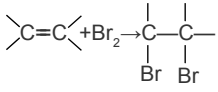
CHAPTER 27

ANALYTICAL TEST OF ORGANIC COMPOUNDS

27.1 ALKENE AND ALKYNE

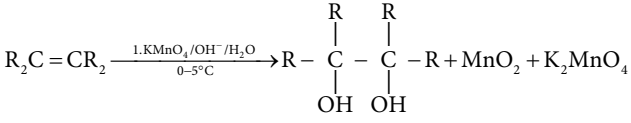
27.1.1 Bromine Water Test

In this test the alkene or alkyne reacts with Br_2 to form an alkyl dibromide, which causes the orange-brown of the Br_2 to disappear. This will be immediate with alkenes, but may take a short while with alkynes. Activated aromatic rings give a false positive in this test.



27.1.2 Baeyer's Reagent

In this test the alkene or alkyne is oxidized to a diol (alkene) or diketone (alkyne), which uses up the purple permanganate solution and produces manganese dioxide, a brown precipitate. It may also give a positive test for aryl amines, aldehydes, and alcohols, which can also be oxidized.



27.1.3 Metal alkynide Test

When terminal alkyne is treated with ammonical $AgNO_3$ to produce silver alkynide

$$R-C\equiv CH + AgNO_3 / NH_4OH \rightarrow \underset{\text{(grey-coloured ppt.)}}{R-C\equiv C-Ag\downarrow}$$

When terminal alkyne is treated with ammonical Cu_2Cl_2 to produce red-coloured ppt.

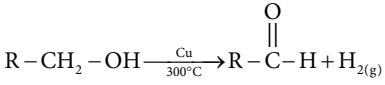
$$R-C\equiv C-H + Cu_2Cl_2 / NH_4OH \rightarrow \underset{\text{(red-coloured ppt.)}}{R-C\equiv C-Cu\downarrow}$$

27.2 ALCOHOL

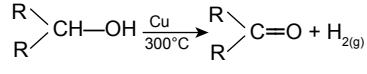
27.2.1 Dehydrogenation Test

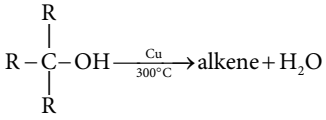
When alcohol vapours are passed through red hot Cu at 300°C, they react differently

(a) Primary alcohol undergoes dehydrogenation to produce aldehyde



(b) Secondary alcohol also undergoes dehydrogenation to produce ketone

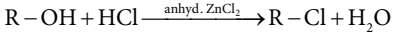


(c) Tertiary alcohol undergoes dehydration to produce alkene 

27.2.2 Lucas Test

In this method, alcohol is treated with equimolar mixture of anhydrous $ZnCl_2$ and Conc. HCl also called Lucas reagent at room temperature to produce alkyl chloride.

Lucas reagent provides an analytical test to distinguish primary, secondary and tertiary alcohol.

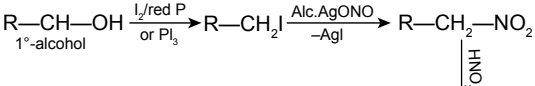


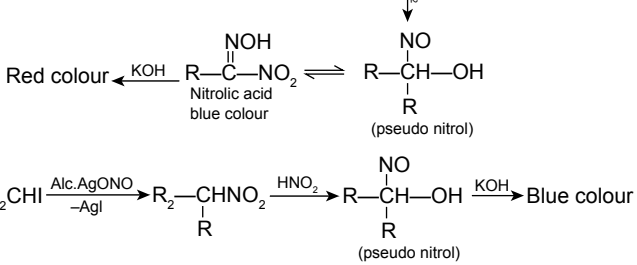
1. Tertiary alcohol gives white turbidity immediately.
2. Secondary alcohol gives white turbidity in few minutes.
3. Primary alcohol do not give white turbidity at room temperature.

Note:

Though benzyl or allyl alcohol are primary still they produce white turbidity immediately due to high stability of carbonation produced during the reaction.

27.2.3 Victor Meyer's Test





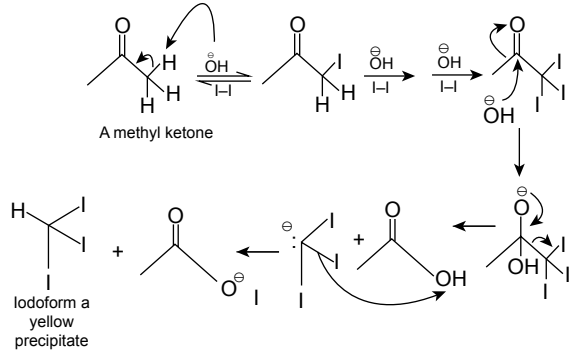
27.2.4 Iodoform Test

Compound which give +ve iodoform test have any one of the following structural features:

(i) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-$ (ii) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$ (iii) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-$

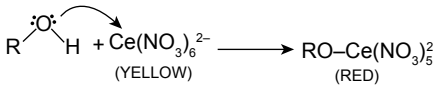
(iv) $ICH_2-\overset{\displaystyle O}{\overset{\|}{C}}-$ (v) $I_2CH-\overset{\displaystyle O}{\overset{\|}{C}}-$ (vi) $I_3C-\overset{\displaystyle O}{\overset{\|}{C}}-$

When a compound having any one of the above structural feature is treated with I_2 in presence of alkali like NaOH or KOH or $Ca(OH)_2$, etc. iodoform as a yellow precipitate is obtained.



27.2.5 Ceric Ammonium Nitrate Test

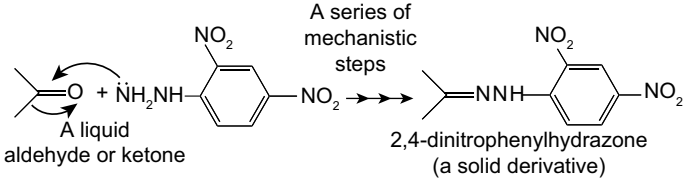
Alcohols react with ceric nitrate reagent to produce a colour change (yellow to red), whereas carbonyl compounds do not react. Note that changing the groups attached to certain inorganic ions such as Ce^{4+} results in a change to the electronic structure, which results in a colour change. Production of a magenta color therefore indicates the presence of an alcohol group.



27.3 ALDEHYDE AND KETONE

27.3.1 2,4-DNP Test

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine reagent to form yellow, orange, or reddish-orange precipitates, whereas alcohols do not react. Formation of a precipitate therefore indicates the presence of an aldehyde or ketone. The precipitate from this test also serves as a solid derivative.

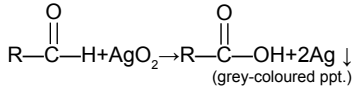


27.3.2 Tollen's Test

When $AgNO_3$ is treated with NH_4OH, white precipitate of Ag_2O is produced.

$2AgNO_3 + 2NH_4OH \rightarrow Ag_2O\downarrow + 2NH_4NO_3 + H_2O$

$Ag_2O + 4NH_4OH \rightarrow 2[Ag(NH_3)_2]OH + 3H_2O$



Tollen's reagent due to this complex dissolves again in solution. $2[Ag(NH_3)_2]OH \xrightarrow{\Delta} Ag_2O + H_2O + 4NH_3$

Compounds which give positive test with Tollen's reagent are:

(i) Aldehydes (ii) HCOOH (iii) α-hydroxy ketone
(iv) $CHCl_3$ (v) Terminal alkyne (vi) Hydroxyl amine

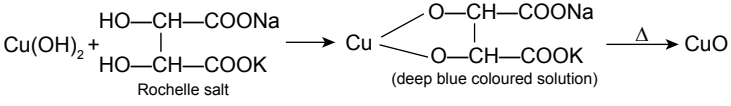
27.3.3 Fehling's Test

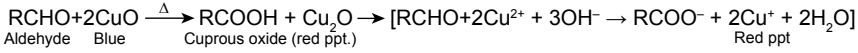
Fehling's reagent is prepared by mixing equal volume of Fehling's solution I and Fehling's solution II.

Fehling's solution I $\xrightarrow{\text{Contains}}$ $CuSO_4$ or some other cupric salt

Fehling's solution II $\xrightarrow{\text{Contains}}$ alkaline solution of Rochelle salt (sodium potassium tarterate)

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





Compounds which give +ve test with Fehling's reagent are:

(i) Aliphatic aldehydes (ii) HCOOH (iii) α-hydroxyl ketone
(iv) $CHCl_3$ (v) Terminal alkyne

Fehling's reagent can be used to distinguish between aliphatic and aromatic aldehydes.

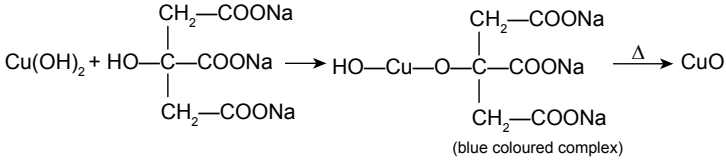
27.3.4 Benedict's Test

Benedict's reagent is prepared by mixing equal volume of Benedict solution I with Benedict solution II.

Benedict solution I $\xrightarrow{\text{Contains}}$ alkaline solutions of sodium citrate

Benedict solution II $\xrightarrow{\text{Contains}}$ Cu^{2+} salt

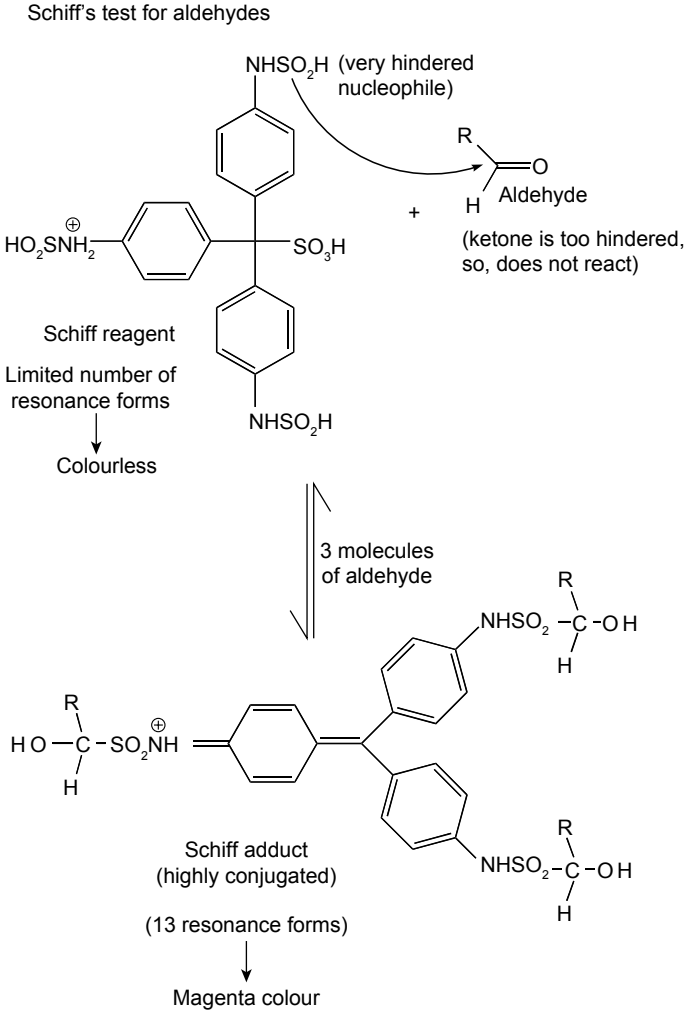
$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 + Na_2SO_4$



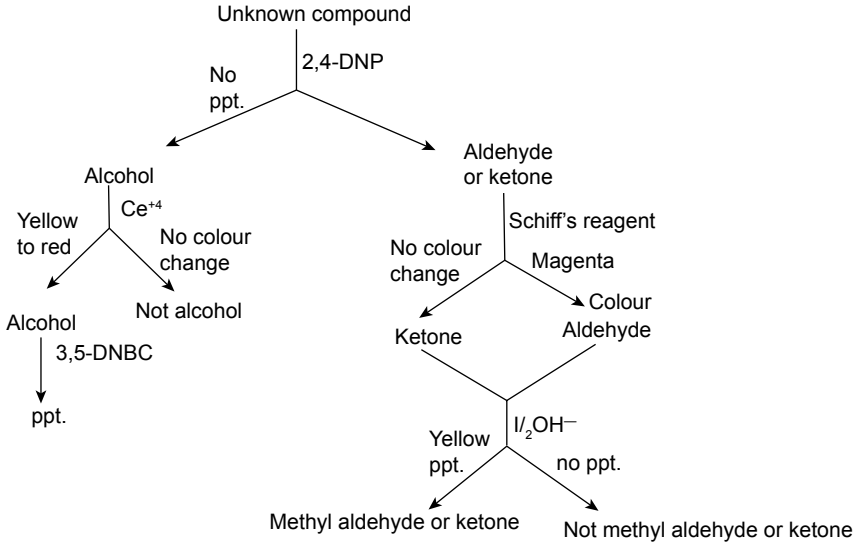
- All compounds which give positive test with Fehling's reagent also give similar test with Benedict's reagent.

27.3.5 Schiff's Test

The Schiff's reagent acts as a nucleophile that adds to the carbonyl group of an aldehyde. Because this nucleophile is extremely bulky, a ketone, which is more sterically crowded than an aldehyde at the carbonyl carbon, does not react with Schiff's reagent, and thus does not produce the magenta color. Production of the magenta colour therefore indicates that the unknown compound is an aldehyde and not a ketone. Note that, generally, more extended systems of conjugation lead to coloured compounds, whereas the Schiff reagent itself has a limited system of conjugation, the adduct with an aldehyde has an extended system of conjugation, resulting in a highly coloured compound.



Identification of an unknown organic compound



where 3,5 – DNBC is 3, 5-dinitrobenzyol chloride.

27.4 AMINES

27.4.1 Carbyl Amine Test

When primary amine whether it is aliphatic or aromatic is treated with $CHCl_3$ and alcoholic KOH a bad smelling compound isocyanide is produced.

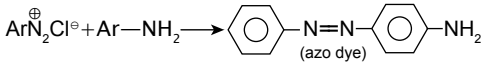
$$R-NH_2 + CHCl_3 + \text{alc. KOH} \rightarrow R-N\equiv C + 3KCl + H_2O$$

27.4.1.1 Azo dye test

When aliphatic primary amine is treated with HNO_2 or $NaNO_2$ Conc. HCl at low temperature it undergoes diazotization to produce colourless alcohols.

However, when aromatic primary amine is treated with $NaNO_2$ and or Conc. HCl at 0–5°C. An aryl diazonium salt which undergoes diazo coupling with aromatic amine to produce coloured azo dye.

$$Ar-NH_2 \xrightarrow[HCl]{NaNO_2} \underset{\substack{\text{Aryl}\\ \text{diazonium}\\ \text{chlorire}}}{ArN_2^+Cl^-} + 2H_2O + NaCl$$

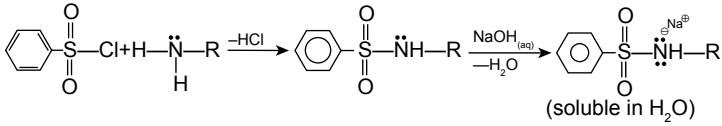


$$R-NH_2 \xrightarrow[HCl]{NaNO_2} R-OH + N_2\uparrow$$

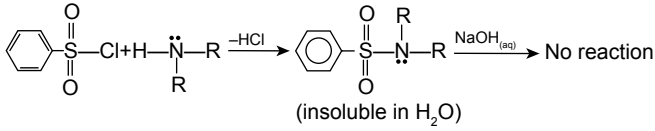
27.4.2 Hinsberg's Test

In this method amine mixture is treated with Hinsberg's reagent, i.e., $C_6H_5SO_2Cl$. **(Benzene sulphonyl chloride)** where they react differently.

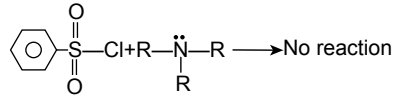
Primary amine reacts with Hinsberg's reagent to produce a substituted sulphonamide which is soluble in aq. alkali.



Secondary amine reacts with Hinsgerg's reagent to produce N, N–dialkyl sulphonamide which is insoluble in aq. alkali.



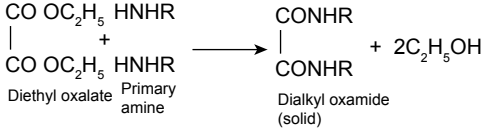
Tertiary amine does not react at all with Hinsberg's reagent.



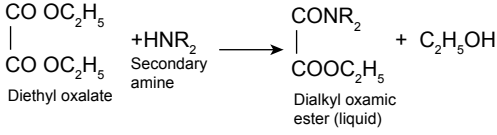
27.4.3 Hofmann's Test

In this method, amine mixture is treated with Hofmann's reagent, i.e., ethyl oxalate where they react differently

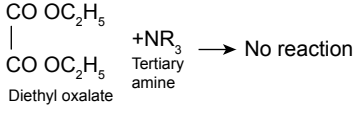
- Primary amine reacts with Hofmann's reagent to produce a substituted oxamide which is a crystalline solid.



- Secondary amines reacts with Hofmann's reagent to produce N, N – dialkyl oxamic ester which is a high boiling liquid.

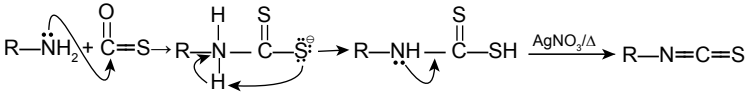


- Tertiary amine does not react at all with Hoffmann's reagent



27.4.4 Hofmann's Mustard Oil Test

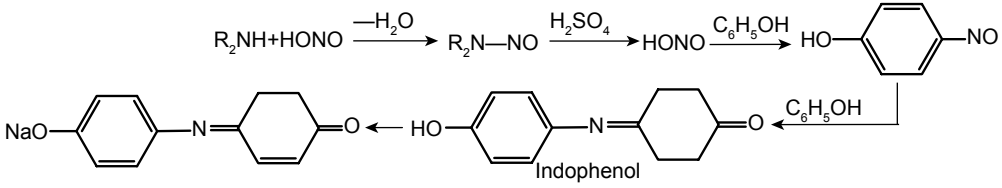
When primary amine is treated with CS_2, then N-alkyl dithiocarbamic acid is produced which on decomposition with $AgNO_3$ and $HgCl_2$ produces alkyl isothiocyanate, an oily compound having mustard oil smell along with formation of black precipitate of HgS. Secondary and tertiary amines do not give this test and therefore this is a confirmatory test of a primary amine.



where $H_2S \xrightarrow{HgCl_2} Hgs\downarrow + 2HCl$

27.4.5 Liebermann's Nitroso Test

This test is given only by 2° amine whether it is aliphatic or aromatic. 2° amine is converted into nitroso amine by treating the amine with HNO_2. On warming with phenol and Conc. H_2SO_4 brown on red colour is formed at first which changes to blue then to green colour changes to red on dilution and further to greenish blue or violet on treatment with alkali.

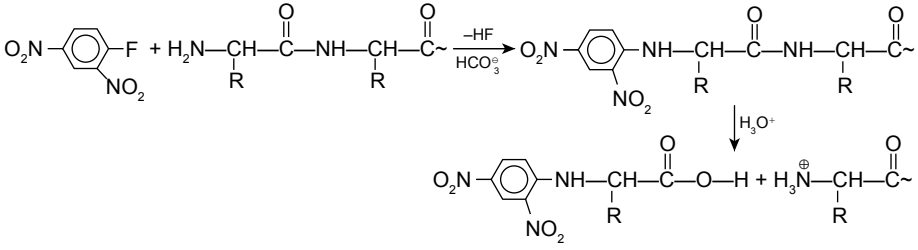


27.5 PROTEIN CHEMISTRY

27.5.1 Sanger's Test

When 2,4-dinitro-fluoro-benzene (DNFB) is treated with polypeptide in a solution, an aromatic nucleophilic substitution takes place involving the free amine group of the N-terminal residue.

Subsequent hydrolysis of the polypeptide gives, a mixture of amino acids in which N-terminal amino acid bear a label of 2,4-dinitrophenyl group.



27.5.2 Ninhydrin Test

When a protein is treated with ninhydrin, a violet or purple-coloured anion is produced.