

## *Aldehydes and ketones*

Aldehydes and ketones are important chemicals in many ways. They play a major part in many of the aromas and flavours associated with food and also with wine. A brain bank in the USA where over 3000 healthy and diseased human brains are stored in methanal (formaldehyde) and used for medical research. Artists use methanal too. Various animals, including whole sheep and cattle, preserved in methanal.

Many ketones have distinctive smells. Patients with diabetes lack the hormone insulin; which breaks down glucose in the blood. The body utilises fats as an alternative energy source, leading to a build-up of ketones in the blood and urine that may eventually cause convulsions and diabetic coma. The distinctive smell of ketones on the breath can be a giveaway, but by testing the level of ketones in the urine, diabetes can be controlled and diabetic coma can be avoided in a much more reliable way.

### *The nature of carbonyl compounds*

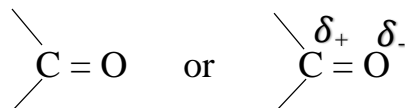
Alkenes are unsaturated hydrocarbons containing a C=C double bond. Aldehyde and ketones contain a C=O group called a carbonyl group.

The bond between the two carbon atoms in an alkene consists of a  $\sigma$  bond (sigma bond) and a  $\pi$  bond (pi bond), each containing two electrons. Both carbon atoms are of identical electronegativity, so the electron density is equally distributed and the double bond is not polar.

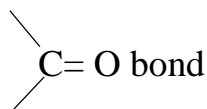
### *The carbonyl group*

In the group,  $R_2C=O$ , the carbon atom forms three single  $\sigma$  bonds, which are coplanar. The unused P orbital of the carbon atom overlaps with one of the unused P orbitals of the oxygen atom to form a  $\pi$  orbital.

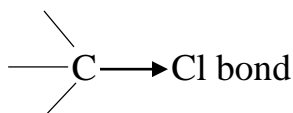
The  $\pi$  electrons in the  $C=O$  bond are extensively polarized. The electrons in the  $\sigma$  and  $\pi$  bonds are drawn towards the more electronegative oxygen atom. To represent this polarization the carbonyl group is written as



Since  $\pi$  electrons are polarized much more extensively than  $\sigma$  electrons, the dipole in a



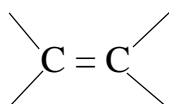
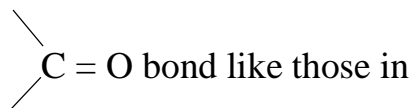
Is greater than that in a

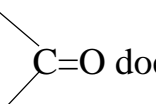
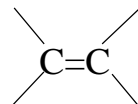


The electronic structure of the carbonyl group is responsible for the reactions of aldehydes and ketones.

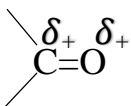
### *Comparison with the alkene group*

The carbonyl group resembles the alkene group in that both groups contain a  $\sigma$  bond and a  $\pi$  bond between the bonded atoms. One might expect that the  $\pi$  electrons in the



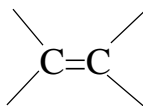
❖ **Note:**  does not react with electrophiles as does 

Would react with electrophiles, such as  $\text{Br}_2$  and  $\text{HBr}$ . This does not happen. The reason is that the oxygen atom in the carbonyl group, being electronegative, is able to keep control of the  $\pi$  electrons and does not make them available for bonding to an electrophile. To summarise:



Polar bond

The electron-deficient carbon atom is attacked by nucleophiles.

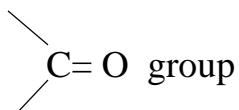


Non-polar bond

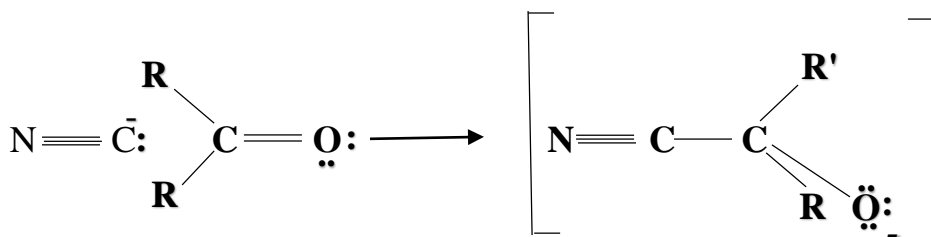
The double bond is attacked by electrophiles.

## *Attack by nucleophiles*

Nucleophilic reagents are attracted by the partial positive charge on the carbon atom of the



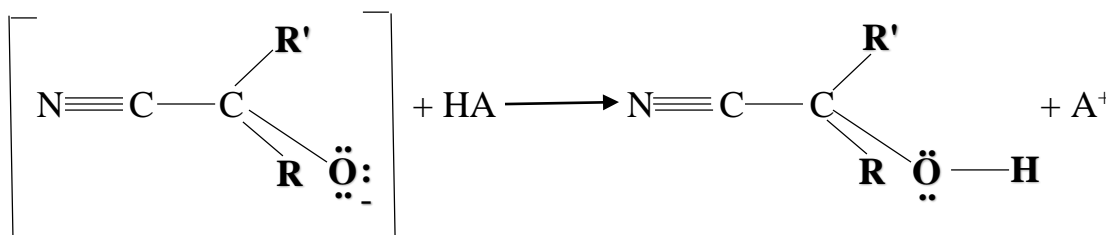
At the approach of a nucleophile (e.g.  $\text{CN}^-$ ), the  $\pi$  electrons are repelled away from the carbon atom towards the oxygen atom. In the reactive intermediate which is formed, oxygen bears a negative charge, and the carbon atom is surrounded by four electron pairs.



Nucleophile attacks  $\text{C}^{\delta+}$

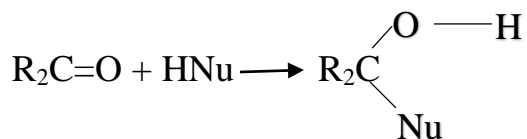
C is 4-valent ; O is negative

The intermediate acts as a base:



❖ The complete reaction is the addition of H Nu across the double bond.

The overall reaction is the addition of HCN across the double bond. In general, if Nu: is the nucleophile



The ease with which the reaction occurs is in contrast with the attack by a nucleophile on a saturated carbon atom.

### *Comparison of aldehydes and ketones*

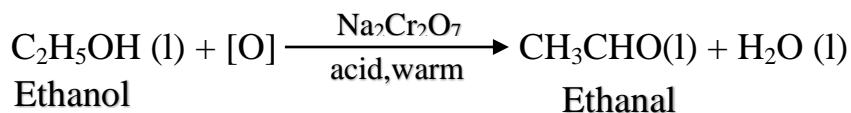
Aldehydes are more reactive than ketones. The reason is chiefly that the presence of two alkyl groups in ketones hinders the approach of attacking reagents to the carbonyl group. Another factor is that alkyl groups are electron-donating and reduce the partial positive charge on the carbonyl atom.

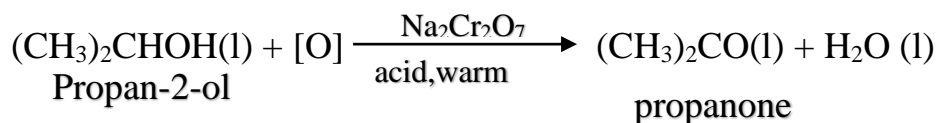
❖ **Note:** Aldehydes are more reactive than ketones.

### *Laboratory preparations:*

#### *From Alcohols:*

Oxidation of primary alcohols gives aldehydes, provided that conditions are controlled to avoid further oxidation to a carboxylic acid. Oxidation of secondary alcohols gives ketones. Acidified sodium dichromate (VI) is often employed for oxidation in the laboratory. The oxidising agent is added slowly to the alcohol. The temperature is kept below the boiling temperature of the alcohol and above that of the carbonyl compound. (Carbonyl compounds are more volatile than the corresponding alcohols). Arranging for an excess of alcohol over oxidant and distilling off the aldehyde as it is formed avoid further oxidation. Ketones are in little danger of further oxidation:





## *Dehydrogenation alcohols*

Catalytic dehydrogenation of alcohols can be used in the laboratory as well as in industry.

Carbonyl compound are made from alcohols.

## *Aromatic ketones by Friedel-Crafts acylation:*

Friedel-crafts acylation gives aromatic ketones. Aromatic ketones are obtained by the Friedel-crafts acylation reaction.

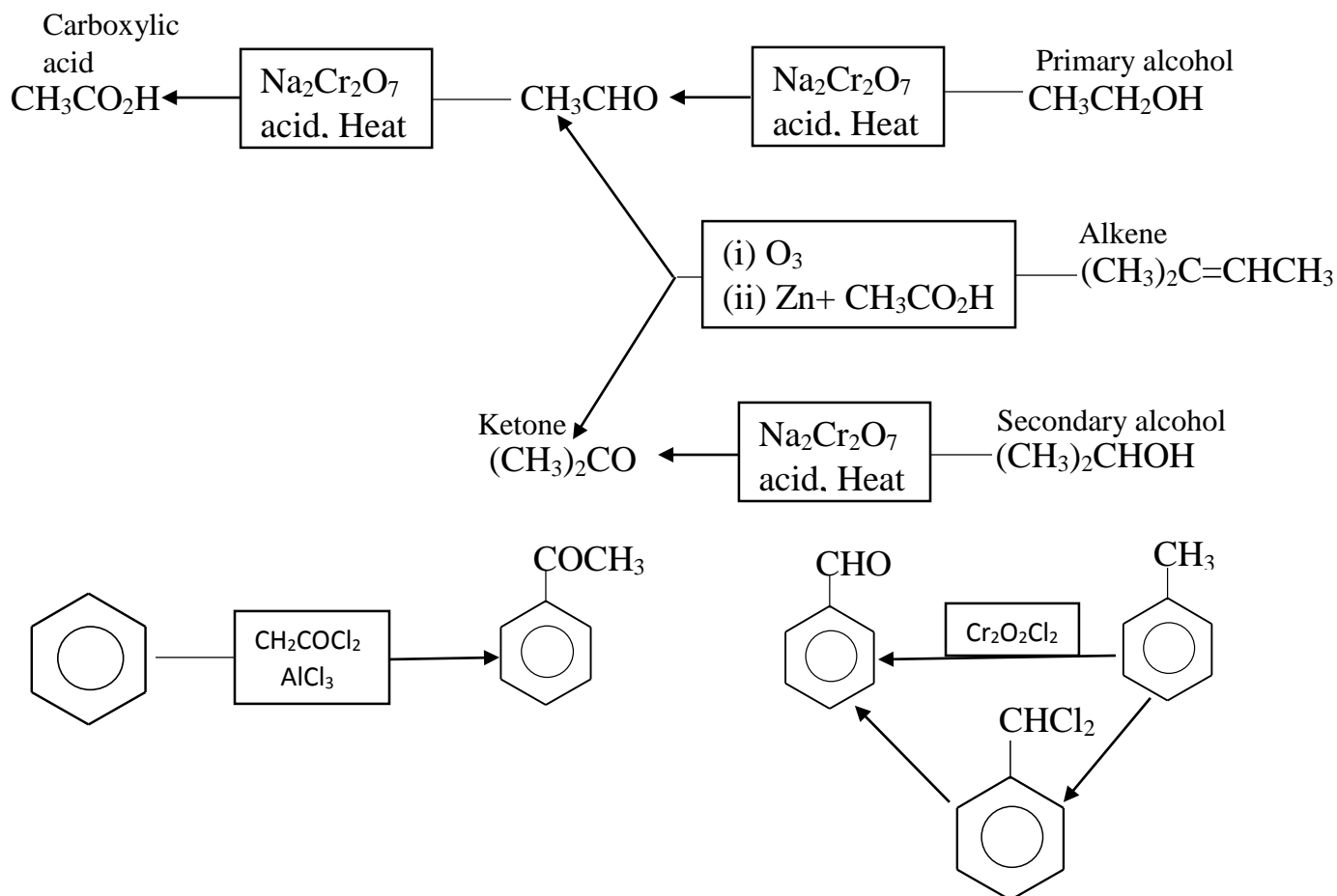


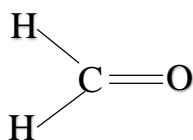
Figure: Methods of preparing Aldehydes and ketones

## *Aldehydes and Ketones*

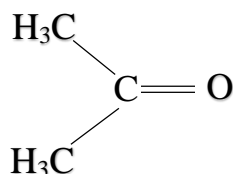
In aldehydes, the carbonyl carbon atom has a hydrogen atom attached to it, together with either a second hydrogen atom or, much more commonly, a

hydrocarbon group, which might be an alkyl group or one containing a benzene ring. Aldehydes can be produced by the oxidation of a primary alcohol.

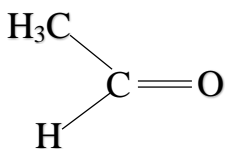
In ketones, the carbonyl group has two hydrocarbon groups attached (and so has no hydrogen atoms). These can be either alkyl groups or groups containing benzene rings.



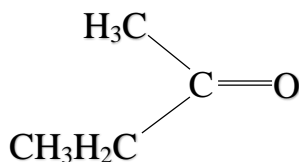
Methanal (formaldehyde)



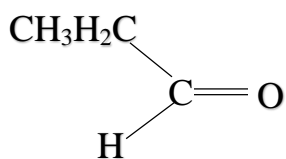
Propanone (acetone)



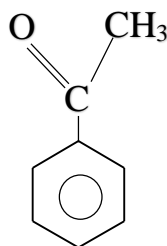
Ethanal (acetaldehyde)



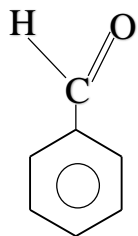
butanone



Propanal

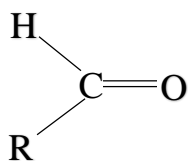


Phenylethanone

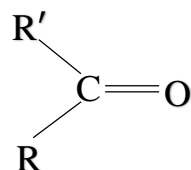


Benzenecarbaldehyde (benzaldehyde)  
aldehyde

Figure: Some simple aldehyde and ketone



aldehyde



Ketone

Figure: The general formula of aldehyde and ketone

a) Aldehydes

Formula	Name
HCHO	Methanal (formerly formaldehyde)
CH <sub>3</sub> CHO	Ethanal (formerly acetaldehyde)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHO	Pentanal
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO	Phenylethanal
C <sub>6</sub> H <sub>5</sub> CHO	Benzenecarbaldehyde (or benzaldehyde)

## b) Ketones

Formula	Name
$\text{CH}_3\text{COCH}_3$	Propanone (formerly acetone)
$\text{CH}_3\text{COCH}_2\text{CH}_3$	Butanone (formerly ethyl methyl ketone)
$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}_3$	Pentan-2-one
$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	Pentan-3-one
$\text{C}_6\text{H}_5\text{COCH}_3$	Phenylethanone

**Table:** The names of some Aldehydes and ketones

### *Physical properties of the aldehydes and ketones*

The physical properties of the aldehydes and the ketones are influenced by the presence of the carbonyl group. Aldehydes and ketones occupy territory part way between the alkanes ( very volatile, with only **van der waals** weak intermolecular forces) and the alcohols ( low volatility, with van der waals forces and much stronger hydrogen bonds between the molecules) . The carbonyl group cannot take part in hydrogen bonding, but there are permanent dipole- dipole interactions between aldehyde molecules and between ketone molecules. This gives them boiling temperatures which are higher than those of the corresponding alkanes, but lower than those of the corresponding alcohols.

A further point about the boiling temperature of the aldehydes and ketones is that molecules of straight-chain isomers can pack closer together than those of branched-chain molecules. This means that the forces between molecules of straight- chain isomers are stronger than those between molecules of branched-chain isomers, so the boiling temperatures of straight-chain isomers are higher. For example, butanal boils at  $72^\circ\text{C}$  , while 2-methylpropanal boils at  $64^\circ\text{C}$  ; pentan-2-one has a boiling point of  $102^\circ\text{C}$  compared to  $94^\circ\text{C}$  for 3-methylbutan-2-one.

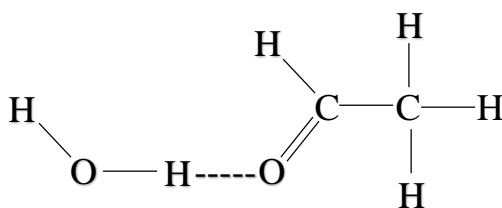
Both the families of carbonyl compounds have members with strong odours, but the aldehydes are particularly responsible for imparting characteristic smells and flavours to a variety of foods and are also one of the groups of substances responsible for the bouquet of good wines.



## *Solubility of aldehydes and ketones in water*

Aldehydes and ketones composed of small molecules- such as methanal, ethanal and propanone are miscible with water in all proportions, but this decrease with increasing chain length.

The reason for the solubility is that they can form hydrogen bonds with water molecules even though they cannot form hydrogen bonds with themselves.



**Fig:** Hydrogen bonding between water molecules and ethanal molecules is stronger than the intermolecular bonds in the pure aldehyde.

**Dispersion forces** and **dipole-dipole** attractions between the aldehyde or ketone and the water molecules will also exist. Forming these attractions releases energy, which helps to supply the energy needed to separate the water molecules and aldehyde or ketone molecules from each other so that they can mix together. As chain length increases, the hydrocarbon portions of the molecules prevent such attractions occurring.

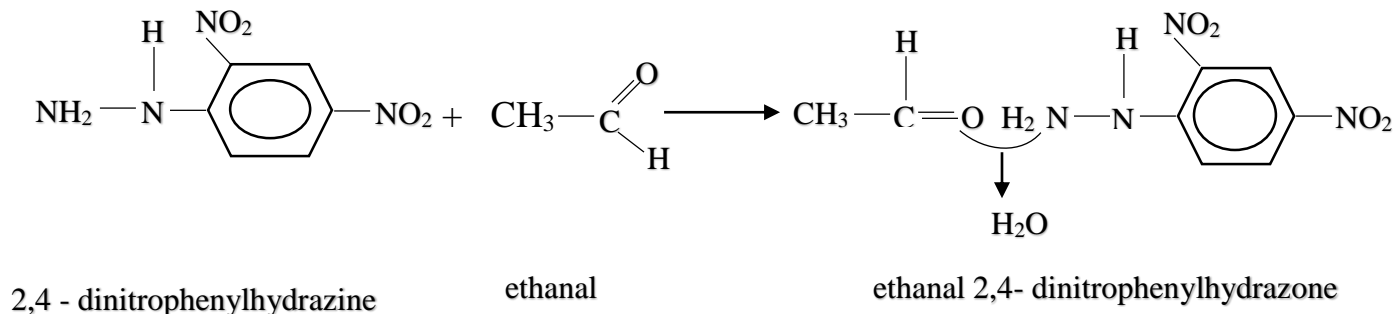
## *Testing and identifying carbonyl compounds*

All aldehydes and ketones contain the carbonyl group, C=O . In this section we are going to consider a chemical test that can be used to identify a particular aldehyde or ketone.

### *Brady's reagent*

Brady's reagent (2,4-dinitrophenylhydrazine) is a red –orange solid, usually supplied wet to reduce the risk of explosion.

Aldehydes and ketones react with Brady's reagent to form yellow/ orange /red crystalline solids. These solids are called 2,4-dinitrophenylhydrazine derivatives. They have no practical use other than in identifying aldehydes and ketones.



The reaction that takes place is a **condensation reaction** –this involves addition followed by the elimination of water. The derivative can be removed by filtration and purified by recrystallization.

These compounds have characteristic melting temperatures which can be compared with values given in data books. The melting temperatures for the derivatives of some carbonyl compounds.

Carbonyl compound	Melting temperature of 2,4-dinitrophenylhydrazone
Methanal	166
Ethanal	168
Propanal	155
Butanal	126
Benzaldehyde	237
Propanone	126
Butanone	115
Pentan-3-one	156

**Table:** Melting temperatures for some 2,4-dinitrophenylhydrazones.

## ***Why use Brady's reagent:***

Hydroxylamine, hydrazine, or dinitrohydrazine, for example. 2,4-dinitrophenylhydrazine derivatives are less soluble and therefore crystalline out more easily, so it is more useful.

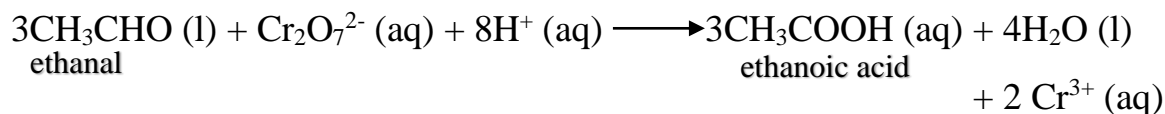
Another compound which forms derivatives with aldehydes and ketones in condensation reactions is hydroxylamine,  $\text{NH}_2\text{OH}$ . Draw the displayed formula of the derivative formed by propanone with hydroxylamine.

## ***Reactions of carbonyl compounds***

### ***Oxidation reaction of aldehydes:***

There are many similarities in the reactions of aldehydes and ketones with a wide variety of reagents. However, they can be readily distinguished by the way in which they react with oxidising agents. Aldehydes have a hydrogen atom that forms part of the functional group. This hydrogen is activated by the carbonyl group and, as a result, aldehydes are readily oxidised to carboxylic acids by even quite mild oxidizing agents. In contrast, ketones have no such hydrogen atom and so they are very resistant to oxidation – they only react after prolonged treatment with a very strong oxidizing agent.

The oxidation of aldehydes can be carried out by warming with a solution of potassium dichromate(VI) acidified with sulfuric acid. For example:



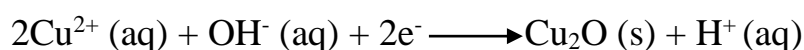
### ***Testing carbonyl compounds:***

There are three reactions that are regularly used as qualitative tests to determine if an unknown compound is an aldehyde or a ketone. These are Fehling's solution, Tollens' reagent and acidified dichromate (VI) ions. The most common tests to identify aldehydes and ketones all involve oxidation reactions.

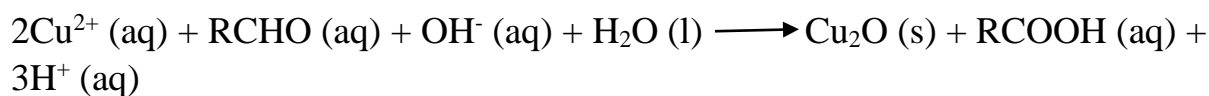
## ***Fehling's or Benedict solution***

This contains an aqueous alkaline solution containing  $\text{Cu}^{2+}$  ions. Normally these would give a precipitate of copper(II) hydroxide under these conditions, but in Fehling's solution the copper(II) ions are prevented from precipitating by complexing them with 2,3-dihydroxybutanedioate ions.

If an aldehyde is warmed with Fehling's solution then the aldehyde is oxidised to a carboxylic acid, and the Fehling's solution is reduced, giving a red-brown precipitate of copper (I) oxide. The half equations are:



so overall:



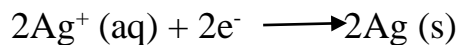
If a ketone is warmed with Fehling's solution in the same way then there is no reaction- so the two can be distinguished by this method.

## ***Tollens' reagent***

This is produced by dissolving silver nitrate in water and adding aqueous ammonia. Silver (I) oxide is formed as a precipitate initially but this dissolves as more ammonia is added forming a complex- the diamminesilver (I) ion,  $[\text{Ag}(\text{NH}_3)_2]^{+}$ .

When Tollens' reagent is warmed gently with an aldehyde, the aldehyde is oxidised and the silver(I) ions in the complex are reduced to form silver metal. When careful preparation, this coats the inside of the test tube as a silver mirror- or less successfully as a black precipitate. For this reason the reaction is known as the 'silver mirror test'.

The half reactions are:



If a ketone warmed with the same reagent, there is no reaction.

## *Reduction reactions of aldehydes and ketones*

Aldehydes and ketones are conveniently prepared in the laboratory by the oxidation of alcohols. Partial oxidation of a primary alcohol produced an aldehyde, and oxidation of a secondary alcohol produces a ketone.

These reactions can be reversed by reduction- so aldehydes are readily reduced to primary alcohols, and ketones to secondary alcohols. Suitable reducing agents include lithium tetrahydridoaluminate ( $\text{LiAlH}_4$ ) dissolved in dry ether

( ethoxyethane), or sodium tetrahydridoborate ( $\text{NaBH}_4$ ) dissolved in ethanol.

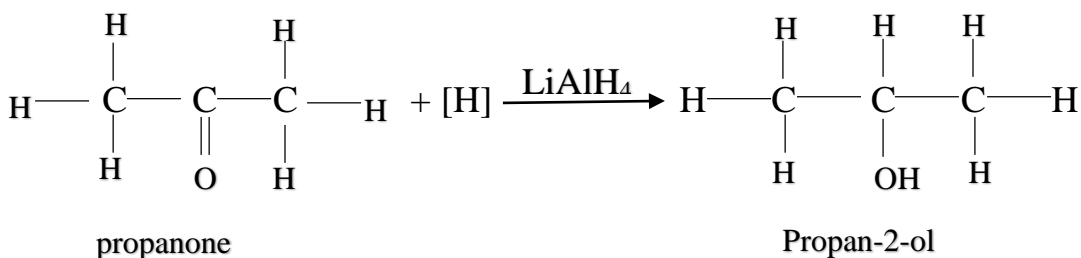
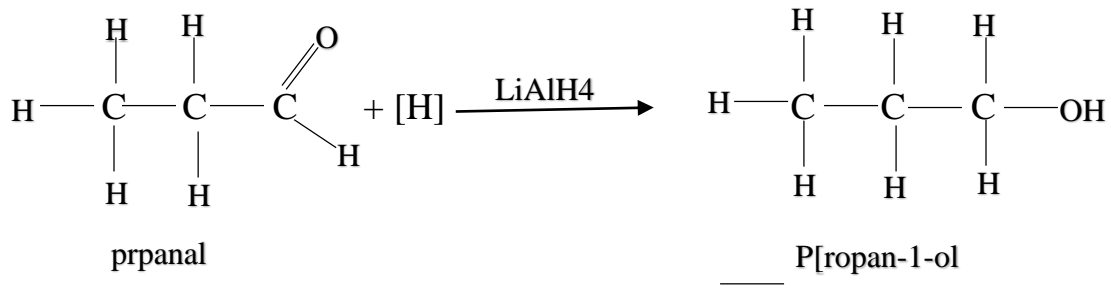


Fig: The reduction of propanal and propanone-[H] is used as an abbreviation for the reducing agent.