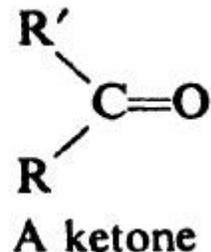
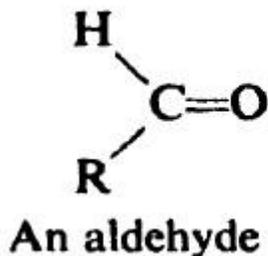


Aldehydes and Ketones

Aldehydes are compounds of the general formula HCHO ; ketones are compounds of the general formula $\text{RR}'\text{CO}$. The groups R and R' may be aliphatic or aromatic.



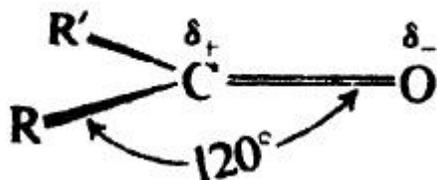
Both aldehydes and ketones contain the carbonyl group, $\text{C}=\text{O}$, and are often referred to collectively as carbonyl compounds. It is the carbonyl group that largely determines the chemistry of aldehydes and ketones.

This difference in structure affects their properties in two ways:

- (a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty;
- (b) aldehydes are usually more reactive than ketones toward nucleophilic addition, the characteristic reaction of carbonyl compounds.

structure of the carbonyl group

Carbonyl carbon is joined to three other atoms by three bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p orbital of the carbon overlaps a p orbital of oxygen to form a π bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon is flat; oxygen, carbonyl carbon, and the two atoms directly attached to carbonyl carbon lie in a plane.



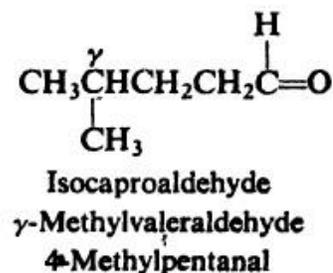
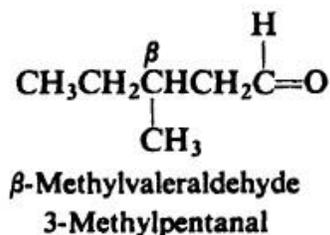
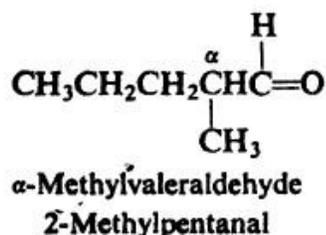
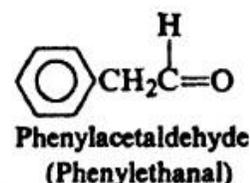
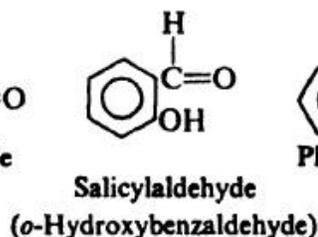
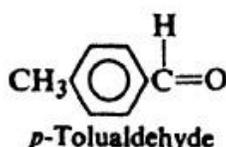
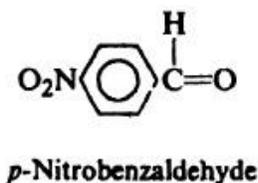
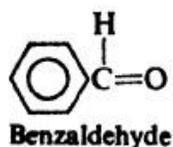
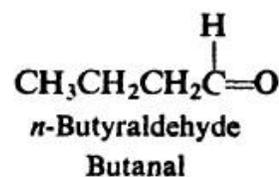
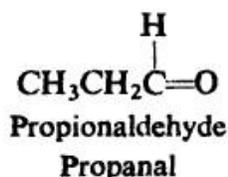
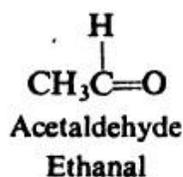
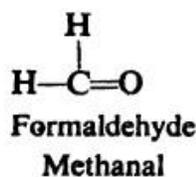
The electrons of the carbonyl double bond hold together atoms of quite different electronegativity, and hence the electrons are not equally shared; in particular, the mobile π cloud is pulled strongly toward the more electronegative atom, oxygen.

The facts are consistent with the orbital picture of the carbonyl group. Electron diffraction and spectroscopic studies of aldehydes and ketones show that carbon, oxygen, and the two other atoms attached to carbonyl carbon lie in a plane; the three bond angles of carbon are very close to 120° . The large dipole

moments of aldehydes and ketones indicate that the electrons of the carbonyl group are quite unequally shared. We shall see how the physical and chemical properties of aldehydes and ketones are determined by the structure of the carbonyl group.

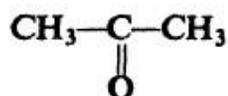
Nomenclature

The common names of aldehydes are derived from the names of the corresponding carboxylic acids by replacing -ic acid by -aldehyde. The IUPAC names of aldehydes follow the usual pattern. The longest chain carrying the CHO group is considered the parent structure and is named by replacing the -e of the corresponding alkane by -al. The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-1. Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to alpha of the common name.

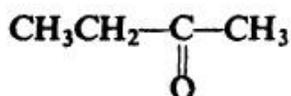


The simplest aliphatic ketone has the common name of acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as a -phenone, as illustrated below.

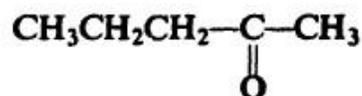
According to the IUPAC system, the longest chain carrying the carbonyl group is considered the parent structure, and is named by replacing the -e of the corresponding alkane with -one. The positions of various groups are indicated by numbers, the carbonyl carbon being given the lowest possible number.



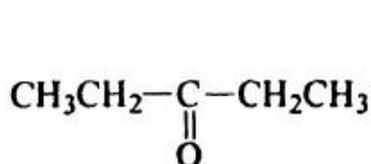
Acetone
Propanone



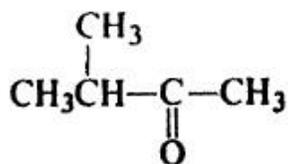
Methyl ethyl ketone
Butanone



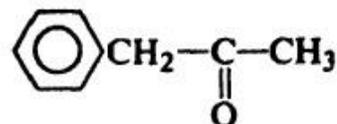
Methyl *n*-propyl ketone
2-Pentanone



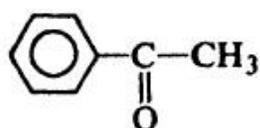
Ethyl ketone
3-Pentanone



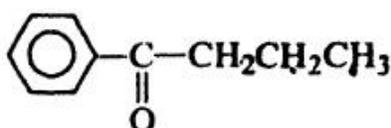
Methyl isopropyl ketone
3-Methyl-2-butanone



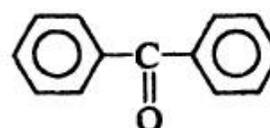
Benzyl methyl ketone
1-Phenyl-2-propanone



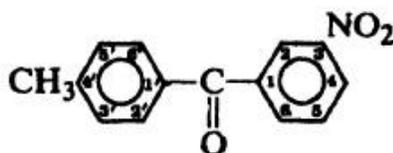
Acetophenone



***n*-Butyrophenone**



Benzophenone



3-Nitro-4'-methylbenzophenone

Physical properties

1-The polar carbonyl group makes aldehydes and ketones polar compounds.

2- they have higher Boiling point than comparable compounds of comparable molecular weight.

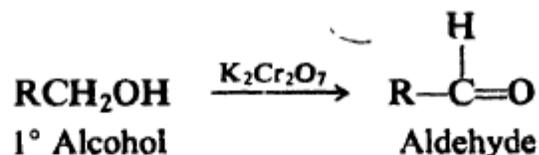
3- they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids.

4-The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons .

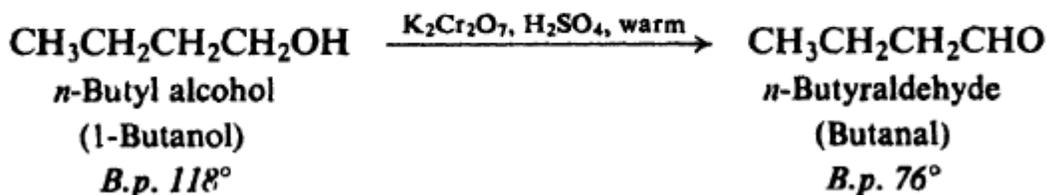
5-Aldehydes and ketones are soluble in the usual organic solvents.

PREPARATION OF ALDEHYDES

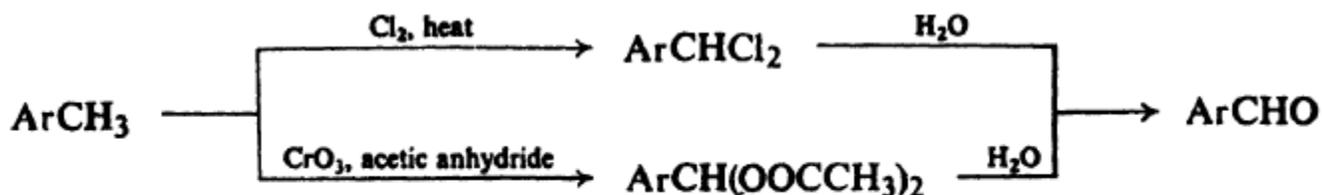
1. Oxidation of primary alcohols



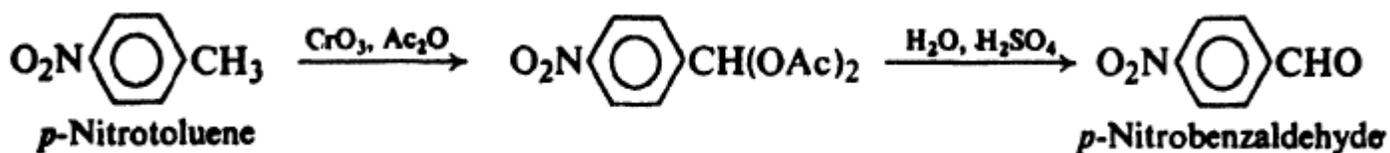
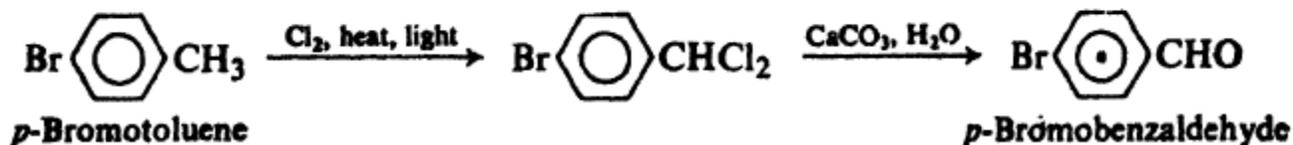
Example:



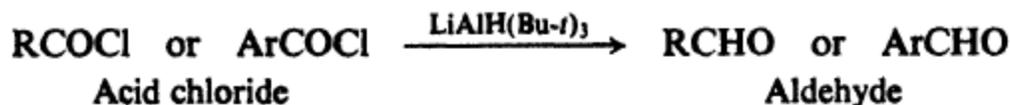
2. Oxidation of methylbenzenes.



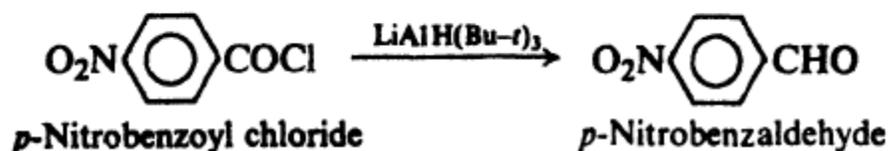
Examples:



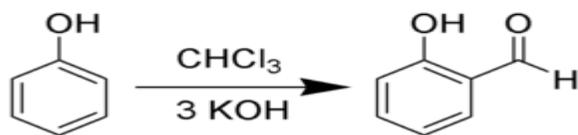
3. Reduction of acid chlorides



Examples:

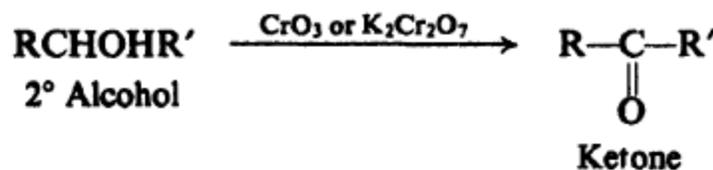


4. Reimer-Tiemann reaction. Phenolic aldehydes.

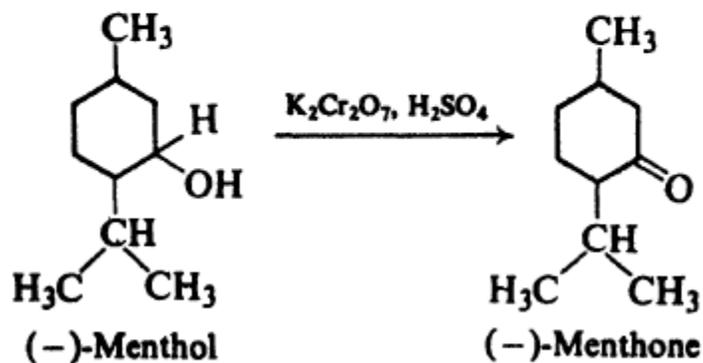


PREPARATION OF KETONES

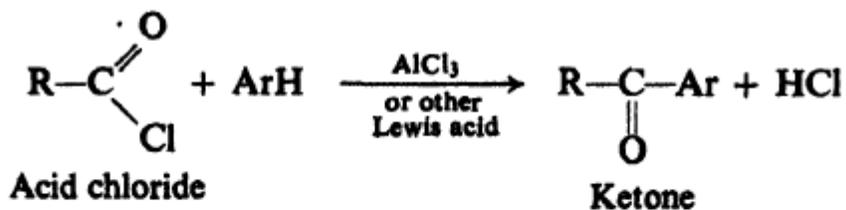
1. Oxidation of secondary alcohols



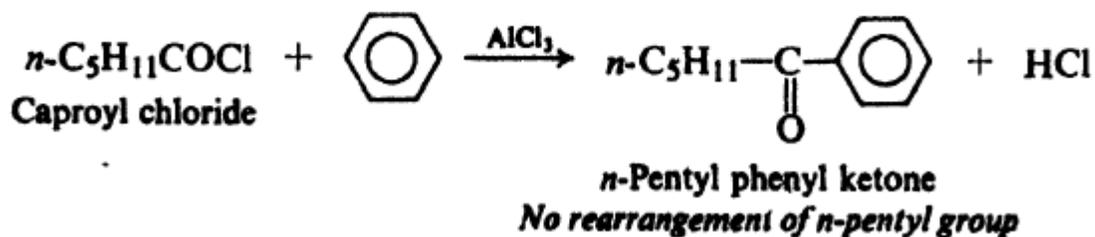
Example:

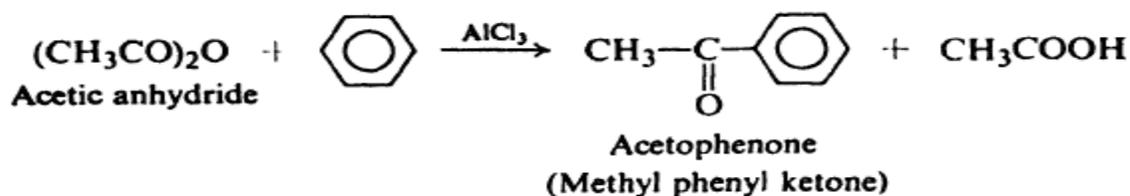
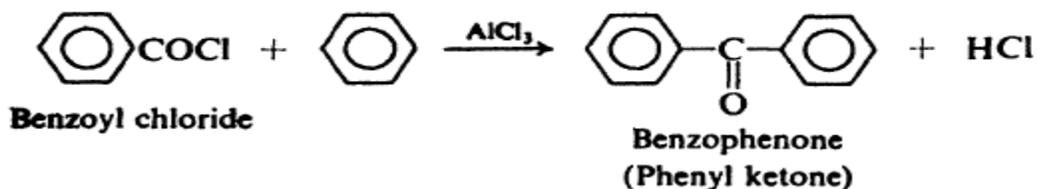


2. Friedel-Crafts acylation

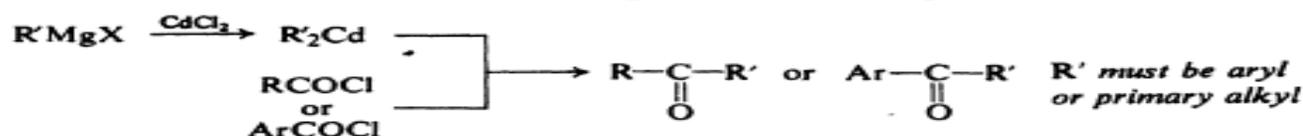


Examples:

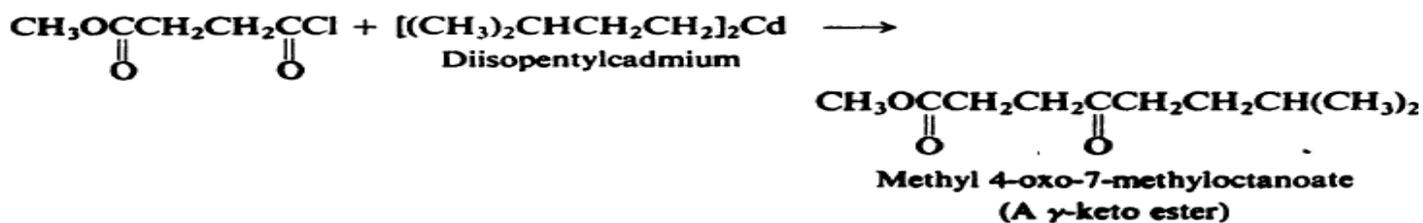
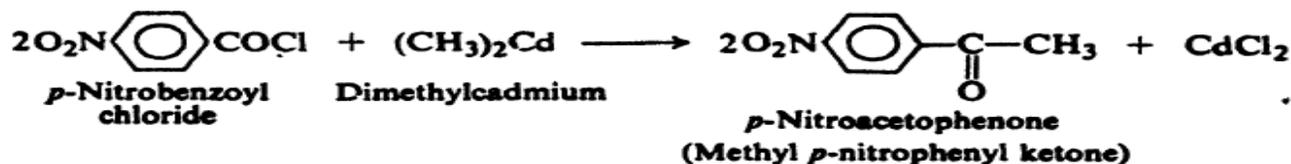
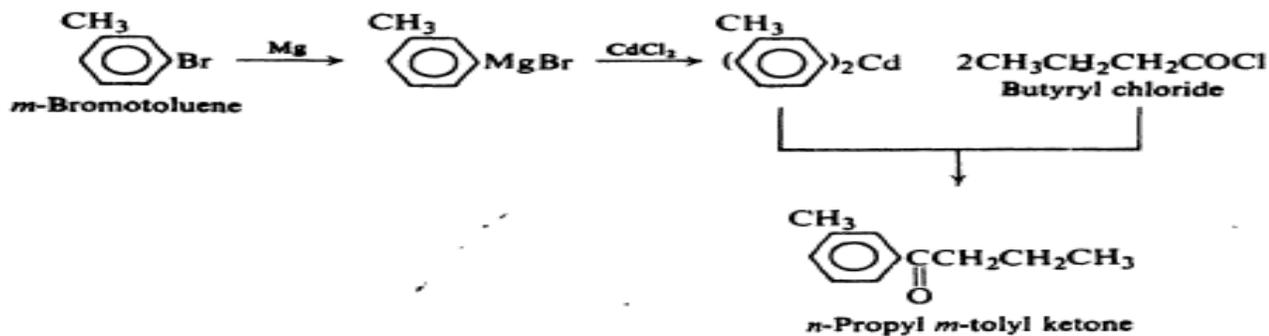
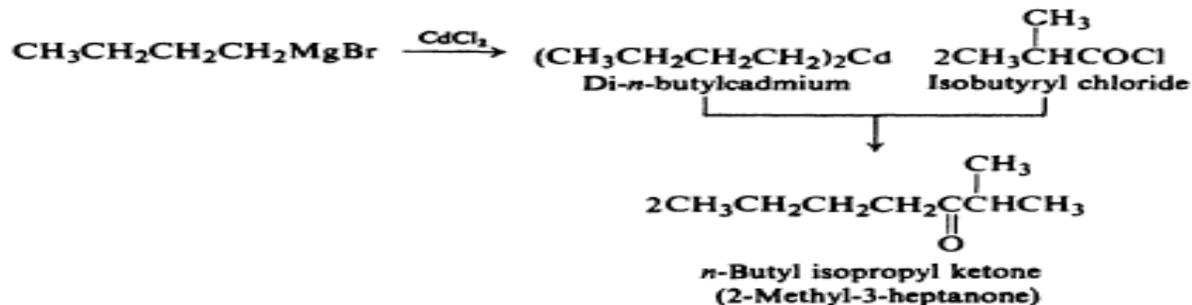




3. Reaction of acid chlorides with organocadmium compounds.

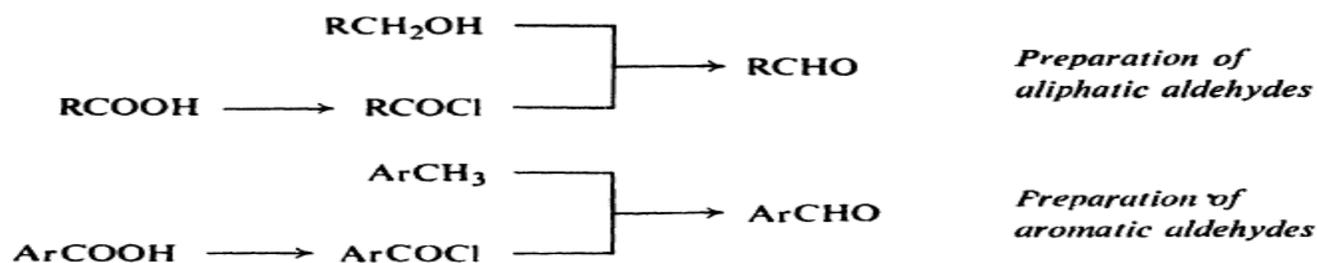


Examples:

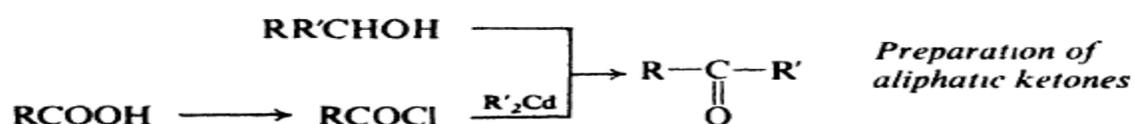


4. Acetoacetic ester synthesis

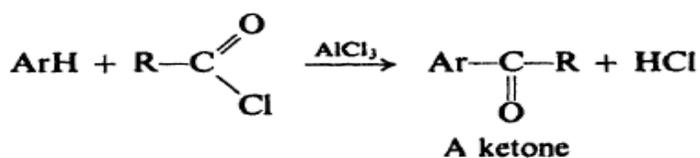
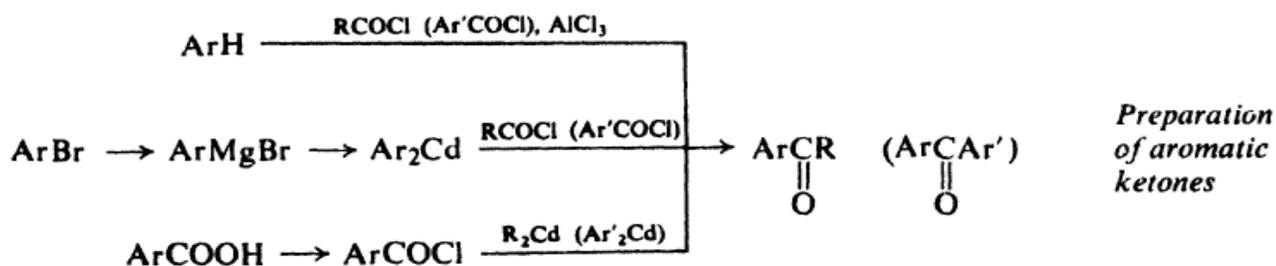
Depending upon the availability of starting materials, aliphatic aldehydes can be prepared from alcohols or acid chlorides of the same carbon skeleton, and aromatic aldehydes can be prepared from methylbenzenes or aromatic acid chlorides.



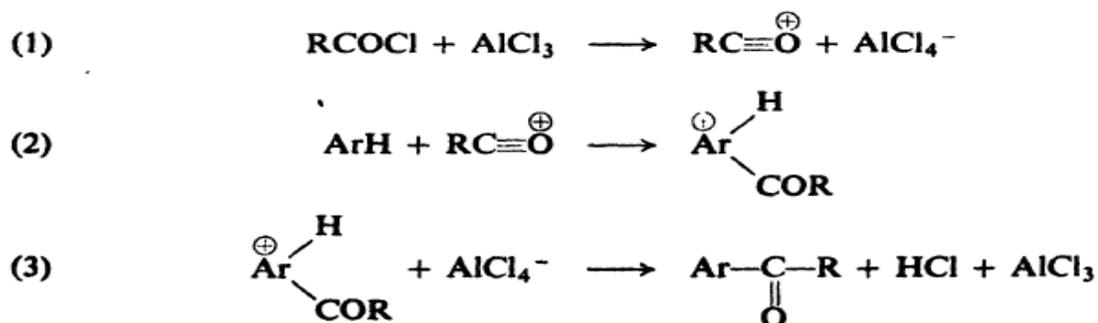
Aliphatic ketones are readily prepared from the corresponding secondary alcohols, if these are available. More complicated aliphatic ketones can be prepared by the reaction of acid chlorides with organocadmium compounds.



Aromatic ketones containing a carbonyl group attached directly to an aromatic ring are conveniently prepared by Friedel-Crafts acylation



The most likely mechanism for Friedel-Crafts acylation is analogous to the carbonium ion mechanism for Friedel-Crafts alkylation and involves the following steps:

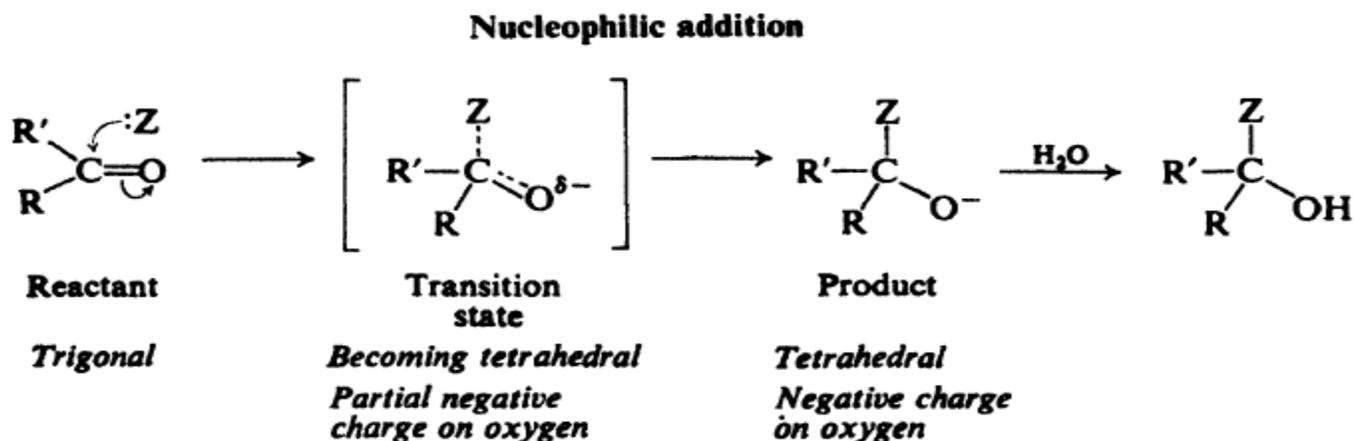


Reactions. Nucleophilic addition

The carbonyl group, C=O, governs the chemistry of aldehydes and ketones. It does this in two ways: (a) by providing a site for nucleophilic addition, and

(b) by increasing the acidity of the hydrogen atoms attached to the alpha carbon.

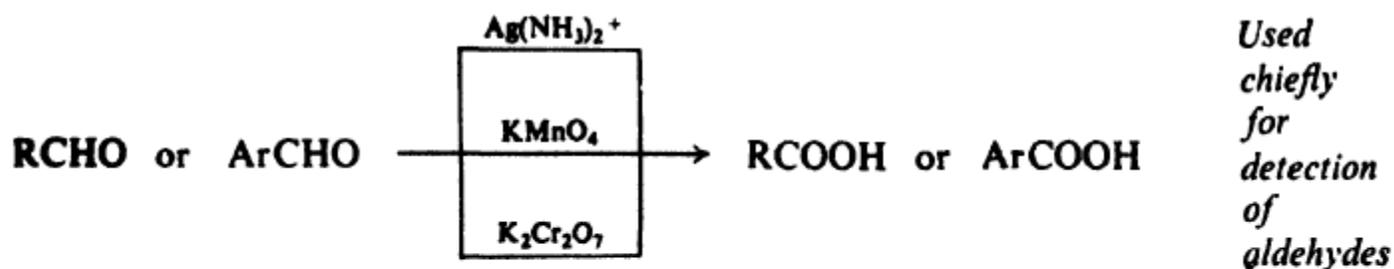
What kind of reagents will attack such a group? Since the important step in these reactions is the formation of a bond to the electron-deficient (acidic) carbonyl carbon, the carbonyl group is most susceptible to attack by electron-rich, nucleophilic reagents, that is, by bases! The typical reaction of aldehydes and ketones is nucleophilic addition.



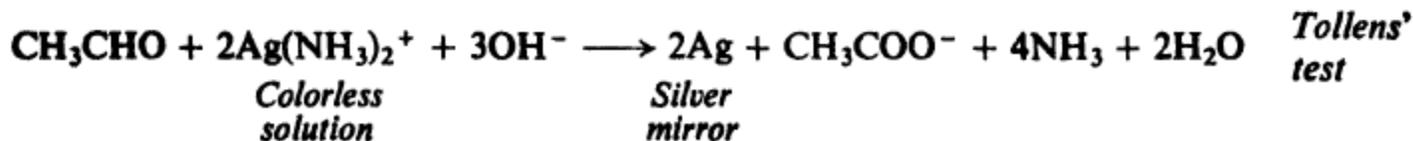
REACTIONS OF ALDEHYDES AND KETONES

1. Oxidation.

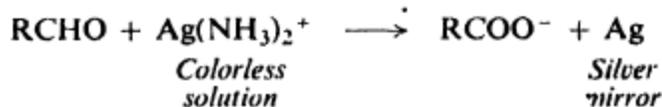
(a) Aldehydes



Examples:



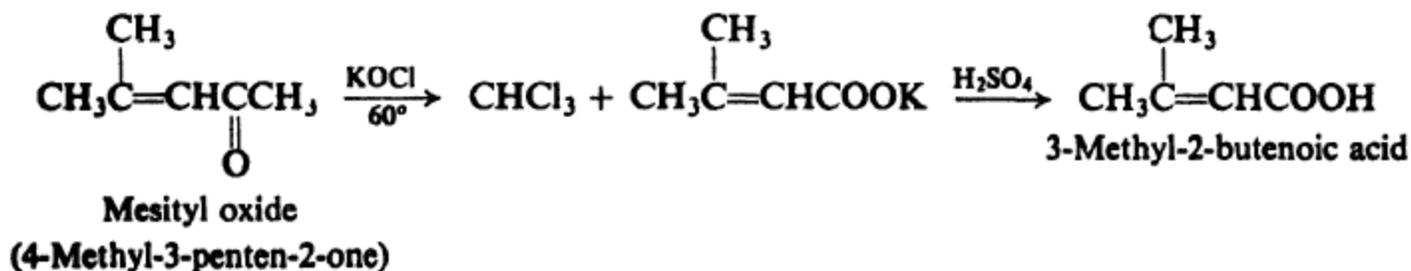
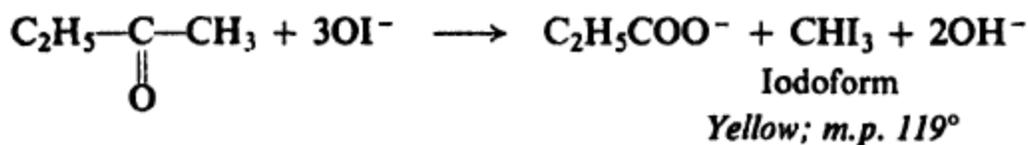
Tollens' reagent contains the silver ammonia ion, $\text{Ag}(\text{NH}_3)_2^+$. Oxidation of the aldehyde is accompanied by reduction of silver ion to free silver (in the form of a *mirror* under the proper conditions).



(b) Methyl ketones

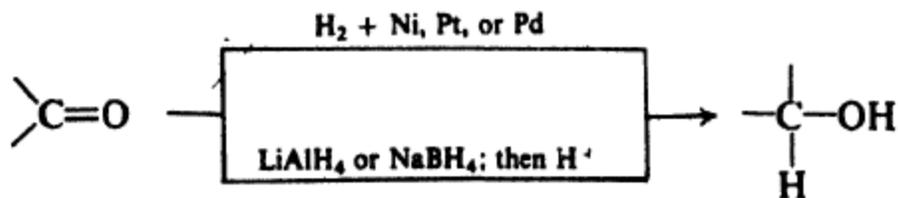


Examples:

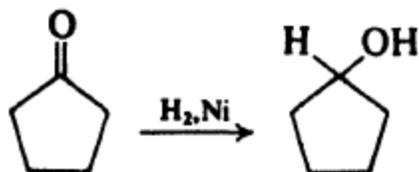


2. Reduction

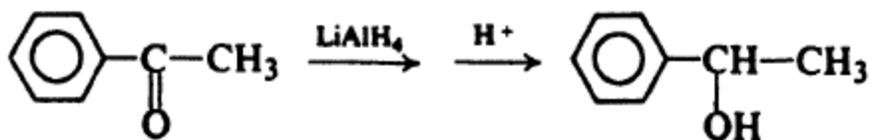
(a) Reduction to alcohols.



Examples:



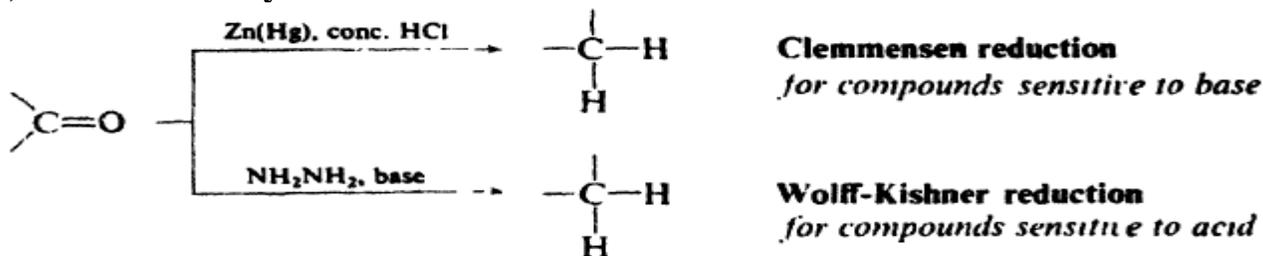
Cyclopentanone Cyclopentanol



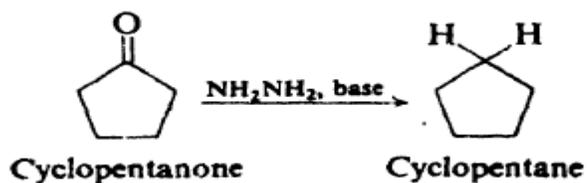
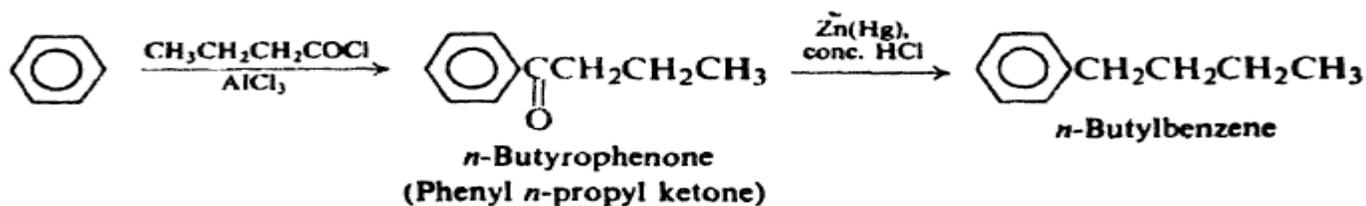
Acetophenone

α -Phenylethyl alcohol

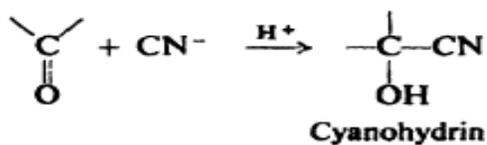
(b) Reduction to hydrocarbons.



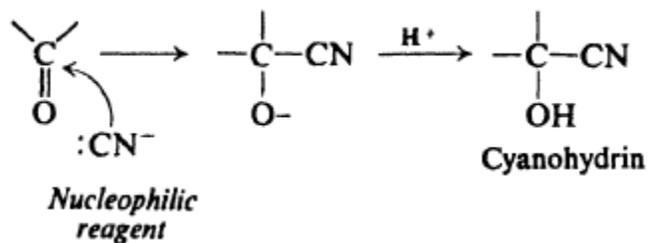
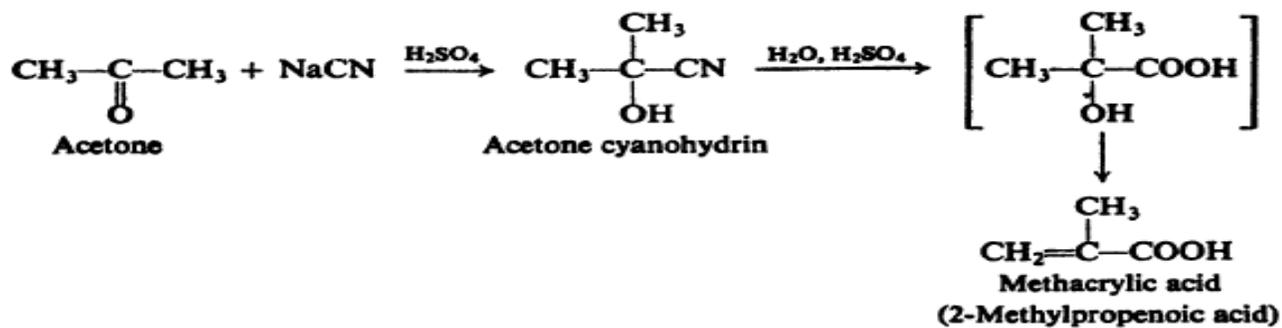
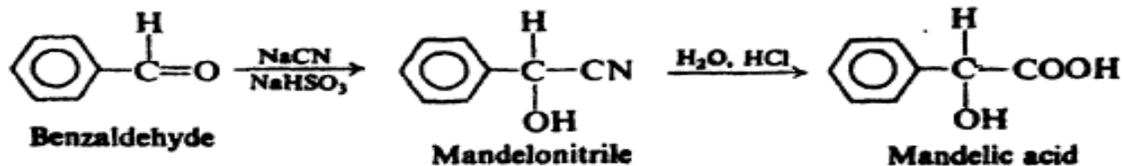
Examples:



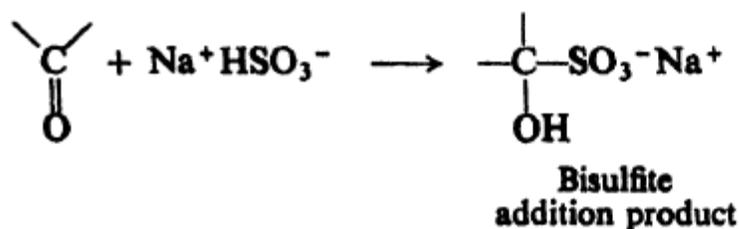
5. Addition of cyanide. Cyanohydrin formation



Examples:

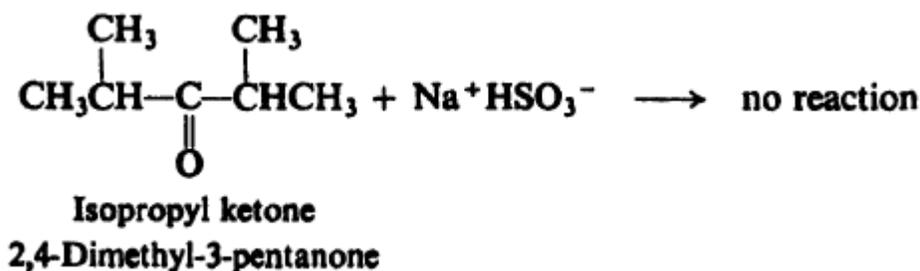
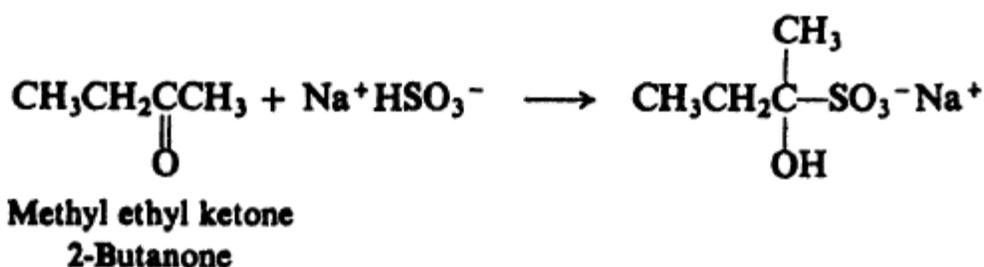
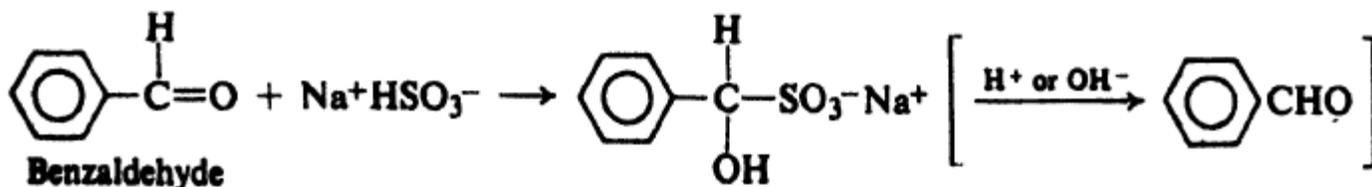


5. Addition of bisulfite.

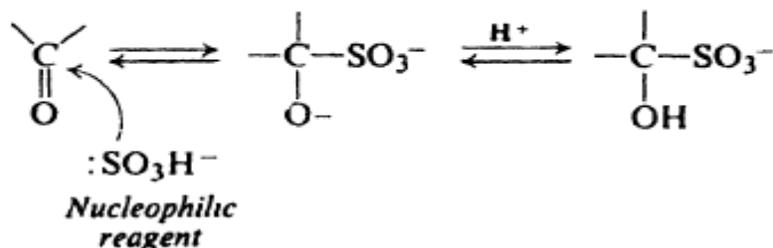


*Used in purification
Not for hindered ketones*

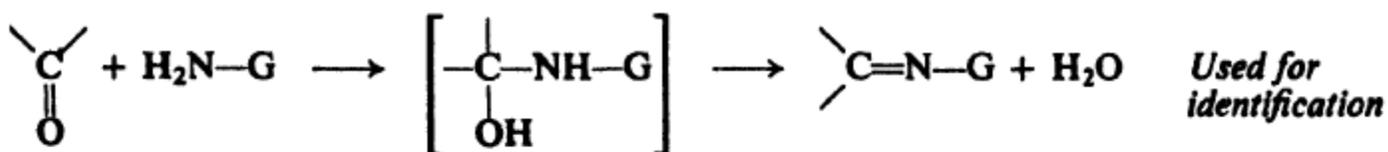
Examples:



Addition involves nucleophilic attack by bisulfite ion on carbonyl carbon, followed by attachment of a hydrogen ion to carbonyl oxygen:

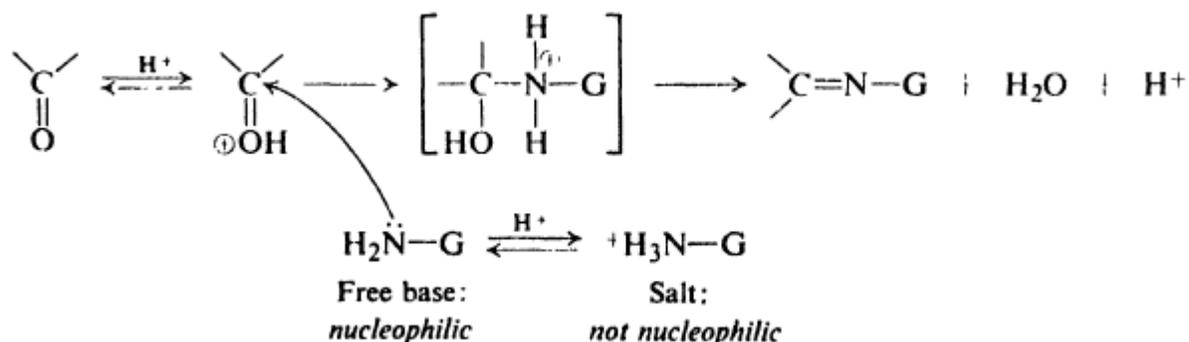
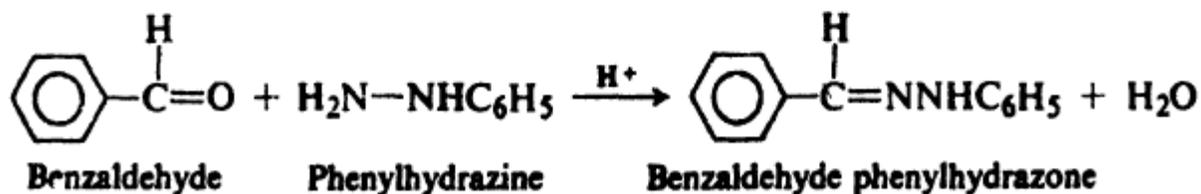
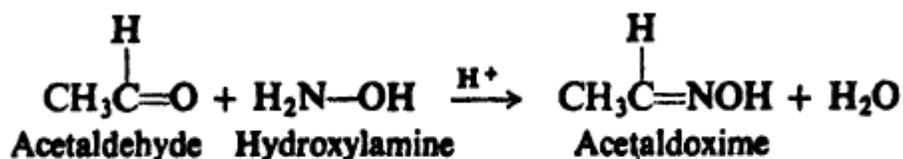


6. Addition of derivatives of ammonia.

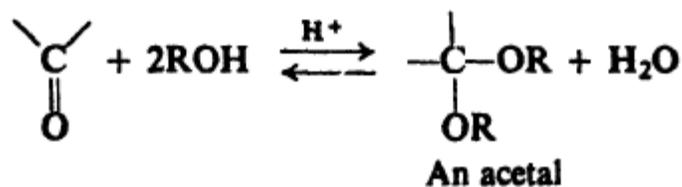


$\text{H}_2\text{N}-\text{G}$		Product	
$\text{H}_2\text{N}-\text{OH}$	Hydroxylamine	$\begin{array}{c} \diagup \\ \text{C}=\text{NOH} \\ \diagdown \end{array}$	Oxime
$\text{H}_2\text{N}-\text{NH}_2$	Hydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{NNH}_2 \\ \diagdown \end{array}$	Hydrazone
$\text{H}_2\text{N}-\text{NHC}_6\text{H}_5$	Phenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{NNHC}_6\text{H}_5 \\ \diagdown \end{array}$	Phenylhydrazone
$\text{H}_2\text{N}-\text{NHCONH}_2$	Semicarbazide	$\begin{array}{c} \diagup \\ \text{C}=\text{NNHCONH}_2 \\ \diagdown \end{array}$	Semicarbazone

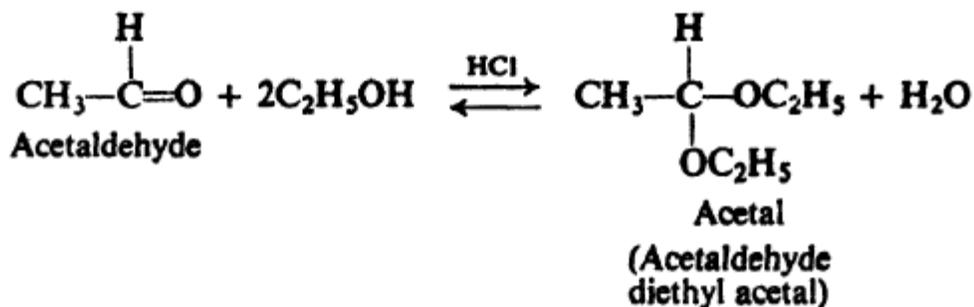
Examples:



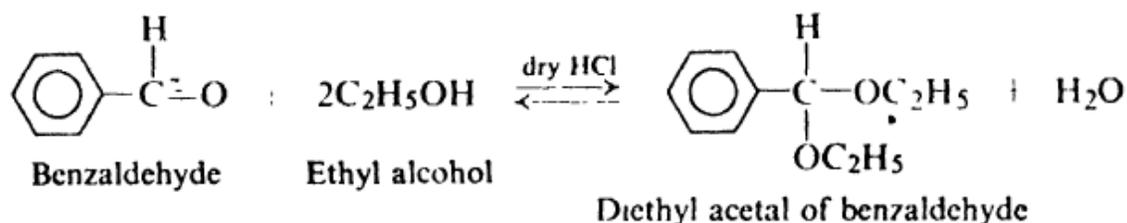
7. Addition of alcohols. Acetal formation.



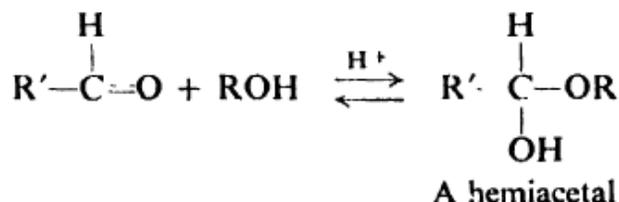
Example:



The reaction is carried out by allowing the aldehyde to stand with an excess of the anhydrous alcohol and a little anhydrous acid, usually hydrogen chloride. In the preparation of ethyl acetals the water is often removed as it is formed by means of the azeotrope of water, benzene, and ethyl alcohol

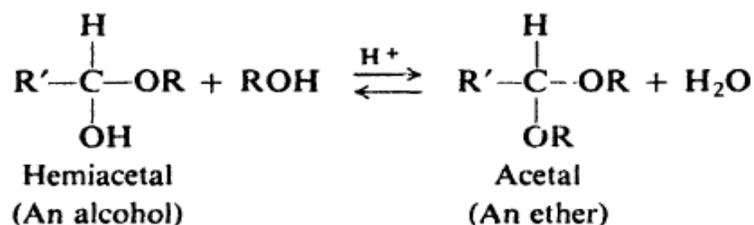


There is good evidence that in alcoholic solution an aldehyde exists in equilibrium with a compound called a **hemiacetal**:

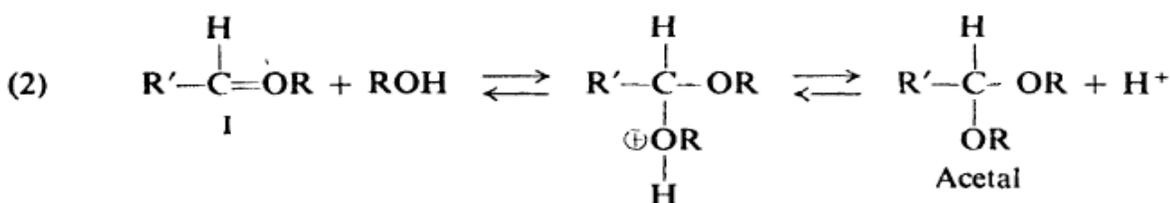
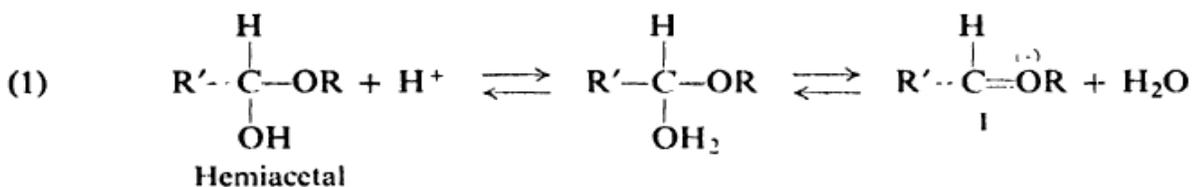


A hemiacetal is formed by the addition of the nucleophilic alcohol molecule to the carbonyl group; it is both an ether and an alcohol. With a few exceptions, hemiacetals are too unstable to be isolated.

In the presence of acid the hemiacetal, acting as an alcohol, reacts with more of the solvent alcohol to form the acetal, an ether:



The reaction involves the formation (step 1) of the ion I, which then combines (step 2) with a molecule of alcohol to yield the protonated acetal. As we can see,

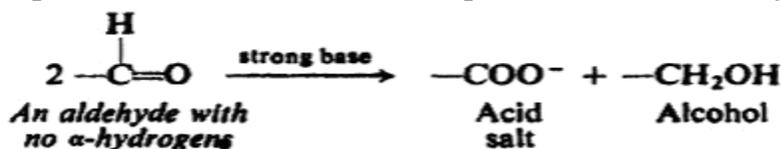


Acetal formation thus involves :-

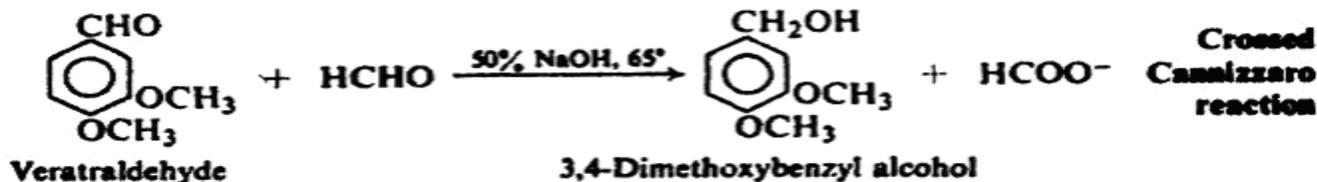
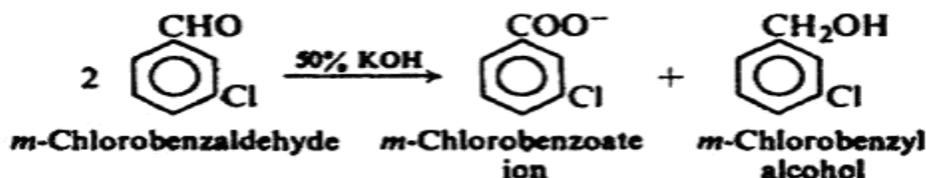
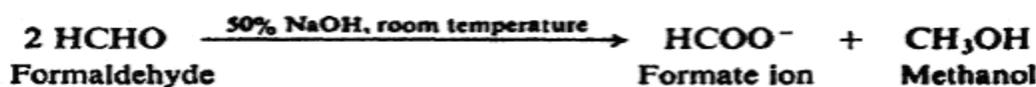
- (a) nucleophilic addition to a carbonyl group, and
- (b) ether formation via a carbonium ion.

(8) Cannizzaro reaction

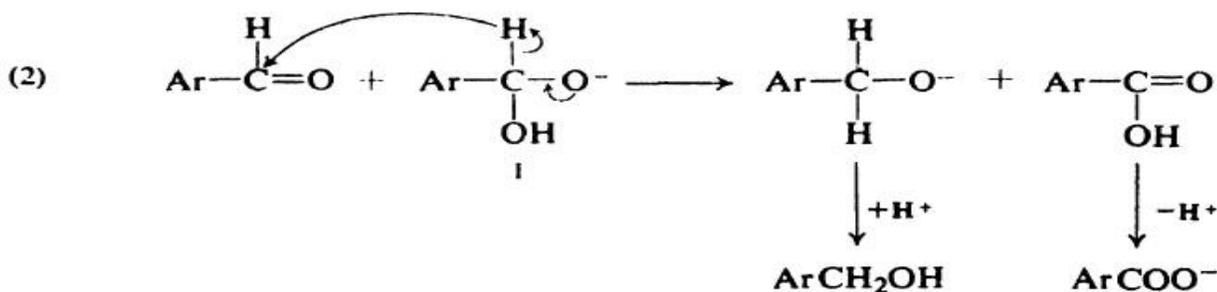
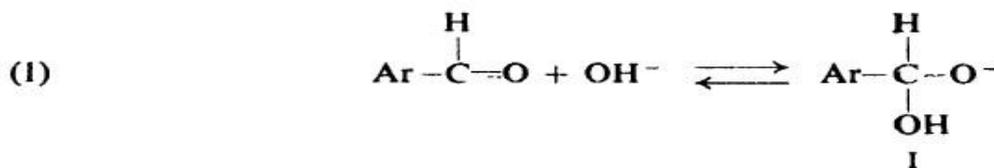
In the presence of concentrated alkali, aldehydes containing no α -hydrogens undergo self-oxidation-and-reduction to yield a mixture of an alcohol and a salt of a carboxylic acid. This reaction, known as the Cannizzaro reaction, is generally brought about by allowing the aldehyde to stand at room temperature with concentrated aqueous or alcoholic hydroxide.



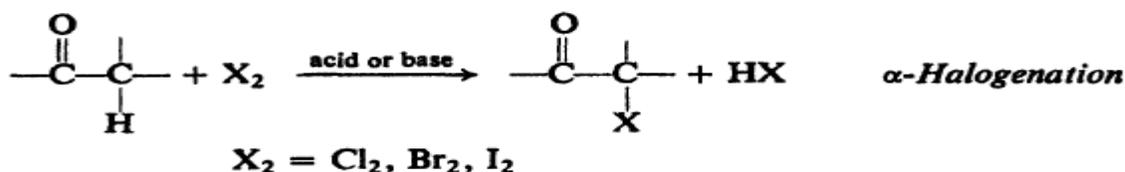
Examples:



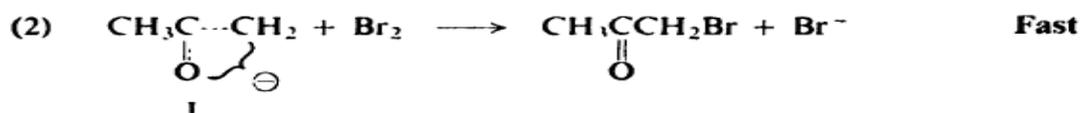
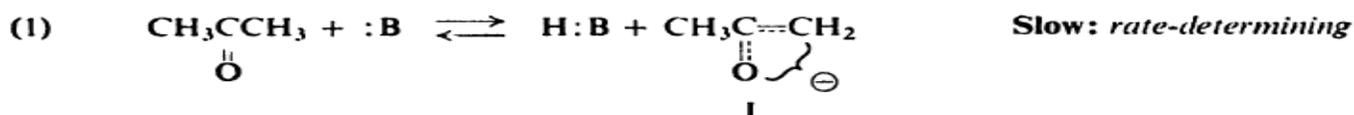
Two successive additions



9. Halogenation of ketones.



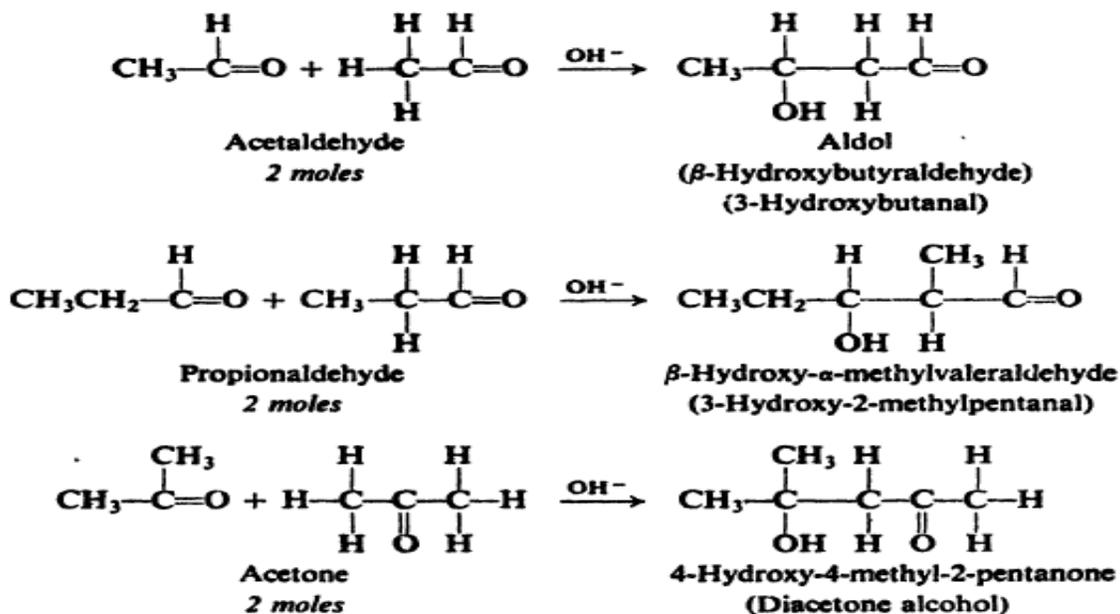
The kinetics is quite consistent with the following mechanism. The base



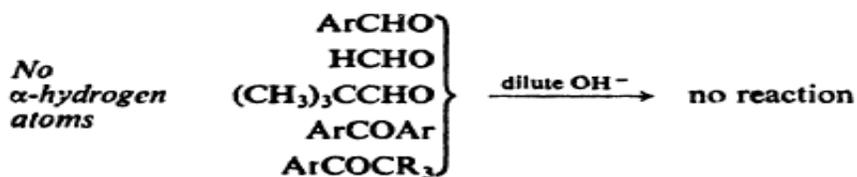
10. Addition of carbanions.

(a) Aldol condensation

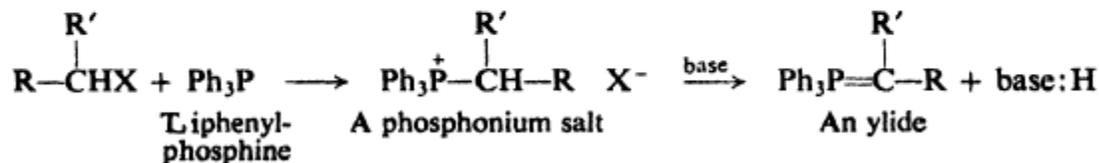
Under the influence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may combine to form a β -hydroxyaldehyde or β -hydroxyketone. This reaction is called the aldol condensation. In every case the product results from addition of one molecule of aldehyde (or ketone) to a second molecule in such a way that the α -carbon of the first becomes attached to the carbonyl carbon of the second. For example:



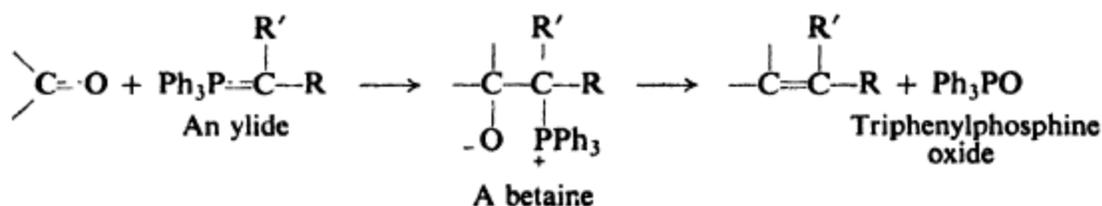
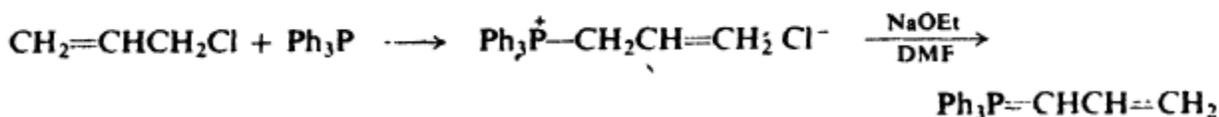
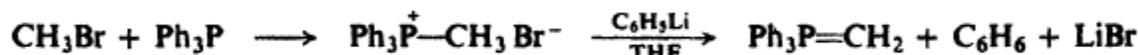
If the aldehyde or ketone does not contain an α -hydrogen, a simple aldol condensation cannot take place. For example:



The preparation of ylides is a two-stage process, each stage of which belongs to a familiar reaction type: nucleophilic attack on an alkyl halide, and abstraction of a proton by a base.



Many different bases have been used—chiefly alkoxides and organometallics—and in a variety of solvents. For example:



is the nucleophilic attack on carbonyl carbon by an *ylide* to form a *betaine* which—often spontaneously—undergoes elimination to yield the product. For example:

