Structural Identification

Introduction

The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory.

In order to establish the correct structure of an organic compound, it is necessary to detect skeleton of compound, elements and functional groups present in the organic compound.

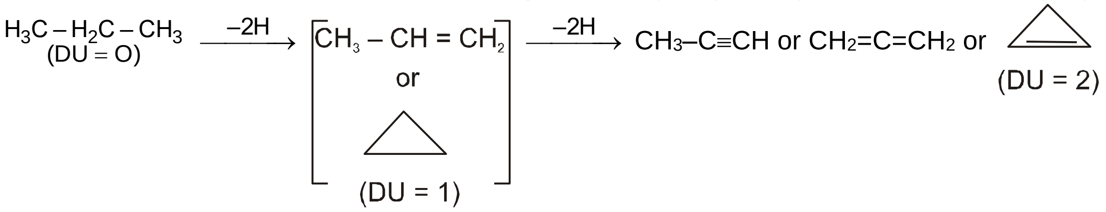
Section (A) : Degree of unsaturation and catalytic hydrogenation

1. Hydrogen deficiency index:

The presence of double bonds or rings within a molecule is indicated by a quantity called hydrogen deficiency index.

Applications : To indentify the no. of π bonds or rings and also helpful in determining the structure of the molecule.

Definition : Deficiency of 2H atoms with respect to fully saturated acyclic hydrocarbon is equivalent to One HDI It is also known as Double Bond Equivalence (DBE) or degree of unsaturation (DU).



$$\boxed{\text{Degree of unsaturation (D.U.)} = \frac{(2n+2)-(\text{No.of H atoms}+\text{No.of X atoms}-\text{No.of N atoms})}{2}}$$

Where n = number of carbon atoms in the molecule

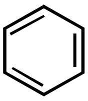
Note : Total no. of cyclic rings + double bonds will give us degree of unsaturation.

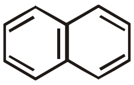
One double bond = one DU
One ring = one DU
One triple bond = two DU

Ex. (i) $CH_2=CH_2$ DU = $\frac{(2\times2+2)-4}{2}$ = 2/2 = 1

(ii)

DU = 2

(iii)

DU = 4

(iv)

DU = 7

(v) C_6H_6O DU = $\frac{(2n+2)-6}{2} = \frac{14-6}{2} = 4$

(vi) C_6H_5Cl D.U. = $\frac{14-(5+1)}{2} = 4$

2. Catalytic hydrogenation :

Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature.

All Carbon–Carbon π bonds(C=C, C≡C) get hydrogenate. The reaction can't be stopped at any intermediate stage.

Note : **(i)** Aromatic π bonds are stable at room temperature but can be hydrogenated at high temperature.

(ii) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.

(iii) The no. of moles of H_2 consumed by 1 mole of compound is equal to the no. of π bonds.

(iv) During catalytic hydrogenation *carbon skelton* does not change.

Application : This reaction gives an information about molecule that the molecule is saturated or unsaturated.

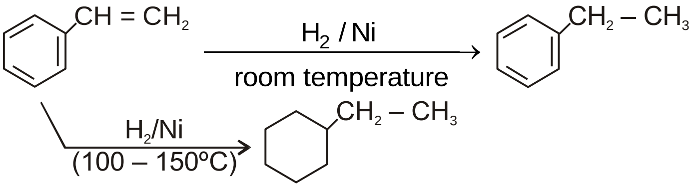
General reaction :

(a) $R{-}CH{=}CH{-}R + H_2 \xrightarrow{Ni} R{-}CH_2{-}CH_2{-}R$

(b) $$\begin{tikzcd} R{-}C{\equiv}C{-}R + 2H_2 \arrow[r, "Ni/Pt/Pd"] \arrow[d, "H_2"] & R{-}CH_2{-}CH_2{-}R \\ \underset{\text{(Not isolated)}}{R-CH=CH-R} \arrow[r, "H_2"] & R{-}CH_2{-}CH_2{-}R \end{tikzcd}$$

(c) $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{2H_2/Ni} CH_3{-}CH_2{-}CH_2{-}CH_3$

(d)



Section (B) : Monochloroination & ozonolysis reactions

3. Monohalogenation :

When an alkane or a cycloalkane is treated with halogen (Cl_2, Br_2, F_2, I_2), a photochemical reaction takes place, in which a C–H bond cleaves and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.

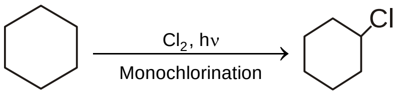
Applications : If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers.**

Conclusion : Hence, it can be concluded that the total no. of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical Hydrogens or non-equivalent Hydrogens or chemically different Hydrogens.

Note : In aromatic hydrocarbons, the hydrogen atoms of the side-chain are chlorinated, but H-atoms of Benzene ring are stable.

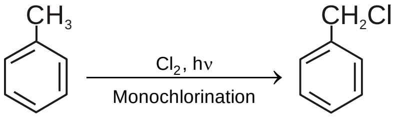
Ex. (i) $CH_4 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu} CH_3Cl + HCl$ ¼1–Monochloroproduct½

(ii)



+ HCl ¼1–Monochloroproduct½

(iii)



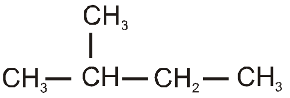
¼1–Monochloroproduct½

Note : Only one monochloro product is formed because aromatic H atoms are inert towards this reaction.

(iv) $CH_3{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 2 Products (structure isomers)

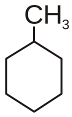
(v) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 3 Products (structure isomers)

(vi)



$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_2{-}CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 4 Products (structure isomers)

(vii)



$\xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 5 Products (structure isomers)

4. Ozonolysis :

Ozonolysis reaction is used to determine the position of C=C, C≡C in a molecule. In this reaction Alkene, Alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

(i) Reductive ozonolysis

Reagents are : (1) O_3 (ozone) (2) Zn or $(CH_3)_2S$ and H_2O or CH_3COOH

The products are carbonyl compounds (aldehydes or ketones).

(ii) Oxidative ozonolysis

Reagents are : (1) O_3 (ozone) (2) H_2O_2 or H_2O

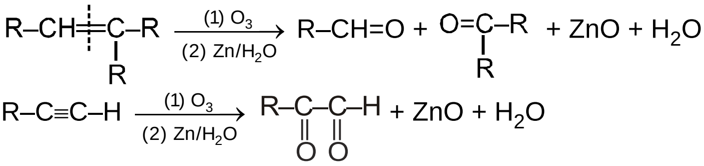
The products are ketones and/or acids.

Note : (i) Ozonolysis does not interfere with other functional groups.

(ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General Reaction :

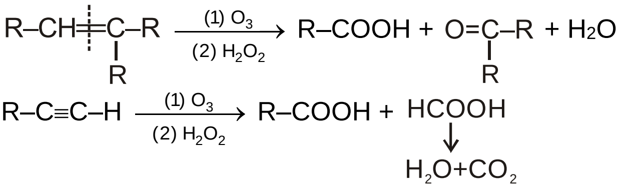
(i) Reductive ozonolysis



$$R{-}CH{=}\underset{\displaystyle R}{\underset{|}{C}}{-}R \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} R{-}CH{=}O + O{=}\underset{\displaystyle R}{\underset{|}{C}}{-}R + ZnO + H_2O$$

$$R{-}C{\equiv}C{-}H \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H + ZnO + H_2O$$

(ii) Oxidative ozonolysis



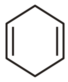
$$R{-}CH{=}\underset{\displaystyle R}{\underset{|}{C}}{-}R \xrightarrow[(2)\ H_2O_2]{(1)\ O_3} R{-}COOH + O{=}\underset{\displaystyle R}{\underset{|}{C}}{-}R + H_2O$$

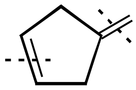
$$R{-}C{\equiv}C{-}H \xrightarrow[(2)\ H_2O_2]{(1)\ O_3} R{-}COOH + \underset{\substack{\downarrow \\ H_2O+CO_2}}{HCOOH}$$

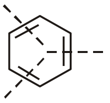
Ex. (a) $CH_2{=}CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2{=}O + CH_2{=}O$

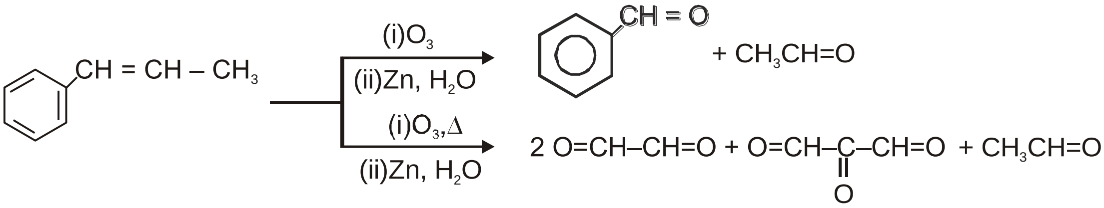
(b) $CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3{-}CH_2{-}CH{=}O + O{=}CH_2$

(c) $CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2{=}O + O{=}CH{-}CH_2{-}CH{=}O + O{=}CH{-}CH_3$

(d)  $\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ $2OHC{-}CH_2{-}CHO$ (Propandial)

(e)  $\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ $O{=}CH{-}CH_2{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH{=}O + O{=}CH_2$

(f)  $\xrightarrow[(2)\ H_2O_2]{(1)\ O_3(\Delta)}$ $3\ O = \overset{\displaystyle H}{\overset{|}{C}} - \overset{\displaystyle H}{\overset{|}{C}} = O$ (Ethanedial) or (glyoxal)

(g) 

5. Practical Organic Chemistry (POC) :

When we are looking for the information regarding the functional nature of the compound then we go for the following lab test.

Section (C & D) : Test for acidic hydrogen, unsaturation & functional groups

(1) 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 : Those H atoms which is attached with more electronegative atoms like O,N,S,X, C_{sp}.

General reaction : $Z-Ⓗ + Na \rightarrow \overset{-}{Z}\overset{+}{Na} + \frac{1}{2}H_2\uparrow$

Ex.

(a) $R-NH_2 \xrightarrow{Na} R-NHNa + \frac{1}{2}H_2\uparrow$

(b) $R-SH \xrightarrow{Na} RSNa + \frac{1}{2}H_2\uparrow$

(c) $R-COOH \xrightarrow{Na} R-COONa + \frac{1}{2}H_2\uparrow$

(d) $PhOH \xrightarrow{Na} PhONa + \frac{1}{2}H_2\uparrow$

(e) $R—OH + Na \rightarrow R—O^-Na^+ + \frac{1}{2}H_2\uparrow$

(f) $R—SO_3H + Na \rightarrow R—SO_3^-Na^+ + \frac{1}{2}H_2\uparrow$

(g) $R—C\equiv CH + Na \rightarrow R—C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$

(h) $R—CH=CH_2 + Na \rightarrow$ No reaction.

(i) $R — CH_2—O —CH_3 + Na \rightarrow$ No reaction.

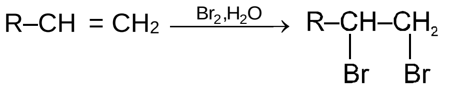
(j) $HCl \xrightarrow{Na} NaCl + \frac{1}{2}H_2\uparrow$

(2) Test for unsaturation :

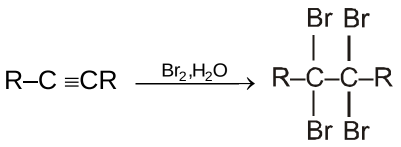
(i) Bromine water test ($Br_2 + H_2O$, Red-brown solution) :

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

$R–CH_2–CH_3 \xrightarrow{Br_2,H_2O}$ no reaction



$R–CH=CH_2 \xrightarrow{Br_2,H_2O} R–CH(Br)–CH_2(Br)$ Red-brown colour disappears



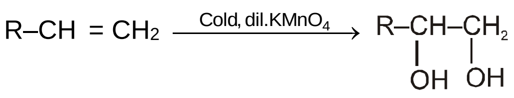
$R–C\equiv CR \xrightarrow{Br_2,H_2O} R–CBr_2–CBr_2–R$ Red-brown colour disappears

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

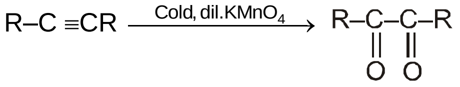
(ii) Baeyer reagent (Cold dil. alkaline $KMnO_4$ Pink/purple solution) :

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

$R–CH_2–CH_3 \xrightarrow{Cold,\ dil.KMnO_4}$ no reaction



$R–CH=CH_2 \xrightarrow{Cold,\ dil.KMnO_4} R–CH(OH)–CH_2(OH)$ Purple colour disappears



$R–C\equiv CR \xrightarrow{Cold,\ dil.KMnO_4} R–\underset{\Vert}{C}(O)–\underset{\Vert}{C}(O)–R$ Purple colour disappears

$$\boxed{2KMnO_4 \longrightarrow K_2O + \underset{\substack{\uparrow \\ \text{Brown solution}}}{2MnO_2} + 3\,[O]}$$

(3) Test for terminal Alkyne

(i) Tollen’s reagent [$AgNO_3$ + NH_4OH or $\{Ag(NH_3)_2\}^+ OH^{\ominus}$] :

Tollen’s Reagent gives white precipitate (Silver alkynide) with terminal alkyne.

$$R\text{–}C \equiv CH \xrightarrow{AgNO_3+NH_4OH} R\text{–}C{\equiv}CAg + NH_4NO_3$$

White precipitate

(ii) Ammonical cuprous chloride (Cu_2Cl_2 + NH_4OH) :

It gives red precipitate with terminal alkyne.

$$2\ R\text{–}C \equiv CH \xrightarrow{Cu_2Cl_2+NH_4OH} 2\ R\text{–}C \equiv CCu \downarrow + 2NH_4Cl + 2H_2O$$

Red precipitate

(4) Test for alcohols :

(i) 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 used to distinguish between 1°, 2°, 3° alcohol because 1°, 2°, 3° alcohols react with different rates.

(a) 1° alcohol $R\text{–}CH_2\text{–}OH \xrightarrow{\text{conc. HCl+anhydrous } ZnCl_2} R\text{–}CH_2\text{–}Cl$

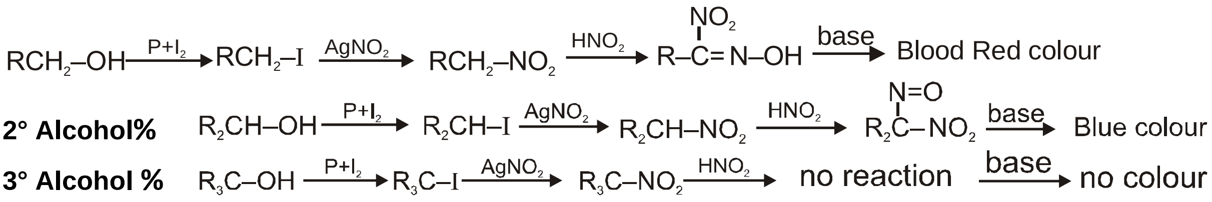
(does not give appreciable reaction or gives white turbidity in 30 min.)

(b) 2° alcohol $R_2CH\text{–}OH \xrightarrow{\text{conc. HCl+anhydrous } ZnCl_2} R_2CH\text{–}Cl$ (gives white turbidity in 5 min.½

(c) 3° alcohol $R_3C\text{–}OH \xrightarrow{\text{conc. HCl+anhydrous } ZnCl_2} R_3C\text{–}Cl$ (gives white turbidity immediately)

*** Phenols and enols do not give Lucas test.**

(ii) Victor Mayer test :



1° Alcohol%

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

2° Alcohol%

$$R_2CH\text{–}OH \xrightarrow{P+I_2} R_2CH\text{–}I \xrightarrow{AgNO_2} R_2CH\text{–}NO_2 \xrightarrow{HNO_2} R_2\overset{N=O}{\overset{|}{C}}\text{–}NO_2 \xrightarrow{base} \text{Blue colour}$$

3° Alcohol %

$$R_3C\text{–}OH \xrightarrow{P+I_2} R_3C\text{–}I \xrightarrow{AgNO_2} R_3C\text{–}NO_2 \xrightarrow{HNO_2} \text{no reaction} \xrightarrow{base} \text{no colour}$$

(iii) Cerric Ammonium Nitrate test : (Group reagent for alcohols)

Alcohols(1°,2°,3°) also give characteristic red colour with cerric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$ solution.

(5) Test for phenol or enol :

Neutral $FeCl_3$ test :

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

$$6\ PhOH + FeCl_3 \longrightarrow [(PhO)_6Fe]^{3-} + 3HCl + 3H^+$$

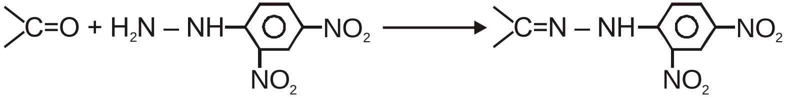
(Coloured complex)

*** It does not give positive test with alcohol.**

(6) Test for carbonyl compounds :

2, 4-DNP ¼2, 4-Dinitrophenyl hydrazine+½Test :

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



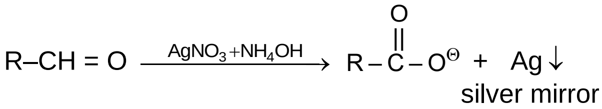
2, 4-DNP

(yellow–orange precipitate of Hydrazone)

(7) Test for aldehydes :

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

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



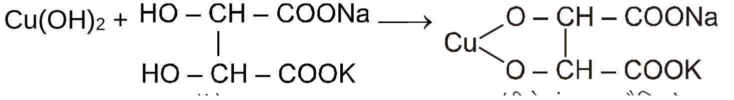
$$R{-}CH = O \xrightarrow{AgNO_3+NH_4OH} R{-}\overset{\overset{O}{\|}}{C}{-}O^{\ominus} + \underset{\text{silver mirror}}{Ag\downarrow}$$

Note : HCOOH also gives this test.

(b) Fehling's solution :

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate.
There are two solutions in Fehling solution,
Solution (A) : $CuSO_4$ solution and
Solution (B) : Alkaline solution of sodium potassiumtartarate.
When these two solutions are mixed we get deep blue coloured solution.

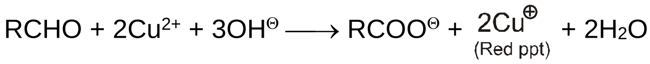
$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



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.

$$R{-}CHO + \underset{\text{Blue}}{2CuO} \longrightarrow RCOOH + Cu_2O \text{ (Red ppt)}$$

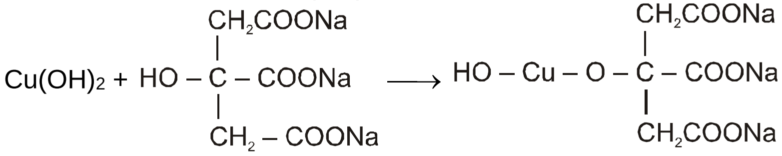


$$RCHO + 2Cu^{2+} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt)}}{2Cu^{\oplus}} + 2H_2O$$

(c) Benedict solution :

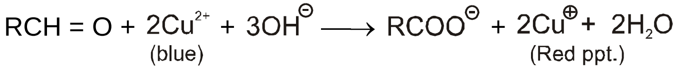
It also consists of two solutions.
Solution (A) : $CuSO_4 \longrightarrow$ solution and
Solution (B) : Alkaline solution of sodium Citrate.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



(Blue colour)

Aldehyde gives positive test with Benedict solution.



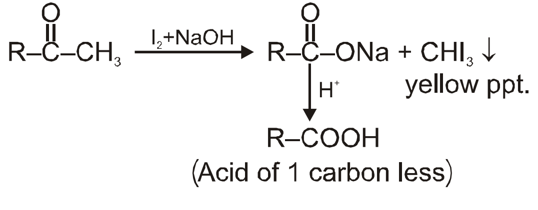
$$RCH = O + \underset{\text{(blue)}}{2Cu^{2+}} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt.)}}{2Cu^{\oplus}} + 2H_2O$$

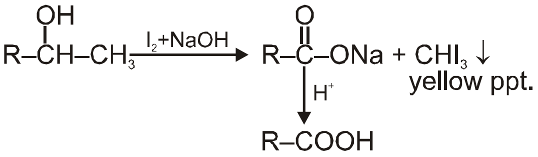
(d) Schiff's reagent :

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 gives** Fehling and Bendict **test.**

(8) Iodoform test :

Reagents : I_2 + NaOH or NaOI ¼Where R = H, alkyl, aryl group½
Acetaldehyde, all methyl ketones & ethyl alcohol give Iodoform test.





$$R\text{–}\overset{OH}{\overset{|}{C}H}\text{–}CH_3 \xrightarrow{I_2+NaOH} R\text{–}\overset{O}{\overset{||}{C}}\text{–}ONa + CHI_3\downarrow \ \text{yellow ppt.} \quad \xrightarrow{H^+} R\text{–}COOH$$

(9) Test for acids/esters/amides :

(i) Sodium bicarbonate test ($NaHCO_3$) %

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

$HCl + NaHCO_3 \longrightarrow NaCl + H_2CO_3$

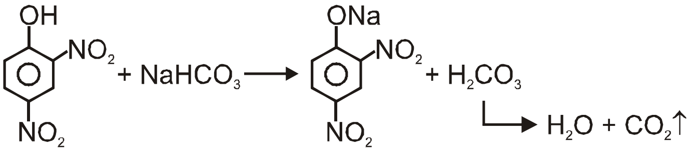
$\quad \longrightarrow H_2O + CO_2\uparrow$

$RCOOH + NaH\overset{*}{C}O_3 \longrightarrow R\text{–}COONa + H_2\overset{*}{C}O_3$

$\quad \longrightarrow H_2O + \overset{*}{C}O_2\uparrow$

$RSO_3H + NaHCO_3 \longrightarrow RSO_3Na + H_2CO_3$

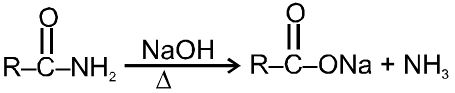
$\quad \longrightarrow H_2O + CO_2\uparrow$



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

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

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



$$R\text{–}\overset{O}{\overset{||}{C}}\text{–}NH_2 \xrightarrow[\Delta]{NaOH} R\text{–}\overset{O}{\overset{||}{C}}\text{–}ONa + NH_3$$

(**iv**) **Esters** are sweet (fruity) smelling liquids.

When react with NaOH & Phenophthalein then pink colour will disappear on heating.

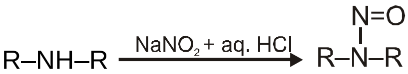
RCOOR' + NaOH + Phenophthalein (Pink) $\xrightarrow{\Delta}$ R COOH + R' OH (Colourless solution)

(10) Test for amines :

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

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

1° Aromatic Amine : $Ph\text{–}NH_2 \xrightarrow[(0\text{–}5°C)]{NaNO_2 + \text{aq. HCl}} Ph\text{–}\overset{+}{N_2}\overset{\ominus}{Cl}$ ¼diazonium salt)

2° Amine : 

$R\text{–}NH\text{–}R \xrightarrow{NaNO_2 + \text{aq. HCl}} R\text{–}\overset{N=O}{\overset{|}{N}}\text{–}R$ (N-Nitroso amine) yellow oily liquid

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

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

1° Amine (Aliphatic or Aromatic) %

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

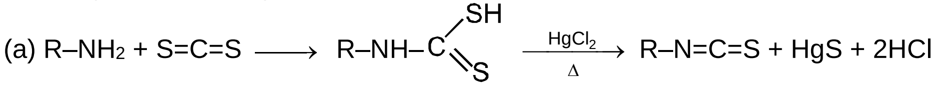
(unpleasent smell of isocyanide)

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

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

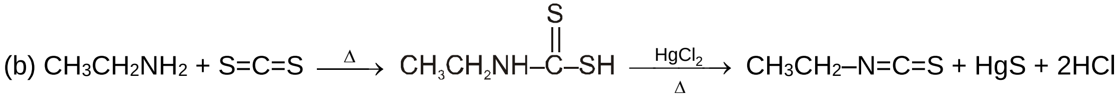
(iii) Hofmann mustard oil test

It is a test for 1° 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 isothiocyanates having smell like mustard oil.



(a) $R{-}NH_2 + S{=}C{=}S \longrightarrow R{-}NH{-}C(SH){=}S \xrightarrow[\Delta]{HgCl_2} R{-}N{=}C{=}S + HgS + 2HCl$

Dithioethylcarbamic acid Alkylisothiocyanate



(b) $CH_3CH_2NH_2 + S{=}C{=}S \xrightarrow{\Delta} CH_3CH_2NH{-}\overset{\overset{S}{||}}{C}{-}SH \xrightarrow[\Delta]{HgCl_2} CH_3CH_2{-}N{=}C{=}S + HgS + 2HCl$

(1° amine) Ethyl isothiocyanate

Similarly aniline gives phenlyisothiocyanate

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

Phenylisothiocyanate

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

(iv) Hinsberg reagent ($C_6H_5SO_2Cl$) :

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

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

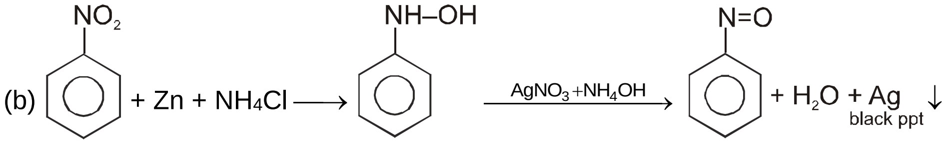
2° Amine : $R_2NH + PhSO_2Cl \xrightarrow{\text{Pyridine}} R_2N{-}SO_2{-}Ph \xrightarrow{\text{Base}}$ Compund is **insoluble** in base.

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

(11) Test of nitro group : (Mulliken-Barker's test)

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

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



(12) Test for carbohydrates & sugars

Molisch test :

This is a general test for carbohydrates. One or two drops of alcoholic solution of α-naphthol is added to 2 ml glucose solution. 1 ml of conc. H_2SO_4 solution is added carefully along the sides of the test tube. The formation of a violet ring at the junction of two liquids confirms the presence of a carbohydrate or sugar.

Barfoed test : It is given by reducing sugars.

(13) Test for amino acids and proteins :

Ninhydrin Test : This is used to detect the presence of amino acids & proteins.

Xanthoproteic test & Biuret test are given by proteins.

Section (E) : Elements detection

(1) 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).

$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$; $2H + CuO \xrightarrow{\Delta} Cu + H_2O$

$CO_2 + Ca(OH)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O$; $\underset{\text{White}}{5H_2O + CuSO_4} \xrightarrow{\Delta} \underset{\text{Blue}}{CuSO_4.5H_2O}$

(2) 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 so formed on 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 $FeCl_3$.

$$Na + C + N + S \longrightarrow NaSCN$$

$$\text{Neutral } FeCl_3 + NaSCN \longrightarrow Fe(SCN)_3$$

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