a) Brisk effervescence with aq. $NaHCO_3$ solution.

(b) HCOOH alone gives silver mirror test with Tollen's reagent.

(c) Blue litmus → red

(d) Give fruity smell on reaction with alcohols.

9. Phenols:

(a) Violet colouration with neural $FeCl_3$

(b) Liebermann test

(c) White ppt with Br_2 water

(d) Brisk effervescence with aq. $NaHCO_3$ is observed in case of Nitrophenols.

10. Primary amines:

(a) Carbylamine reaction → Isonitriles have very distinctive foul odors

(b) Hoffmann mustard oil reaction → Oily liquid with mustard like smell.

11. Aromatic 1° amine → diazo test

12. Amide boil with NaOH → NH_3

13. Nitrobenzene → Mullikqn Baker test → Treat it with $ZnNH_4Cl$ then boil with Tollen's reagent → Silver mirror will appear

(A) ELEMENTAL ANALYSIS Lassaigne method (Detection of elements)			
Element	**Sodium Extract (S.E.)**	**Confirmed Test**	**Reaction**
Nitrogen	$Na+C+N \xrightarrow{\Delta} NaCN$ (S.E.)	S.E. + $FeSO_4$ + NaOH, boil and cool, + $FeCl_3$ + conc. HCl Blue or green colour	$Feso_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaOH \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 + 3$ NaCl Prussian blue
Sulphur	$2Ns + S \xrightarrow{\Delta} Na_2S$ (S.E.)	(i) S.E. + sodium nitro prusside (A) A deep violet colour. (ii) S.E. + CH_3COOH + $(CH_3COO)_2Pb$ A black ppt.	(i) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ Deep violet (ii) $Na_2S + (CH_3COO)_2Pb$ $\xrightarrow{CH_3COOH} PhS\downarrow + 2CH_3COONa$ black ppt.
Halogen	$Na + Cl \xrightarrow{\Delta} NaCl$ (S.E.)	S.E. + $HNO_3 = AgNO_3$ (i) White ppt. so lub le in aq NH_3 confirms Cl (ii) Yellow ppt partially so lub le in aq. NH_3 confirm br (iii) Yellow ppt inso lub le in aq NH_3 confirms I	$NaX + AgNO_3 \xrightarrow{HNO_3} AgZ\downarrow$ $AgCl + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl$ White ppt soluble
Nitrogen and Sulphur together	$Na + C + N + S \xrightarrow{\Delta}$ NaCNS (S.E.)	As in test for nitrogen; instead of greed or blue colour, blood red coloration confirms presence of N and S both	$NaCNS + FeCl_2 \longrightarrow [Fe(CNS)]Cl_2 + naCl$ Blood red colour