

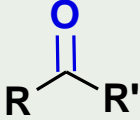
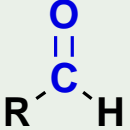
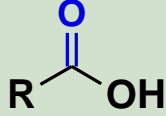
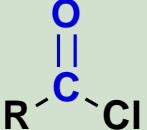
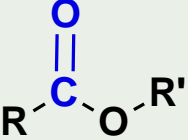
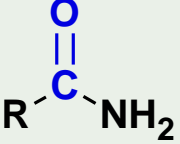
# Fundamentals of Organic Chemistry

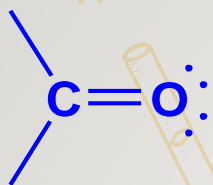
The background is a light-colored illustration of a chemistry laboratory. It features various pieces of glassware such as flasks, beakers, and test tubes, some on stands. A DNA double helix is also depicted. In the bottom right corner, there is a petri dish with several colonies. The overall style is that of a hand-drawn or sketched illustration in a light brown or tan color.

CHEM 245

## 3. Aldehydes & Ketones

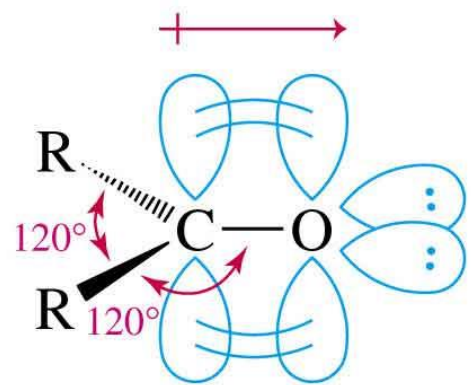
## Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	



## The carbonyl group

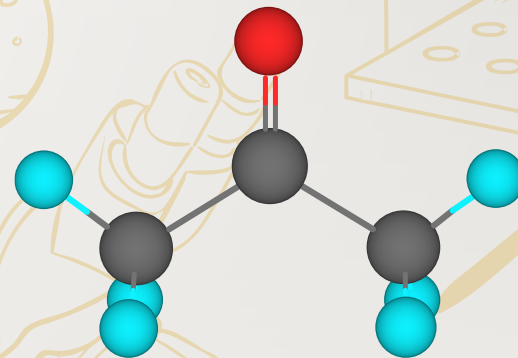
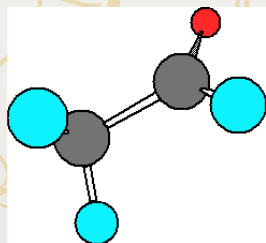
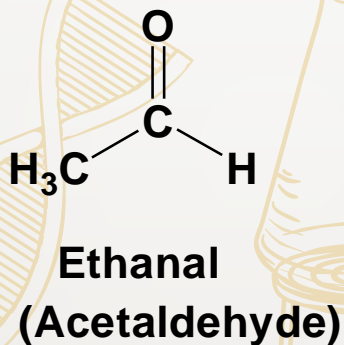
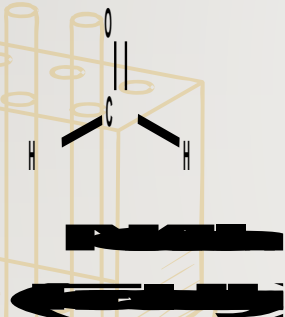
- Carbon is  $sp^2$  hybridized.
- C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.



	<i>length</i>	<i>energy</i>
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)

# Structure aldehydes & ketones

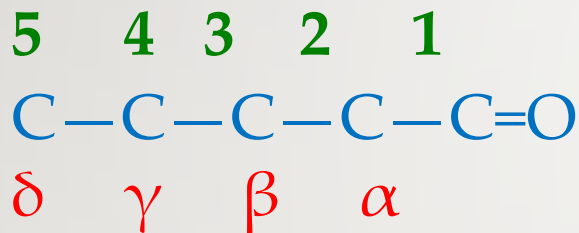
- The functional group of an aldehyde is a carbonyl group bonded to an H atom and a carbon atom.
- The functional group of a ketone is a carbonyl group bonded to two carbon atoms.



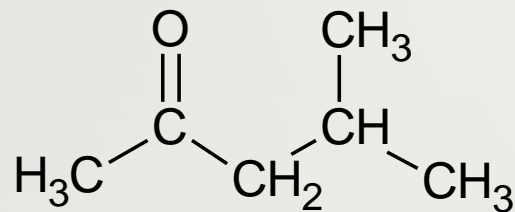
## Nomenclature

Common names of aldehydes and ketones are derived from the common names of the corresponding carboxylic acids.

Thus you must first know something about the nomenclature of carboxylic acids



used in common names

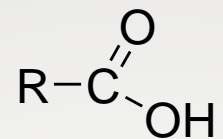


Methyl isobutyl ketone

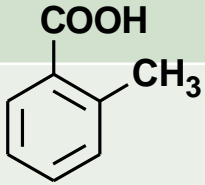
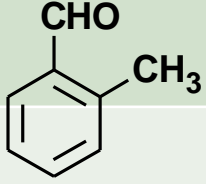
(MIBK)



# Carboxylic acids:



R-COOH, R-CO<sub>2</sub>H,

Carboxylic Acids		Aldehydes	
HCO <sub>2</sub> H	formic acid	HCHO	Formaldehyde
CH <sub>3</sub> CO <sub>2</sub> H	acetic acid	CH <sub>3</sub> CHO	Acetaldehyde
CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H	propionic acid	CH <sub>3</sub> CH <sub>2</sub> CHO	Propionaldehyde
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	butyric acid	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Buteraldehyde
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	valeric acid	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Valeraldehyde
	o-Toluic acid		o-Tolualdehyde



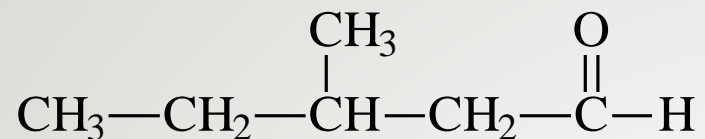
## IUPAC names:

The parent chain is the longest chain that contains the carbonyl group.

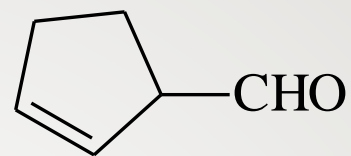
For an aldehyde, change the suffix from **-e** to **-al**.

For an unsaturated aldehyde, change the infix from **-an-** to **-en-**; the location of the suffix determines the numbering pattern.

For a cyclic molecule in which **-CHO** is bonded to the ring, add the suffix **-carbaldehyde**



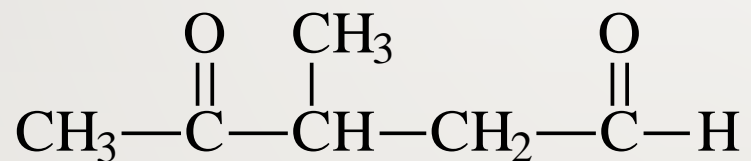
3-methylpentanal



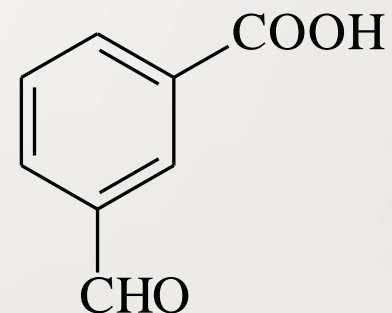
2-cyclopentene carbaldehyde

### Name as Substituent

- On a molecule with a higher priority functional group, C=O is *oxo-* and -CHO is *formyl*.
- Aldehyde priority is higher than ketone.



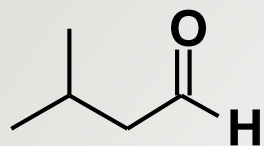
3-methyl-4-oxopentanal



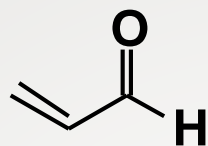
3-formylbenzoic acid



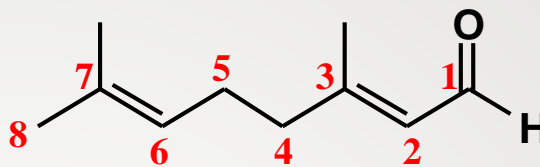
## Nomenclature: Aldehydes



**3-Methylbutanal**

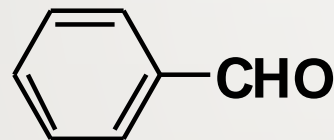


**2-Propenal  
(Acrolein)**

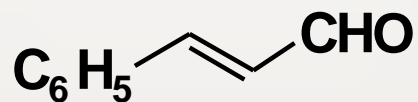


**(2E)-3,7-Dimethyl-2,6-octadienal  
(Geranial)**

- The IUPAC naming uses the common names benzaldehyde, cinnamaldehyde, formaldehyde and acetaldehyde.



**Benzaldehyde**

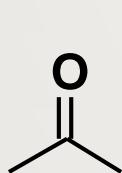


***trans*-3-Phenyl-2-propenal  
(Cinnamaldehyde)**

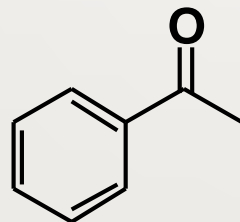
# Nomenclature: Ketones

## IUPAC names

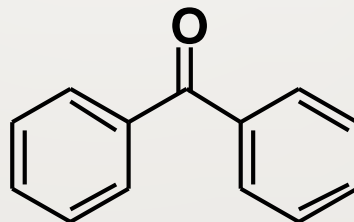
- The parent alkane is the longest chain that contains the carbonyl group.
- For a ketone, change the suffix **-e** to **-one**.
- Number the chain to give C=O the smaller number.
- IUPAC uses the common names acetone, acetophenone, and benzophenone.



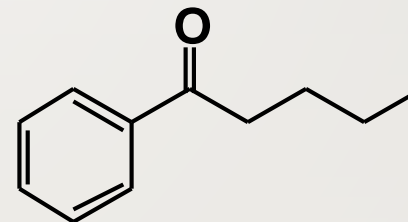
**Propanone**  
(Acetone)



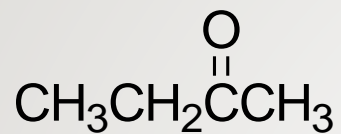
**Acetophenone**



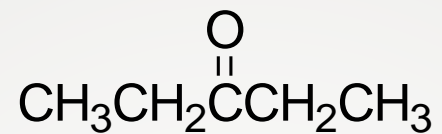
**Benzophenone**



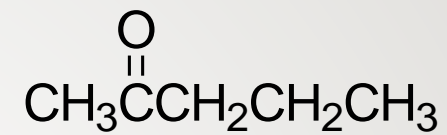
**1-Phenyl-1-pentanone**



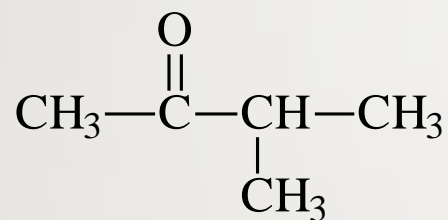
2-butanone



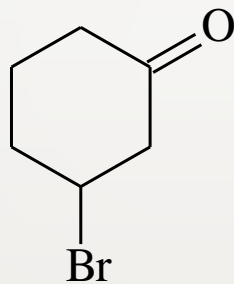
3-pentanone



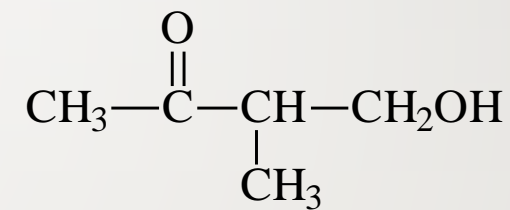
2-pentanone



3-methyl-2-butanone



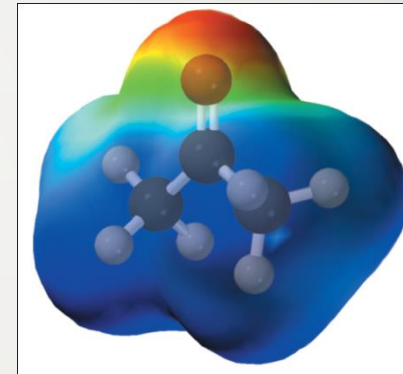
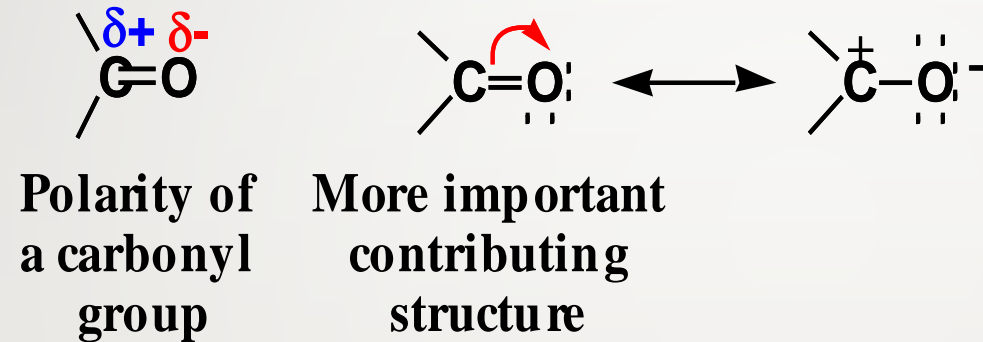
3-bromocyclohexanone



4-hydroxy-3-methyl-2-butanone

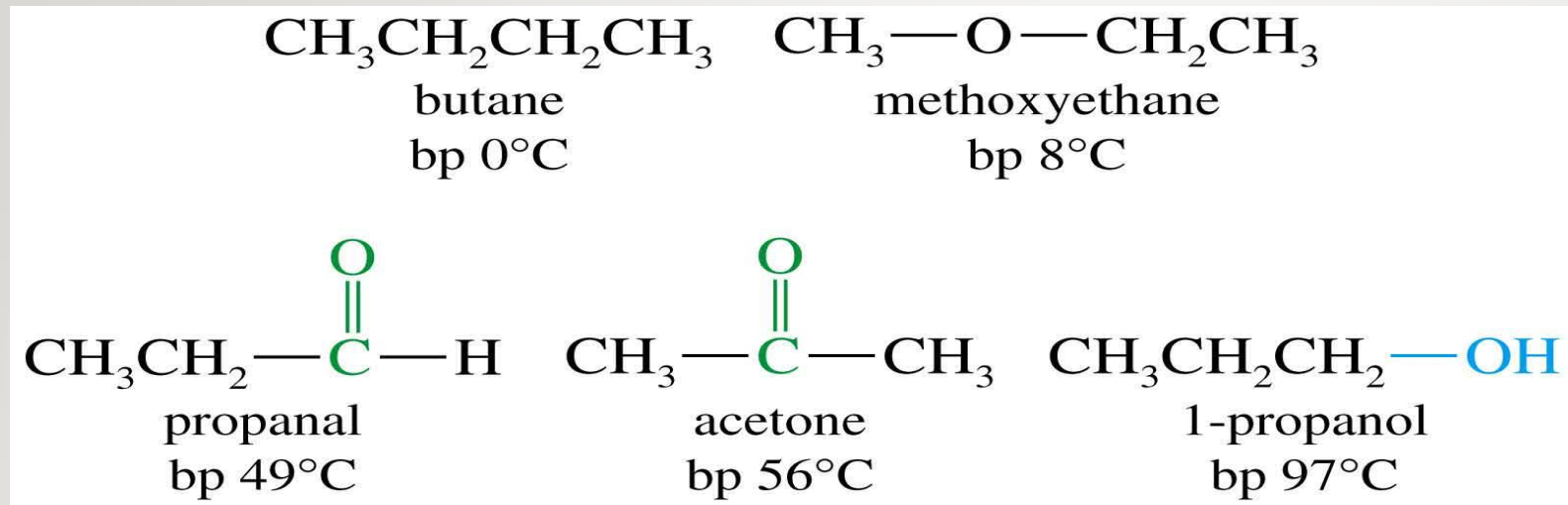
# Physical Properties

Oxygen is more electronegative than carbon (3.5 vs 2.5) and, therefore, a C=O group is polar.

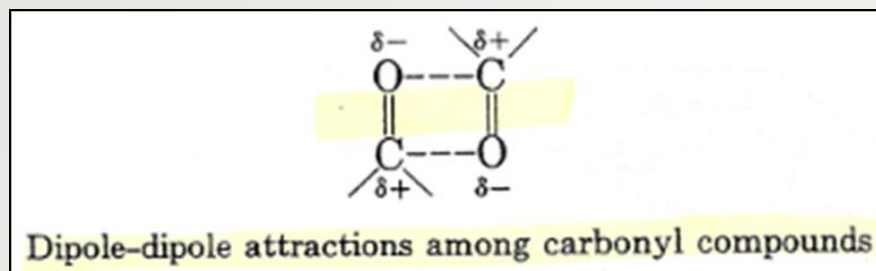


Aldehydes and ketones are polar compounds and interact in the pure state by dipole-dipole interaction.

They have higher boiling points and are more soluble in water than nonpolar compounds of comparable molecular weight.

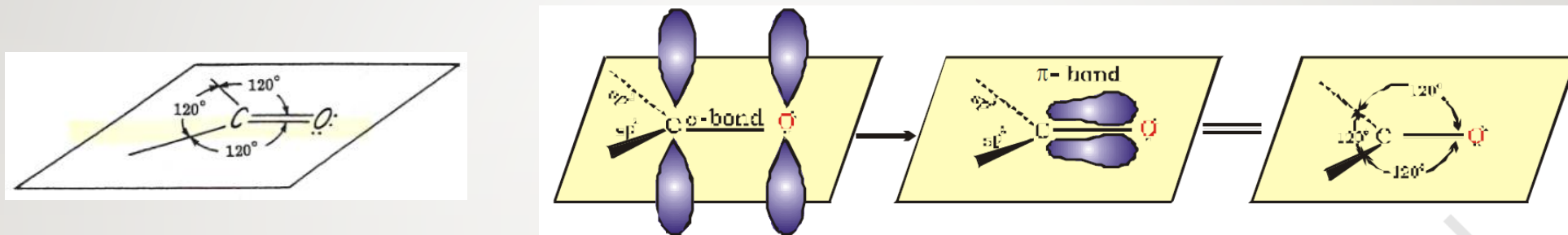


Cannot H-bond to each other, so lower boiling point than comparable alcohol.



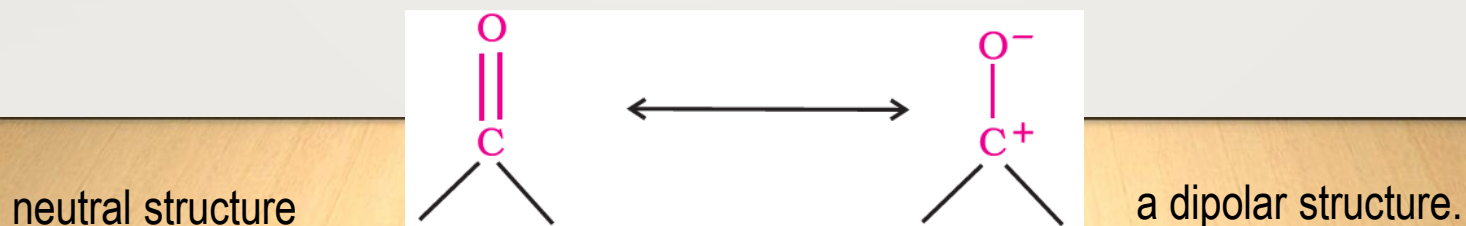
## Structure of the Carbonyl Group

- The carbonyl carbon atom is  **$sp^2$ -hybridised** and forms **three sigma ( $\sigma$ ) bonds and one  $\pi$ -bond**.
- In addition, **the oxygen atom also has two non bonding electron pairs**.
- The **bond angles are approximately  $120^\circ$**  as expected of a trigonal coplanar structure



Orbital diagram for the formation of carbonyl group

- The carbon-oxygen double bond **is polarized** due to higher electronegativity of oxygen relative to carbon.
- Hence, **the carbonyl carbon is an electrophilic** (Lewis acid), and **carbonyl oxygen, a nucleophilic** (Lewis base).
- The high polarity of the carbonyl group is explained on the basis of **resonance**.



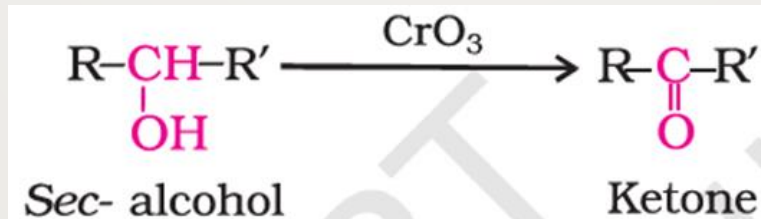
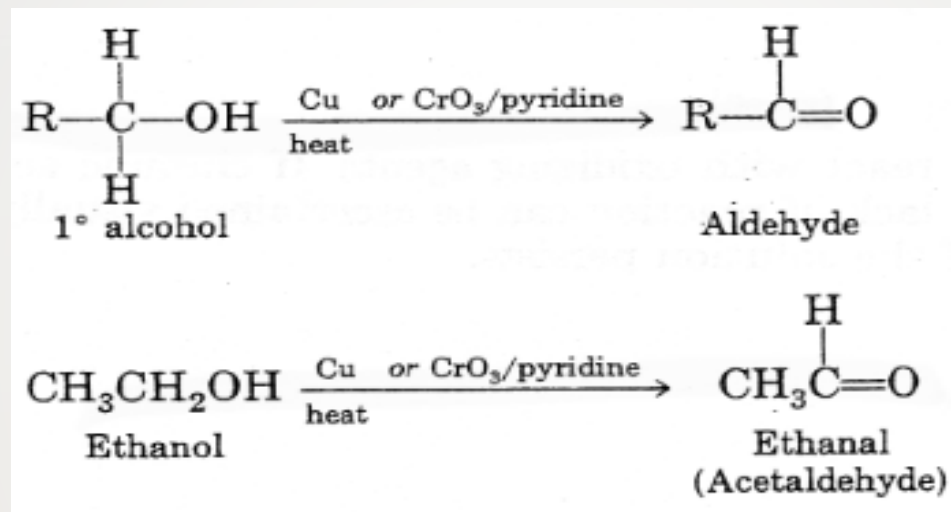
# Solubility

- Good solvent for alcohols.
- Lone pair of electrons on oxygen of carbonyl can accept a hydrogen bond from O-H or N-H.
- The **lower aldehydes and ketones** are soluble in water such as acetone and acetaldehyde are miscible in water.
- As the hydrocarbon portion of the molecule increases, the solubility in water decreases rapidly.
- Aldehydes and ketones with more than six carbons are essentially insoluble in water.

# Preparation of Aldehydes and Ketones

## 1. By oxidation of Alcohols

Aldehydes and ketones are generally prepared by **oxidation of primary and secondary alcohols**, respectively.

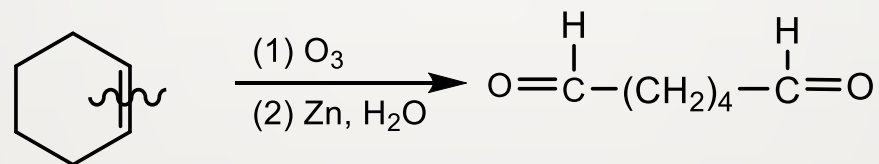
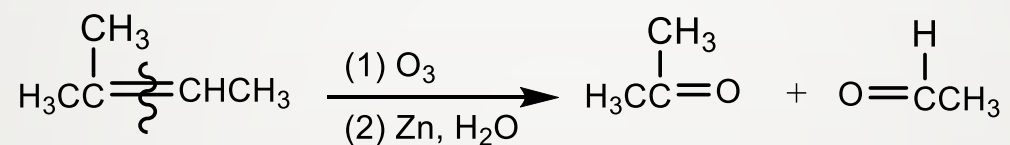
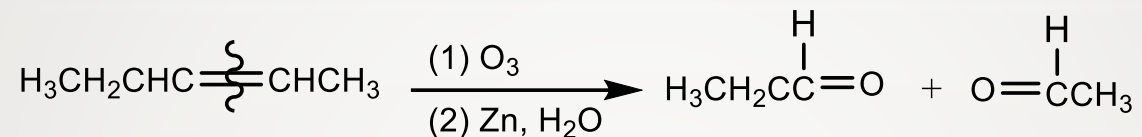




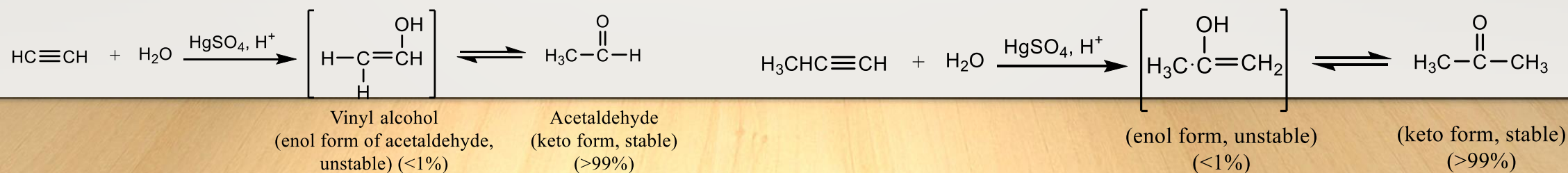
# Preparation of Aldehydes and Ketones

## 2. From Hydrocarbons

**(i) Ozonolysis of Alkenes:** Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.



**(ii) Hydration of Alkynes:** Addition of water to ethyne in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  gives acetaldehyde. All other alkynes give ketones in this reaction



# Preparation of Aldehydes and Ketones

## 2. From Hydrocarbons

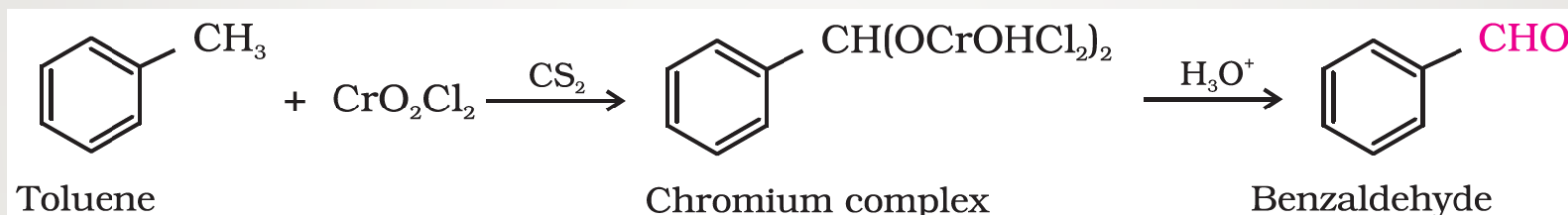
### (iii) By oxidation of methylbenzene

Strong oxidizing agents oxidize toluene and its derivatives to benzoic acids.

However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents.

#### (a) Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) (Etard reaction):

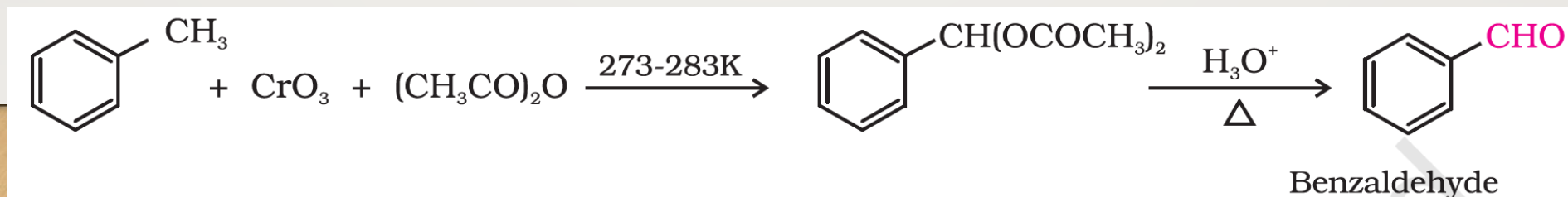
Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



#### (b) Use of chromic oxide ( $\text{CrO}_3$ ):

Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride.

The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



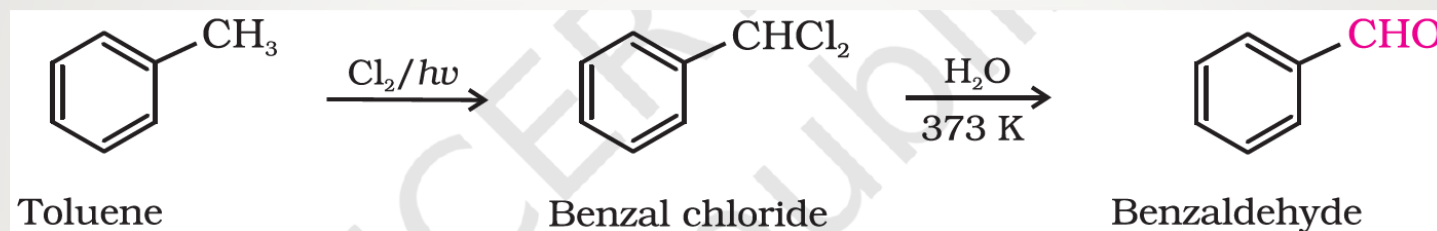
# Preparation of Aldehydes and Ketones

## 2. From Hydrocarbons

### (iv) *By side chain chlorination followed by hydrolysis*

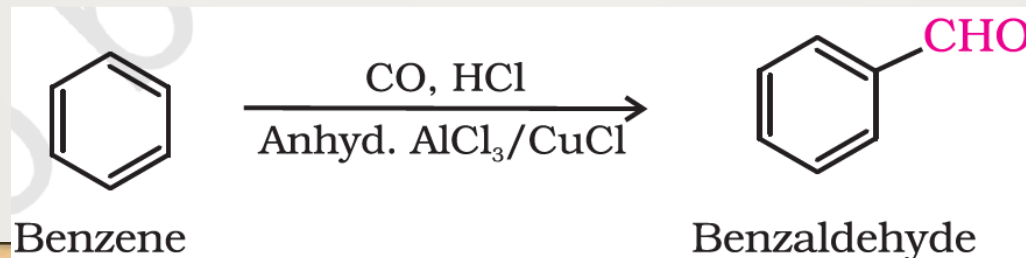
Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

*This is a commercial method of manufacture of benzaldehyde.*



### (v) *By Gatterman – Koch reaction*

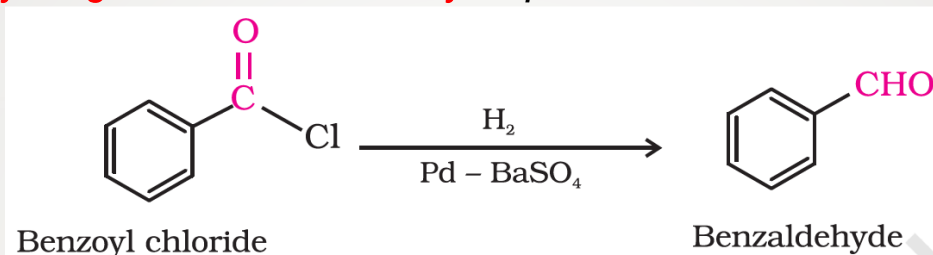
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminum chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



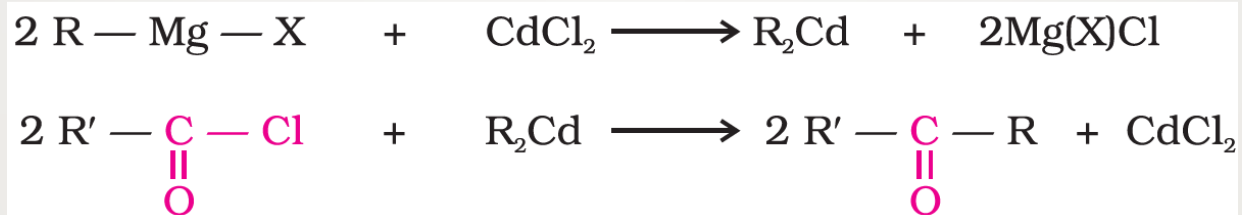
# Preparation of Aldehydes and Ketones

## 3. From Acyl Chloride (Acid Chloride) (*Rosenmund Reduction*)

- Acyl chloride (acid chloride) is *hydrogenated over catalyst*, palladium on barium sulphate, **gives aldehyde**.

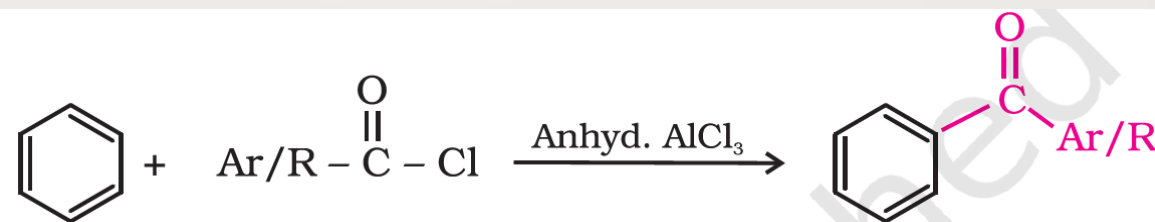


- Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, **gives ketones**.



## 4. From Benzene or Substituted Benzenes (*Friedel-Crafts acylation reaction*)

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminum chloride, it affords the corresponding **ketone**.



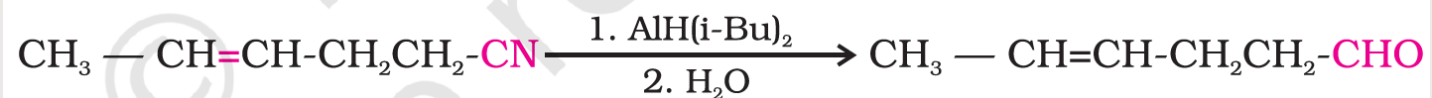
# Preparation of Aldehydes and Ketones

## 5. From Nitriles and Esters (*Stephen Reaction*)

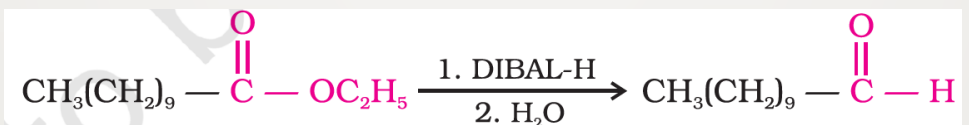
- **Nitriles are reduced** to corresponding imine with stannous chloride in the presence of hydrochloric acid, **which on hydrolysis** give corresponding **aldehyde**.



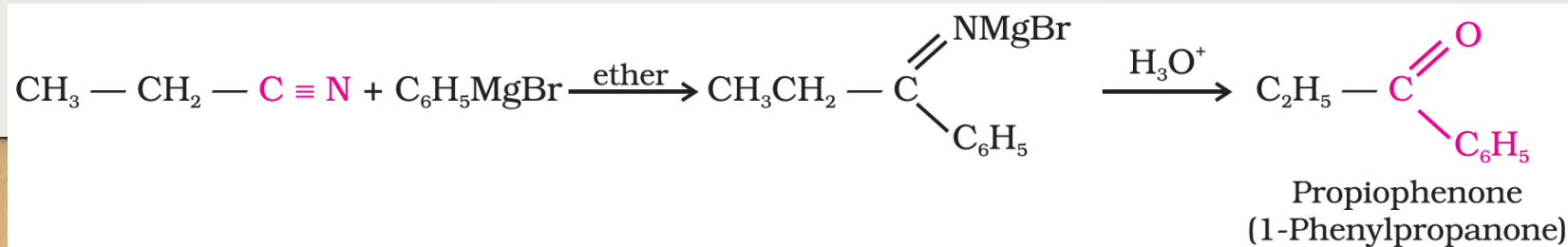
- **Nitriles** are selectively **reduced by diisobutylaluminium hydride**, (DIBAL-H) to imines followed by hydrolysis to **aldehydes**:



- **Esters are also reduced** to **aldehydes** with DIBAL-H.



- **Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.**



# Questions

## Example 12.1

Give names of the reagents to bring about the following transformations:

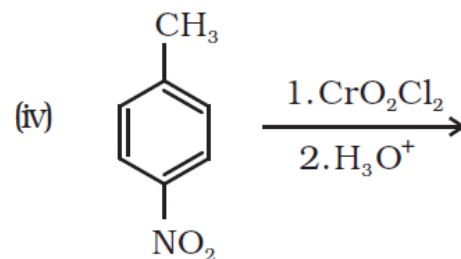
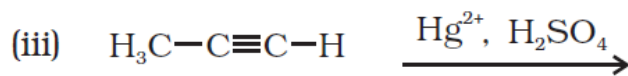
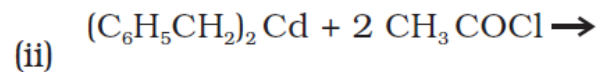
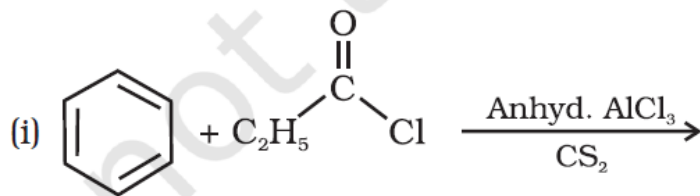
- (i) Hexan-1-ol to hexanal                      (ii) Cyclohexanol to cyclohexanone  
(iii) *p*-Fluorotoluene to *p*-fluorobenzaldehyde                      (iv) Ethanenitrile to ethanal  
(v) Allyl alcohol to propenal                      (vi) But-2-ene to ethanal

## Solution

- (i)  $C_5H_5NH^+CrO_3Cl$  (PCC)                      (ii) Anhydrous  $CrO_3$   
(iii)  $CrO_3$  in the presence of acetic anhydride /  
1.  $CrO_2Cl_2$  2. HOH                      (iv) (Diisobutyl)aluminium hydride (DIBAL-H)  
(v) PCC                      (vi)  $O_3/H_2O$ -Zn dust

## Intext Question

12.2 Write the structures of products of the following reactions;

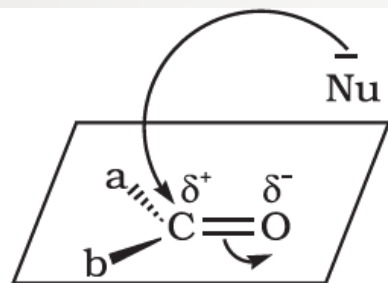


# Chemical Reactions of Aldehydes and Ketones

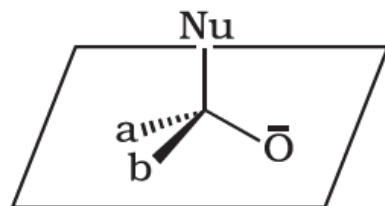
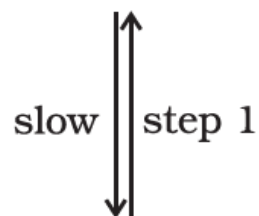
## 1. Nucleophilic Addition Reactions

### (i) Mechanism of Nucleophilic Addition Reactions

2) *The hybridization of carbon changes from  $sp^2$  to  $sp^3$ ; a tetrahedral alkoxide intermediate is produced.*



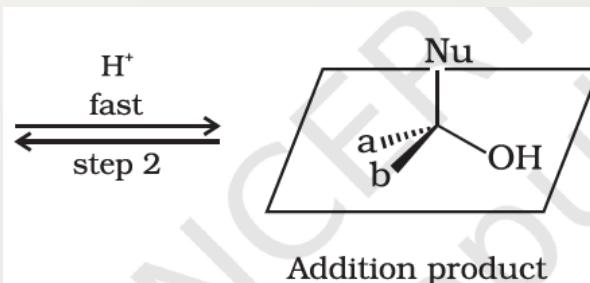
Planar



Tetrahedral intermediate

1) *A nucleophile attacks the electrophilic carbon atom* of the polar carbonyl group from a direction approximately perpendicular to the plane of  $sp^2$  hybridized orbitals of carbonyl carbon.

3) *This intermediate captures a proton from the reaction medium* to give the electrically neutral product.



Addition product

- The net result is addition of  $Nu^-$  and  $H^+$  across the carbon oxygen double bond.

# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions

### (ii) Reactivity

- *Aldehydes are generally more reactive than ketones* in nucleophilic addition reactions due to **steric** and **electronic reasons**.
  - **Sterically**, the presence of two relatively *large substituents in ketones hinders the approach of nucleophile to carbonyl carbon* than in aldehydes having only one such substituent.
  - **Electronically**, aldehydes are more reactive than ketones because *two alkyl groups reduce the electrophilicity of the carbonyl carbon* more effectively than in former.

Example 12.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.



# Questions

Example 12.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

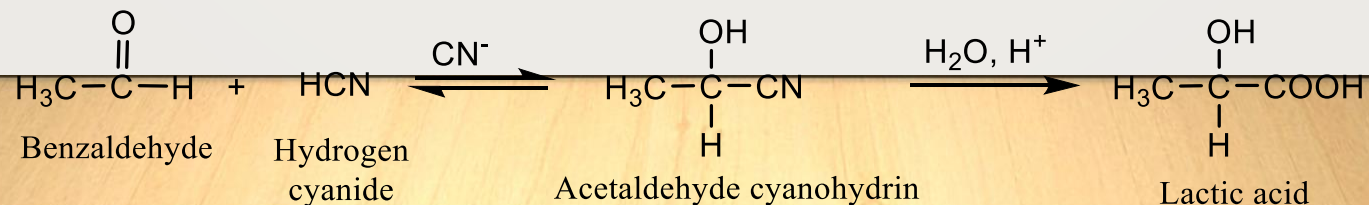
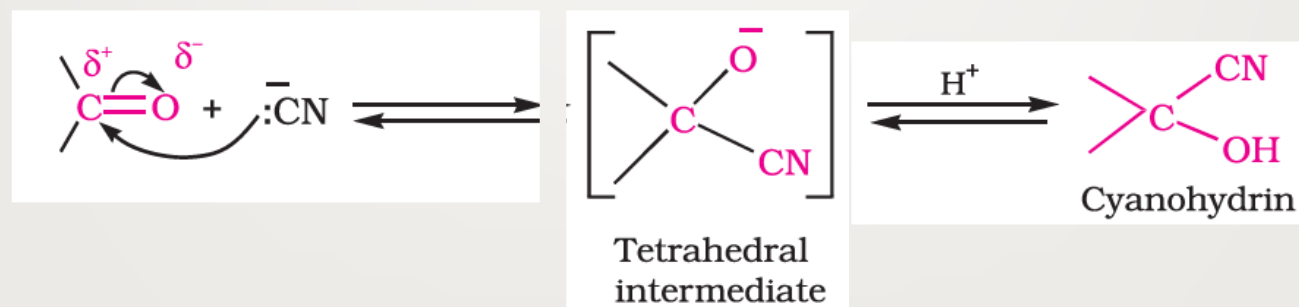
Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions: **Examples**

### (a) Addition of hydrogen cyanide (HCN):

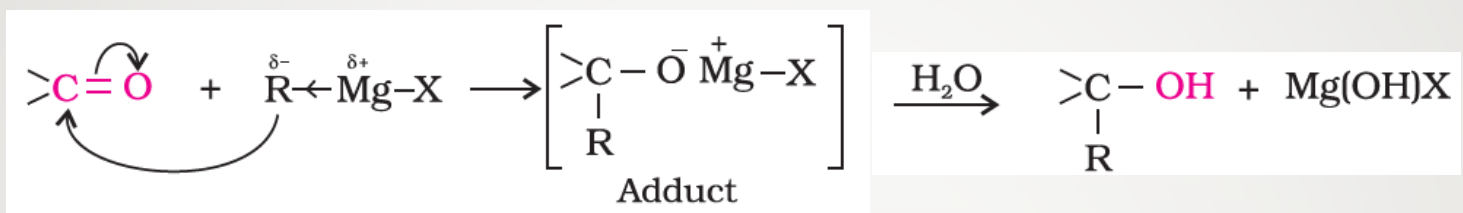
- Aldehydes and ketones react with hydrogen cyanide (HCN) to yield **cyanohydrins**.
- This reaction is catalyzed by a base and the generated cyanide ion (CN<sup>-</sup>) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.
- Cyanohydrins are useful synthetic intermediates.



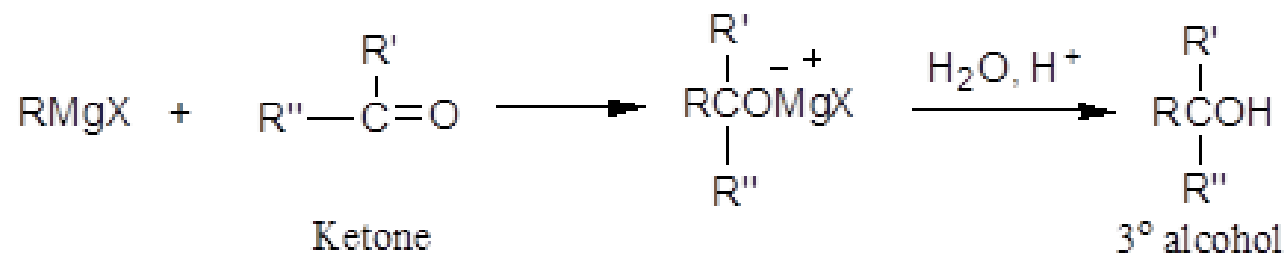
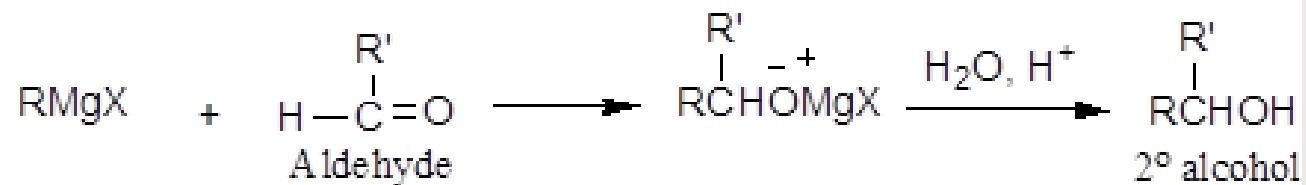
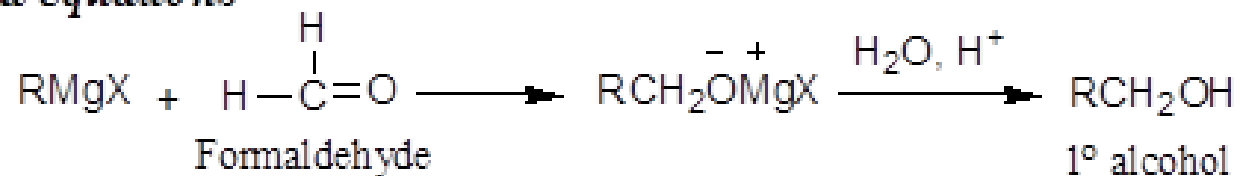
# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions: **Examples**

### (b) Addition of Grignard Reagents:



#### *General equations*

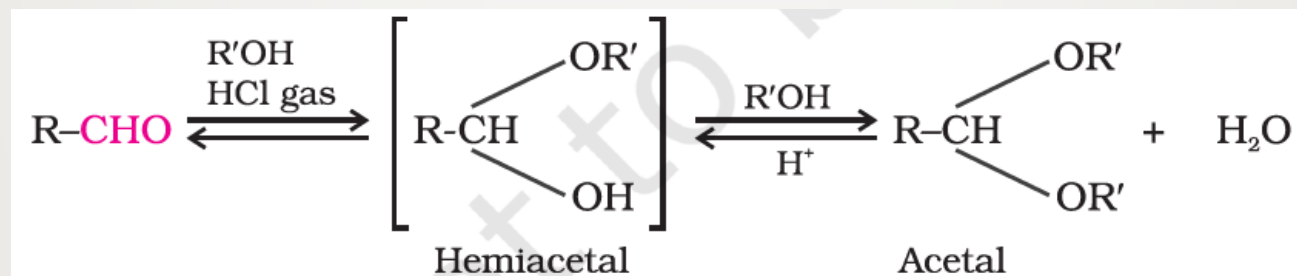


# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions: **Examples**

### (c) Addition of Alcohols:

- Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield **alkoxyalcohol intermediate**, known as **hemiacetals**, which further react with one more molecule of alcohol to give a **gem-dialkoxy compound** known as **acetal**.
- Acetals are hydrolyzed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

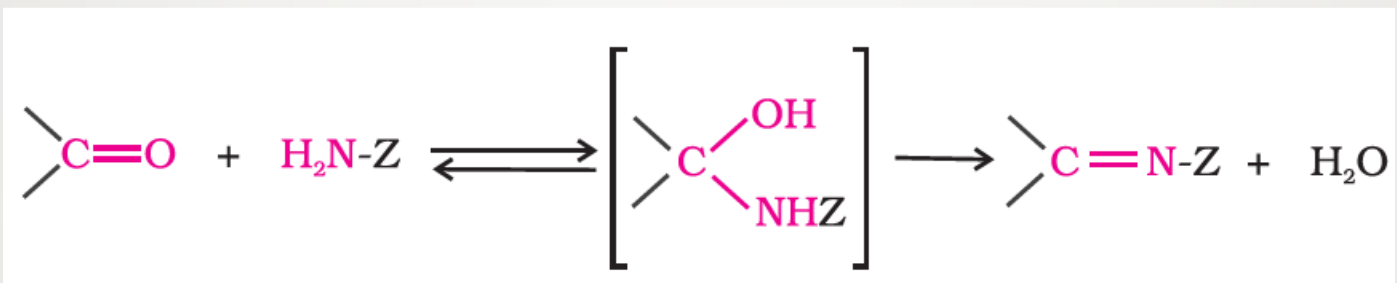


# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions: **Examples**

### (d) Addition of Ammonia and its Derivatives:

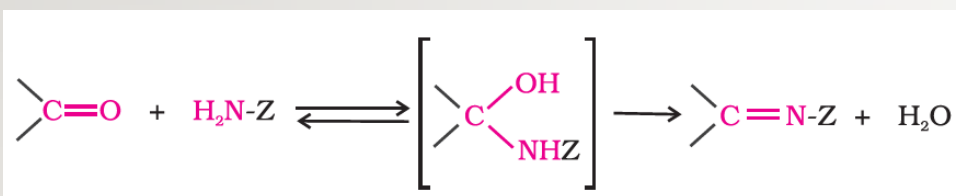
- Nucleophiles, such as ammonia and its derivatives  $\text{H}_2\text{N-Z}$  add to the carbonyl group of aldehydes and ketones.
- The reaction is reversible and **catalyzed by acid**.
- The equilibrium favors the product formation due to **rapid dehydration of the intermediate to form  $>\text{C}=\text{N-Z}$** .

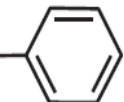

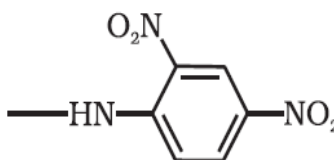
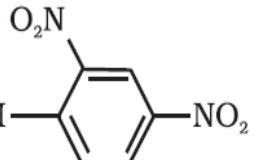

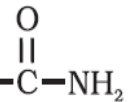


# Chemical Reactions of Aldehydes and Ketones

## 1. Nucleophilic Addition Reactions: **Examples**

### (d) Addition of Ammonia and its Derivatives:



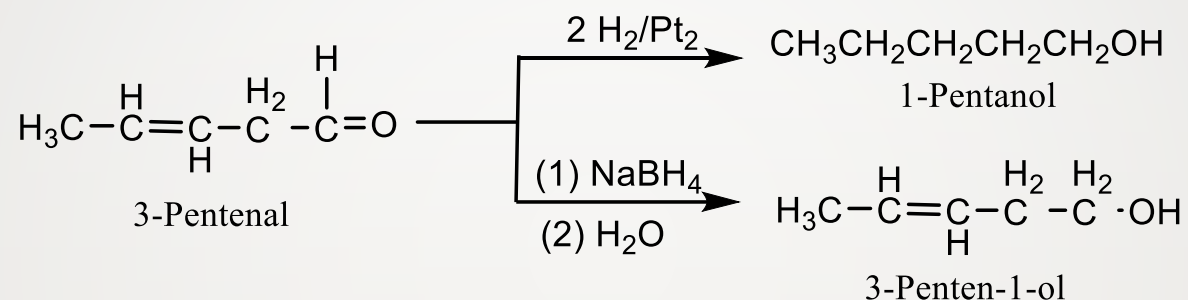
Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\begin{array}{c} \diagup \\ \text{C}=\text{NH} \\ \diagdown \end{array}$	Imine
-R	Amine	$\begin{array}{c} \diagup \\ \text{C}=\text{NR} \\ \diagdown \end{array}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{OH} \\ \diagdown \end{array}$	Oxime
-NH <sub>2</sub>	Hydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}_2 \\ \diagdown \end{array}$	Hydrazone
$\text{—HN—}$ 	Phenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH—} \end{array}$ 	Phenylhydrazone
$\text{—HN—}$ 	2,4-Dinitrophenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH—} \end{array}$ 	2,4 Dinitrophenylhydrazone
$\text{—NH—}$ 	Semicarbazide	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH—} \end{array}$ 	Semicarbazone

# Chemical Reactions of Aldehydes and Ketones

## 2. Reduction

### (i) Reduction to alcohols:

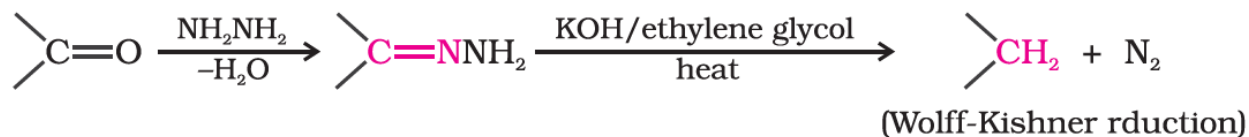
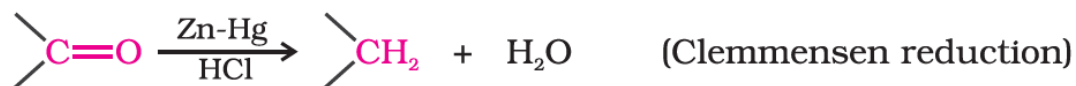
Aldehydes and ketones are **reduced to primary and secondary alcohols** respectively by sodium borohydride ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ) as well as by catalytic hydrogenation



### (ii) Reduction to hydrocarbons:

The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with:

- zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction].
- hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.



# Chemical Reactions of Aldehydes and Ketones

## 3. Oxidation

**Aldehydes are easily oxidized to carboxylic acids** on treatment with *common oxidizing agents* like nitric acid, potassium permanganate, potassium dichromate, etc. Even *mild oxidizing agents*, mainly Tollens' reagent and Fehlings' reagent also oxidize aldehydes.



### (i) Tollens' Test:

- On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal.
- The reaction occurs in alkaline medium.



### (ii) Fehling's Test:

- Fehling reagent comprises of two solutions, **Fehling solution A** is aqueous copper sulphate and **Fehling solution B** is alkaline sodium potassium tartarate.
- Aldehyde are oxidized to carboxylate anion with Fehling's reagent, and a reddish brown precipitate is obtained.





# Chemical Reactions of Aldehydes and Ketones

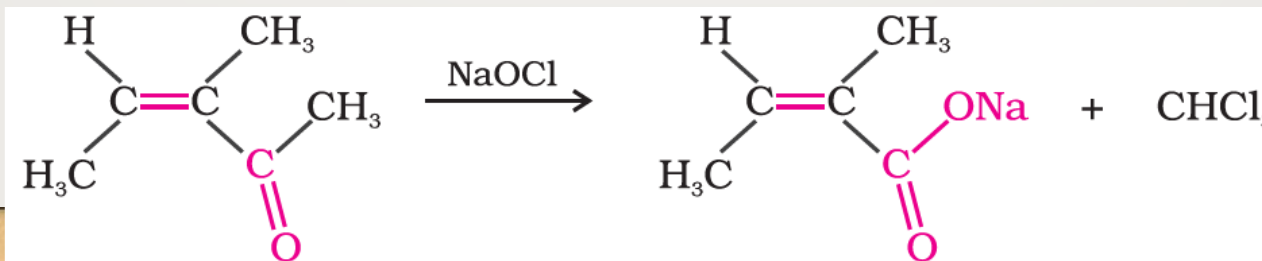
## 3. Oxidation

### (iii) Oxidation of Methyl Ketones by Haloform Reaction:

- Aldehydes and ketones having *at least one methyl group linked to the carbonyl carbon atom* (**methyl ketones**) are *oxidized by sodium hypohalite* to
  - sodium salts of corresponding carboxylic acids* having one carbon atom less than that of carbonyl compound.
  - The methyl group is converted to haloform.



- This oxidation does not affect a carbon-carbon double bond**, if present in the molecule.

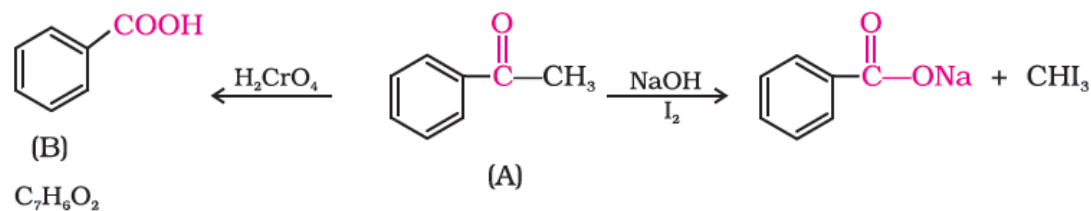
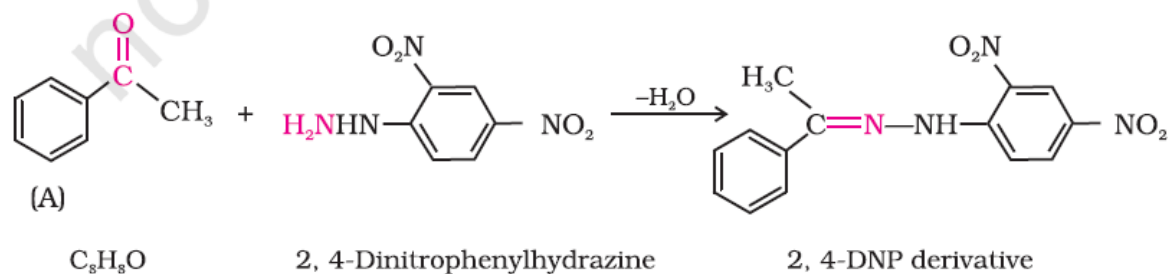


# Questions

**Example 12.4** An organic compound (A) with molecular formula  $C_9H_8O$  forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula  $C_7H_6O_2$ . Identify the compounds (A) and (B) and explain the reactions involved.

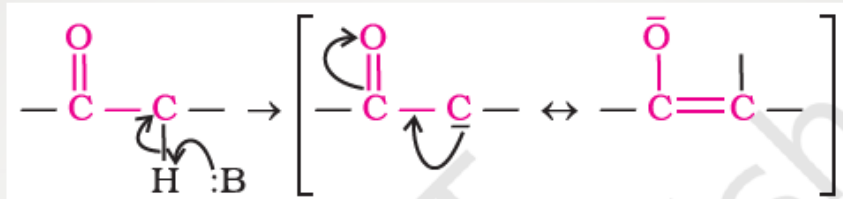
**Solution** (A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows:



# Chemical Reactions of Aldehydes and Ketones

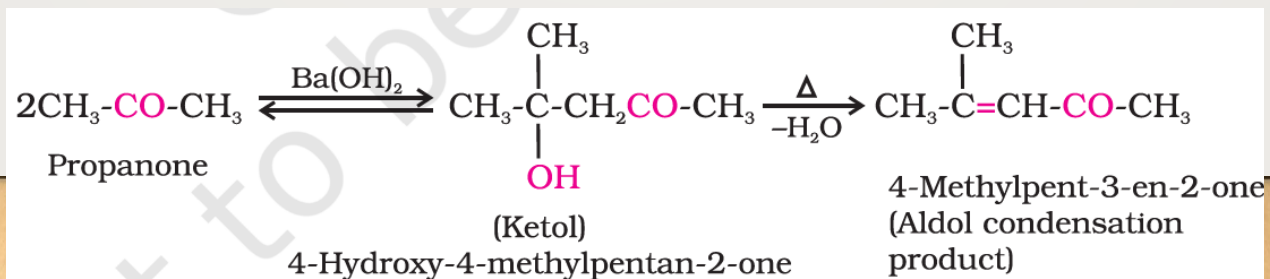
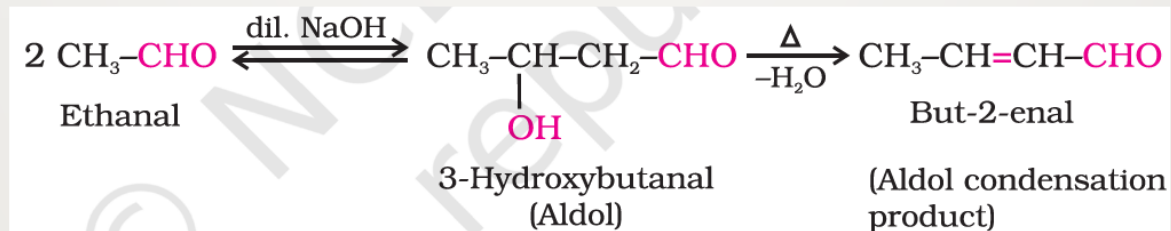
## 4. Reactions due to $\alpha$ -hydrogen



- The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is *due to the strong electron withdrawing effect of the carbonyl group and resonance stabilization of the conjugate base.*

### (i) Aldol condensation:

Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst *to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxyl ketones (ketol), respectively.*



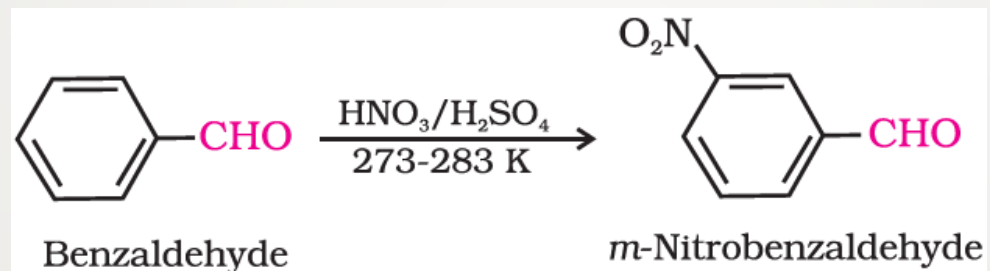


# Chemical Reactions of Aldehydes and Ketones

## 5. Other Reactions

### (ii) Electrophilic Substitution Reaction:

- Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



# Questions

## Intext Questions

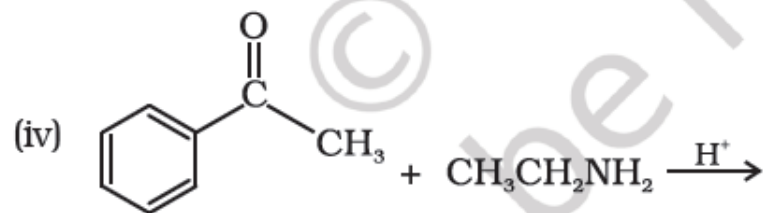
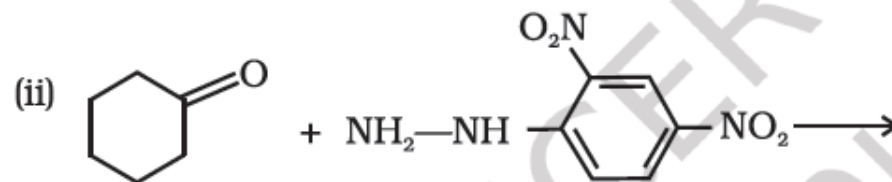
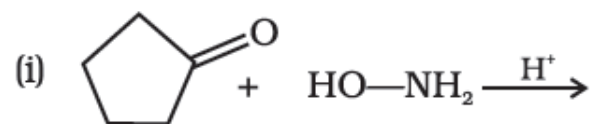
**12.4** Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.

(ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

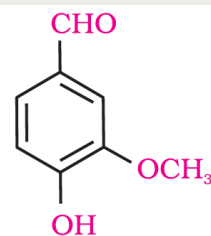
*Hint:* Consider steric effect and electronic effect.

**12.5** Predict the products of the following reactions:

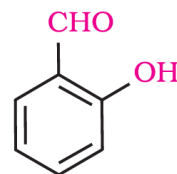


# Uses of Aldehydes and Ketones

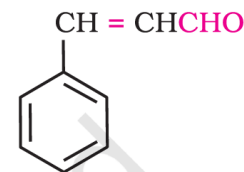
- *In chemical industry* aldehydes and ketones are used as *solvents, starting materials and reagents for the synthesis of other products.*
- *Formaldehyde* is well known as formalin (40%) solution used to *preserve biological specimens* and to *prepare Bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues* and *other polymeric products.*
- *Acetaldehyde* is used primarily as a starting material in the *manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers* and *drugs.*
- *Benzaldehyde* is used in *perfumery* and in *dye industries.*
- *Acetone and ethyl methyl ketone* are common *industrial solvents.*
- They add fragrance and flavor to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



Vanillin



Salicylaldehyde



Cinnamaldehyde