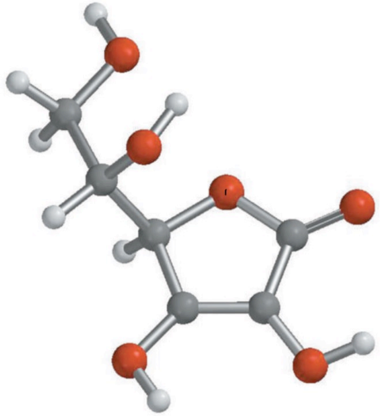
CHEM 245

Organic Chemistry II

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 244

CREDIT HOURS; 2 (2+0)



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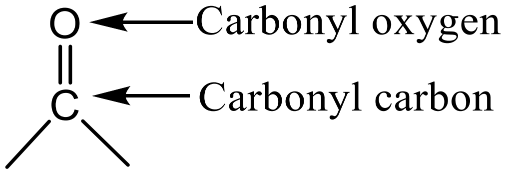
Carbonyl Compounds; Aldehydes and Ketones

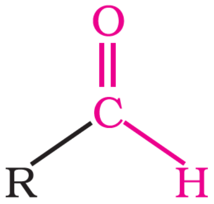
Based on NCERT

Carbonyl Compounds

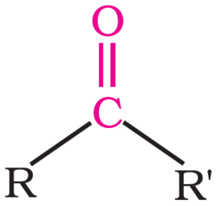
- **Organic compounds** containing carbon-oxygen double bond (>C=O) called ***carbonyl group***, which is one of the most important functional groups in organic chemistry.
- In **aldehydes**, the carbonyl group is bonded to a carbon and hydrogen.
- In the **ketones**, the carbonyl group is bonded to two carbon atoms.
- In **Carboxylic acids**, the carbonyl group is bonded to oxygen.
- Their **Carboxylic acids derivatives** (e.g. esters, anhydrides, amides and acyl halides).



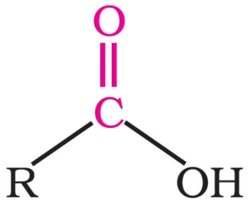
The carbonyl group



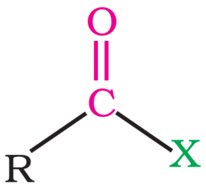
Aldehyde



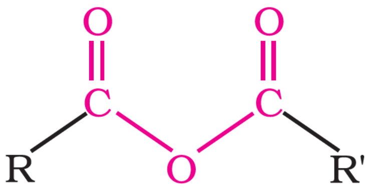
Ketone



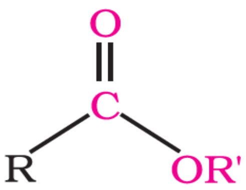
Carboxylic acid



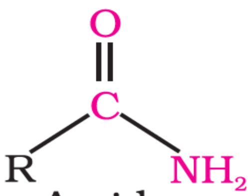
Acyl halide; X = (Halogen)



Acid anhydride



Ester



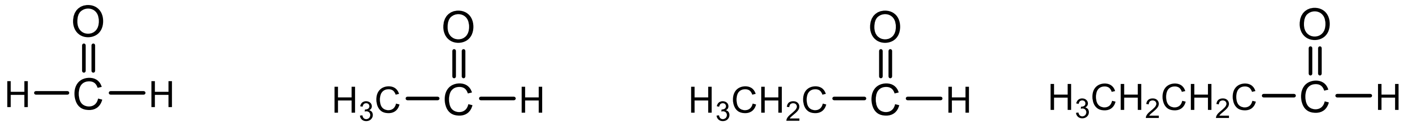
Amide

Aldehydes and Ketones

Nomenclature of Aldehydes

A) Common Names

- The **common names of most aldehydes** are derived from the common names of the corresponding carboxylic acids by *replacing the ending –ic of acid with aldehyde*.

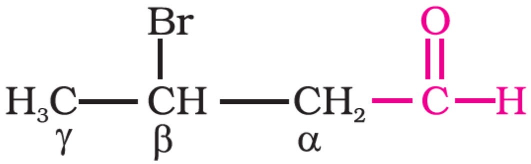


$H-\overset{\overset{O}{\|}}{C}-H \quad H_3C-\overset{\overset{O}{\|}}{C}-H \quad H_3CH_2C-\overset{\overset{O}{\|}}{C}-H \quad H_3CH_2CH_2C-\overset{\overset{O}{\|}}{C}-H$

Common name:	Formaldehyde	Acetaldehyde	Propionaldehyde	Butyraldehyde
IUPAC name:	Methanal	Ethanal	Propanal	Butanal

- The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc.

The α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on.



$\underset{\gamma}{H_3C}-\underset{\beta}{\overset{\overset{Br}{|}}{CH}}-\underset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-H$

β-Bromobutyraldehyde

Nomenclature of Aldehydes

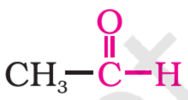
B) IUPAC System

- **Aliphatic aldehydes** are named by **dropping the suffix -e** from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and **replacing it with the suffix *-al***.

Alkane - e + *al* = Alkanal

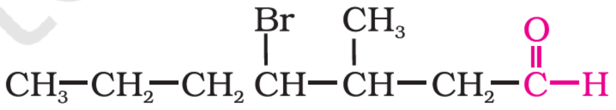
  - In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group.

    The CHO group is assigned the number 1 position.



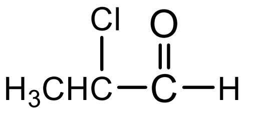
$CH_3-\overset{\overset{O}{\|}}{C}-H$

Ethanal



$CH_3-CH_2-CH_2\overset{\overset{Br}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-H$

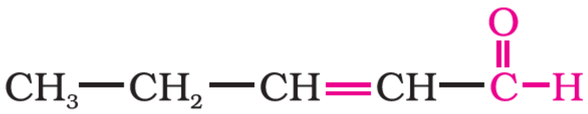
4-Bromo-3-methylheptanal



$H_3CH\overset{\overset{Cl}{|}}{C}-\overset{\overset{O}{\|}}{C}-H$

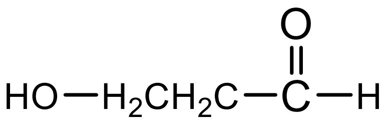
2-Chloropropanal

  - **The CHO group takes precedence over other functional groups such as -OH, C=C, or C-C triple bond.**



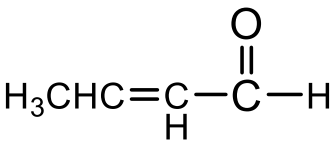
$CH_3-CH_2-CH=CH-\overset{\overset{O}{\|}}{C}-H$

Pent-2-enal



$HO-H_2CH_2C-\overset{\overset{O}{\|}}{C}-H$

3-Hydroxypropanal

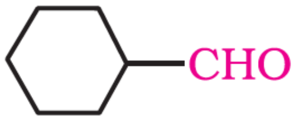


$H_3CHC=\underset{H}{C}-\overset{\overset{O}{\|}}{C}-H$

2-Butenal

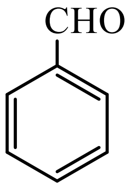
Nomenclature of Aldehydes

- When the **aldehyde group is attached to a ri**ng, the *suffix carbaldehyde is added after the full name of the cycloalkane*.

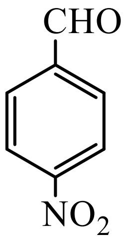


Cyclohexanecarbaldehyde

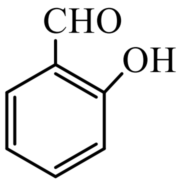
- The name of the simplest **aromatic aldehyde** carrying the aldehyde group on a benzene ring is benzenecarbaldehyde.
- However, **the common name benzaldehyde is also accepted by IUPAC**.
- **Other aromatic aldehydes** are hence named as **substituted benzaldehydes**.



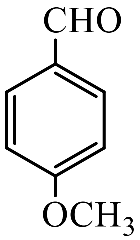
Benzaldehyde
(Benezenecarbaldehyde)



p-Nitrobenzaldehyde
4-Nitrobenzaldehyde
4-Nitrobenzenecarbaldehydealdehyde



o-Hydroxybenzaldehyde
(Salicylaldehyde)



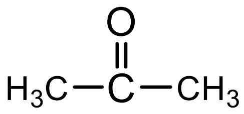
p-Methoxybenzaldehyde
(Anisaldehyde)

Nomenclature of Ketones

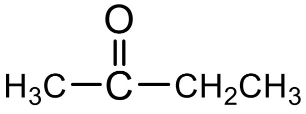
A) Common Names

- The **common names of ketones** are derived by naming two alkyl or aryl groups bonded to the carbonyl group.

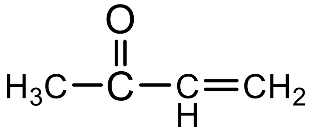
Alkyl ketone


$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

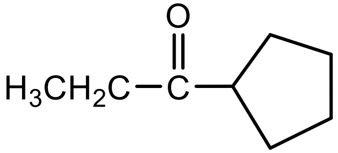
Acetone
(Dimethyl ketone)


$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$

Methyl ethyl ketone

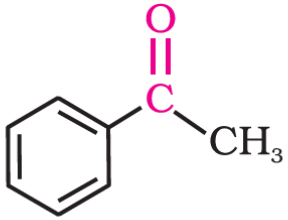

$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{H}{C}=CH_2$

Methyl vinyl ketone

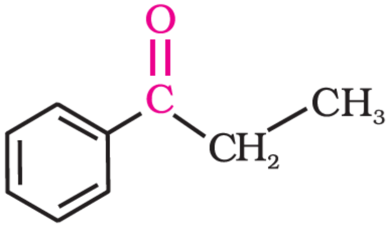


Ethyl cyclopentyl ketone

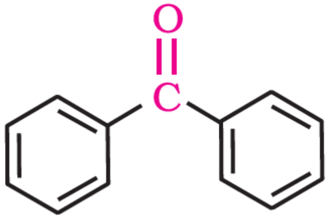
- Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.



Acetophenone



Propiophenone



Benzophenone

- The **locations of substituents** are indicated by Greek letters, α α', β β' and so on beginning with the carbon atoms next to the carbonyl group, indicated as αα'.

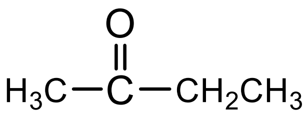
Nomenclature of Ketones

B) IUPAC System

- We find the longest continuous chain carrying the carbonyl group.
- Name the parent structure by **dropping the suffix –e**, and replacing it with the **suffix *-one***.

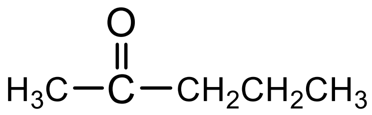
Alkane - e + *one* = Alkanone

- The **numbering** begins from the end nearer to the carbonyl group.
- The **substituents** are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain.



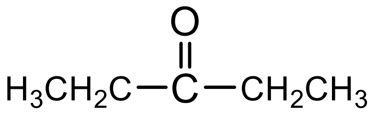
$H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

Butanone



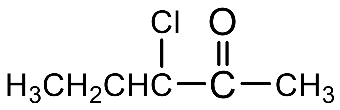
$H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$

2-Pentanone
(*not* 4-Pentanone)



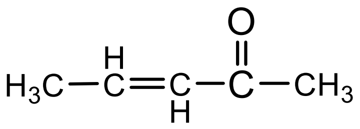
$H_3CH_2C-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

3-Pentanone



$H_3CH_2CH\overset{\overset{Cl}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

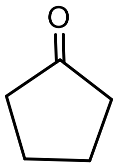
3-Chloro-2-pentanone
(*not* 3-Chloro-4-pentanone)



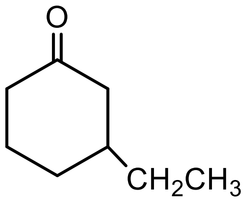
$H_3C-\overset{H}{C}=\underset{H}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

3-Penten-2-one
(*not* 2-Penten-4-one)

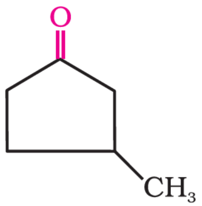
- For **cyclic ketones**, numbering always starts from the C=O group; the carbonyl carbon is numbered one.



Cyclopentanone

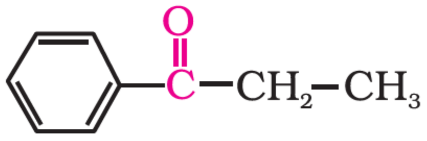


3-Ethlcyclohexanone
(*not* 5-Methylcyclohexanone)

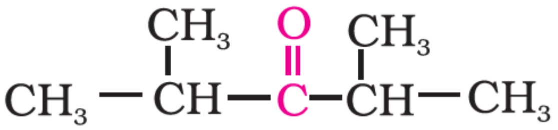


3-Methylcyclopentanone

Nomenclature of Aldehydes and Ketones; Examples

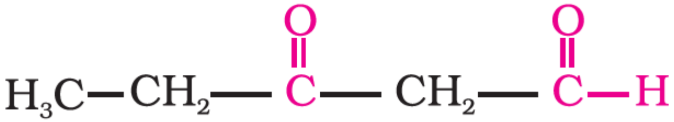


1-Phenylpropan-1-one



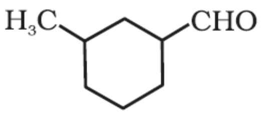
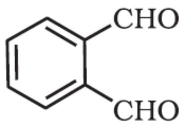
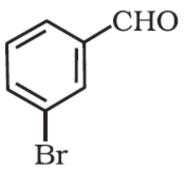
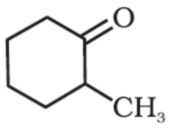
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

2,4-Dimethylpentan-3-one



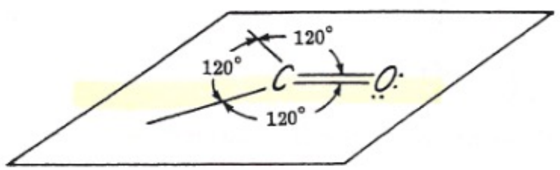
$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

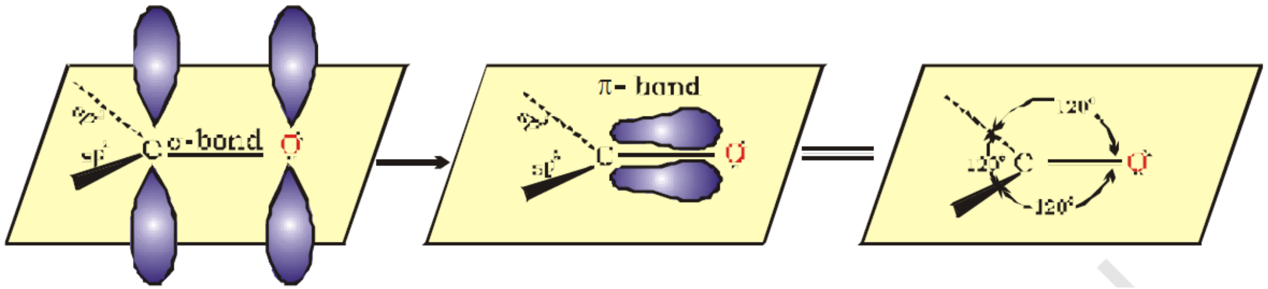
3-Oxopentanal

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

Structure of the Carbonyl Group

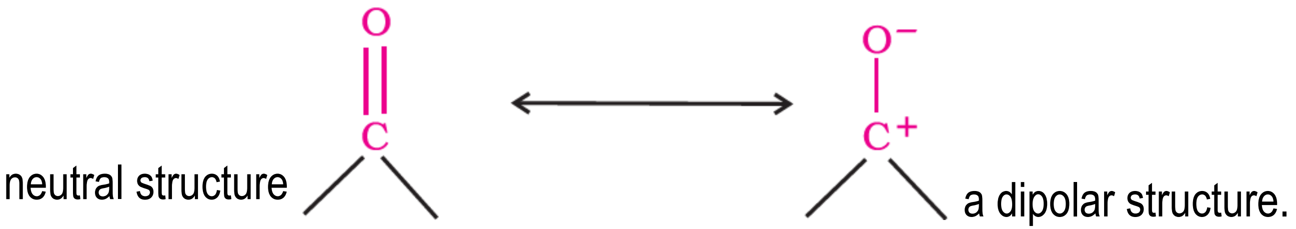
- The carbonyl carbon atom is ***sp*²-hybridised** and forms ***three sigma (σ) bonds and one π-bond***.
- In addition, *the oxygen atom also has two non bonding electron pairs*.
- The **bond angles are approximately 120°** as expected of a trigonal coplanar structure





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**.



neutral structure

a dipolar structure.

Questions

Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde
(ii) 3-Hydroxybutanal
(iii) 2-Hydroxycyclopentane carbaldehyde
(iv) 4-Oxopentanal
(v) Di-sec. butyl ketone
(vi) 4-Fluoroacetophenone

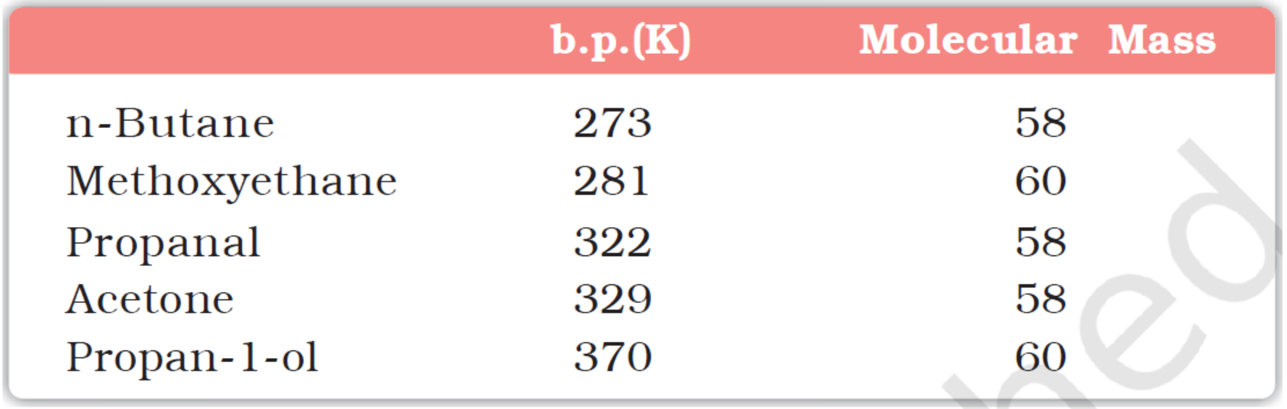
Physical Properties of Aldehydes and Ketones

○ Physical State

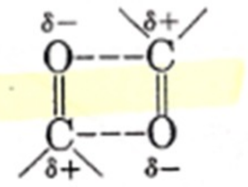
- **Methanal** is a gas at room temperature.
- **Ethanal** is a volatile liquid.
- **Other aldehydes and ketones** are liquid or solid at room temperature.

○ Boiling Points

- The boiling points of aldehydes and ketones are **higher than hydrocarbons and ethers** of comparable molecular masses.
- Also, their boiling points are **lower than those of alcohols** of similar molecular masses *due to absence of intermolecular hydrogen bonding*.



	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60



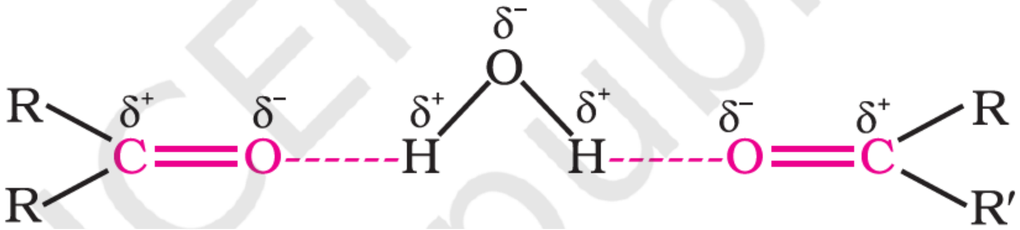
Dipole-dipole attractions among carbonyl compounds

Dipole-dipole attractions, although important, are not as strong as interactions due to hydrogen bonding.

Physical Properties of Aldehydes and Ketones

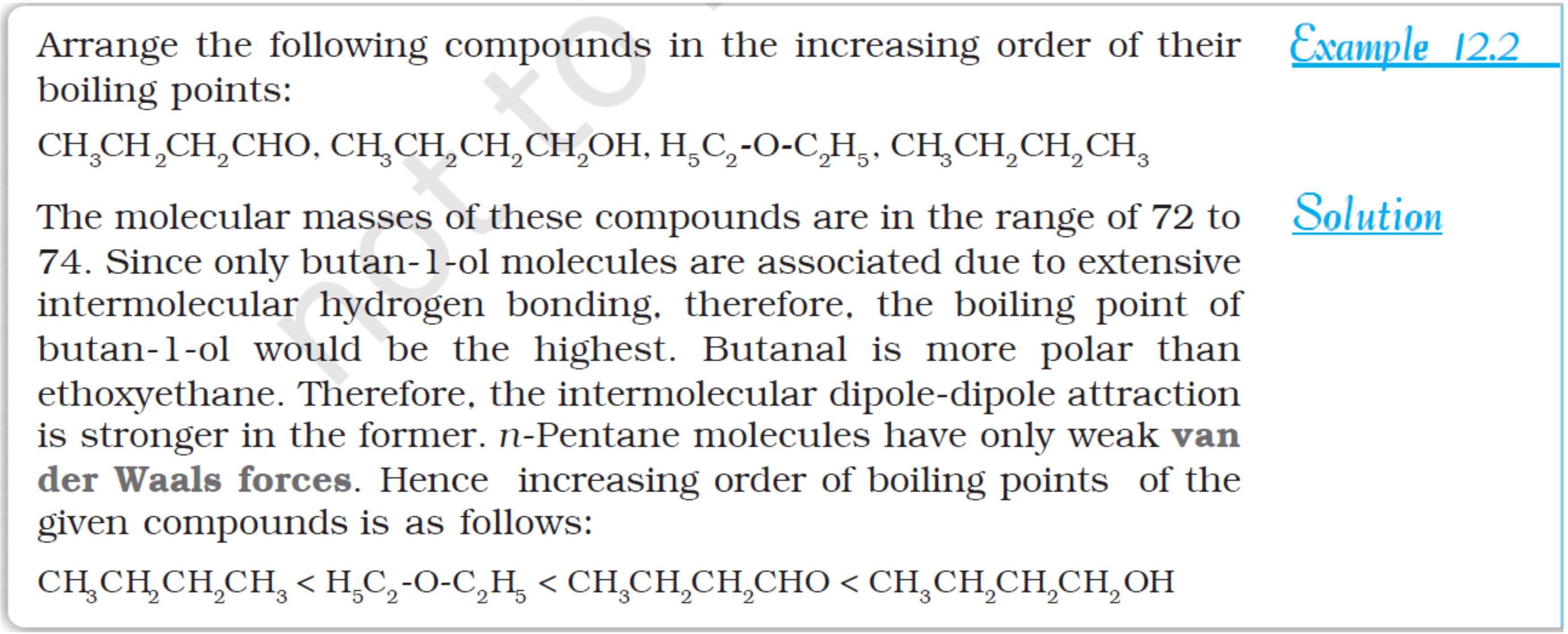
○ Solubility in Water

- The ***lower members of aldehydes and ketones*** such as methanal, ethanal and propanone are ***miscible with water*** in all proportions, because *they form hydrogen bond with water*.



- However, *the solubility of aldehydes and ketones decreases* rapidly *on increasing the length of alkyl chain*.
- All aldehydes and ketones are *fairly soluble in organic solvents* like benzene, ether, methanol, chloroform, etc.
- The lower aldehydes have sharp pungent odors.
- As the size of the molecule increases, the odor becomes less pungent and more fragrant.
- In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavoring agents.

Questions



Arrange the following compounds in the increasing order of their boiling points:

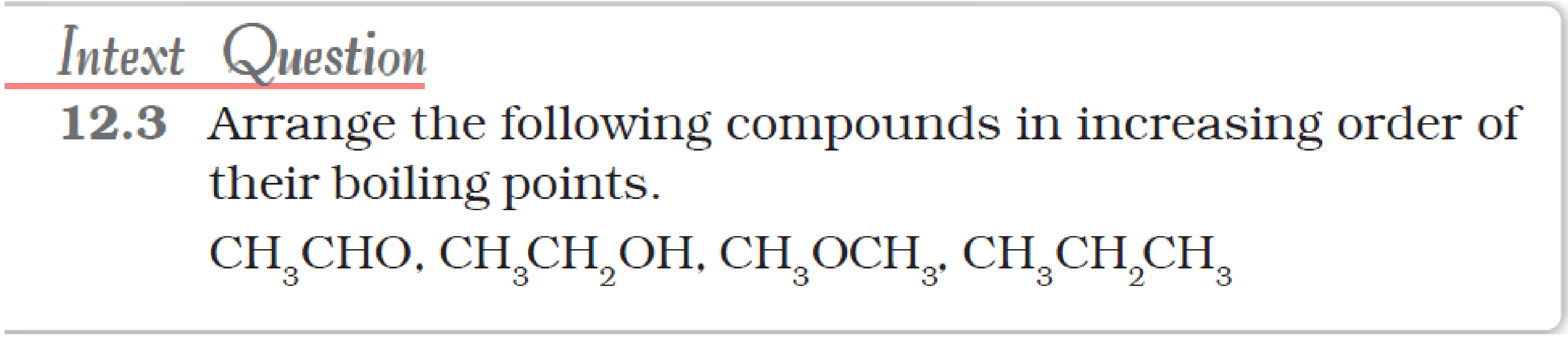
Example 12.2

$CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, H_5C_2-O-C_2H_5, $CH_3CH_2CH_2CH_3$

Solution

The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. *n*-Pentane molecules have only weak **van der Waals forces**. Hence increasing order of boiling points of the given compounds is as follows:

$CH_3CH_2CH_2CH_3 < H_5C_2\text{-O-}C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$



Intext Question

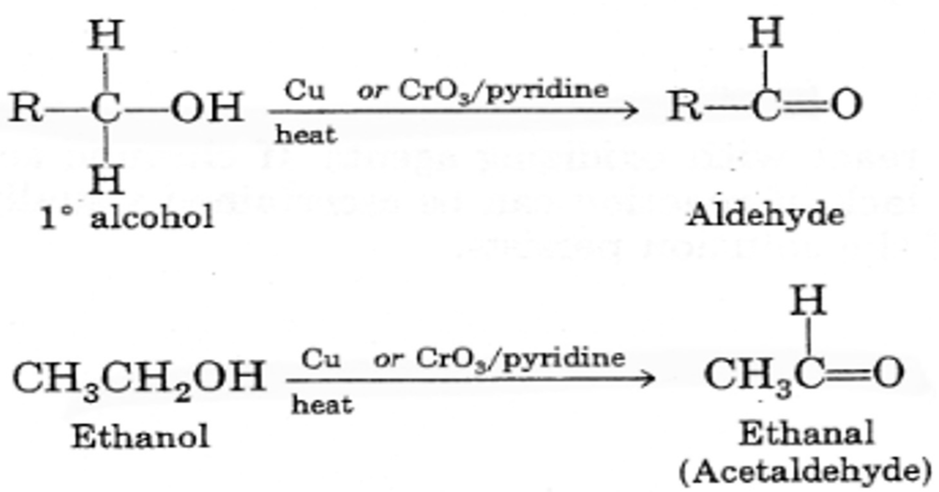
12.3 Arrange the following compounds in increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Preparation of Aldehydes and Ketones

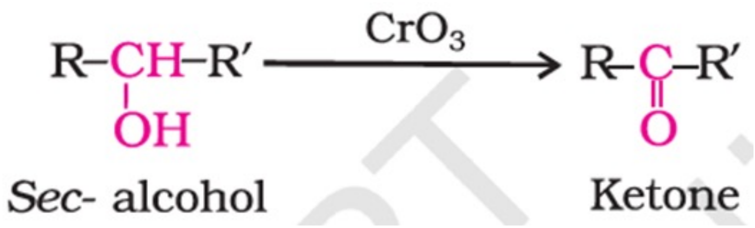
1. By oxidation of Alcohols

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



$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow[\text{heat}]{\text{Cu} \quad or\ CrO_3/\text{pyridine}} R-\overset{\overset{H}{|}}{C}=O$$

$$CH_3CH_2OH \xrightarrow[\text{heat}]{\text{Cu} \quad or\ CrO_3/\text{pyridine}} CH_3\overset{\overset{H}{|}}{C}=O$$

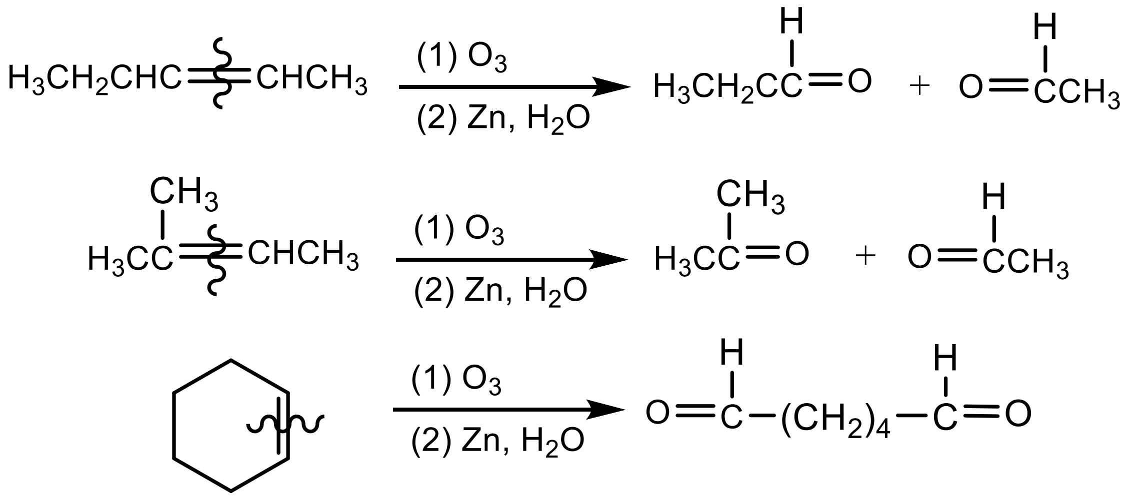


$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} R-\underset{\underset{O}{\|}}{C}-R'$$

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.*

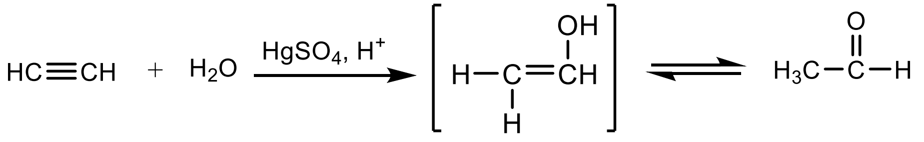


$$H_3CH_2CHC{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3CH_2C\overset{H}{C}{=}O + O{=}\overset{H}{C}CH_3$$

$$H_3C\overset{CH_3}{C}{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3C\overset{CH_3}{C}{=}O + O{=}\overset{H}{C}CH_3$$

$$\xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} O{=}\overset{H}{C}-(CH_2)_4-\overset{H}{C}{=}O$$

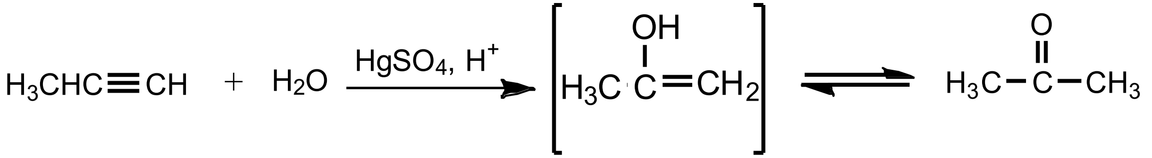
(ii) Hydration of Alkynes: *Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction*



$$HC{\equiv}CH + H_2O \xrightarrow{HgSO_4,\ H^+} \left[H-\underset{H}{C}{=}\overset{OH}{C}H \right] \rightleftharpoons H_3C-\overset{O}{\overset{\|}{C}}-H$$

Vinyl alcohol (enol form of acetaldehyde, unstable) (<1%)

Acetaldehyde (keto form, stable) (>99%)



$$H_3CHC{\equiv}CH + H_2O \xrightarrow{HgSO_4,\ H^+} \left[H_3C\overset{OH}{C}{=}CH_2 \right] \rightleftharpoons H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

(enol form, unstable) (<1%)

(keto form, stable) (>99%)

Preparation of Aldehydes and Ketones

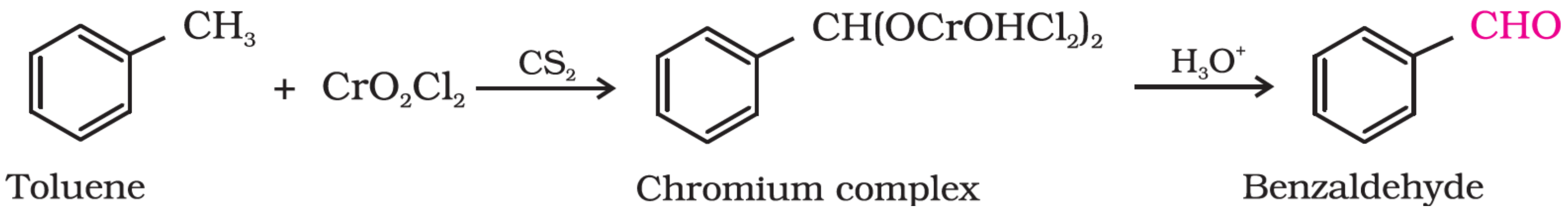
2. From Hydrocarbons

(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.

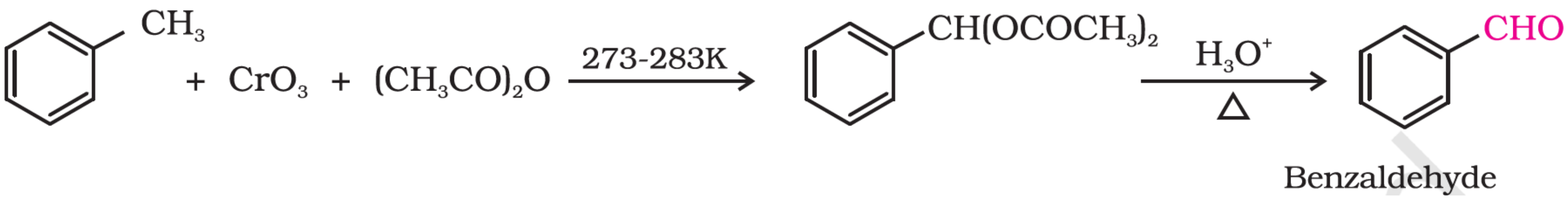
(a) Use of chromyl chloride (CrO_2Cl_2) (Etard reaction):

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



(b) Use of chromic oxide (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.



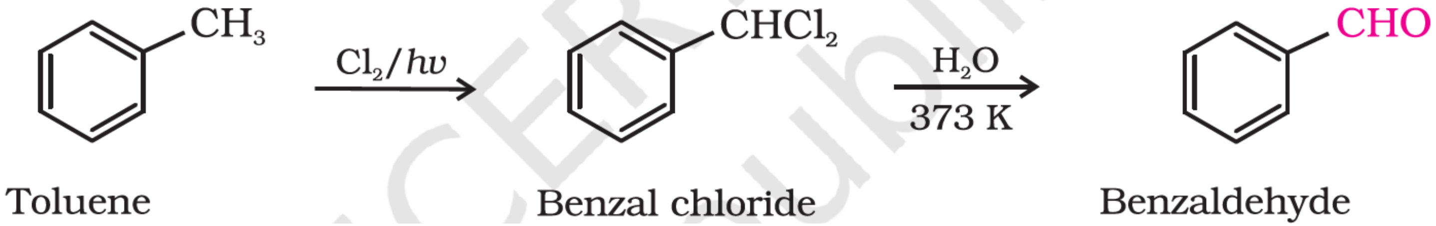
Preparation of Aldehydes and Ketones

2. From Hydrocarbons

(iv) By side chain chlorination followed by hydrolysis

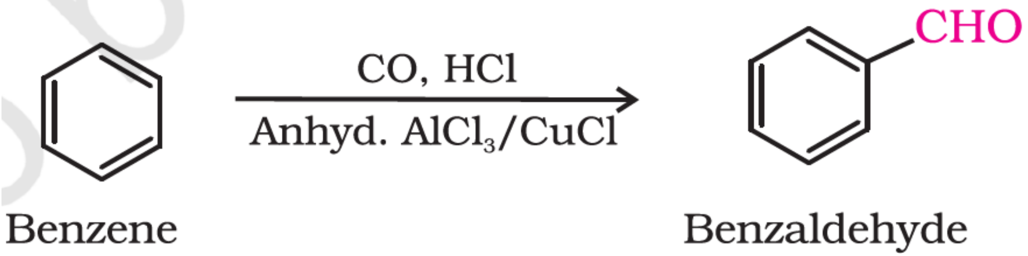
Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

This is a commercial method of manufacture of benzaldehyde.



(v) By Gatterman – Koch reaction

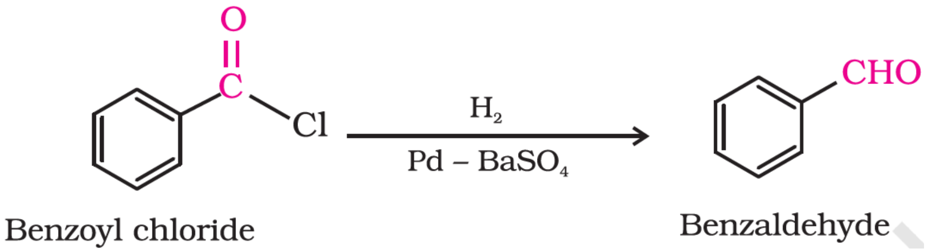
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminum chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



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**.*



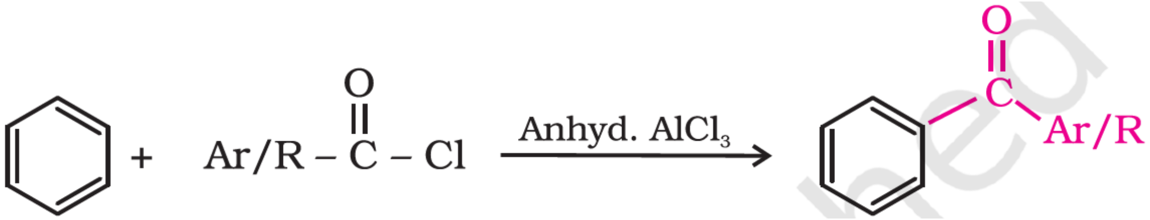
- *Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, **gives ketones**.*

$$2\,R - Mg - X \quad + \quad CdCl_2 \longrightarrow R_2Cd \quad + \quad 2Mg(X)Cl$$

$$2\,R' - \underset{\underset{O}{\|}}{C} - Cl \quad + \quad R_2Cd \longrightarrow 2\,R' - \underset{\underset{O}{\|}}{C} - R \; + \; CdCl_2$$

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*)

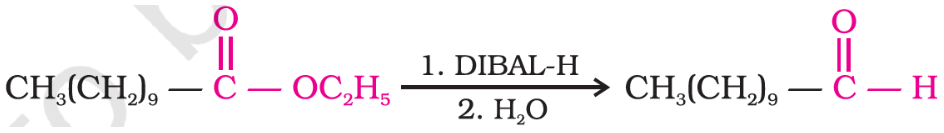
- ***Nitriles are reduced*** *to corresponding imine with stannous chloride in the presence of hydrochloric acid,* ***which on hydrolysis*** *give corresponding* ***aldehyde****.*

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

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

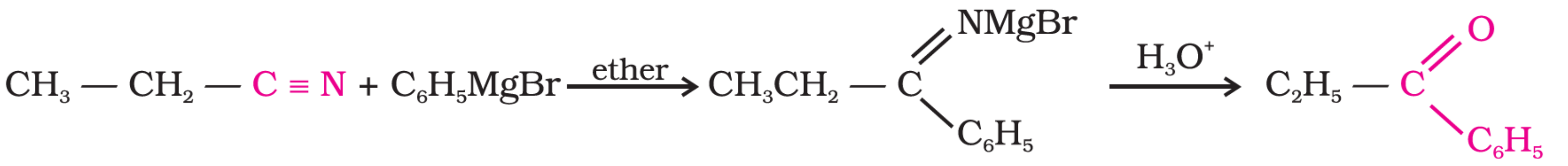
$$CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CHO$$

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



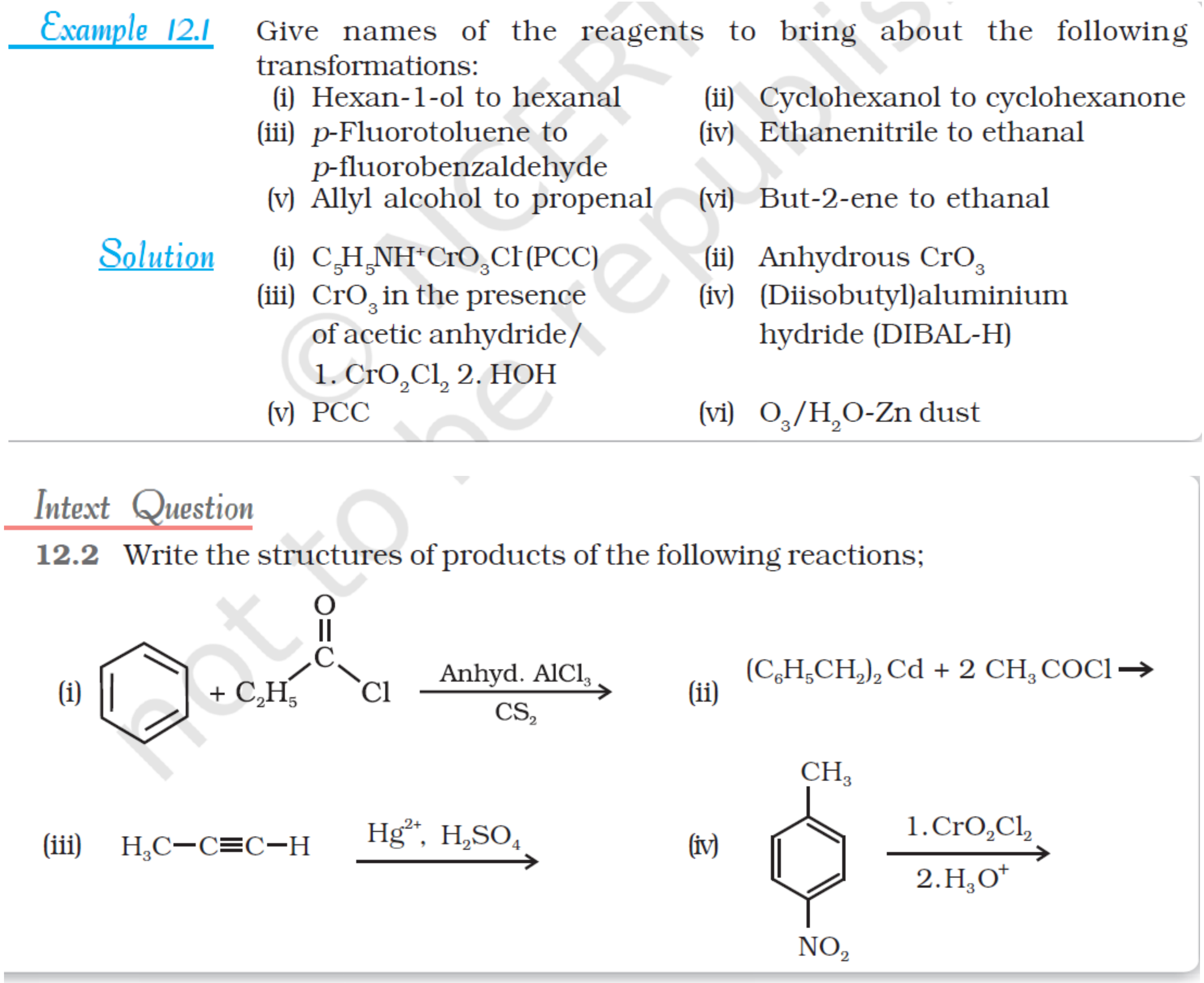
$$CH_3(CH_2)_9 - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9 - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

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



Propiophenone
(1-Phenylpropanone)

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;

(i) $+\ C_2H_5\overset{\overset{O}{\|}}{C}Cl \xrightarrow[CS_2]{\text{Anhyd. AlCl}_3}$

(ii) $(C_6H_5CH_2)_2Cd + 2\ CH_3COCl \longrightarrow$

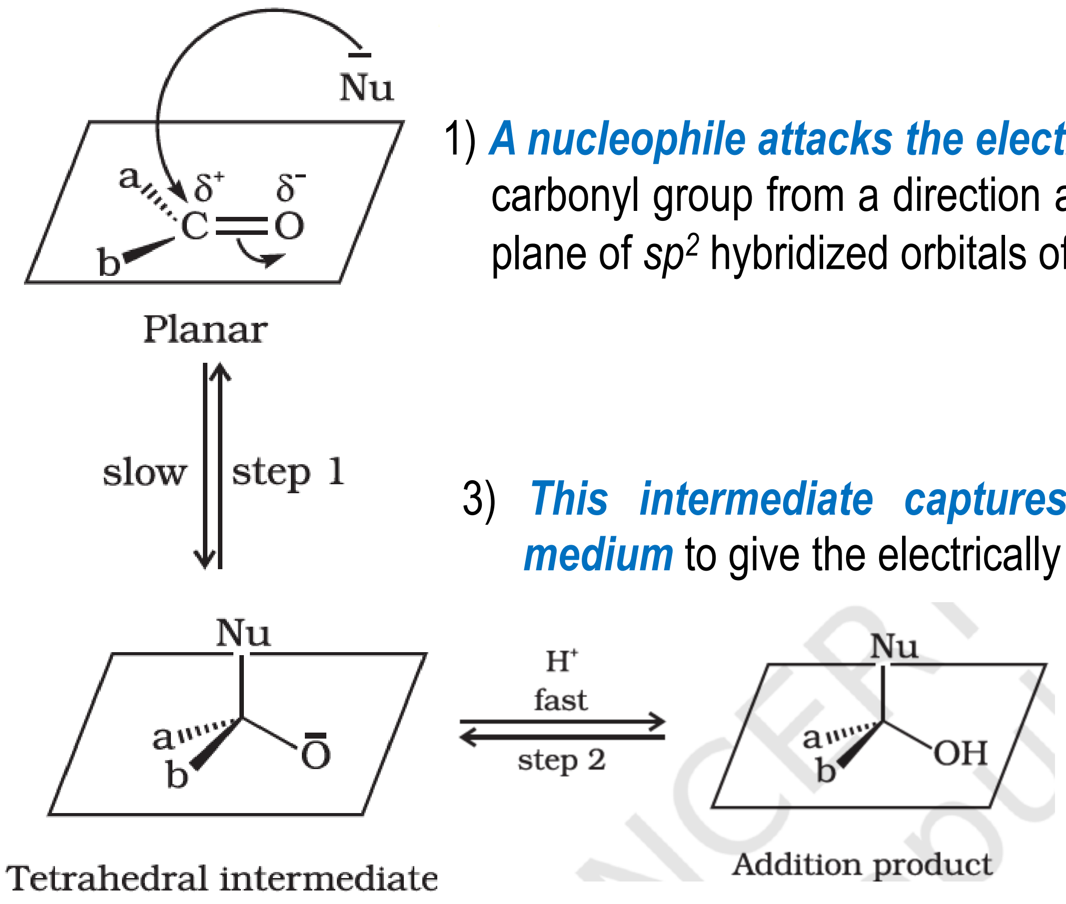
(iii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iv) $\xrightarrow[2.H_3O^+]{1.CrO_2Cl_2}$

Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions

(i) Mechanism of Nucleophilic Addition Reactions



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.

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

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

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

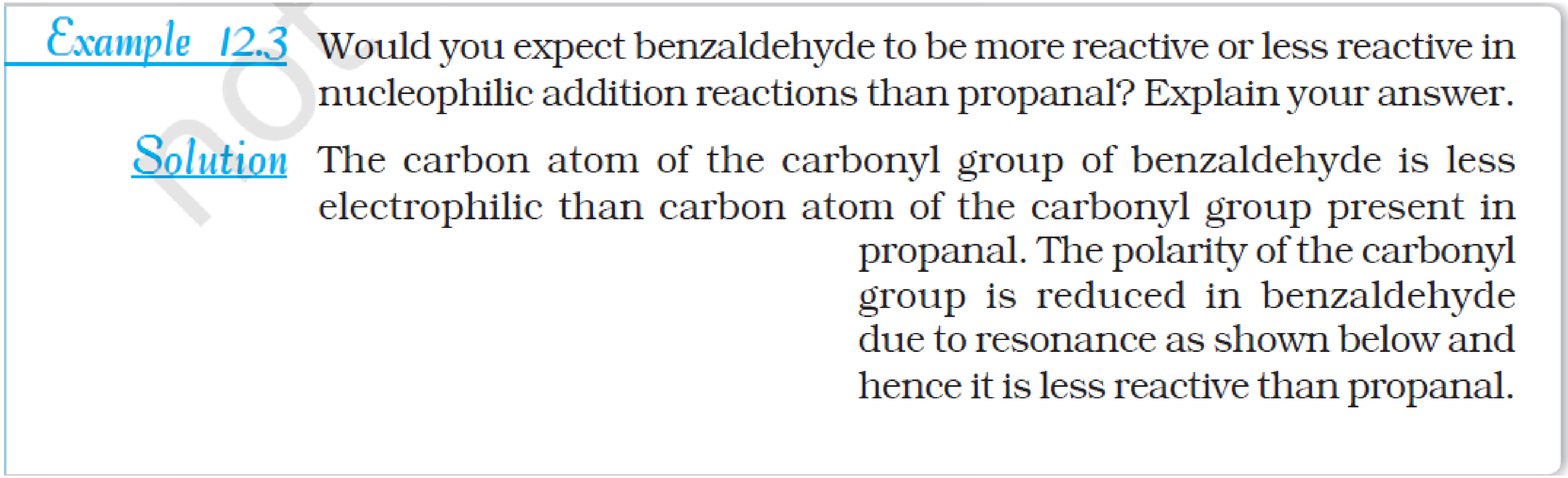
Chemical Reactions of Aldehydes and Ketones

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.

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.

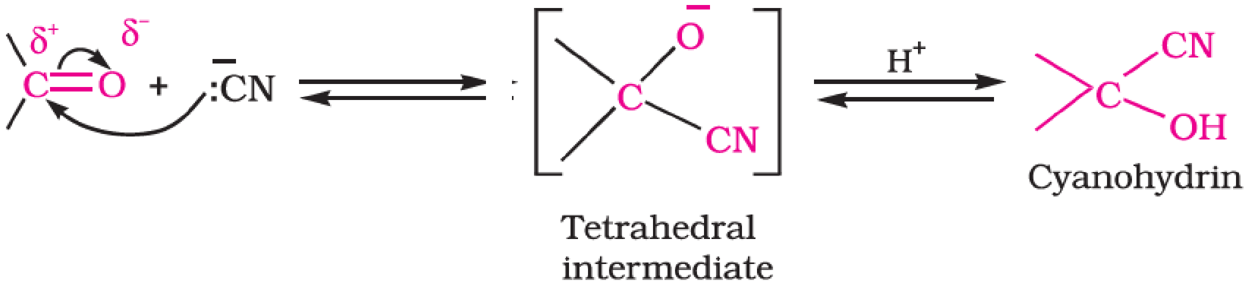
Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: Examples

(a) Addition of hydrogen cyanide (HCN):

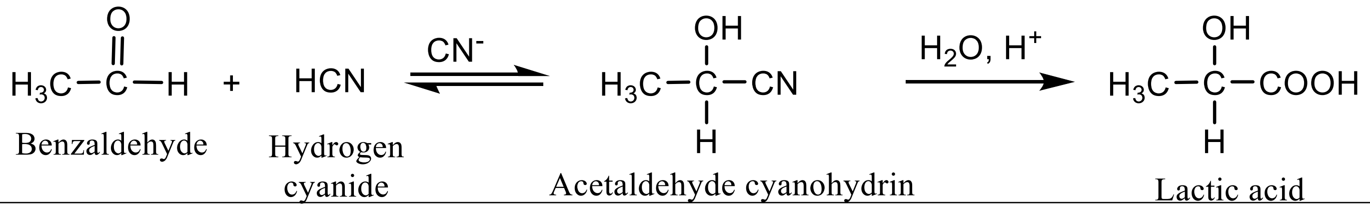
- Aldehydes and ketones react with hydrogen cyanide (HCN) to yield **cyanohydrins**.
- This reaction is catalyzed by a base and the generated cyanide ion (CN-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.
- Cyanohydrins are useful synthetic intermediates.

$$HCN + OH^- \rightleftharpoons :\overline{C}N + H_2O$$



Tetrahedral intermediate

Cyanohydrin



$$H_3C-\overset{O}{\overset{\|}{C}}-H + HCN \xrightleftharpoons{CN^-} H_3C-\underset{H}{\overset{OH}{C}}-CN \xrightarrow{H_2O,\ H^+} H_3C-\underset{H}{\overset{OH}{C}}-COOH$$

Benzaldehyde

Hydrogen cyanide

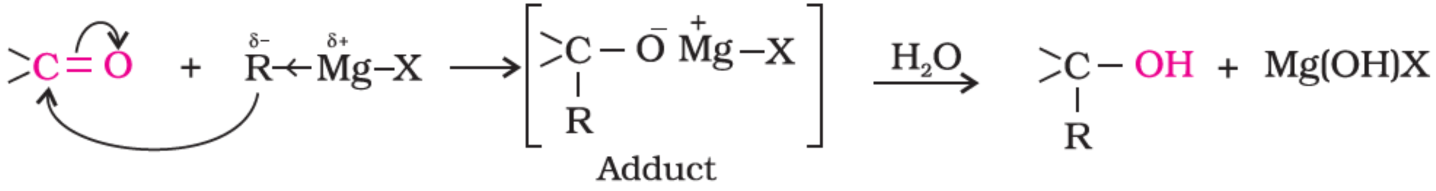
Acetaldehyde cyanohydrin

Lactic acid

Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: Examples

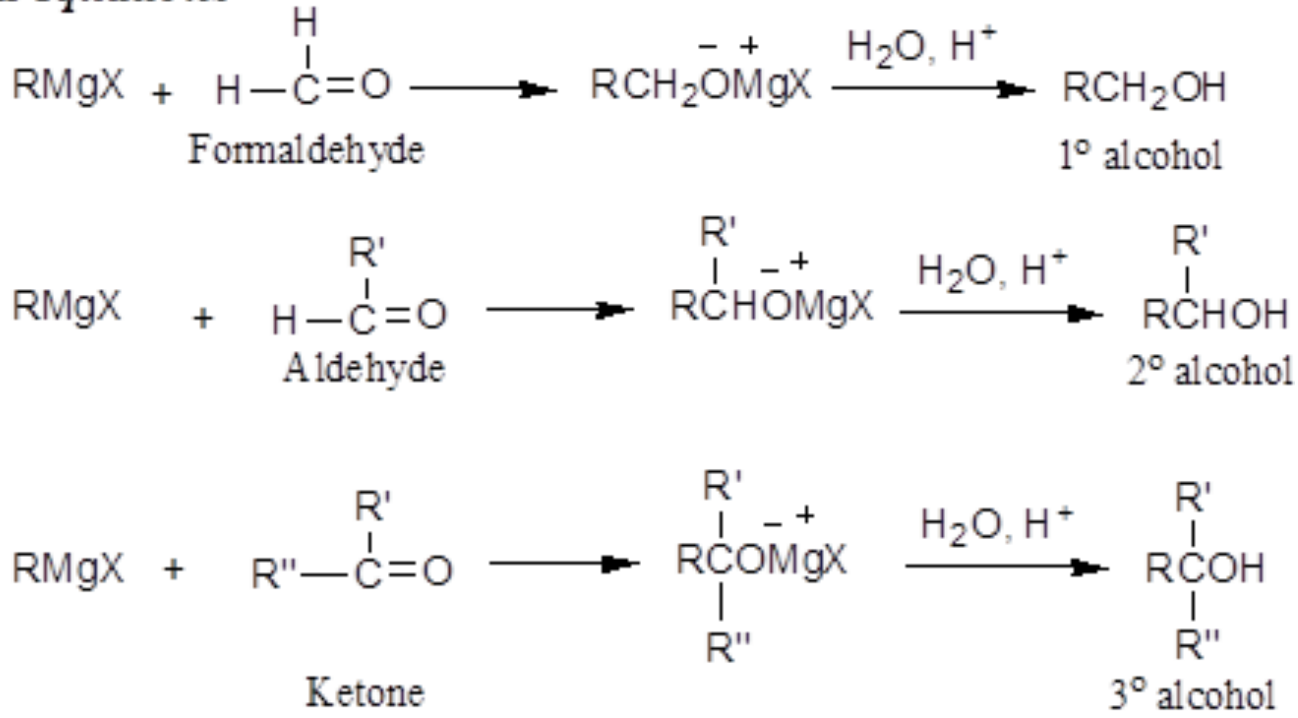
(b) Addition of Grignard Reagents:



$$>C=O + \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X \longrightarrow \left[>\underset{R}{\underset{|}{C}}-\bar{O}\,\overset{+}{Mg}-X\right] \xrightarrow{H_2O} >\underset{R}{\underset{|}{C}}-OH + Mg(OH)X$$

Adduct

General equations



$$RMgX + H-\overset{H}{\overset{|}{C}}=O \longrightarrow RCH_2\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} RCH_2OH$$

Formaldehyde — 1° alcohol

$$RMgX + H-\overset{R'}{\overset{|}{C}}=O \longrightarrow R\overset{R'}{\overset{|}{C}}H\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} R\overset{R'}{\overset{|}{C}}HOH$$

Aldehyde — 2° alcohol

$$RMgX + R''-\overset{R'}{\overset{|}{C}}=O \longrightarrow R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}OH$$

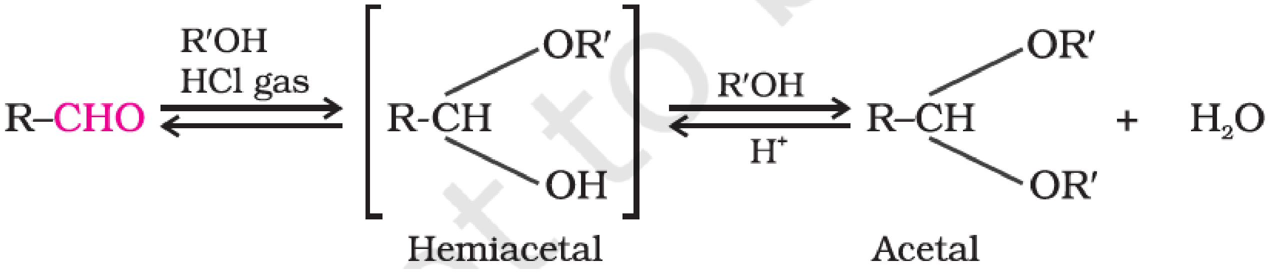
Ketone — 3° alcohol

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.

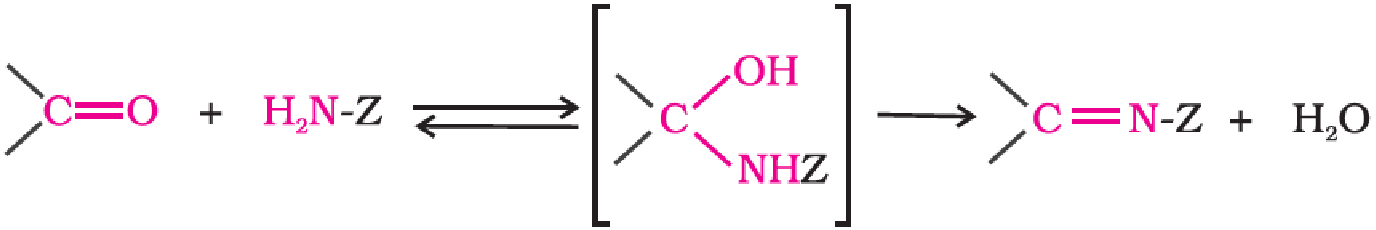


Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: Examples

(d) Addition of Ammonia and its Derivatives:

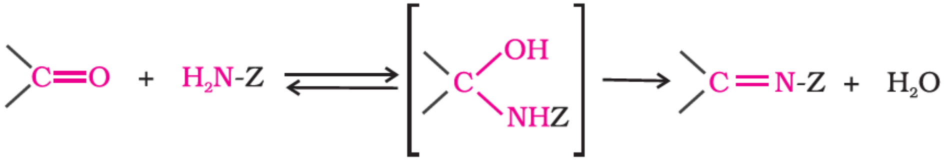
- Nucleophiles, such as ammonia and its derivatives $H_2N\text{-}Z$ add to the carbonyl group of aldehydes and ketones.
- The reaction is reversible and catalyzed by acid.
- The equilibrium favors the product formation due to rapid dehydration of the intermediate to form >C=N-Z.



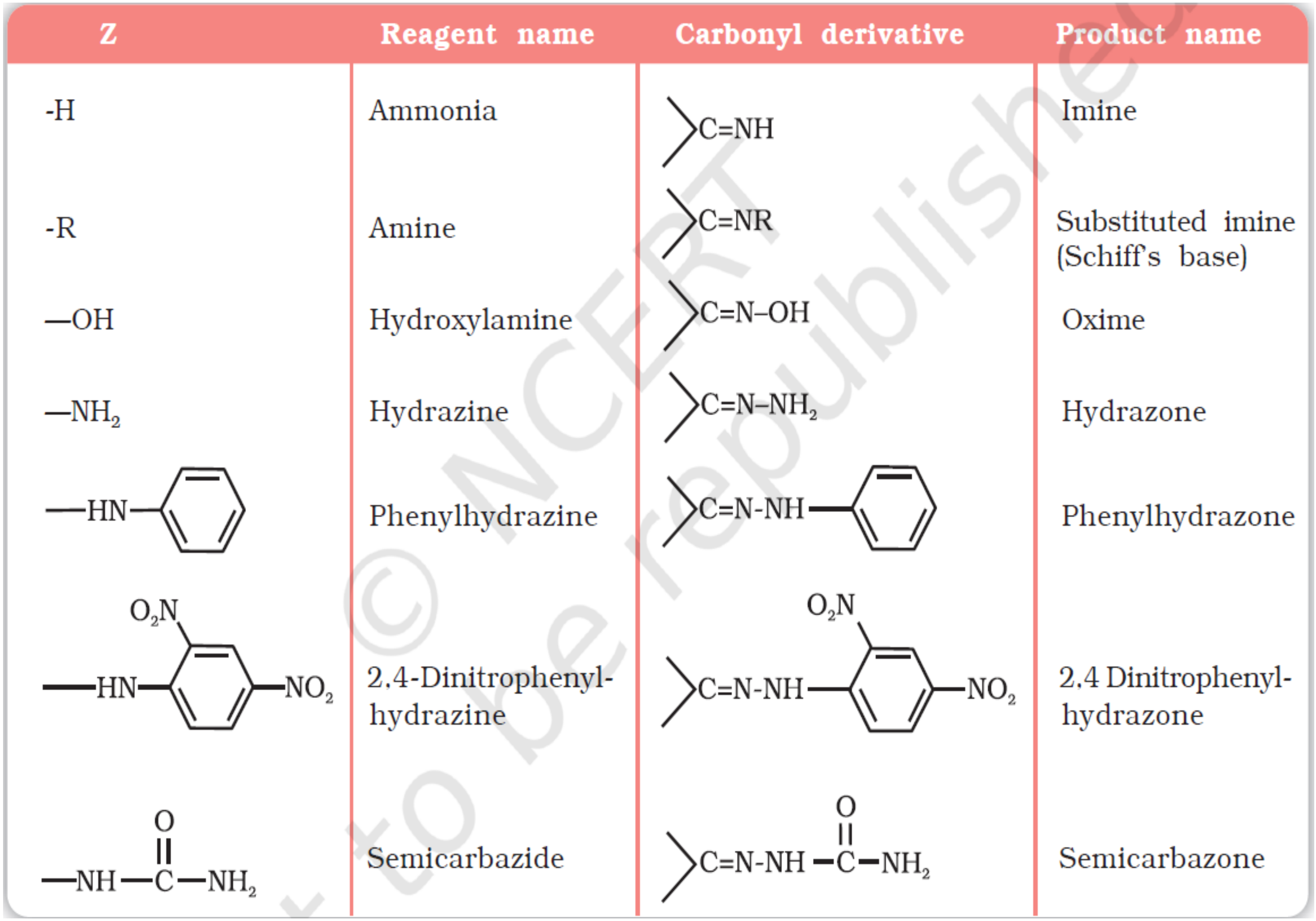
Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: Examples

(d) Addition of Ammonia and its Derivatives:



$$>C=O + H_2N\text{-}Z \rightleftharpoons \left[>C\begin{matrix} OH \\ NHZ \end{matrix} \right] \longrightarrow >C=N\text{-}Z + H_2O$$



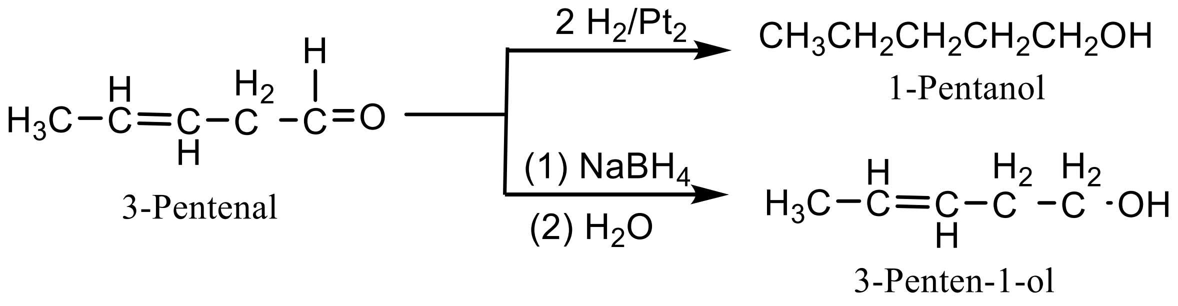
Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
$-OH$	Hydroxylamine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
—HN—	Phenylhydrazine	$>C=N-NH-$	Phenylhydrazone
O_2N —HN— NO_2	2,4-Dinitrophenyl-hydrazine	O_2N $>C=N-NH-$ NO_2	2,4 Dinitrophenyl-hydrazone
$-NH-\overset{O}{\overset{\|}{C}}-NH_2$	Semicarbazide	$>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$	Semicarbazone

Chemical Reactions of Aldehydes and Ketones

2. Reduction

(i) Reduction to alcohols:

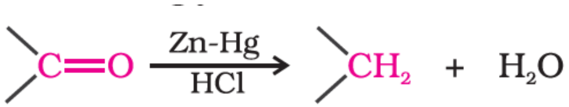
Aldehydes and ketones are ***reduced to primary and secondary alcohols*** respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation



(ii) Reduction to hydrocarbons:

The carbonyl group of aldehydes and ketones is reduced to 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.



(Clemmensen reduction)

(Wolff-Kishner rduction)

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.

$$\text{R-CHO} \xrightarrow{[O]} \text{R-COOH}$$

(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.

$$\text{RCHO} + 2[Ag(NH_3)_2]^+ + 3\,\bar{O}H \longrightarrow \text{RCO}\bar{O} + 2Ag + 2H_2O + 4NH_3$$

(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.

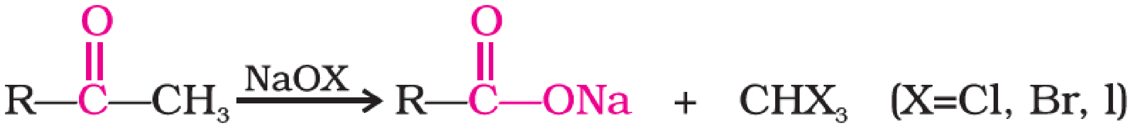
$$\text{R-CHO} + 2Cu^{2+} + 5\bar{O}H \longrightarrow \text{RCO}\bar{O} + \underset{\text{Red-brown ppt}}{Cu_2O} + 3H_2O$$

Chemical Reactions of Aldehydes and Ketones

3. Oxidation

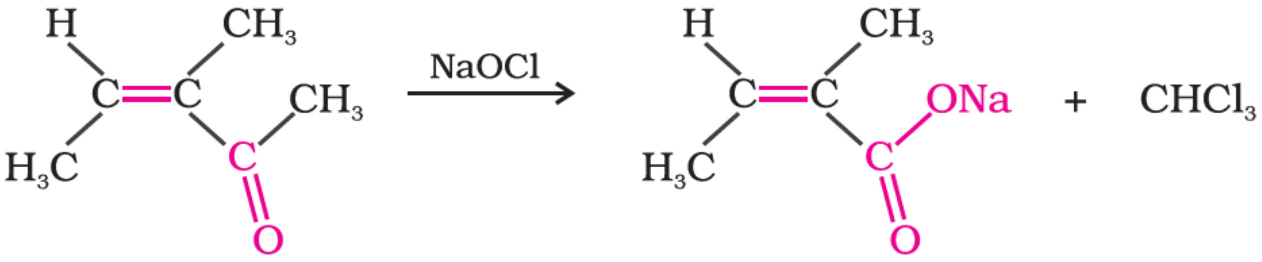
(iii) Oxidation of Methyl Ketones by Haloform Reaction:

- 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.

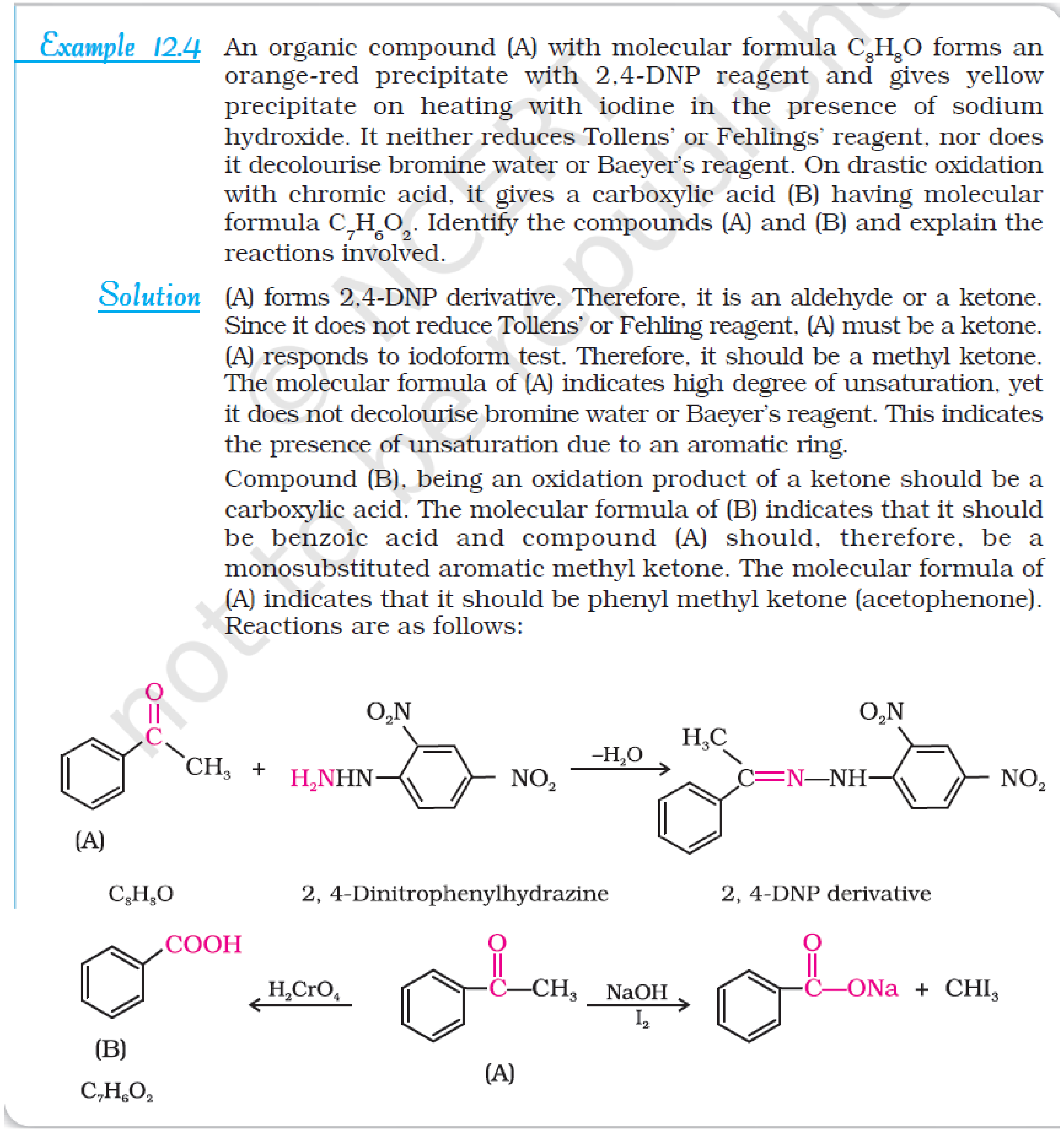


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-ONa \quad + \quad CHX_3 \quad (X=Cl,\ Br,\ I)$$

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



Questions



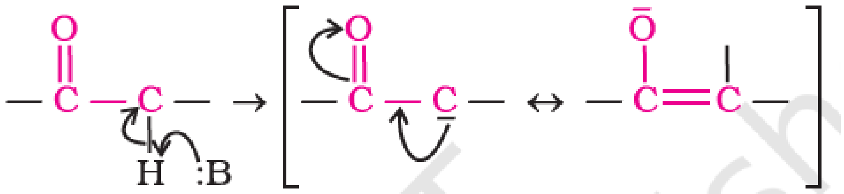
Example 12.4 An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or 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

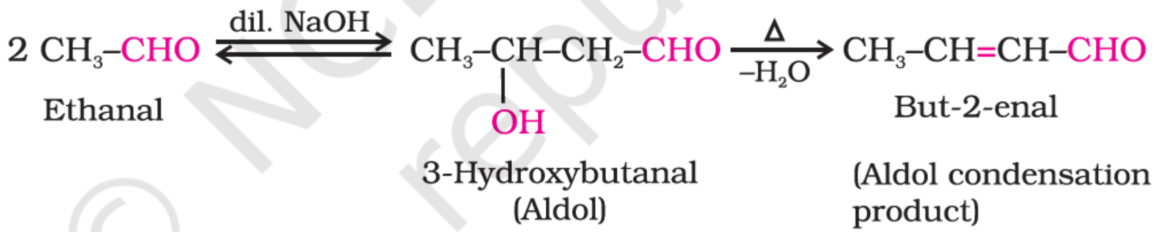
4. Reactions due to α-hydrogen



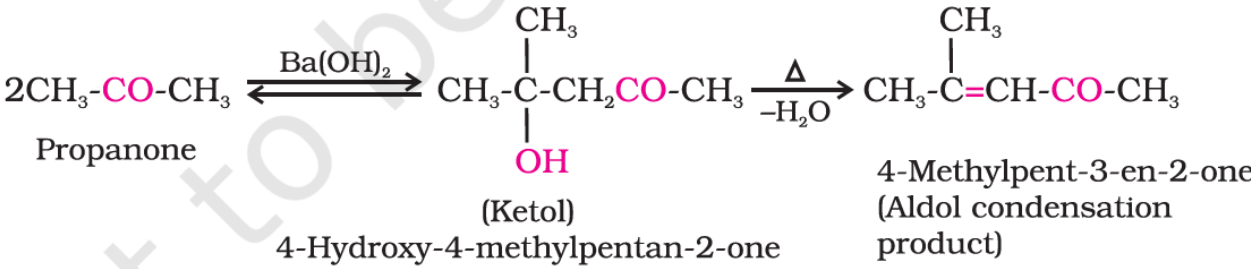
- The acidity of α-hydrogen atoms of carbonyl compounds is *due to the strong electron withdrawing effect of the carbonyl group* and *resonance stabilization of the conjugate base*.

(i) Aldol condensation:

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



$$2\ CH_3-CHO \xrightleftharpoons{\text{dil. NaOH}} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$



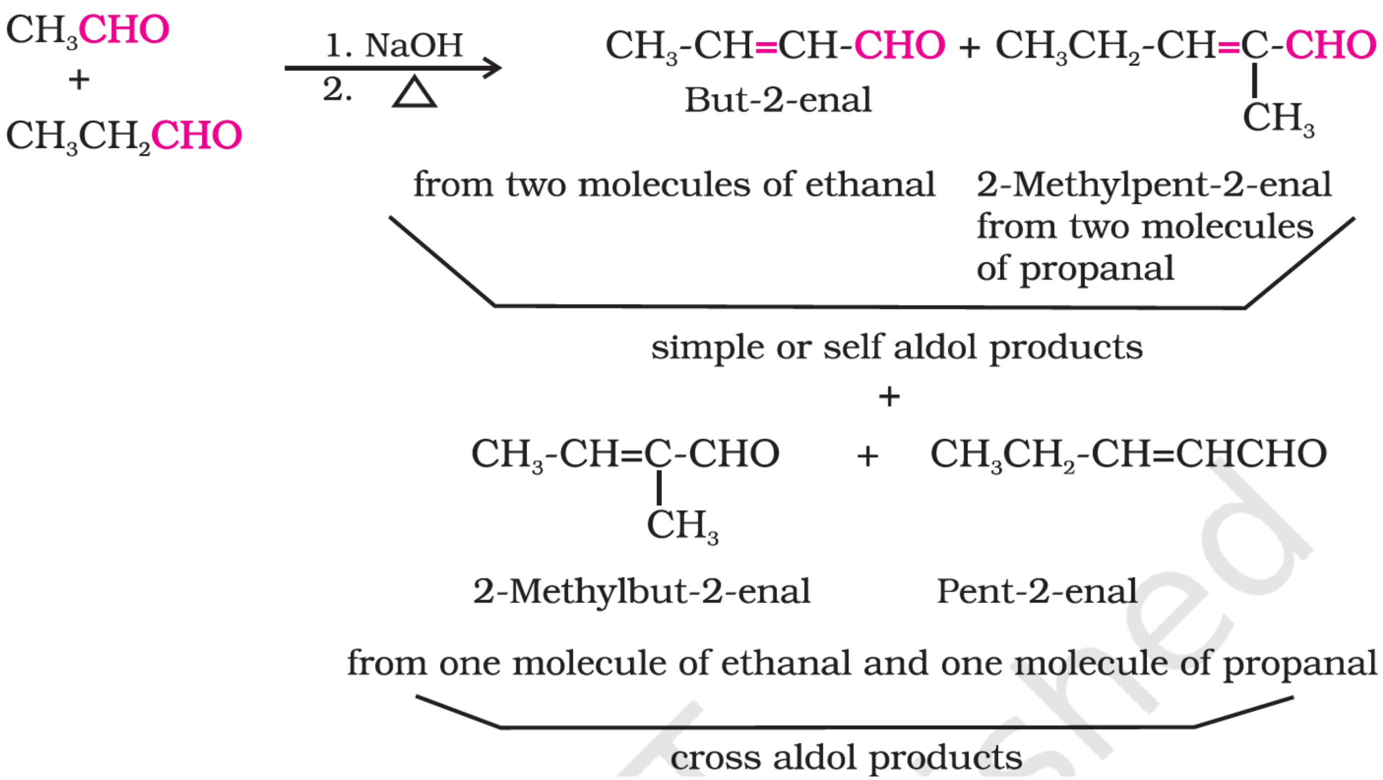
$$2CH_3-CO-CH_3 \xrightleftharpoons{Ba(OH)_2} CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2CO-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CO-CH_3$$

Chemical Reactions of Aldehydes and Ketones

4. Reactions due to α-hydrogen

(ii) Cross aldol condensation

- When aldol condensation is carried out **between two different aldehydes and / or ketones**, it is called cross aldol condensation.
- If both of them contain α-hydrogen atoms, it gives a mixture of four products.



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH} \underbrace{\underset{\text{But-2-enal}}{CH_3\text{-}CH{=}CH\text{-}CHO} + \underset{CH_3}{CH_3CH_2\text{-}CH{=}\overset{}{C}\text{-}CHO}}_{\text{simple or self aldol products}}$$

from two molecules of ethanal

2-Methylpent-2-enal from two molecules of propanal

simple or self aldol products

+

$$\underbrace{\underset{CH_3}{CH_3\text{-}CH{=}C\text{-}CHO} + CH_3CH_2\text{-}CH{=}CHCHO}_{\text{cross aldol products}}$$

2-Methylbut-2-enal

Pent-2-enal

from one molecule of ethanal and one molecule of propanal

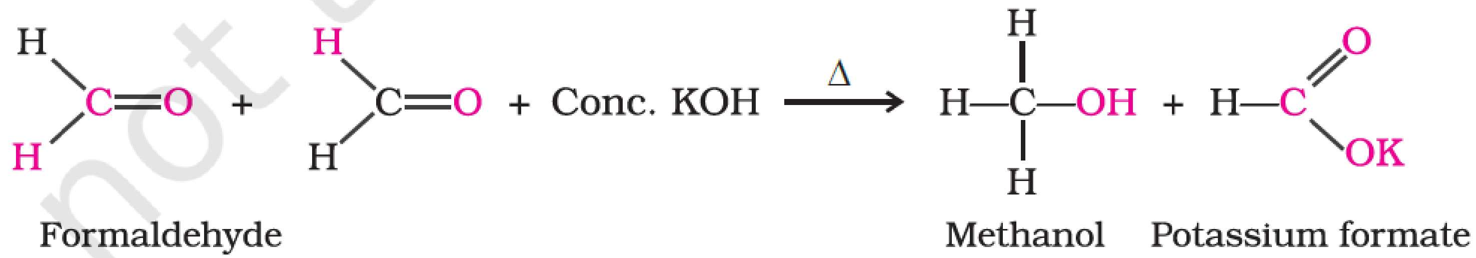
cross aldol products

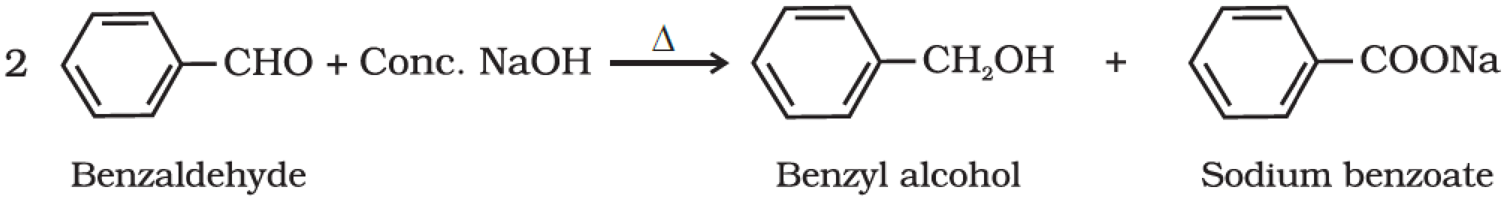
Chemical Reactions of Aldehydes and Ketones

5. Other Reactions

(i) Cannizzaro Reaction:

- **Aldehydes which do not have an α-hydrogen atom**, ***undergo self oxidation and reduction*** (disproportionation) reaction on heating with concentrated alkali.
- *One molecule of the aldehyde is reduced to alcohol* while *another is oxidized to carboxylic acid salt*.



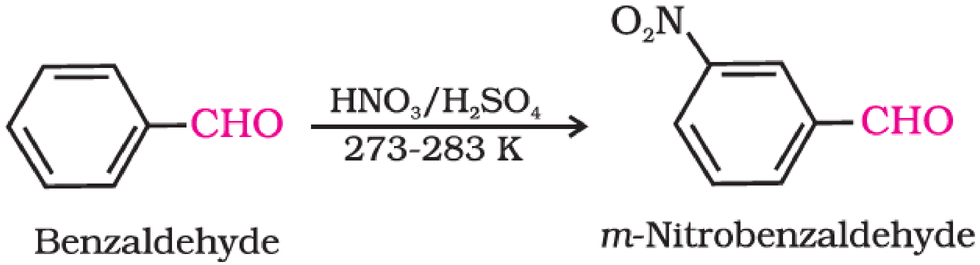


Chemical Reactions of Aldehydes and Ketones

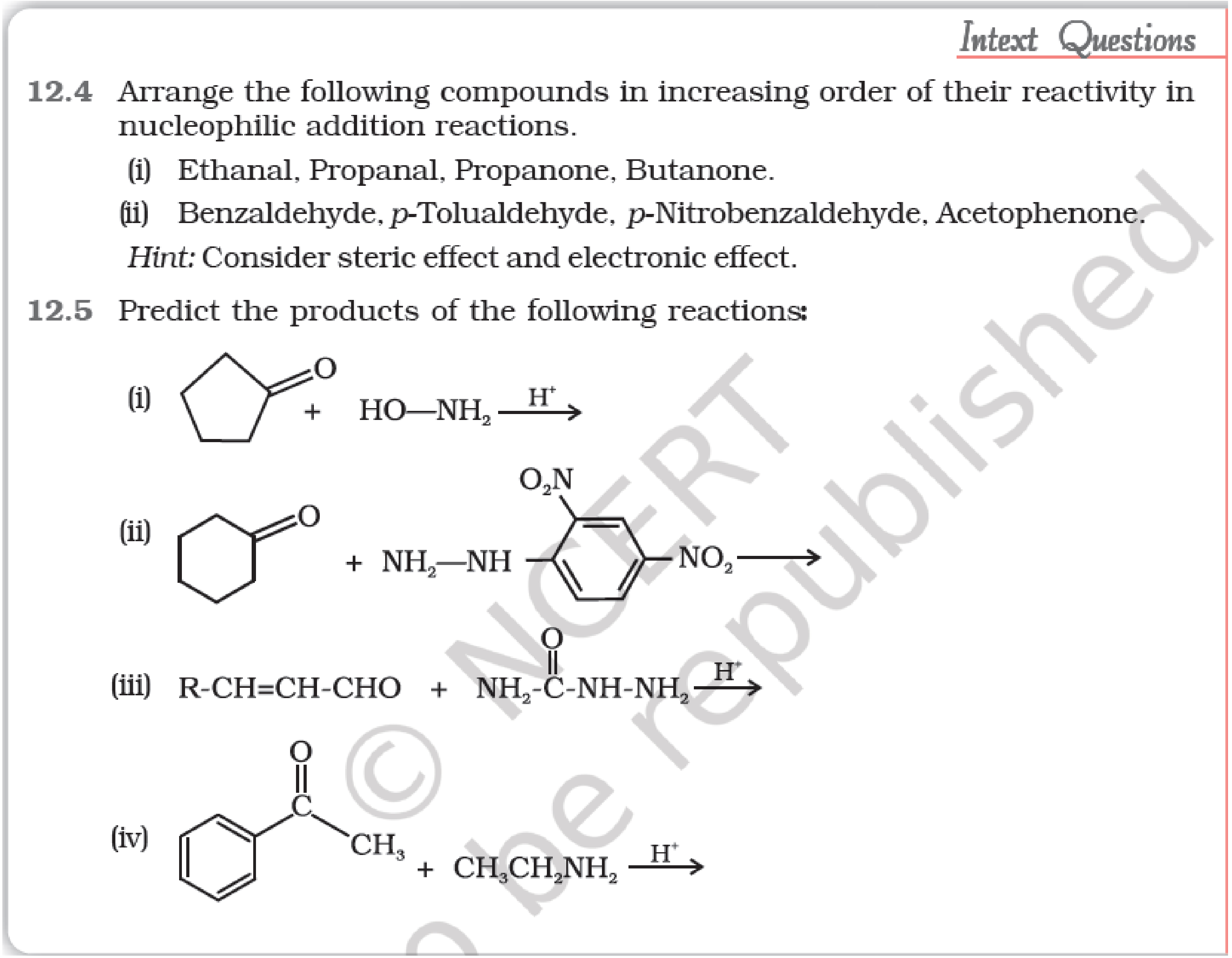
5. Other Reactions

(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:

(i) $+ \ HO—NH_2 \xrightarrow{H^+}$

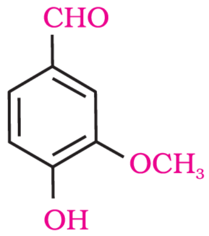
(ii) $+ \ NH_2—NH$ O_2N $NO_2 \longrightarrow$

(iii) $R\text{-}CH{=}CH\text{-}CHO \ + \ NH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}NH_2 \xrightarrow{H^+}$

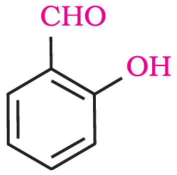
(iv) CH_3 $+ \ CH_3CH_2NH_2 \xrightarrow{H^+}$

Uses of Aldehydes and Ketones

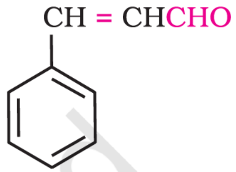
- *In chemical industry* aldehydes and ketones are used as *solvents*, *starting materials and reagents for the synthesis of other products*.
- *Formaldehyde* is well known as formalin (40%) solution used to *preserve biological specimens* and to *prepare Bakelite (a phenol-formaldehyde resin)*, *urea-formaldehyde 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