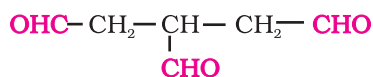


4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde



Propane-1,2,3-tricarbaldehyde

[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

The common and IUPAC names of some aldehydes and ketones are given in Table 12.1.

Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	<i>m</i> -Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
CH ₃ COCH ₂ CH ₂ CH ₃	Methyl <i>n</i> -propyl ketone	Pentan-2-one
(CH ₃) ₂ CHCOCH(CH ₃) ₂	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one

12.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2 -hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p -orbital and forms a π -bond with oxygen by overlap with p -orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π -electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a trigonal coplanar structure (Figure 12.1).

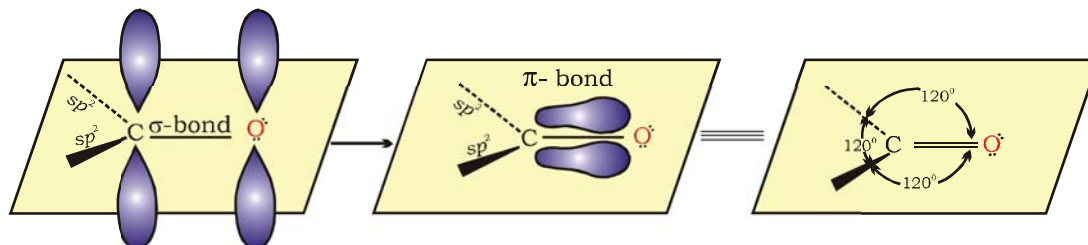
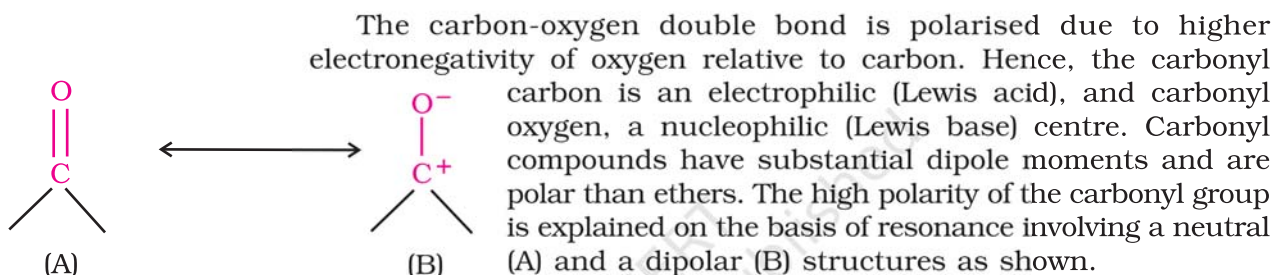


Fig.12.1 Orbital diagram for the formation of carbonyl group



Intext Questions

12.1 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 |

12.2 Preparation of Aldehydes and Ketones

Some important methods for the preparation of aldehydes and ketones are as follows:

12.2.1 Preparation of Aldehydes and Ketones

1. By oxidation of alcohols

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (Unit 11, Class XII).

2. By dehydrogenation of alcohols

This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively (Unit 11, Class XII).

3. From hydrocarbons

- (i) *By ozonolysis of alkenes:* As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes,

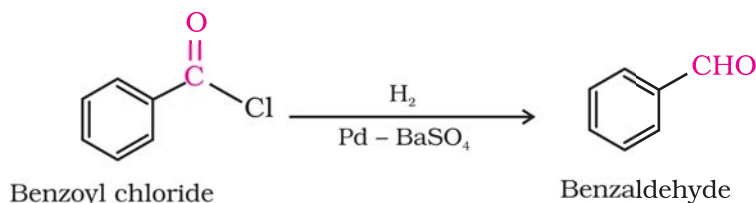
ketones or a mixture of both depending on the substitution pattern of the alkene (Unit 13, Class XI).

(ii) *By 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 (Unit 13, Class XI).

12.2.2 Preparation of Aldehydes

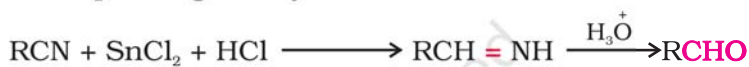
1. From acyl chloride (acid chloride)

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.



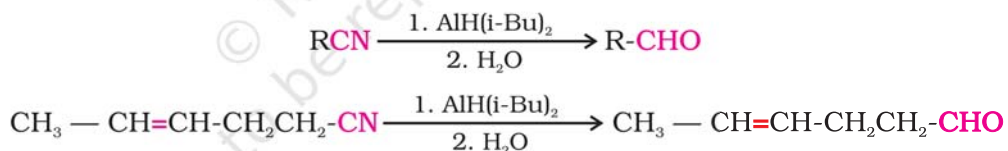
2. From nitriles and esters

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

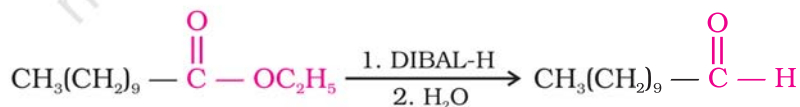


This reaction is called **Stephen** reaction.

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



Similarly, esters are also reduced to aldehydes with DIBAL-H.



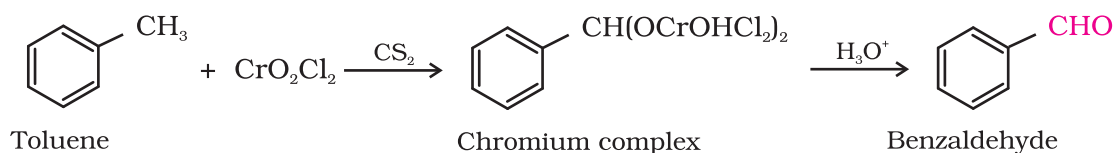
3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

(i) *By oxidation of methylbenzene*

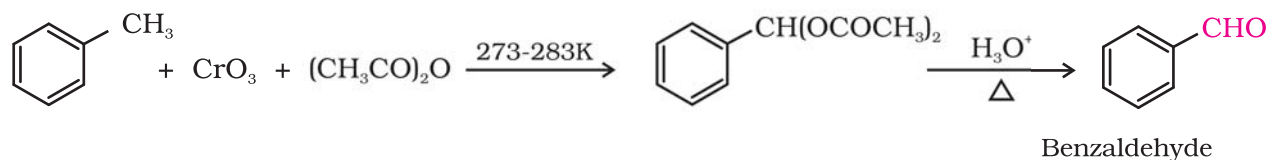
Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

(a) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



This reaction is called **Etard reaction**.

(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.



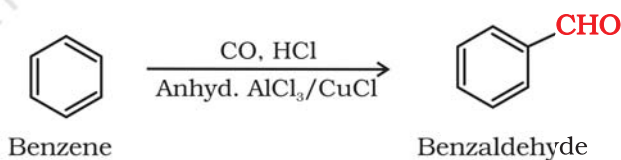
(ii) *By side chain chlorination followed by hydrolysis*

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



(iii) *By Gatterman - Koch reaction*

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

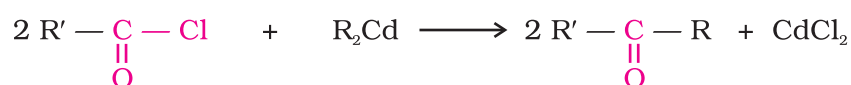
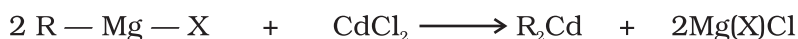


This reaction is known as **Gatterman-Koch** reaction.

12.2.3 Preparation of Ketones

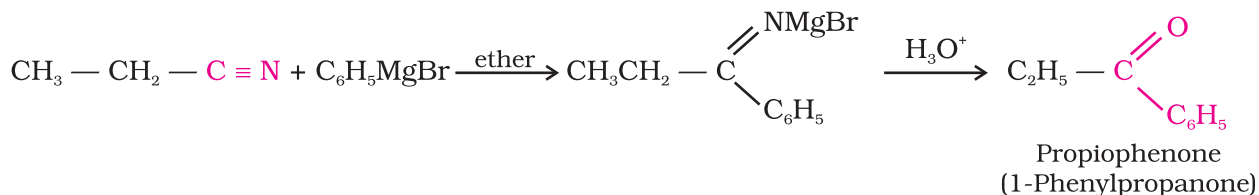
1. From acyl chlorides

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



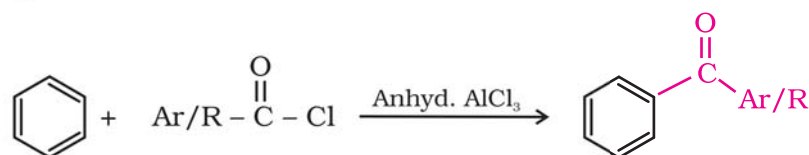
2. From nitriles

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



3. From benzene or substituted benzenes

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.



Example 12.1

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

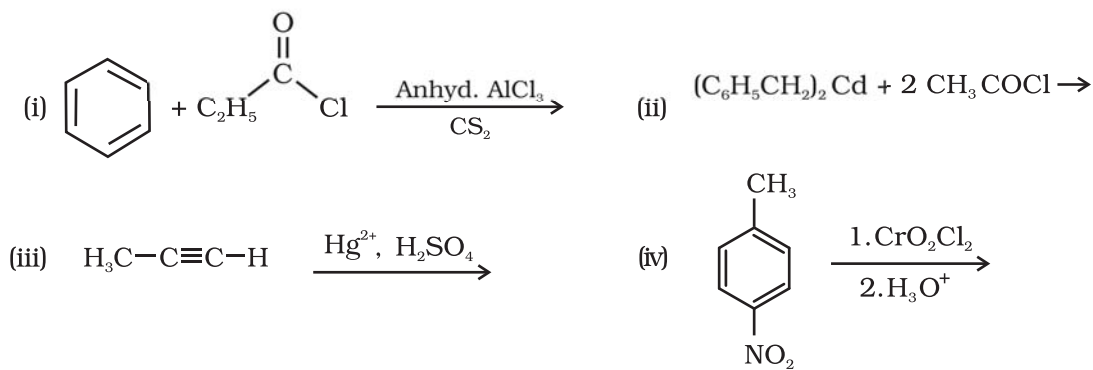
- | | |
|---|------------------------------------|
| (i) Hexan-1-ol to hexanal | (ii) Cyclohexanol to cyclohexanone |
| (iii) <i>p</i> -Fluorotoluene to <i>p</i> -fluorobenzaldehyde | (iv) Ethanenitrile to ethanal |
| (v) Allyl alcohol to propenal | (vi) But-2-ene to ethanal |

Solution

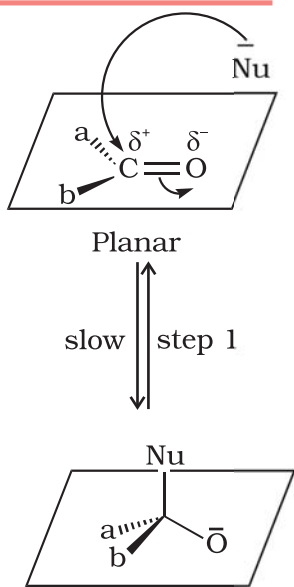
- | | |
|--|---|
| (i) $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}$ (PCC) | (ii) Anhydrous CrO_3 |
| (iii) CrO_3 in the presence of acetic anhydride/
1. CrO_2Cl_2 2. HOH | (iv) (Diisobutyl)aluminium hydride (DIBAL-H) |
| (v) PCC | (vi) $\text{O}_3/\text{H}_2\text{O}$ -Zn dust |

Intext Question

12.2 Write the structures of products of the following reactions;



12.4 Chemical Reactions



Tetrahedral intermediate

Addition product

Fig.12.2: Nucleophilic attack on carbonyl carbon

Intext Question

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



Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions.

1. Nucleophilic addition reactions

Contrary to electrophilic addition reactions observed in alkenes (refer Unit 13, Class XI), the aldehydes and ketones undergo nucleophilic addition reactions.

(i) Mechanism of nucleophilic addition reactions

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon (Fig. 12.2). The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced. 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 as shown in Fig. 12.2.

(ii) Reactivity

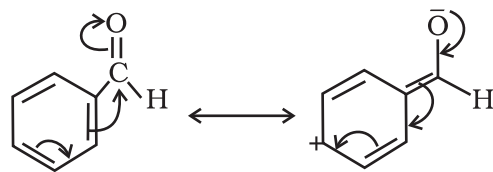
Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. 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

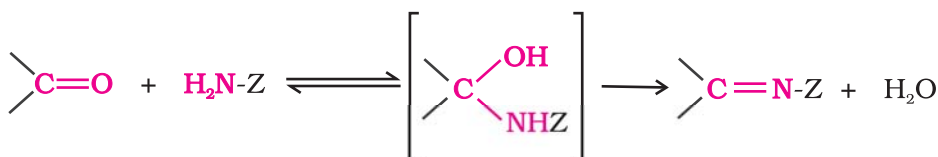
The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in



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.


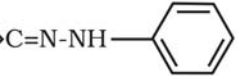
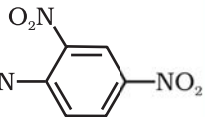
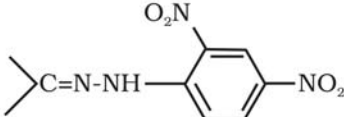

the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

- (e) *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 catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>\text{C}=\text{N-Z}$.



Z = Alkyl, aryl, OH, NH_2 , $\text{C}_6\text{H}_5\text{NH}$, NHCONH_2 , etc.

Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones ($>\text{C}=\text{N-Z}$)

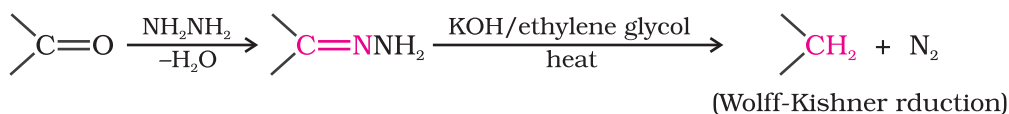
Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\text{>C}=\text{NH}$	Imine
-R	Amine	$\text{>C}=\text{NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\text{>C}=\text{N-OH}$	Oxime
- NH_2	Hydrazine	$\text{>C}=\text{N-NH}_2$	Hydrazone
-HN- 	Phenylhydrazine	$\text{>C}=\text{N-NH-}$ 	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	$\text{>C}=\text{N-NH-}$ 	2,4 Dinitrophenylhydrazone
-NH- 	Semicarbazide	$\text{>C}=\text{N-NH-C(=O)-NH}_2$	Semicarbazone

* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

2. Reduction

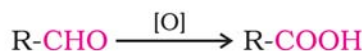
- (i) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4) as well as by catalytic hydrogenation (Unit 11, Class XII).
- (ii) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochloric acid [**Clemmensen**

reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).

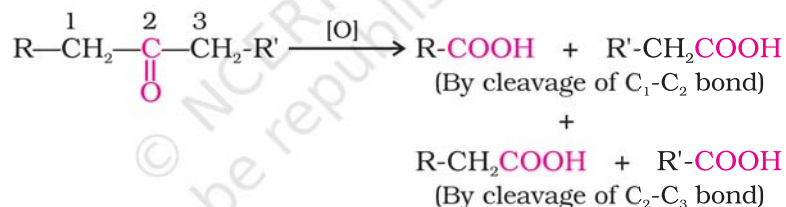


3. Oxidation

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.



Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

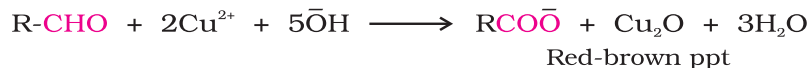


The mild oxidising agents given below are used to distinguish aldehydes from ketones:

- (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 aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

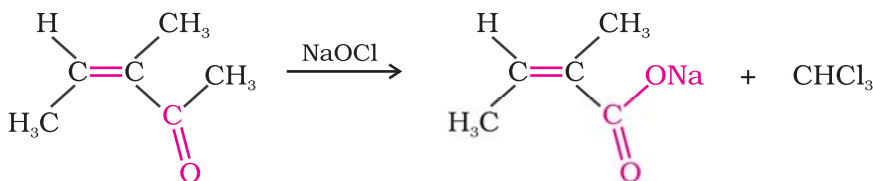


- (ii) **Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



Bernhard Tollens (1841-1918) was a Professor of Chemistry at the University of Gottingen, Germany.

(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 oxidised 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.



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.

Iodoform reaction with sodium hypiodite is also used for detection of CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group which produces CH_3CO group on oxidation.

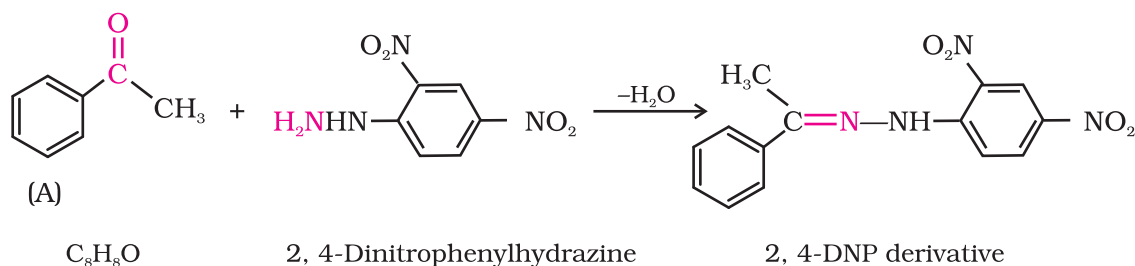
Example 12.4

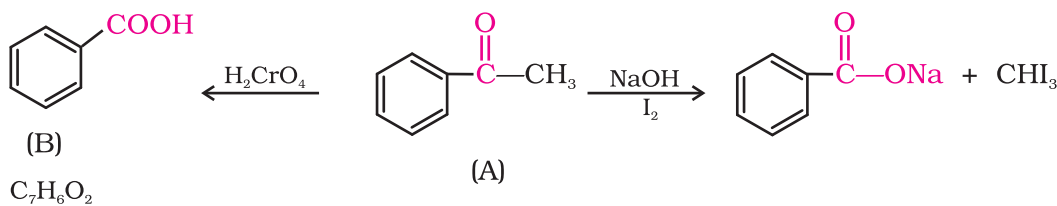
An organic compound (A) with molecular formula $\text{C}_8\text{H}_8\text{O}$ forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. 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:

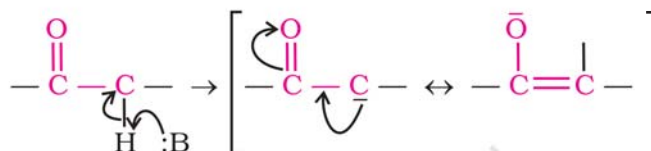




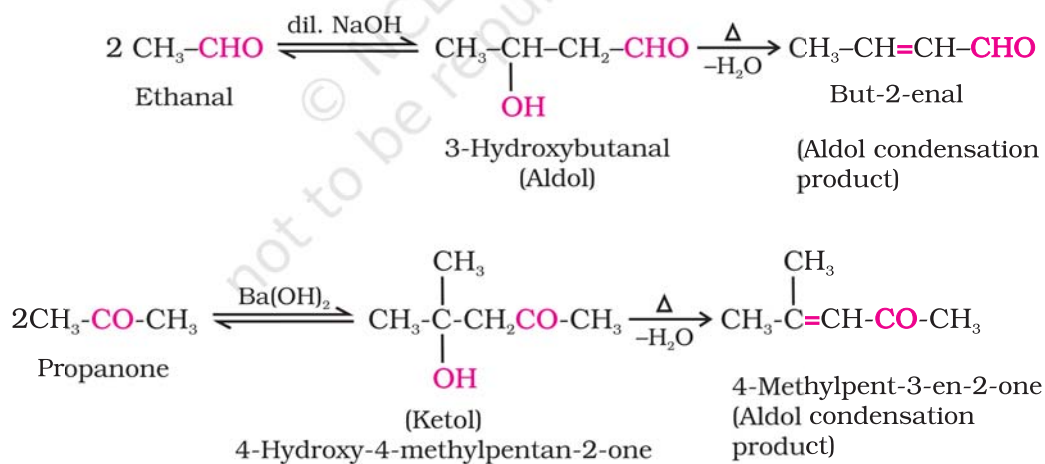
4. Reactions due to α -hydrogen

Acidity of α -hydrogens of aldehydes and ketones: The aldehydes and ketones undergo a number of reactions due to the acidic nature of 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 stabilisation of the conjugate base.

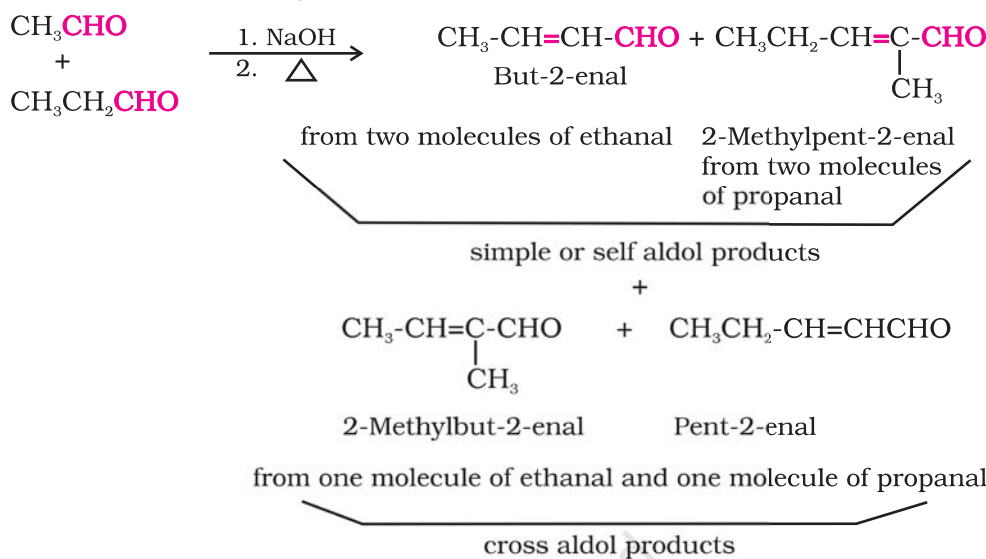


(i) **Aldol condensation:** Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.

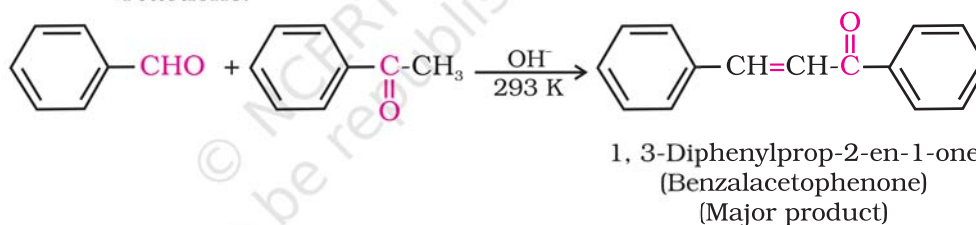


The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give α,β -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

(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. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

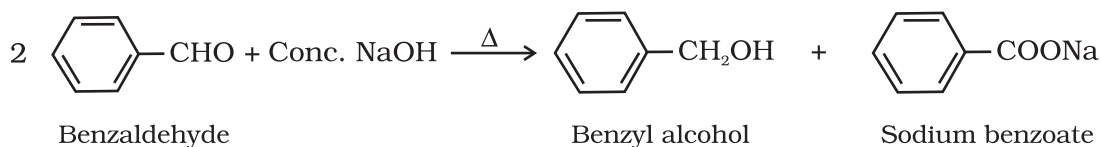
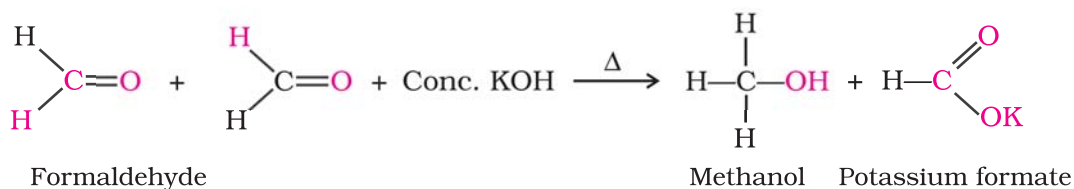


Ketones can also be used as one component in the cross aldol reactions.

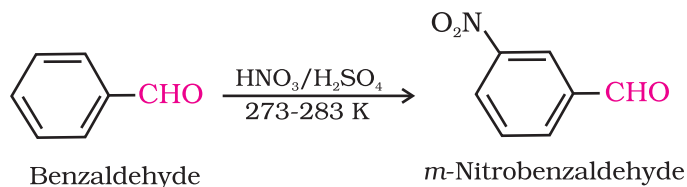


5. Other reactions

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



- (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.



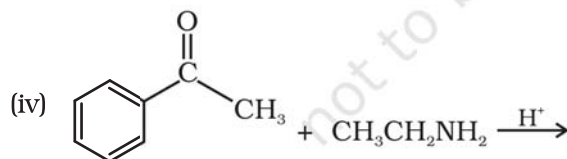
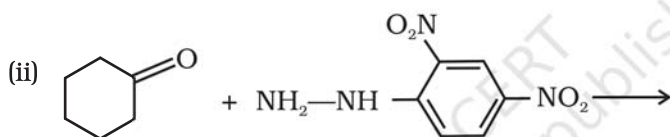
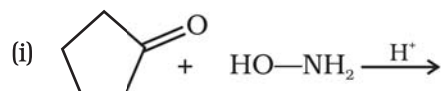
Intext Questions

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.

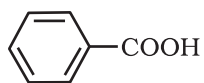
Hint: Consider steric effect and electronic effect.

12.5 Predict the products of the following reactions:



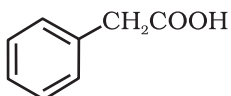
12.5 Uses of Aldehydes and Ketones

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. Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.



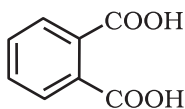
Benzoic acid

Benzenecarboxylic acid
(Benzoic acid)



Phenylacetic acid

2-Phenylethanoic acid

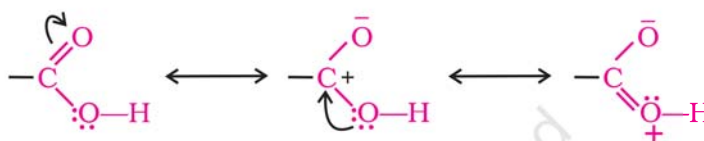


Phthalic acid

Benzene-1, 2-dicarboxylic acid

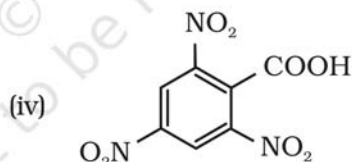
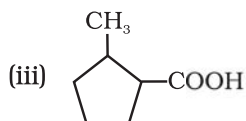
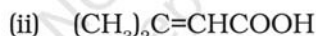
12.6.2 Structure of Carboxyl Group

In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120° . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



Intext Question

12.6 Give the IUPAC names of the following compounds:

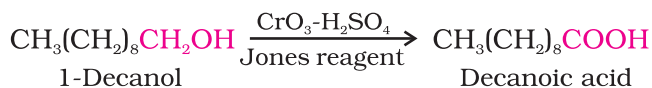
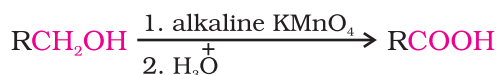


12.7 Methods of Preparation of Carboxylic Acids

Some important methods of preparation of carboxylic acids are as follows.

1. From primary alcohols and aldehydes

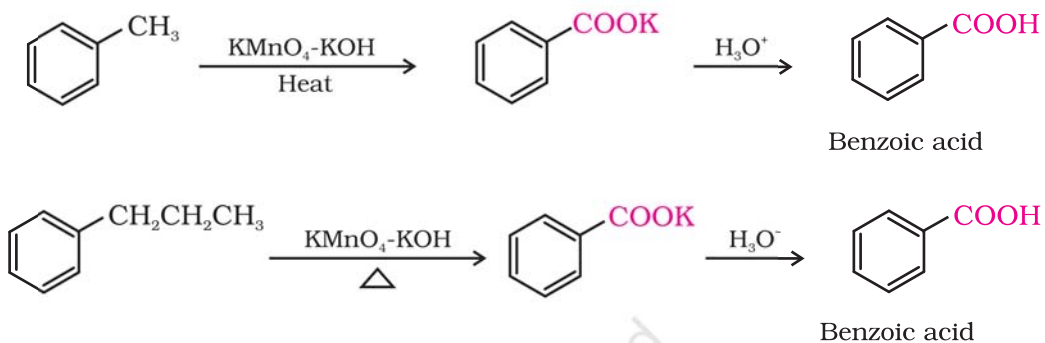
Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO_4) in neutral, acidic or alkaline media or by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).



Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 12.4).

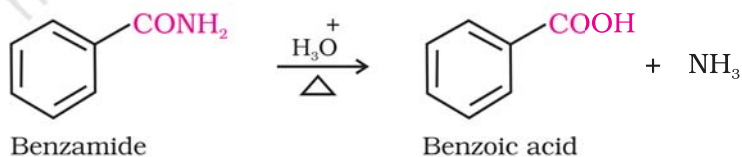
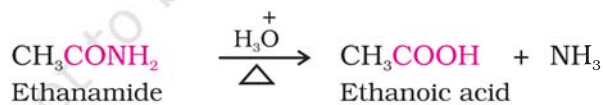
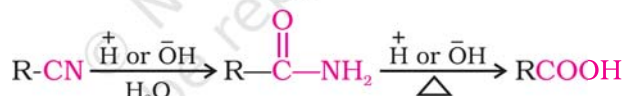
2. From alkylbenzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents (refer Unit 13, Class XI).



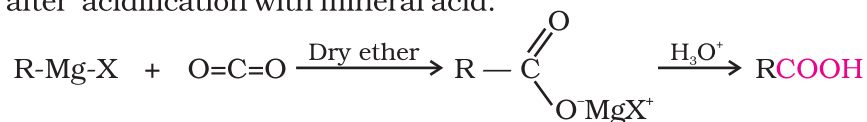
3. From nitriles and amides

Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



4. From Grignard reagents

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.

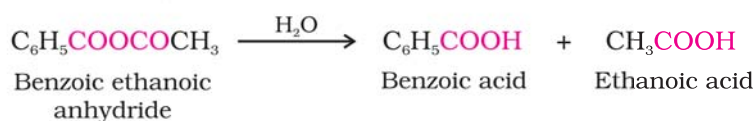
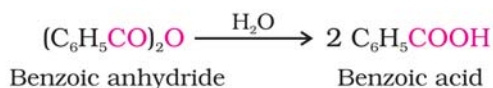
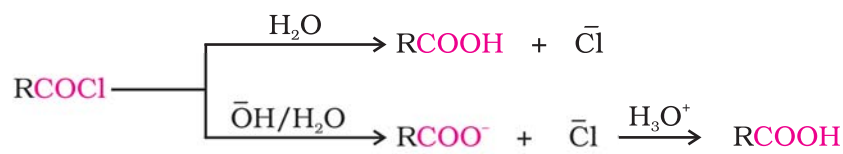


As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 10, Class XII). The above methods

(3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

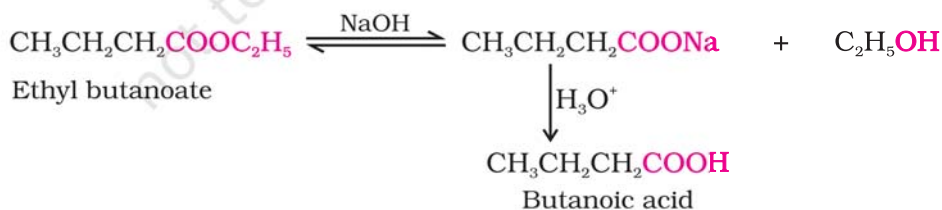
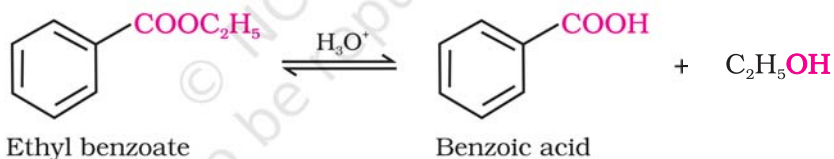
5. From acyl halides and anhydrides

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.



6. From esters

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.

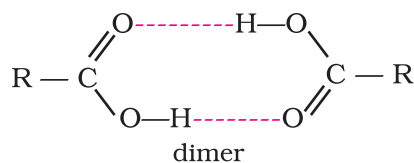


Write chemical reactions to affect the following transformations:

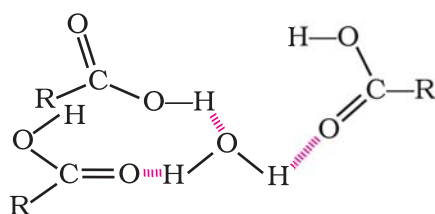
Example 12.5

- (i) Butan-1-ol to butanoic acid
- (ii) Benzyl alcohol to phenylethanoic acid
- (iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid
- (iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
- (v) Cyclohexene to hexane-1,6-dioic acid
- (vi) Butanal to butanoic acid.

12.8 Physical Properties



In vapour state or in aprotic solvent



Hydrogen bonding of RCOOH with H₂O

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

12.9 Chemical Reactions

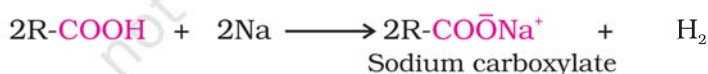
The reaction of carboxylic acids are classified as follows:

12.9.1 Reactions Involving Cleavage of O-H Bond

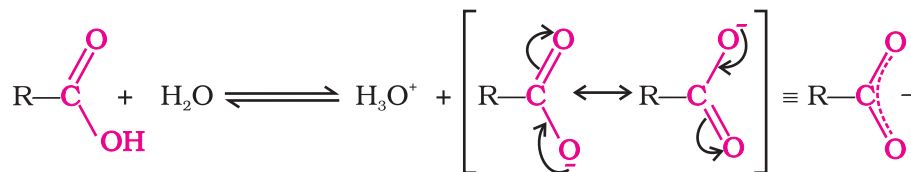
Acidity

Reactions with metals and alkalis

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalis similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.



Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



For the above reaction:

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{H}_2\text{O}][\text{RCOOH}]} \quad K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

where K_{eq} is equilibrium constant and K_a is the acid dissociation constant.

For convenience, the strength of an acid is generally indicated by its $\text{p}K_a$ value rather than its K_a value.

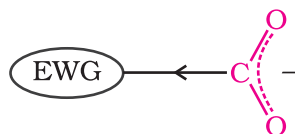
$$\text{p}K_a = -\log K_a$$

The $\text{p}K_a$ of hydrochloric acid is -7.0 , where as $\text{p}K_a$ of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are 0.23 , 4.19 and 4.76 , respectively.

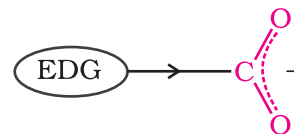
Smaller the $\text{p}K_a$, the stronger the acid (the better it is as a proton donor). Strong acids have $\text{p}K_a$ values < 1 , the acids with $\text{p}K_a$ values between 1 and 5 are considered to be moderately strong acids, weak acids have $\text{p}K_a$ values between 5 and 15 , and extremely weak acids have $\text{p}K_a$ values > 15 .

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols ($\text{p}K_a$ is ~ 16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion (Unit 11, Class XII). Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



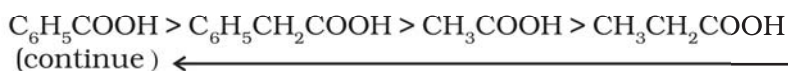
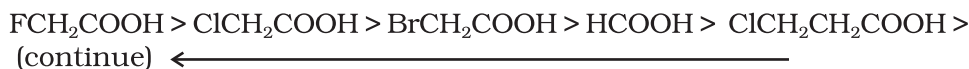
Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is
 $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$

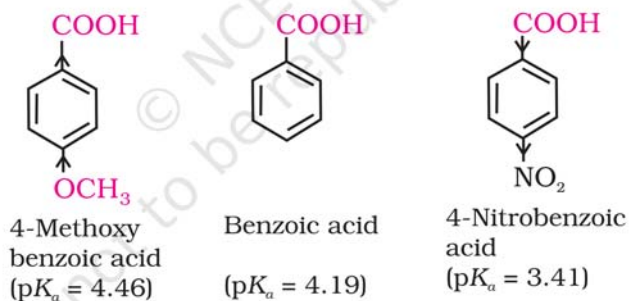
Thus, the following acids are arranged in order of increasing acidity (based on $\text{p}K_a$ values):



Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



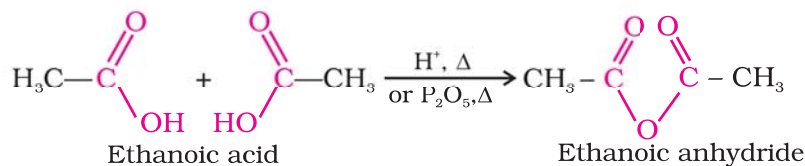
This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



12.9.2 Reactions Involving Cleavage of C-OH Bond

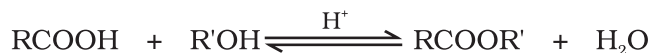
1. Formation of anhydride

Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.

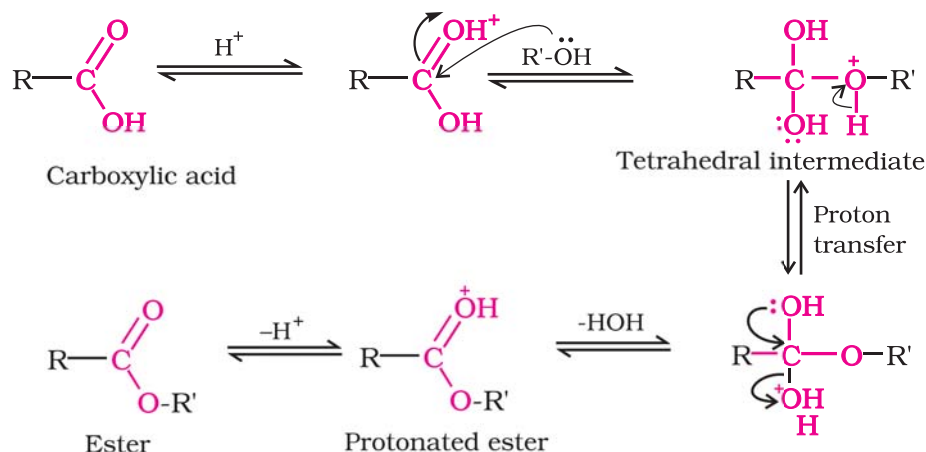


2. Esterification

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.

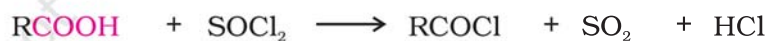


Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $^{-}\text{OH}_2$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



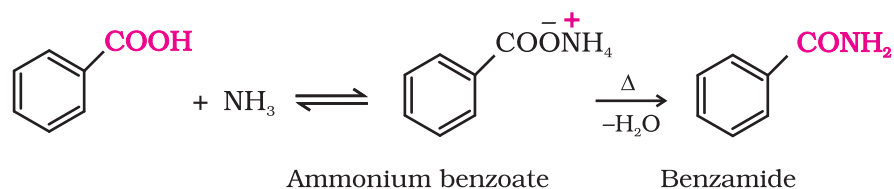
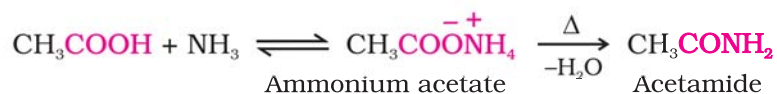
3. Reactions with PCl_5 , PCl_3 and SOCl_2

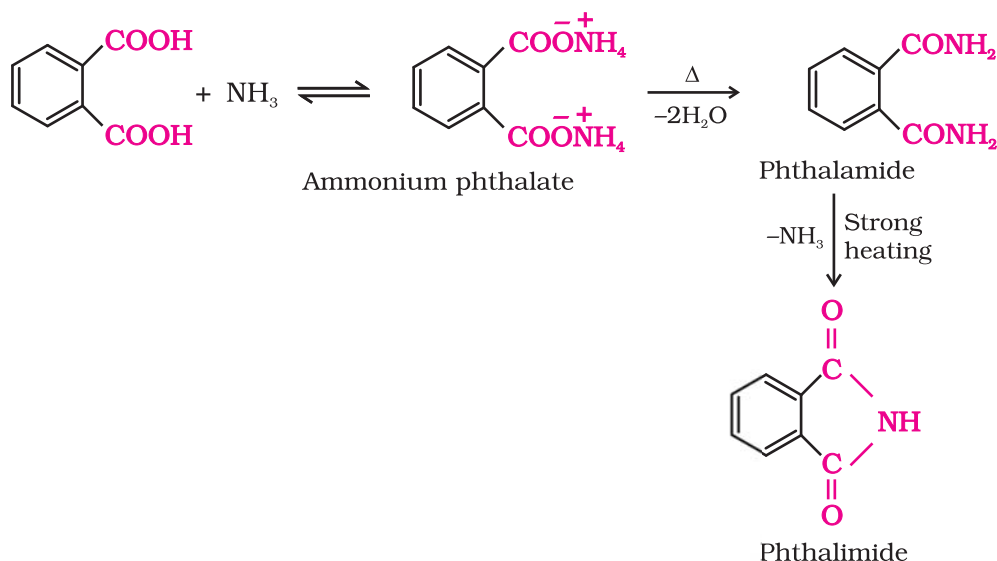
The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5 , PCl_3 or SOCl_2 . Thionyl chloride (SOCl_2) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



4. Reaction with ammonia

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:

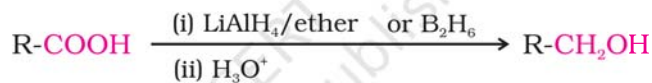




12.9.3 Reactions Involving -COOH Group

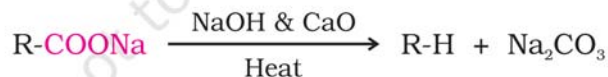
1. Reduction

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.



2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

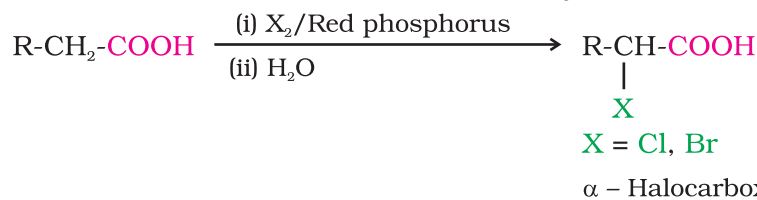


Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Unit 13, Class XI).

12.9.4 Substitution Reactions in the Hydrocarbon Part

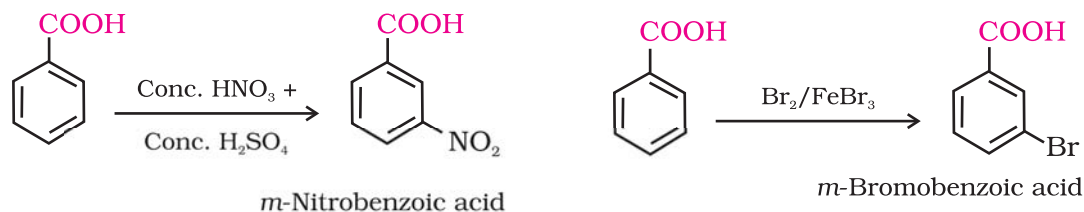
1. Halogenation

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



2. Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



Intext Question

12.8 Which acid of each pair shown here would you expect to be stronger?

(i) $\text{CH}_3\text{CO}_2\text{H}$ or $\text{CH}_2\text{FCO}_2\text{H}$ (ii) $\text{CH}_2\text{FCO}_2\text{H}$ or $\text{CH}_2\text{ClCO}_2\text{H}$

(iii) $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$ or $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$

(iv) $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$ or $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$

12.10 Uses of Carboxylic Acids

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

Summary

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses. The lower members are more soluble in water because they form hydrogen bonds with water. The higher members, because of large size of hydrophobic chain of carbon atoms, are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Aromatic aldehydes may also be prepared by oxidation of (i) methylbenzene with chromyl chloride or CrO_3 in the presence of acetic anhydride, (ii) formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride, and (iii) cuprous chloride or by hydrolysis of benzal chloride. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Ketones are also prepared by reaction of acyl chloride with dialkylcadmium. A good method for the preparation of aromatic ketones is the **Friedel-Crafts acylation** of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN , NaHSO_3 , alcohols (or diols),