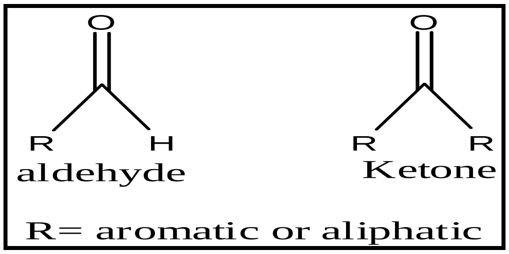
Aldehydes and ketones

All aldehydes have a carbonyl group , bonded on one side to a carbon and on the other side to a hydrogen. In ketones, the carbonyl group is situated between two carbon atoms.



Both aldehydes and ketones contain the carbonyl group, C=O, and are often referred to collectively as carbonyl compounds. However, there is a hydrogen atom attached to the carbonyl group of aldehydes, and there are two organic groups attached to the carbonyl group of 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 to carbonyl compounds.

Nomenclature

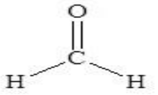
The common names of aldehydes are derived from the names of the corresponding carboxylic acids by replacing -ic add by -aldehyde.

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-l. Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to alpha of the common name.

Summary of Aldehyde Nomenclature rules:

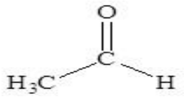
1. Aldehydes take their name from their parent alkane chains. The ***-e*** is removed from the end and is replaced with ***-al***.
2. The aldehyde funtional group is given the #1 numbering location and this number is not included in the name.

3. For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***. Substituent positions are shown with Greek letters.
4. When the -CHO functional group is attached to a ring the suffix –***carbaldehyde*** is added, and the carbon attached to that group is C1.



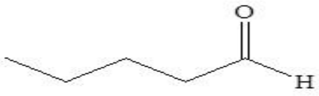
Methanal

(Formaldehyde)



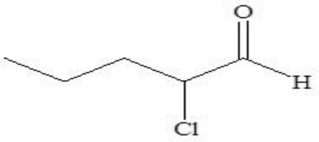
Ethanal

(Acetaldehyde)



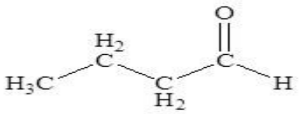
Pentanal

(Valeraldehyde)



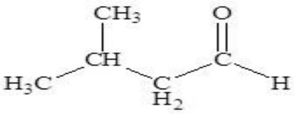
2-Chloropentanal

(a-Chlorovaleraldehyde)



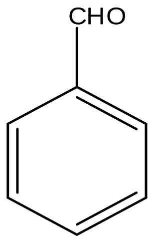
Butanal

(Butyraldehyde)

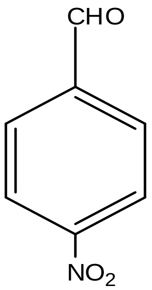


3-Methylbutanal

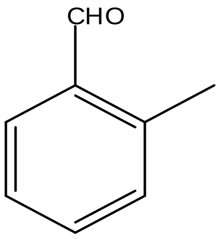
(isovaleraldehyde)



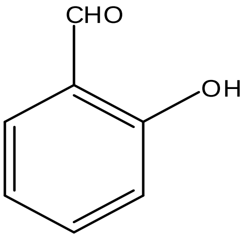
benzaldehyde



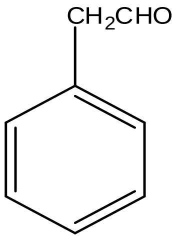
4-nitrobenzaldehyde



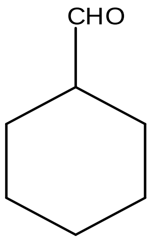
2-methylbenzaldehyde
(o-tolualdehyde)



2-hydroxybenzaldehyde
(salicyldehyde)



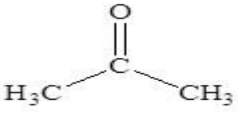
phenylacetaldehyde
(phenylethanal)



cyclohexanecarbaldehyde

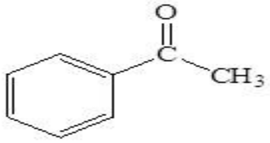
The simplest aliphatic ketone has the common name of acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as a -phenone, as illustrated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



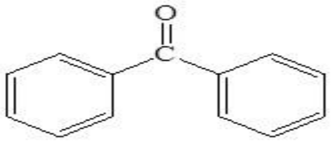
Propanone

(Acetone)



Acetophenone

(Methyl phenyl ketone)

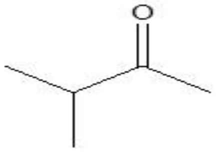


Benzophenone

(Diphenyl ketone)

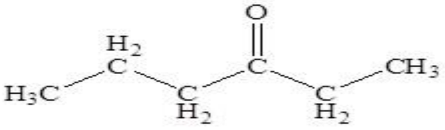
2-Pentanone

(Methyl propyl ketone)



3-Methyl-2-butanone

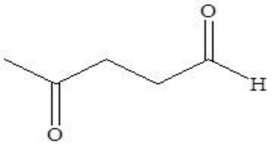
(Methyl isopropyl ketone)



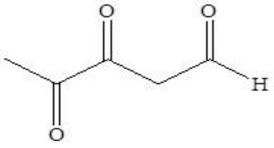
3-Hexanone

(Ethyl propy ketone)

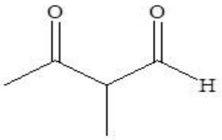
Naming Aldehydes and Ketones in the Same Molecule



4-Oxopentanal

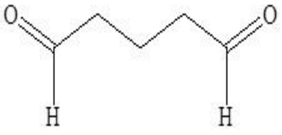


3,4-Dioxopentanal

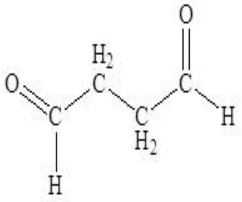


2-Methyl-3-oxo-butanal

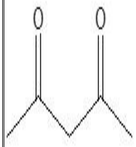
Naming Dialdehydes and Diketones



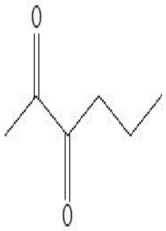
Pentanedial



Butanedial



2,4-Pentanedione

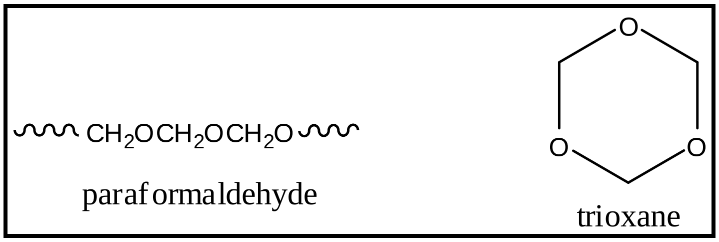


2,3-Hexanedione

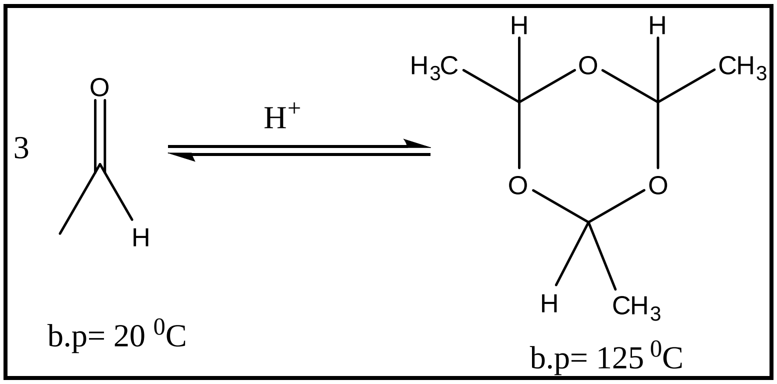
Physical properties

The polar carbonyl group makes aldehydes and ketones polar compounds, and hence they have higher Boiling points has non polar compounds or comparable molecular weight .aldehydes and ketones have lower boiling points than comparable alcohols or carboxylic acids; for example:-
example, compare -**butyraldehyde** (b.p, 76) and **methyl ethyl** ketone (b.p. 80)
n-pentane (b.p. 36) and **ethyl ether** (b.p. 35) on the one hand, and with
n-butyl alcohol (b.p. 118) and **propionic acid** (b.p. 141) on the other.
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 carbones. Aldehydes and ketones are soluble in the usual organic solvents.

Formaldehyde is a gas (b.p. -21), and is handled either as an aqueous solution (Formalin), or as one of its solid polymers: paraformaldehyde (CH_2O)n ,
or trioxane $(CH_2O)_3$. When dry formaldehyde is desired as for Example, for reaction with a Griniard reagent, it is obtained by heating paraformaldehyde or trioxane.



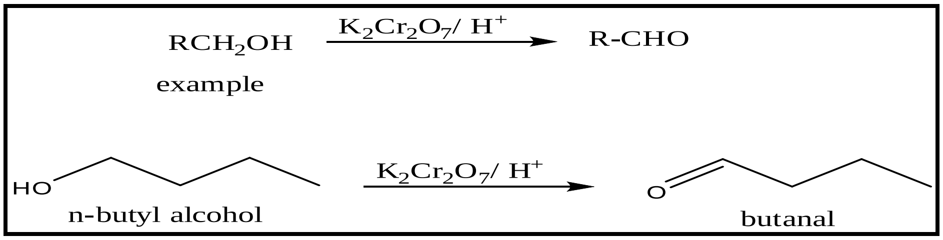
Acetaldehyde (b.p. 20) is often generated from its higher-boiling trimer by heating the trimer with acid:



Preparation of aldehydes

A few of the many laboratory methods of preparing aldehydes and ketones are outlined below; most of these are already familiar to us. Some of the methods involve oxidation or reduction in which an alcohol, hydrocarbon, or acid chloride is converted into an aldehyde or ketone of the same carbon number. Other methods involve the formation of new carbon-carbon bonds, and yield aldehydes or ketones of higher carbon number than the starting materials.

1- Oxidation of primary alcohols



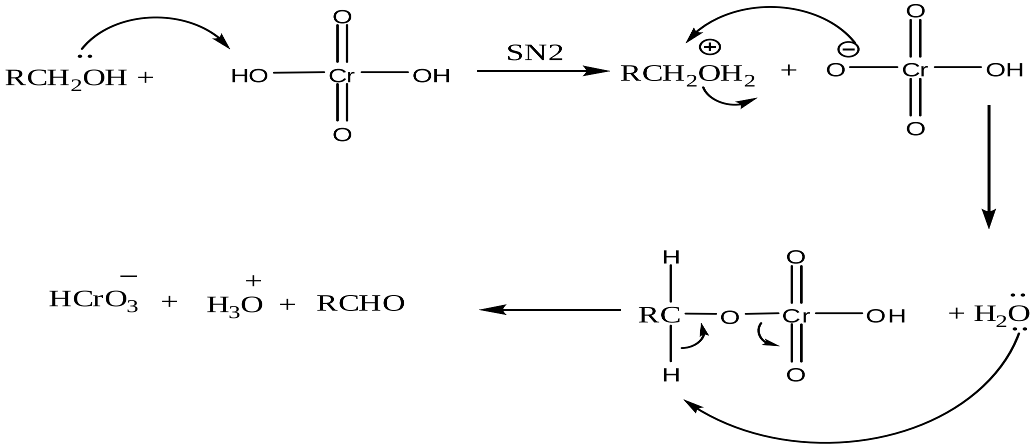
Mechanism

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow H_2Cr_2O_7 + K_2SO_4$$

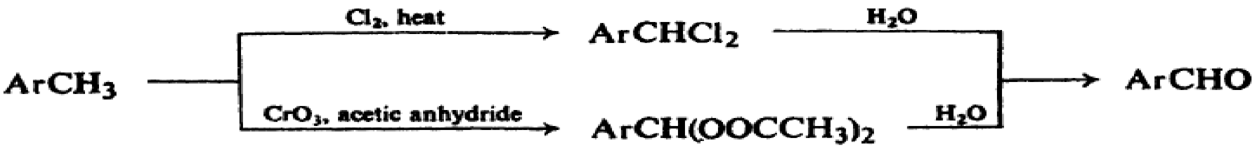
$$H_2Cr_2O_7 + H_2O \longrightarrow 2H_2CrO_4$$

chromic acid

(more oxidized than $K_2Cr_2O_7$)



Oxidation of toluene

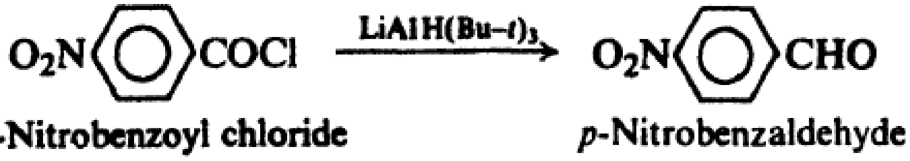


Examples:

3- Reduction of acid chlorides

$$\underset{\text{Acid chloride}}{RCOCl \text{ or } ArCOCl} \xrightarrow{LiAlH(Bu\text{-}t)_3} \underset{\text{Aldehyde}}{RCHO \text{ or } ArCHO}$$

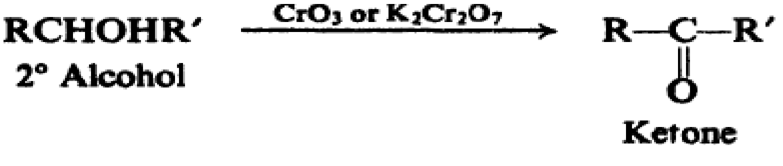
Examples:



- Rimer Tiemann reaction (see chapter 1 for phenol)

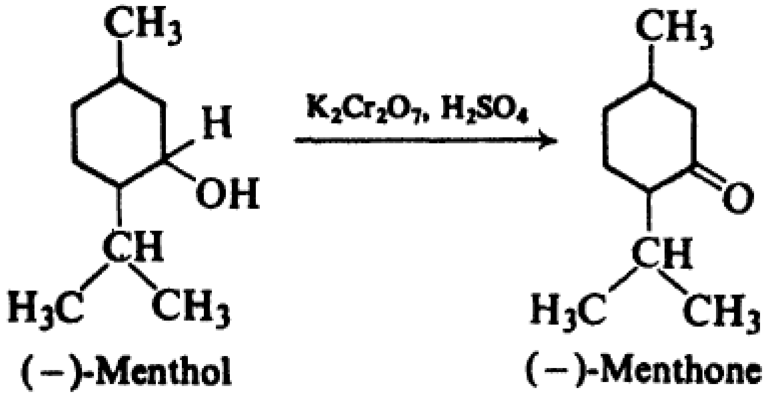
Preparation of ketones

1- Oxidation of secondary alcohols

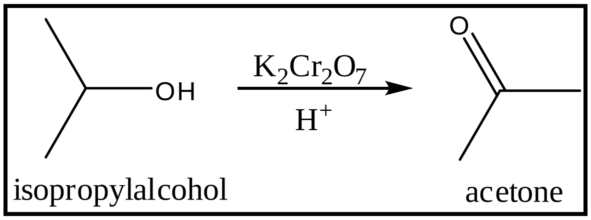


$$\underset{2^\circ \text{ Alcohol}}{RCHOHR'} \xrightarrow{CrO_3 \text{ or } K_2Cr_2O_7} \underset{\text{Ketone}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-R'}$$

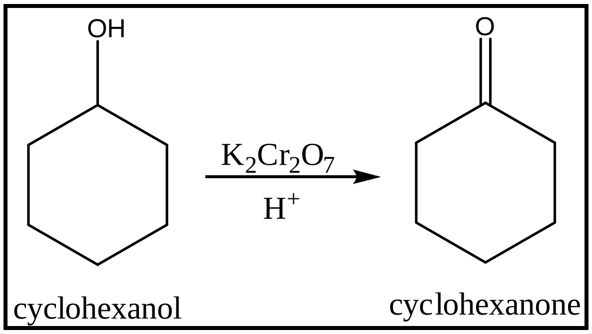
Example



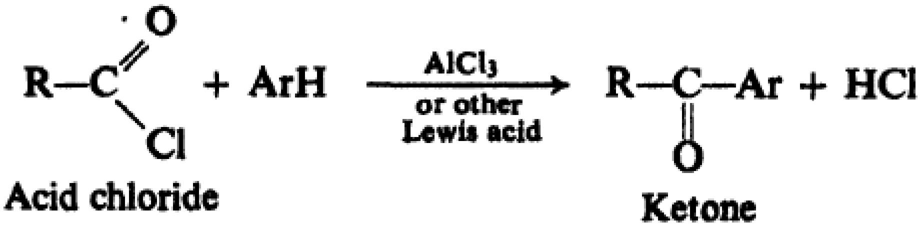
Give the name of the menthol?



Give the mechanism of the title reaction?

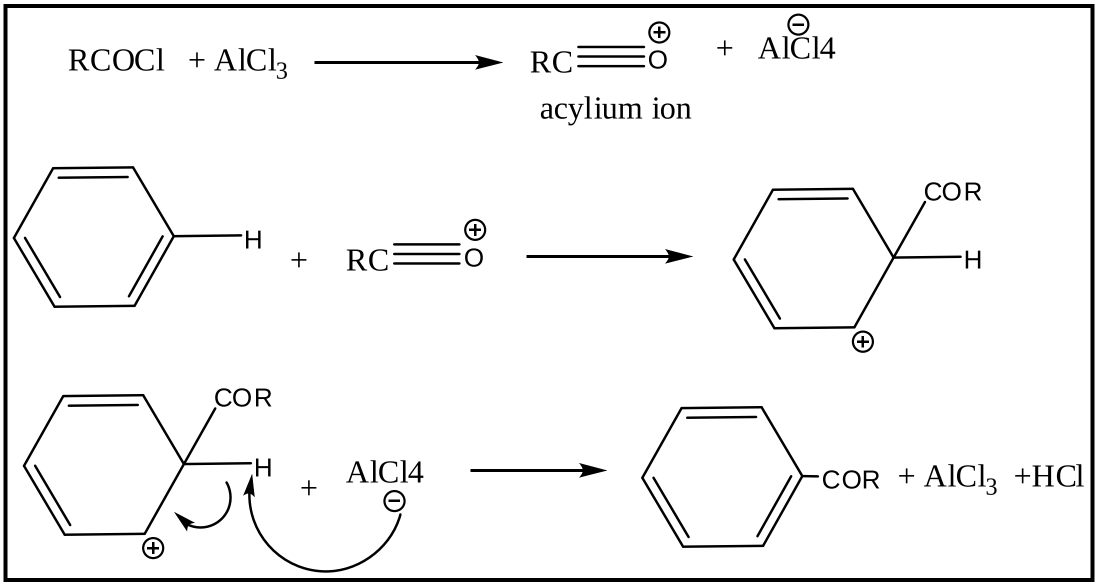


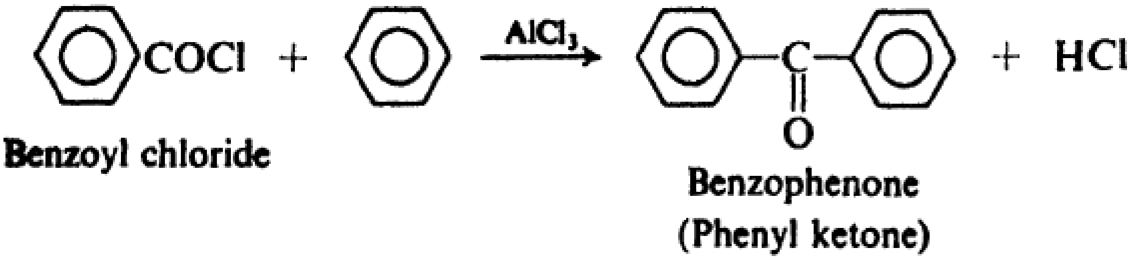
2- Friedel- crafts acylation

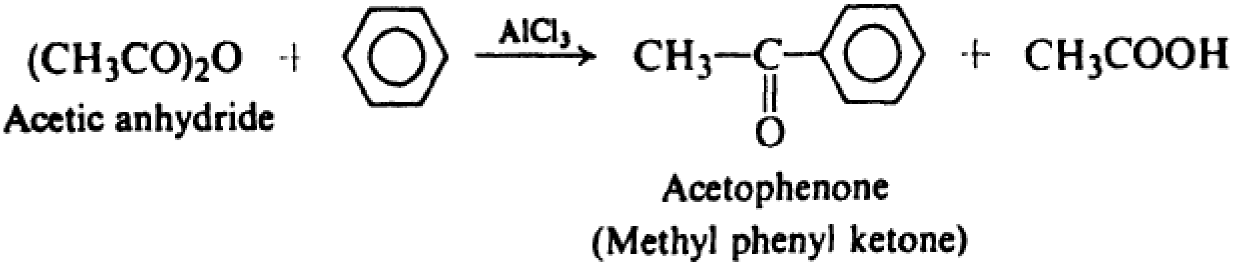


$$R-C(=O)Cl + ArH \xrightarrow[\text{or other Lewis acid}]{AlCl_3} R-C(=O)-Ar + HCl$$

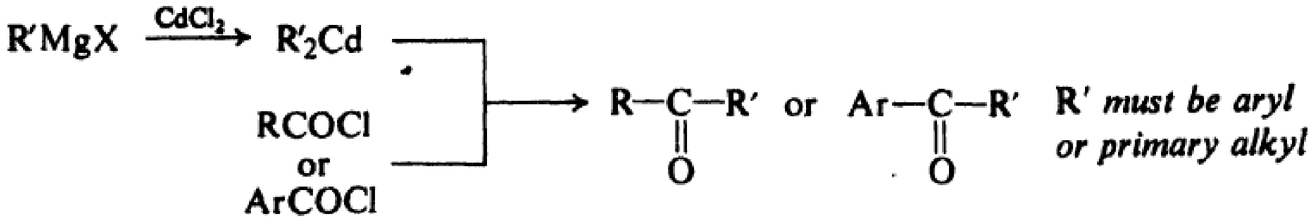
Mechanism



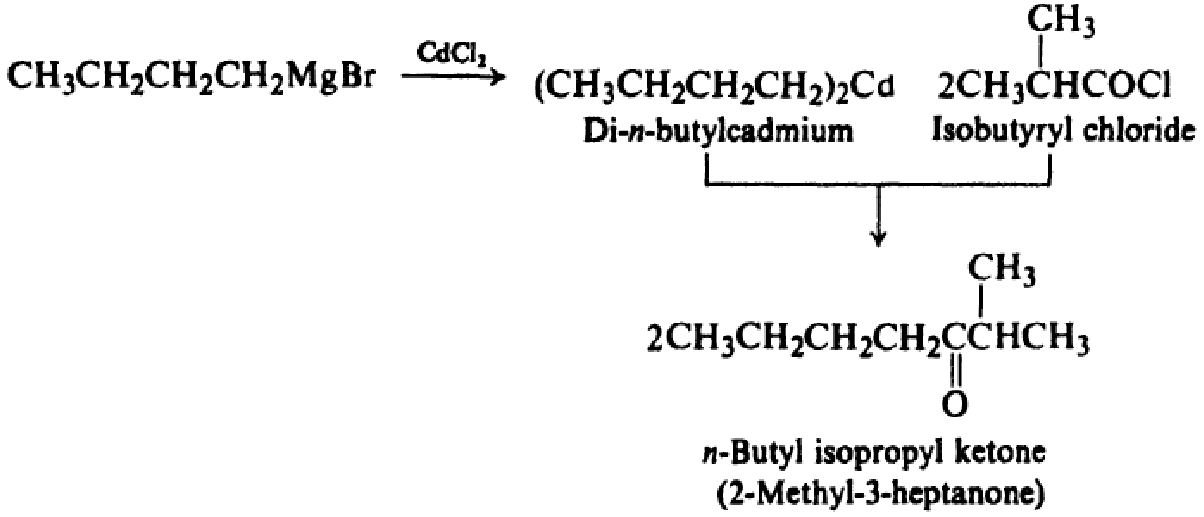




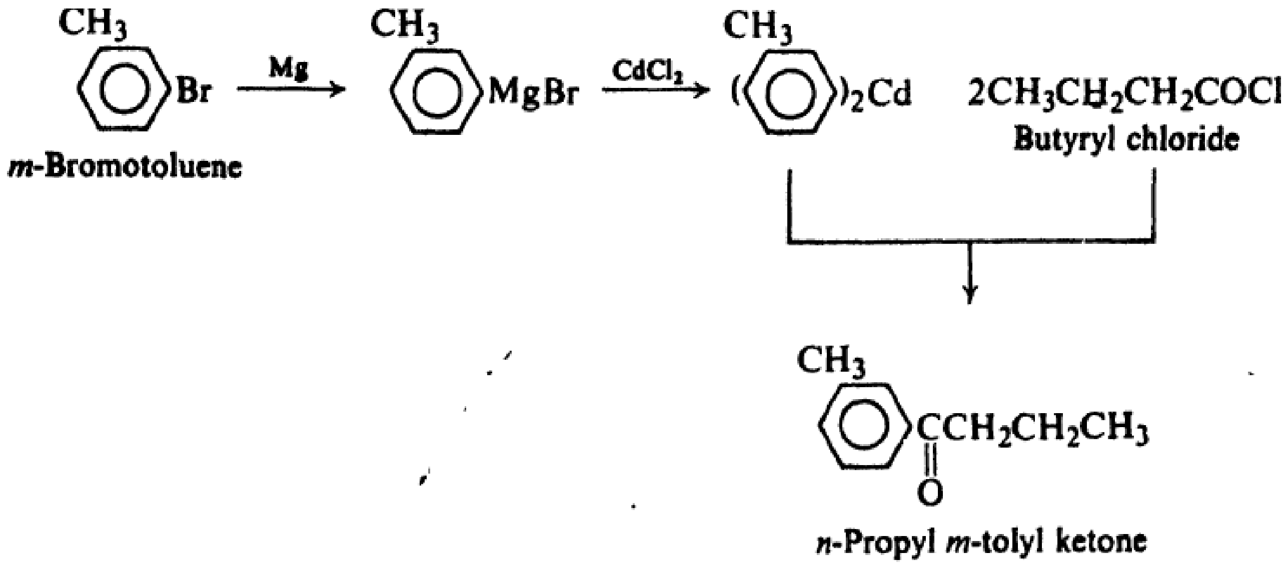
3- **Reaction of acid chlorides with organocadmium compounds.**



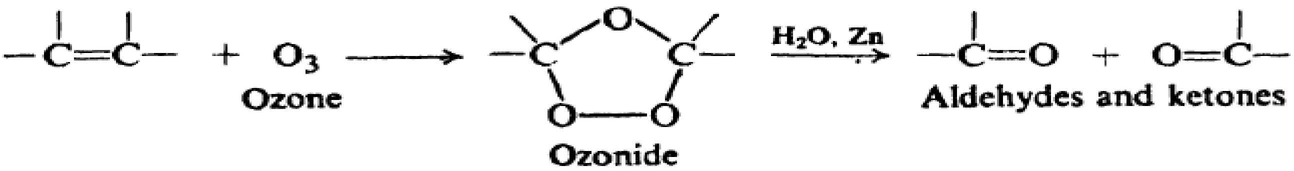
Examples:



Example



4- Oxidation of alkene by ozone



2-methyl-2-pentene + O_3 $\longrightarrow$? (ozonide) $\longrightarrow$? + ?

5- Griniard reagent addition to cyanide compounds: