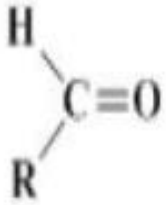
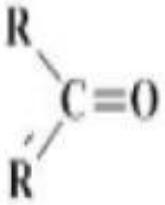
Identification of Aldehydes & Ketones



the general formula for aldehydes



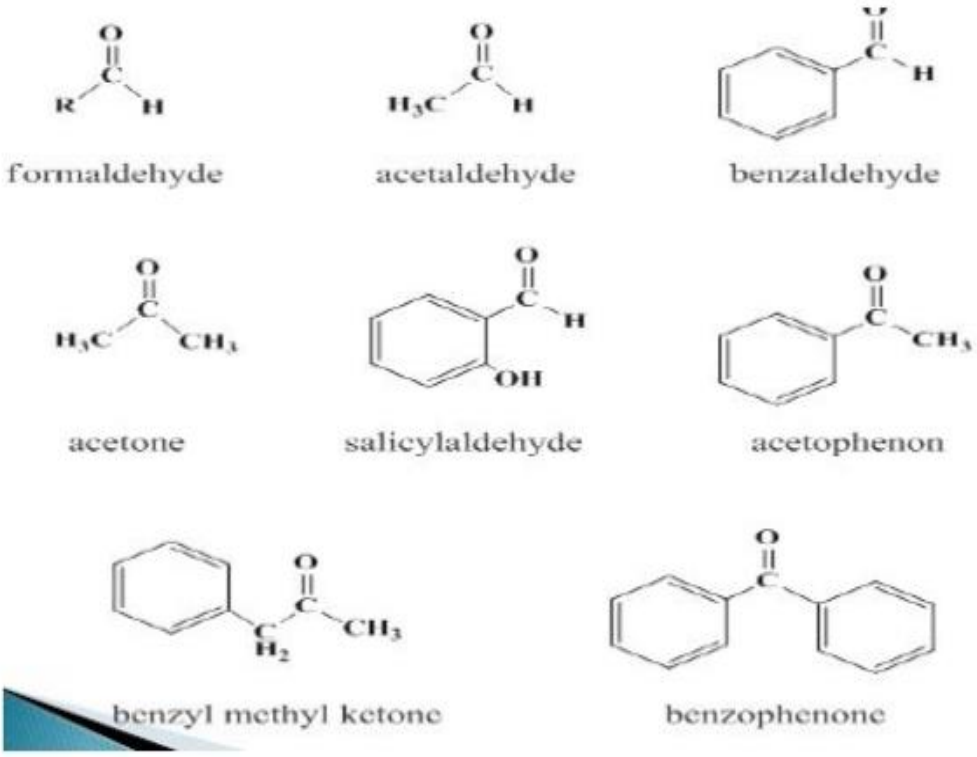
the general formula for ketones

Aim:

To identify the presence of aldehydes or ketones functional group in the given organic compound

Theory:

Aldehydes and ketones constitute an important class of organic compounds containing the carbonyl group. Aldehyde has the structure RCH(=O) while a ketone has the structure of R2C(=O). Where R may be an alkyl, alkenyl, alkynyl or aryl group.



Physical Properties

1. All aldehydes and ketones are liquids except :formaldehyde, which is gas.

2. They are colorless except benzaldehyde, which has a pale yellow colour (due to oxidation) with a characteristic odour.

3. The b.p.s of aldehydes & ketones are lower than those of the alcohols from which they are derived i.e.:isopropyl alcohol boils at 82.5˚C while its oxidation product acetone, boils at 56˚C ; ethanol boils at 78˚C while its oxidation product, acetaldehyde, boils at 21˚C.

4. Aliphatic aldehydes and ketones burn with a blue flame (without smoke) while aromatic ones burn with a yellow smoky flame.

5. Low m.wt aldehydes and ketones (less than 5 carbons) are appreciably soluble in water, although Aromatic ones are insoluble in water, and all of them are soluble in organic solvents.

Chemical Properties

- Both aldehydes and ketones are neutral compounds that don't change the color of litmus paper.
- All reactions of aldehydes and ketones are related to the carbonyl group (the active group).

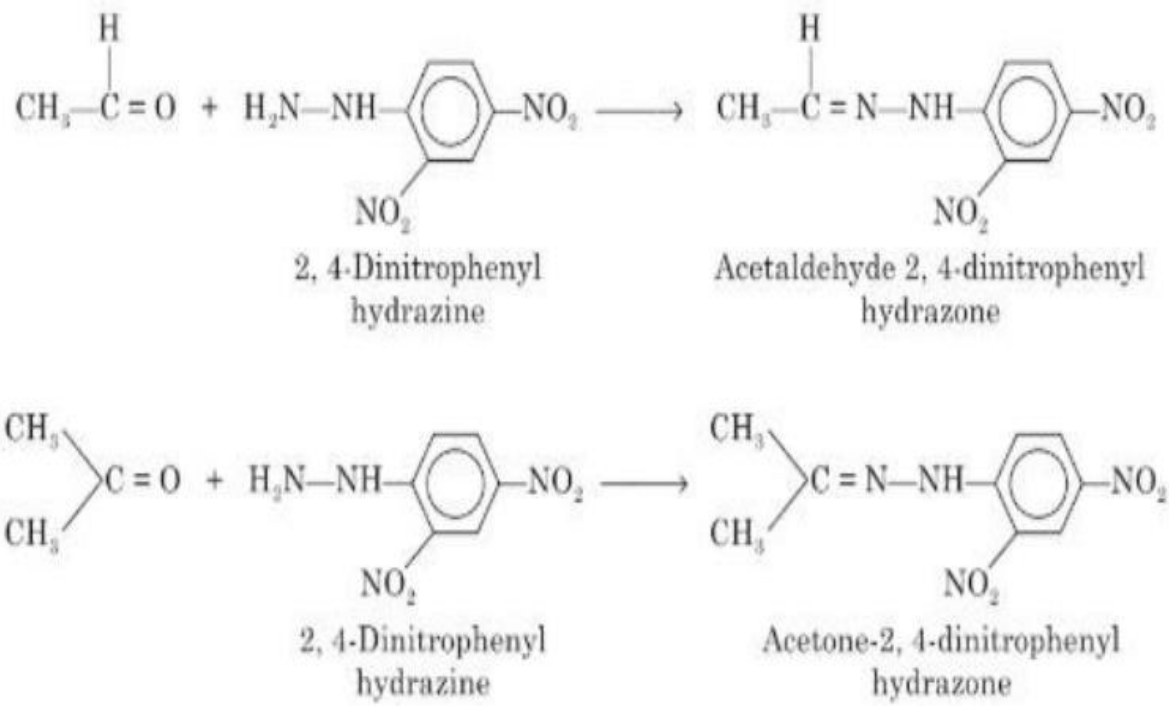
1- General Test

To identify the presence of aldehydes and ketones.

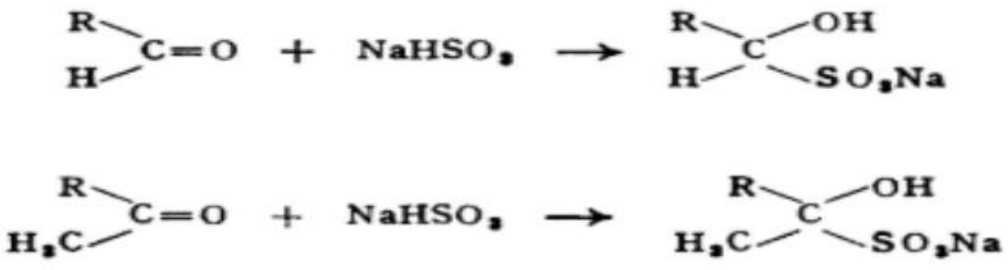
a) 2,4-dinitrophenyl hydrazine test

b) Sodium bisulfite test

a) 2,4-Dinitrophenyl Hydrazine Test: Aldehydes and ketones react with 2,4-dinitrophenylhydrazine gives a yellow to orange precipitate. The chemical reaction is given below.



b) Sodium Bisulfite Test: Aldehydes and ketones combine with sodium bisulfite to for well crystallized water soluble products known as "aldehyde bisulfite" and "ketone bisulfite". The chemical reaction is given below.



2. Differentiation between aldehydes and ketones

Differentiation between aldehydes and ketones is achieved by taking the advantage of the fact that aldehydes can be easily oxidized while ketones cannot(need stronger oxidizing agents).

Two reagents can be used for this purpose :

Tollen's reagent or Fehling's reagent.

Only aldehydes give + ve results with these two reagents

a) Tollen's test (Reduction of ammoniacal silver nitrate)

- Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of NaOH solution.
- Aldehydes show + ve result with this reagent because the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid & the reduction of the silver ions from this reagent to silver element in the form of silver mirror on the inner side of the test tube.

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O + 2NaNO_3 + H_2O$$

(Ag_2O: brown ppt.)

$$Ag_2O + 4NH_4OH \longrightarrow 2Ag(NH_3)_2OH + 3H_2O$$

$$R{-}CHO + 2Ag(NH_3)_2OH \longrightarrow R{-}COO^- + 2Ag^\circ + 4NH_3 + H_2O$$

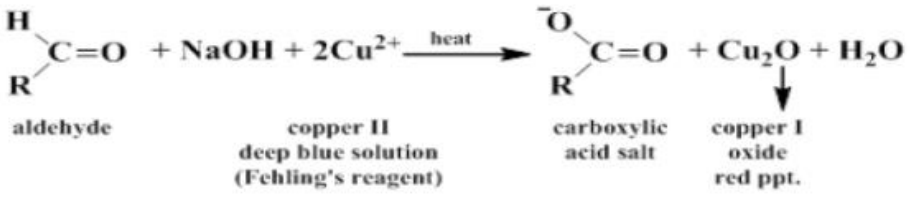
aldehyde — carboxylic acid salt — silver mirror

Procedure

- Add 2-3 drops of **the compound** to 2-3 mL of **Tollen's reagent**, a silver mirror will be formed.
- If no reaction occurs, *warm the test tube* in water bath for few minutes (note that excessive heating will cause the appearance of a false positive test by decomposition of the reagent).
- The formed silver mirror can be washed using dil. nitric acid.
- A **negative** result indicates that the compound is a **ketone**.

b) Reduction of Fehling's reagent

- This test, like Tollen's test, is used to distinguish aldehydes from ketones.
- Only aldehydes can reduce Fehling's reagent (a deep blue solution) to give a red cuprous oxide precipitate.



$$Cu_2O \xrightarrow[\text{aldehyde}]{\text{excess}} Cu^{\circ}$$

copper mirror

Procedure

- Add 5 drops of the compound to 1 mL of Fehling's solution, and then **heat** in water bath for **5 minutes** (with shaking for water insoluble compounds).

- Aldehydes change the color of Fehling's solution from blue to green, orange precipitate, and then red precipitate or copper mirror.
- Ketones don't change the color of this reagent.
- On the other hand, this test does not give a sharp result with aromatic aldehydes.