Carbonyl Compounds

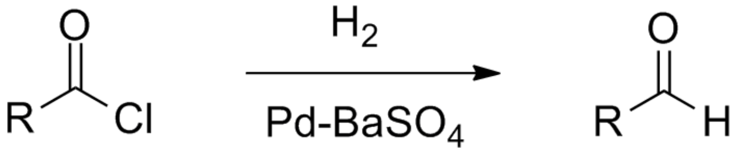
What are Carbonyl Compounds?

Carbonyl compounds are compounds that contain the C=O (carbonyl) group.

Preparation of Aldehydes:

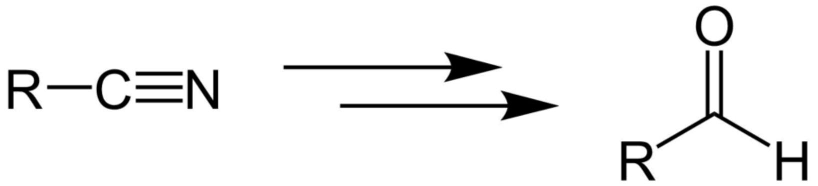
1. Preparation from Acid Chloride (Rosenmund Reduction):

This reaction was named after Karl Wilhelm Rosenmund, who first reported it in 1918. The reaction is a hydrogenation process in which an acyl chloride is selectively reduced to an aldehyde. The reaction, a hydrogenolysis, is catalysed by palladium on barium sulfate, which is sometimes called the Rosenmund catalyst.



2. Preparation from Nitriles:

This reaction involves the preparation of aldehydes (R-CHO) from nitriles (R-CN) using $SnCl_2$ and HCl and quenching the resulting iminium salt ($[R\text{-}CH=NH_2]^+Cl^-$) with water (H_2O). During the synthesis, ammonium chloride is also produced. The reaction is known as **Stephen Aldehyde synthesis**.



3. Preparation from Grignard Reagent:

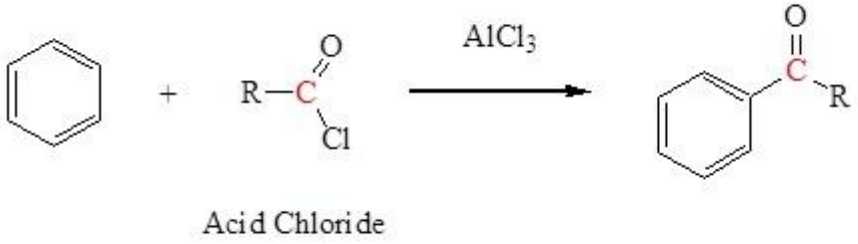
When Grignard Reagent is reacted with HCN followed by hydrolysis aldehyde is produced.

$$\mathrm{RMgX} + \mathrm{HCN} \xrightarrow{\text{dry ether}} \mathrm{RHC{=}NMgX} \xrightarrow{\mathrm{H_3O^{\oplus}}} \mathrm{RCHO}$$

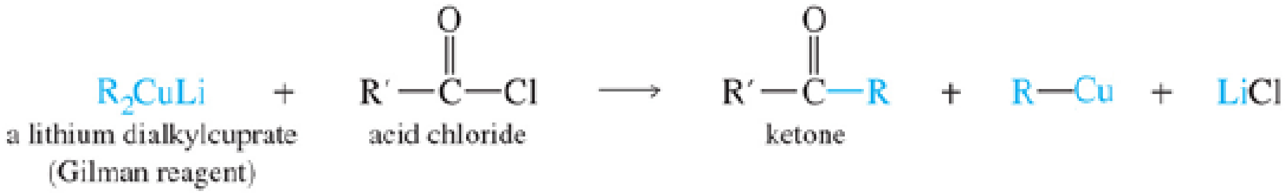
Preparation of Ketones:

1. Preparation from Acid Chloride (Friedel-Crafts Acylation):

Acid chlorides when reacted with benzene in presence of anhydrous $AlCl_3$, aromatic ketone are produced. However, only aromatic ketones can be prepared by following this method.



In order to prepare both aromatic and aliphatic ketones acid chlorides is reacted with lithium dialkylcuprate (Gilman Reagnt).

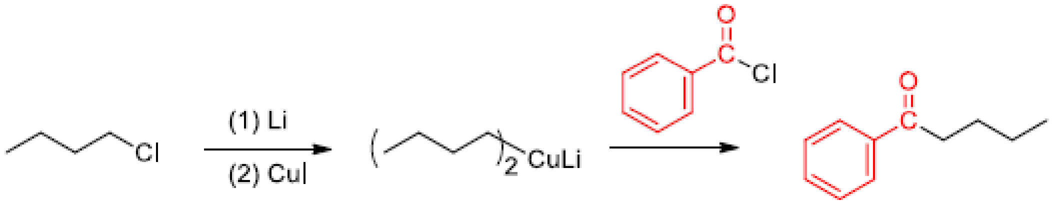


$$R_2CuLi + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \longrightarrow R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + R{-}Cu + LiCl$$

The lithium dialkyl cuprate is produced by the reaction of two equivalents of the organolithium reagent with copper (I) iodide.

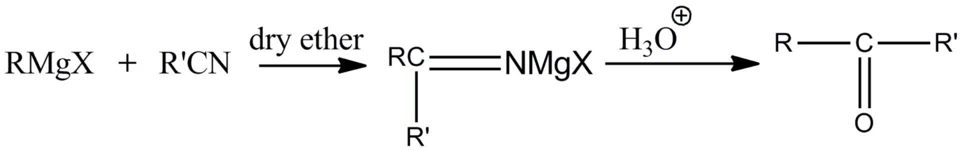
$$2\,R\text{-}Li + CuI \rightarrow R_2CuLi + LiI$$

Example:

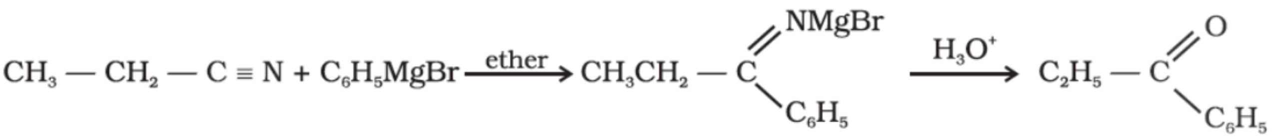


3. Preparation from Nitriles and Grignard Reagents:

When Grignard Reagent is reacted with RCN followed by hydrolysis aldehyde is produced.



$$RMgX + R'CN \xrightarrow{\text{dry ether}} \underset{\underset{\displaystyle R'}{|}}{RC}{=}NMgX \xrightarrow{H_3O^{\oplus}} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R'$$



$$CH_3 - CH_2 - C \equiv N + C_6H_5MgBr \xrightarrow{\text{ether}} CH_3CH_2 - C(=NMgBr)(C_6H_5) \xrightarrow{H_3O^+} C_2H_5 - C(=O)(C_6H_5)$$

Propiophenone
(1-Phenylpropanone)

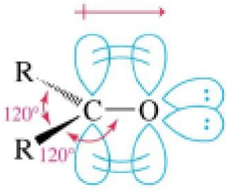
Physical Characteristic of Carbonyl Compounds:

1) The boiling point of carbonyl compounds is higher than the alkanes with similar *Mr*. The boiling point increases with increasing number of carbon atom. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces. Besides temporary dipoles, permanent dipole-dipole forces are also present due to carbonyl compounds being polar. Methanal and ethanal are gases at room temperature, while others are liquids.

2) Carbonyl compounds are soluble in water. This is because they are able to form hydrogen bond with water molecules.

Structure of the Carbonyl groups:

The carbonyl carbon is sp^2 hybridized, and has a partially filled unhybridized p orbital perpendicular to the framework. The picture is shown below:



	length	*energy*
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

The oxygen is also sp^2 hybridized, with the 2 lone pairs occupying sp^2 orbitals. This leaves one electron in a p orbital. The C=O double bond is like a C=C double bond except the carbonyl double bond is shorter and stronger. The carbonyl group has a large dipole moment due to the *polarity* of the double bond. Oxygen is more electronegative than carbon, and so the bond is polarized toward the oxygen.

Reactions of Carbonyl groups:

1. Oxidation of Aldehyde and Ketone:

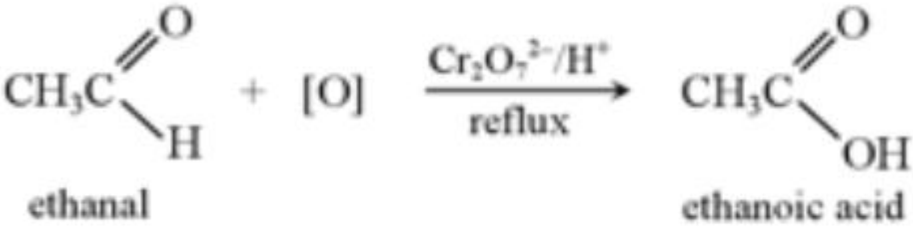
Reagent : Acidified potassium dichromate(VI), $K_2Cr_2O_7$ or acidified potassium manganate(VI), $KMnO_4$

Condition : Heat under reflux

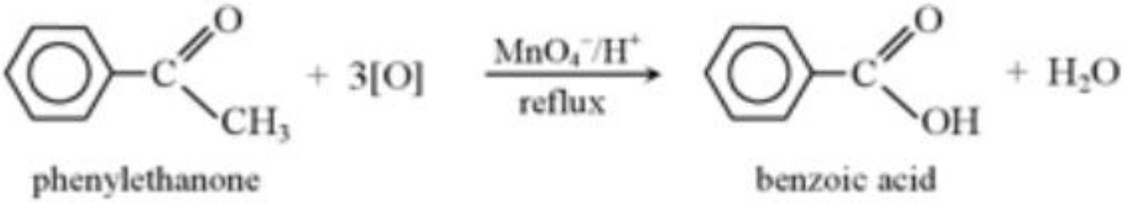
Product : Aldehyde - Carboxylic acid

Ketone - Will not be oxidised.

Aldehydes will be oxidised to **carboxylic acids**. Take ethanal as an example:



Ketones will not be oxidised by acidified $K_2Cr_2O_7$ or $KMnO_4$. The only exception is phenylethanone.



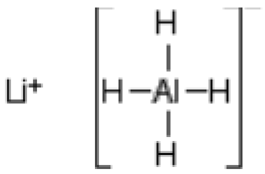
2. Reduction of Aldehyde and Ketone:

<u>Reagent:</u> Lithium tetrahydridoaluminate, $LiAlH_4$ or sodium tetrahydridoborate, $NaBH_4$.

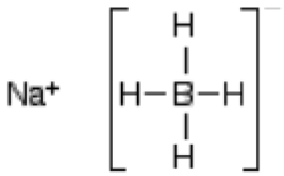
<u>Condition :</u> For $LiAlH_4$ - in dry ether; For $NaBH_4$ - in aqueous alcoholic solution.

<u>Product :</u> Aldehyde - primary alcohol; Ketone - secondary alcohol.

$LiAlH_4$ and $NaBH_4$ are acting as reducing agents as well as providing the nucleophile, H^-. This is a redox reaction as well as a nucleophilic addition reaction.

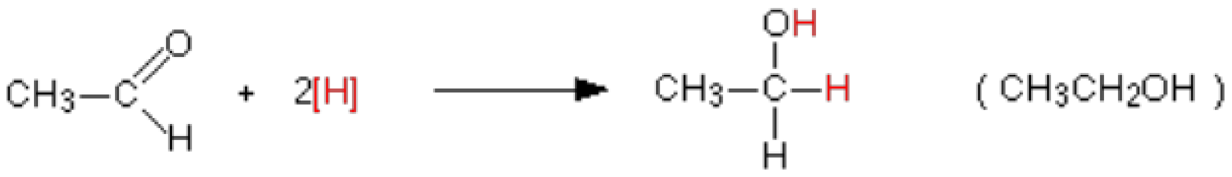


lithium tetrahydridoaluminate

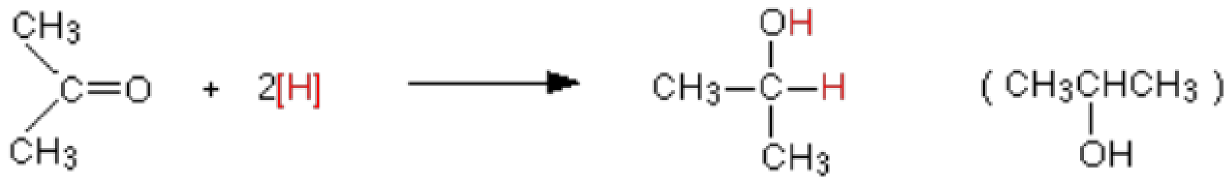


sodium tetrahydridoborate

For aldehydes, **primary alcohols** are formed upon reduction. Take ethanal as an example:

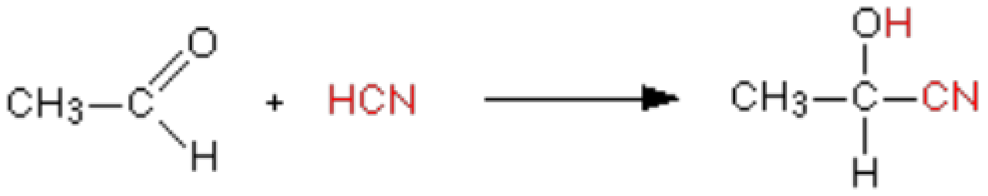


For ketones, secondary alcohols are formed upon reduction. Take propanone as an example:



3. Reaction with HCN:

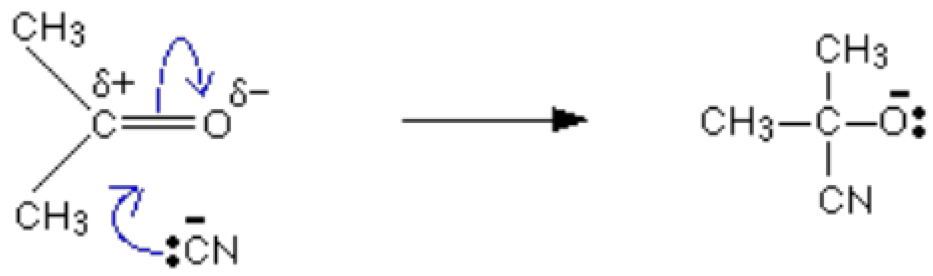
Hydrogen cyanide is not used alone because it is a poisonous gas. Instead, it is produced from the reaction between sodium/potassium cyanide and sulfuric acid. The solution will contain hydrogen cyanide and some free cyanide ions. For aldehydes, take ethanal as an example, 2-hydroxypropanenitrile is produced.



For ketones, take propanone as an example, 2-hydroxy-2-methylpropanenitrile is produced.

The mechanism of this reaction - **nucleophilic addition**:

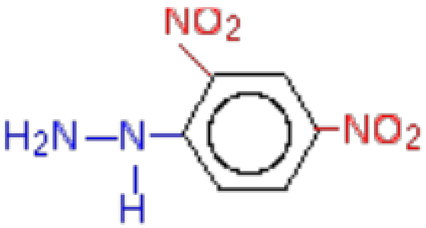
The electron-deficient carbon atom is attacked by the nucleophile, CN^-.



The negative ion formed then picks up a hydrogen ion from hydrogen cyanide, or from the water.

4. Reaction of Carbonyl group with 2,4-dinitrophenylhydrazine(2,4-DNPH):

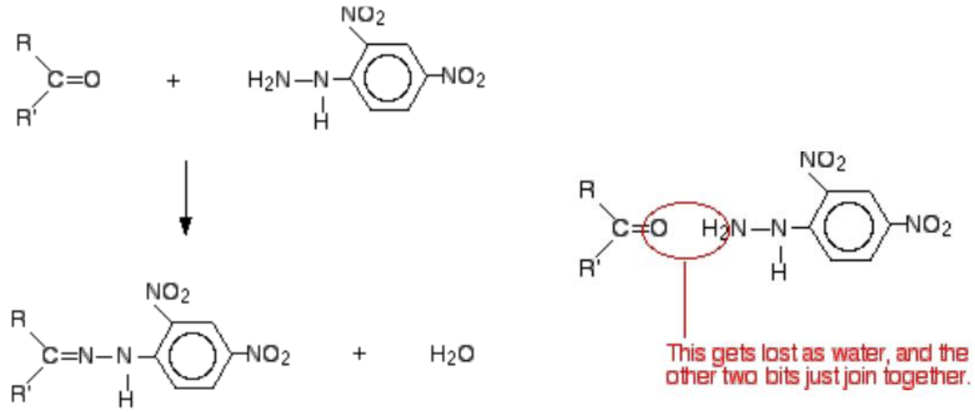
Presence of carbonyl group in any organic compound is tested by using this reaction. 2,4-dinitrophenylhydrazine or 2,4-DNPH can be used **to detect the presence of carbonyl group, C=O**. The structure of 2,4-DNPH is shown below:



2,4-dinitrophenylhydrazine

This test is usually carried out using **Brady's reagent**, that is, a solution of the 2,4-dinitrophenylhydrazine in methanol and sulfuric acid.

A **condensation reaction** occurs when a carbonyl compound is added to 2,4-DNPH. During this reaction, a water molecule is lost. The final compound is seen as orange-yellow precipitate.



This gets lost as water, and the other two bits just join together.

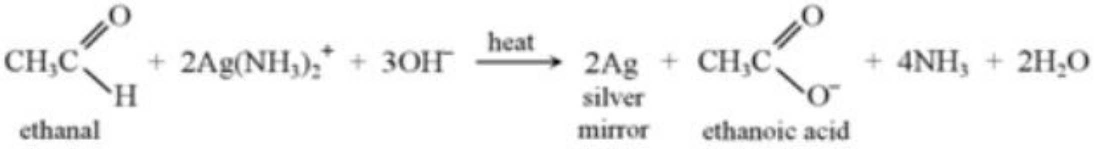
The reaction is same with aldehyde compounds, only R/R' is replaced with H.

5. Reaction of Aldehyde with with Tollens Reagent:

This reaction is specific for aldehydes only, ketones does not give tollens' test. Tollens' reagent contains **diamminesilver(I) ions, $[Ag(NH_3)_2]^+$**. Aldehydes will reduce the diamminesilver(I) ions to metallic silver, aldehyde itself is oxidised to a salt of carboxylic acid.

Therefore, when a few drops of aldehyde is added to the freshly prepared Tollens' reagent, and warmed in a water bath for a few minutes, **a grey precipitate or a silver mirror** is observed only if aldehyde is present.

Take ethanal as an example, the equation is:



How Tollens' reagent is prepared?

To a solution of $AgNO_3$, NaOH solution is added dropwise until a brown precipitate just appears. To this solution aqueous NH_3 is added in equal volume and the light brown precipitate just dissolves. The active species in solution is **$[Ag(NH_3)_2]^+$**.

6. Reaction of Aldehyde with Fehling's Reagent:

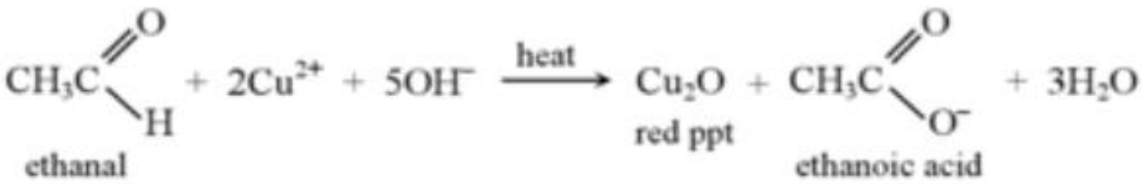
Fehling's Reagent is mixture of Fehling's A and Fehling's B solution. Fehling's A is copper sulfate solution and Fehling'B is alkaline sodium-potassium tartrate solution.

Fehling's solution contains **copper(II) ions complexed with tartrate ions** in sodium hydroxide solution. Complexing the copper(II) ions with tartrate ions prevents precipitation of copper(II) hydroxide. It is a blue solution.

Only aldehydes will reduce the complexed copper(II) ion to copper(I) oxide. Because the solution is alkaline, the aldehyde itself is oxidised to a salt of the corresponding carboxylic acid.

When a few drops of the aldehyde is added to the reagent, and the mixture is warmed gently in a hot water bath for a few minutes, a **red precipitate** is observed only if aldehydes present.

Take ethanal as an example, the equation is:



$$CH_3CHO + 2Cu^{2+} + 5OH^- \xrightarrow{heat} Cu_2O + CH_3COO^- + 3H_2O$$