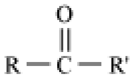
Aldehydes, Ketones and Carboxylic Acids

Nomenclature and Structure of Carbonyl Group

Nomenclature

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

Aldehyde



$$R-\overset{\overset{O}{\|}}{C}-R'$$

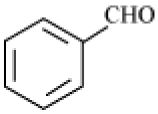
Ketone

Common Names of Aldehydes

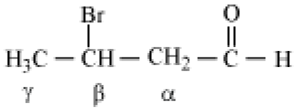
- Often called by their common names instead of IUPAC names
- Derived from the common names of the carboxylic acids by replacing the ending '−ic' of the acid with aldehyde
- Location of the substituent in the carbon chain is indicated by the Greek letters α, β, γ, δ, etc.
- Example:

CH_3CHO

Acetaldehyde



Benzaldehyde

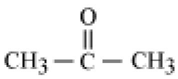


$$\underset{\gamma}{H_3C}-\underset{\beta}{\overset{\overset{Br}{|}}{CH}}-\underset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-H$$

β-Bromobutyraldehyde

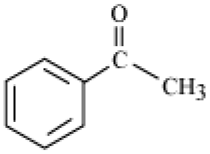
Common Names of Ketones

- Derived by naming two alkyl or aryl groups bonded to the carbonyl group
- Locations of substituents are indicated by the Greek Letters, α, α′, β, β′, and so on
- The simplest dimethyl ketone is called acetone.
- Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.

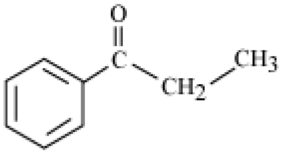


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

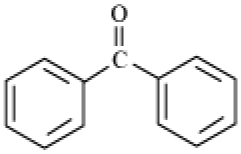
Acetone



Acetophenone



Propiophenone

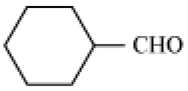


Benzophenone

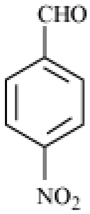
IUPAC Names

- For open-chain aliphatic aldehydes and ketones, IUPAC names are derived from the names of the corresponding alkanes by replacing the ending '−e' with '−al' and '−one' respectively.
- In the case of aldehydes, the longest chain is numbered starting from the carbon of the aldehydic group.
- In the case of ketones, the numbering begins from the end nearer to the carbonyl group.
- Substituents are prefixed in the alphabetical order along with the numerals indicating their positions in the carbon chain.
- Same rule is applicable to cyclic ketones.
- If the aldehydic group is attached to a ring, then the suffix carbaldehyde is added to the full name of cyclohexane.

  Example:



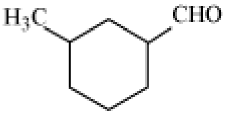
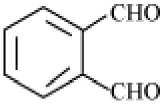
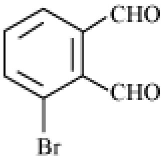
Cyclohexanecarbaldehyde

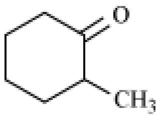


4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde

- The common name benzaldehyde is also accepted by IUPAC.
- Common and IUPAC names of some aldehydes and ketones are listed in the given table.

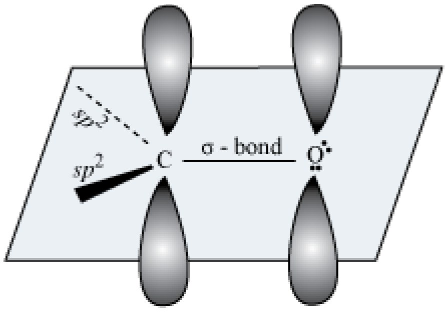
Structure	**Common name**	**IUPAC name**
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexane	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*-Bromophthaldehyde	3-Bromobenzene-1,2-dicarbaldehyde
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

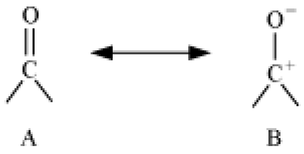
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

Structure of Carbonyl Group

- Carbonyl carbon atom is sp^2 hybridised.
- It forms three sigma (σ) bonds and one pi (π) bond.
- The π bond is formed with oxygen by overlap with *p*-orbital of an oxygen atom.
- Oxygen atom has two non-bonding electron pairs.
- Carbonyl carbon and the three atoms attached to it lie in the same plane.
- π-electron cloud is above and below the plane.
- Bond angles are approximately 120° as is expected of a trigonal co-planar structure.
- Orbital diagram for the formation of carbonyl group is as follows:



- C=O double bond is polarised due to higher electronegativity of oxygen relative to carbon.
- Carbonyl carbon – an electrophile (Lewis acid)
- Carbonyl oxygen – a nucleophile (Lewis base)
- High polarity of the carbonyl group is explained on the basis of resonance involving neutral (A) and dipolar (B) structures as shown below.



Preparation of Aldehydes and Ketones

Important Methods for the Preparation of Aldehydes and Ketones

- **By oxidation of alcohols**

Primary alcohols $\xrightarrow{[o]}$ Aldehydes

Secondary alcohols $\xrightarrow{[o]}$ Ketones

- **By dehydrogenation of alcohols**

Primary alcohols $\xrightarrow{\text{Ag or Cu}}$ Aldehydes

Secondary alcohols $\xrightarrow{\text{Ag or Cu}}$ Ketones

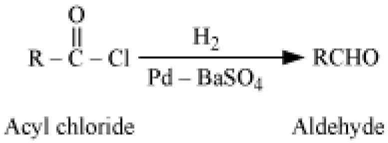
- **From hydrocarbons**
- Ozonolysis of alkenes followed by reaction with Zn dust and water gives aldehydes, ketones, or a mixture of both, depending upon the substitution pattern of the alkene.
- Hydration of alkynes

$$\underset{\text{Ethyne}}{CH \equiv CH} \xrightarrow[H_2SO_4/HgSO_4]{H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

Other alkynes give ketones in this reaction.

Preparation of Aldehydes

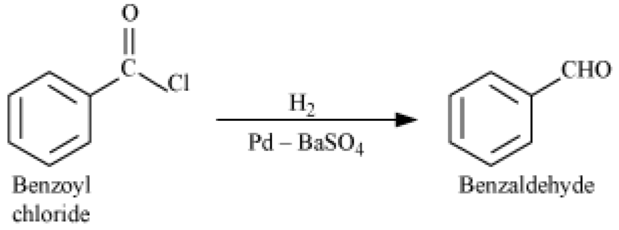
- **From acyl chloride (acid chloride)**



$$\underset{\text{Acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[Pd-BaSO_4]{H_2} \underset{\text{Aldehyde}}{RCHO}$$

- This reaction is called Rosenmund reduction.

- Example:



- **From Nitriles**
- $RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$

  This reaction is called Stephen reaction.

- $R - CN \xrightarrow[2.\ H_2O]{1.\ AlH(i-Bu)_2} R - CHO$

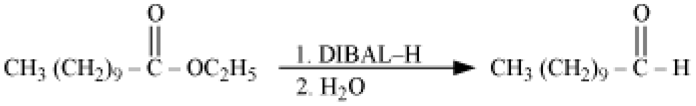
  Example:

$$CH_3 - CH = CH - CH_2 - CH_2 - CN \xrightarrow[2.\ H_2O]{1.\ AlH(i-Bu)_2} CH_3 - CH = CH - CH_2 - CH_2\,CHO$$

- **From esters**

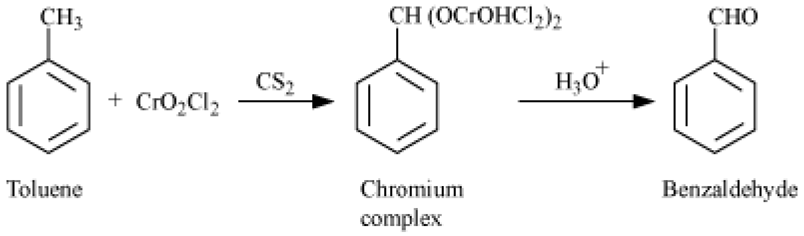
  $Esters \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} Aldehydes$

- Example:



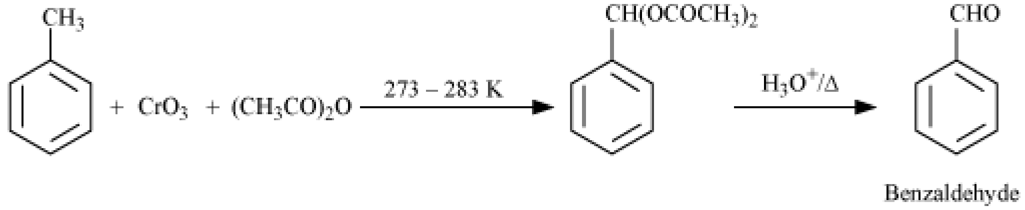
$$CH_3(CH_2)_9 - \overset{\overset{O}{\parallel}}{C} - OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9 - \overset{\overset{O}{\parallel}}{C} - H$$

- **From hydrocarbons**
- By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2)

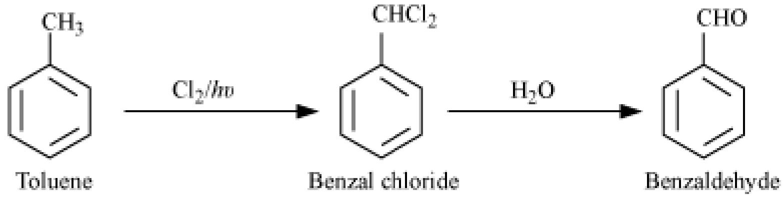


  This reaction is called Etard reaction.

- By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride

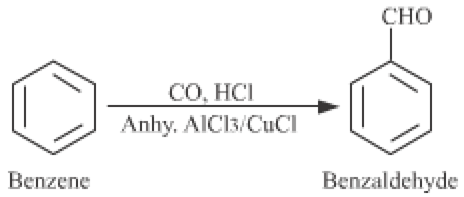


- By side chain chlorination followed by hydrolysis



By Gatterman-Koch reaction

Benzene or its derivative $\xrightarrow[\text{Anhy. AlCl}_3\text{/CuCl}]{\text{CO, HCl}}$ Benzaldehyde or substituted benzaldehyde

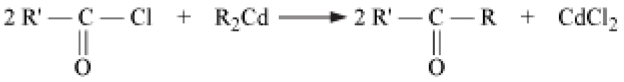


Preparation of Ketones

- **From acyl chlorides**

Treatment of acyl chlorides with dialkylcadmium gives ketones.

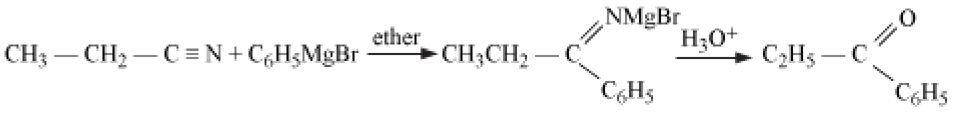
$$2R\text{–}Mg\text{–}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$



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

- **From nitriles**

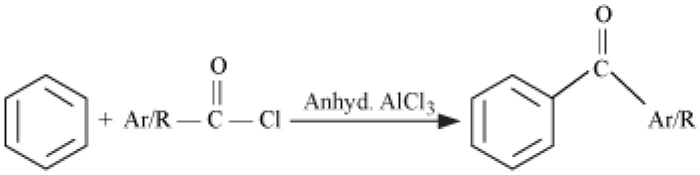
Treatment of nitrile with Grignard reagent followed by hydrolysis gives a ketone.



Propiophenone
(1-Phenylpropanone)

- **From benzene or substituted benzene (Friedel-Craft acylation reaction)**

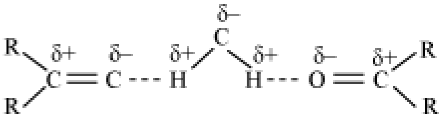
  Treatment of benzene or substituted benzene with acid chloride in presence of anhydrous aluminum chloride gives ketone.



Aldehydes and Ketones - Physical Properties & Chemical Reactions - I

Physical Properties of Aldehydes and Ketones

- Methanal – Gas at room temperature
- Ethanal – Volatile liquid
- Other aldehydes and ketones – Liquid or solid at room temperature
- Boling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.
- Reason: Weak molecular association in aldehydes and ketones, arising out of the dipole–dipole interactions
- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
- Reason: Absence of intermolecular hydrogen bonding
- Lower members of aldehydes and ketones are miscible with water in all proportions.
- Reason: They form hydrogen bonds with water.

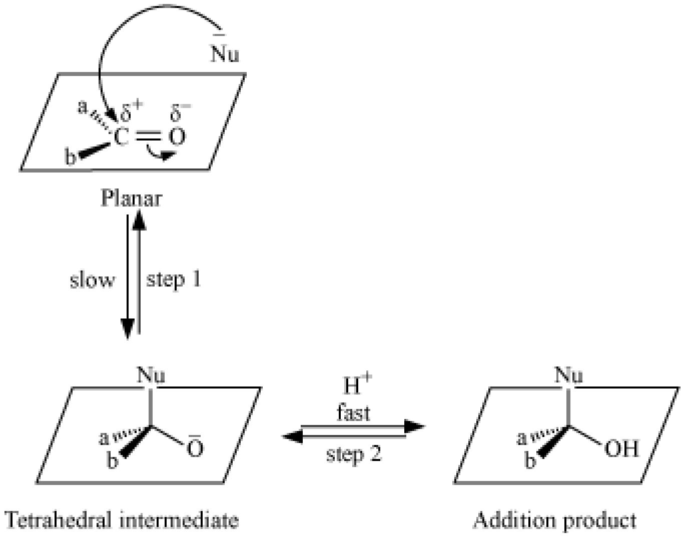


- Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc.
- Lower aldehydes have sharp pungent odours.
- As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

Chemical Reactions – I

Nucleophilic Addition Reaction

- **Mechanism**

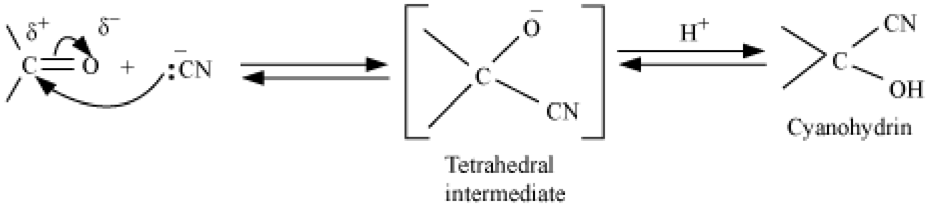


- Nucleophile (Nu^-) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon.
- In the process, hybridisation of carbon changes from sp^2 to sp^3.
- A tetrahedral alkoxide is formed as intermediate.
- **Reactivity**

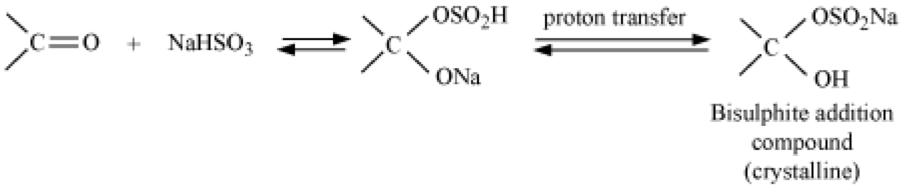
  Aldehydes are more reactive than ketones in nucleophilic addition reactions.
-

- Reason: Steric and electronic reasons
- **Examples:**
- Addition of hydrogen cyanide (HCN)

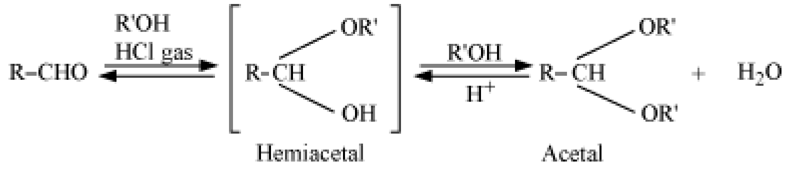
$$HCN + OH^- \longleftrightarrow :\bar{C}N + H_2O$$

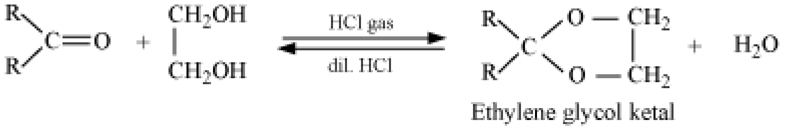


- Addition of sodium hydrogen sulphite ($NaHSO_3$)

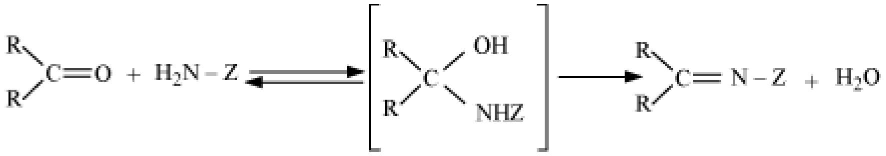


- Addition of alcohols



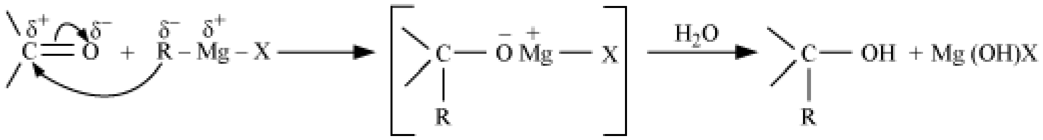


- Addition of ammonia and its derivatives



Z = alkyl, aryl, OH, NH_3, C_6H_5NH, $NHCONH_2$, etc.

- Addition of Grignard reagents



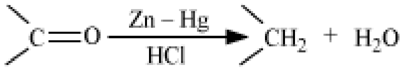
Reduction reactions

- **Reduction to alcohols**

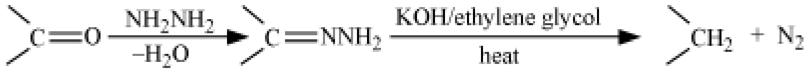
Aldehydes $\xrightarrow[\text{or Catalytic hydrogenation}]{\text{NaBH}_4 \text{ or LiAlH}_4}$ Primary alcohols

Ketones $\xrightarrow[\text{or Catalytic hydrogenation}]{\text{NaBH}_4 \text{ or LiAlH}_4}$ Secondary alcohols

- **Reduction to hydrocarbons**
- Clemmensen reduction



- Wolf–Kishner reduction

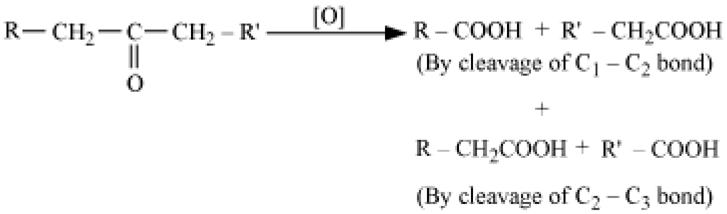


Oxidation reactions

- Aldehydes are oxidised to carboxylic acids by common oxidising agents such as $KMnO_4$, HNO_3, $K_2Cr_2O_7$, etc.

$$R - CHO \xrightarrow{[0]} RCOOH$$

- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On the other hand, ketones are not oxidised by mild oxidising agents.
- Ketones are oxidised under vigorous conditions, i.e., by strong oxidising agents and at elevated temperatures. It involves carbon–carbon bond cleavage.



$$R-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-R' \xrightarrow{[O]} \underset{\text{(By cleavage of } C_1-C_2 \text{ bond)}}{R-COOH + R'-CH_2COOH} + \underset{\text{(By cleavage of } C_2-C_3 \text{ bond)}}{R-CH_2COOH + R'-COOH}$$

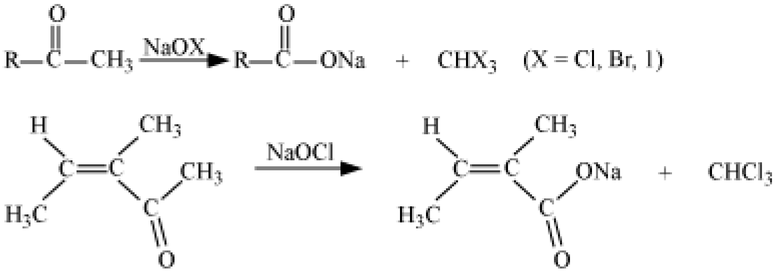
- **Tollen's test**

$$R-CHO+2\left[Ag\left(NH_3\right)_2\right]^+ +3OH^- \longrightarrow RCOO^- +2Ag+2H_2O+4NH_3$$

- **Fehling's Test**

$$R-CHO+2Cu^{2+}+5OH^- \longrightarrow RCOO^- +\underset{\text{red-brown ppt}}{Cu_2O}+3H_2O$$

- **Oxidation of methyl ketones by haloform reaction**

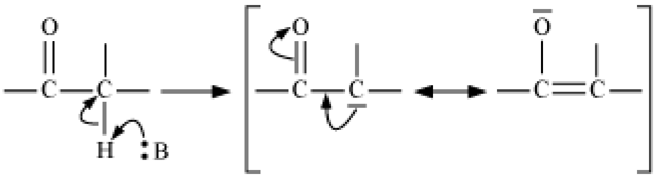


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-ONa + CHX_3 \quad (X = Cl, Br, I)$$

Reactions Due to α-Hydrogen & Uses of Aldehydes and Ketones

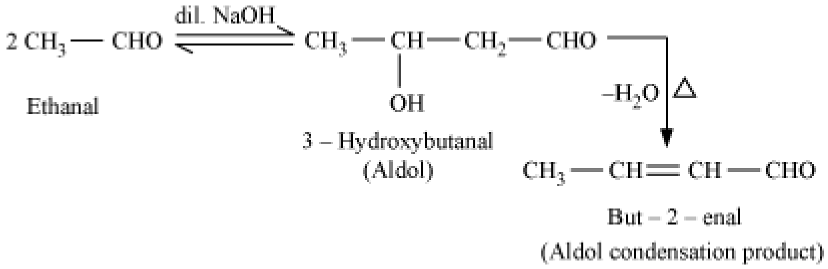
Reactions due to α-Hydrogen

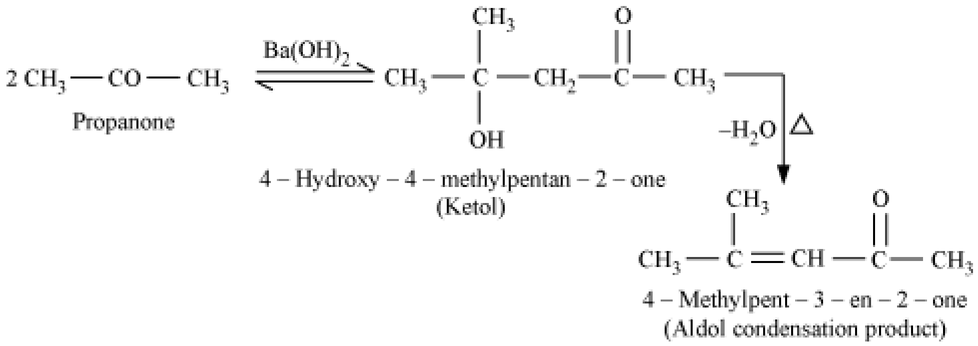
- **α-Hydrogen of aldehydes and ketones are acidic**: They undergo a number of reactions due to the acidic nature of α-hydrogen.
- Reason for the acidity of α-hydrogen: Strong electron-withdrawing effect of the carbonyl group, and resonance stabilisation of the conjugate base



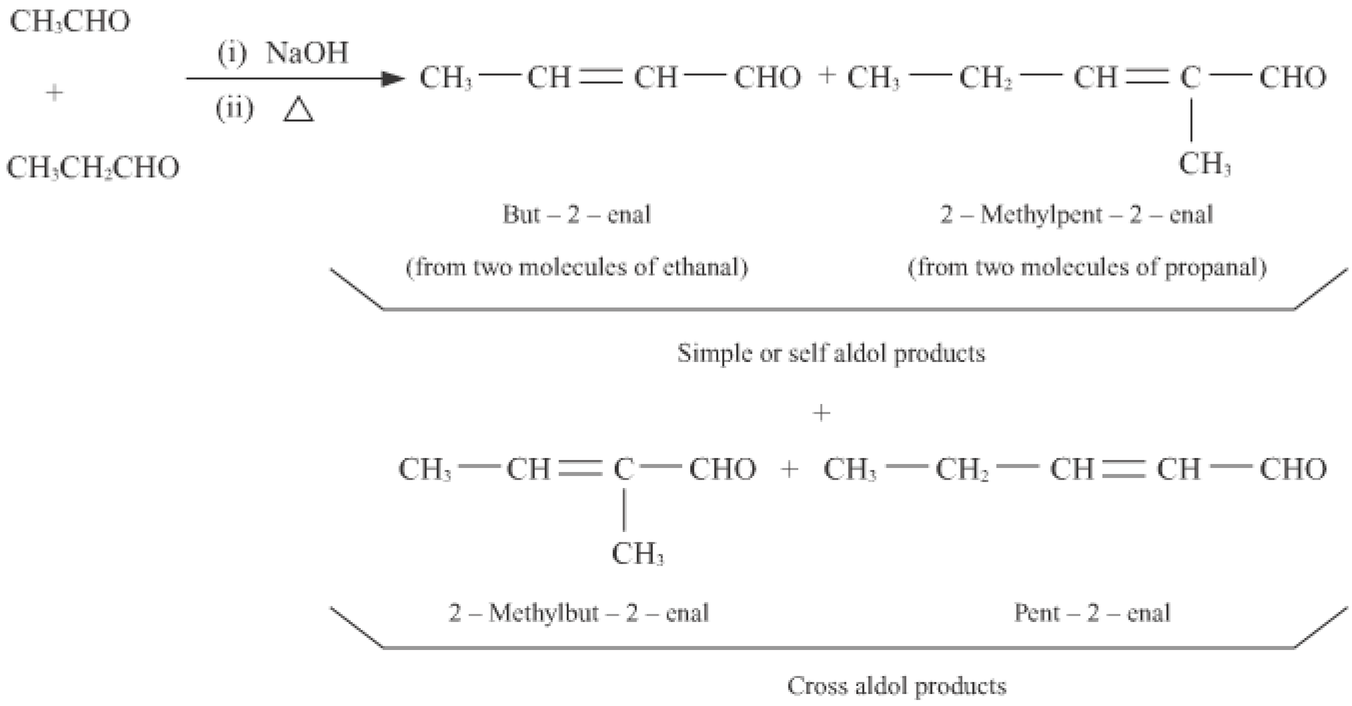
- **Aldol condensation (or aldol reaction)**

Aldehydes and ketones with at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.

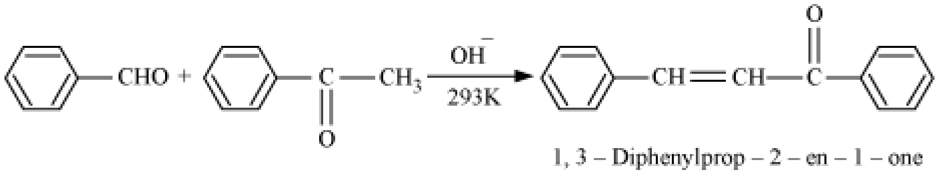




- **Cross-aldol condensation**: Aldol condensation carried out between two different aldehydes and/or ketones
- If both of them contain α-hydrogen atoms, then it gives a mixture of four products.



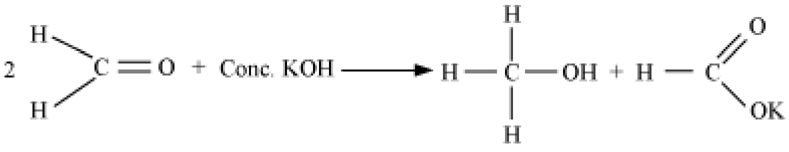
- Ketones can also be used as one component in cross-aldol reactions.



1, 3 – Diphenylprop – 2 – en – 1 – one
{Benzalacetophenone}
(Major product)

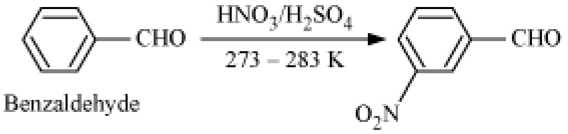
Other Reactions

- **Cannizaro reaction**
- Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with a concentrated alkali.
- Example:



Formaldehyde
Methanol
Potassium formate

- **Electrophilic substitution reaction**
- Aromatic aldehydes and ketones undergo electrophilic substitutions at the ring.
- Carbonyl group acts as a deactivating and *meta*-directing group.



Benzaldehyde
m – Nitrobenzaldehyde

Uses of Aldehydes and Ketones

- As solvents
- As starting materials and reagents for the synthesis of other products
- Formaldehyde {formation (40%) solution}– Used for preserving biological specimens, bakelite, urea formaldehyde glues and other polymers products
- Acetaldehyde – In the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs

- Benzaldehyde – In perfumery and in dye industries
- Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours
- Acetone and ethyl methyl ketone – Common industrial solvents

Carboxyl Group - Nomenclature and Structure & Methods of Preparation

Nomenclature

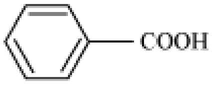
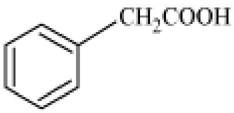
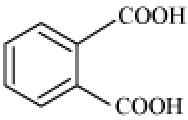
In the IUPAC system, aliphatic carboxylic acids are named as follows:

- By replacing the ending '– e' in the name of the corresponding alkane with '– *oic* acid'
- Carboxylic carbon is numbered one.
- If more than one carboxyl groups are present, then the ending '– *e*' of the alkane is retained.
- The number of carboxyl groups is indicated by adding prefix, *d*, tri, etc. to the term '*oic*'.

The given table lists the common and IUPAC names and structures of some carboxylic acids.

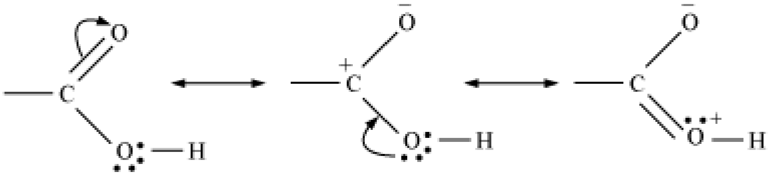
Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid

$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$HOOC-COOH$	Oxalic acid	Ethanedioic acid
$HOOC-CH_2-COOH$	Malonic acid	Propanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butanedioic acid
$HOOC-(CH_2)_3-COOH$	Glutaric acid	Pentanedioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	Hexanedioic acid
$HOOC-CH_2-CH(COOH)-CH_2-COOH$	–	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

Structure of Carboxyl Group

- Carboxyl carbon is less electrophilic than carbonyl carbon because of resonance.



- Bonds to the carboxyl carbon lie in one plane and are separated by about 120°.

Methods of Preparation of Carboxylic Acid

- **From primary alcohols**

$$RCH_2OH \xrightarrow[\text{2. } H_3O^+]{\text{1. Alkaline } KMnO_4} RCOOH$$

$$RCH_2OH \xrightarrow{K_2Cr_2O_7/H^+} RCOOH$$

$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3-H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

- **From primary aldehydes**

$$RCHO \xrightarrow{[O]} R-COOH$$

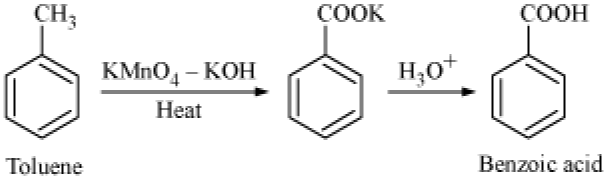
Oxidising agents – HNO_3, $KMnO_4$, $K_2Cr_2O_7$

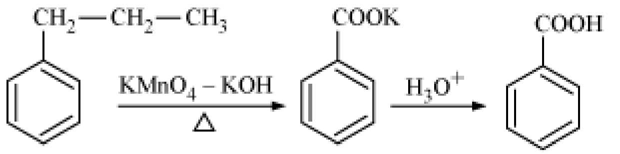
Mild oxidising agents – Tollen’s reagent and Fehling’s reagent

- **From alkyl benzenes**

$$\text{Alkyl benzenes} \xrightarrow[\text{alkaline or acidic } KMnO_4]{\text{Chromic acid or}} \text{Aromatic carboxylic acids}$$

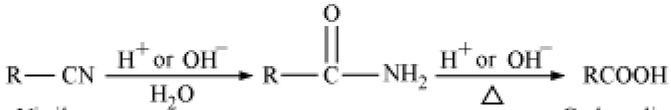
- 1° and 2° alkyl benzene are oxidised in this manner.
- Tertiary group is not affected.





Benzoic acid

- **From nitriles and amides**

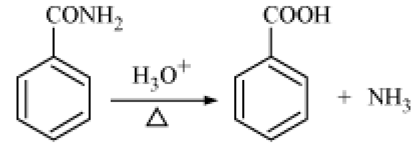


$$R-CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$$

Nitrile Carboxylic acid

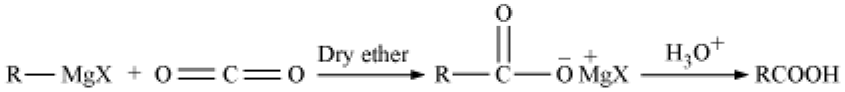
$$CH_3CONH_2 \xrightarrow[\Delta]{H2O^+} CH_3COOH + NH_3$$

Ethanamide Ethanoic acid



Benzamide Benzoic acid

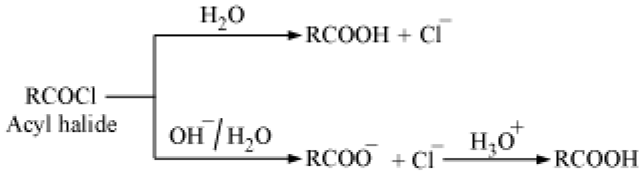
- **From Grignard reagents**



$$R-MgX + O=C=O \xrightarrow{\text{Dry ether}} R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_3O^+} RCOOH$$

Grignard reagent Carboxylic acid

- **From acyl halides**



- **From acyl anhydrides**

$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5COOH$$

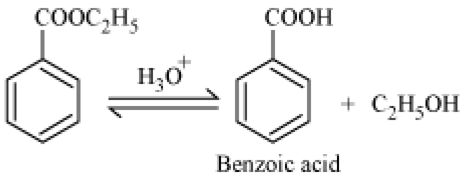
Benzoic anhydride Benzoic acid

$$C_6H_5COO\ COCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$$

Benzoic ethanoic anhydride Benzoic acid Ethanoic acid

- **From esters**
- Ester $\xrightarrow{\text{Acidic hydrolysis}}$ Carboxylic acid

  Example:



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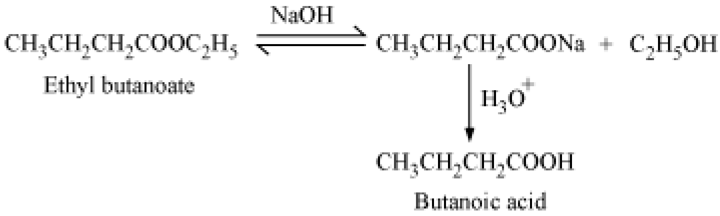
$$\text{Ester} \xrightarrow{\text{Basic hydrolysis}} \text{Carboxylate} \xrightarrow{H_3O^+} \text{Carboxylic acid}$$

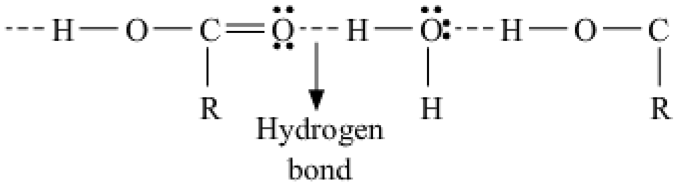
Examples:



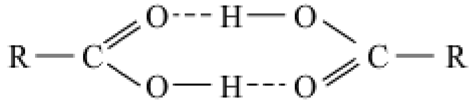
Chemical Reactions of Carboxylic Acids

Physical properties

- Lower carboxylic acids are colourless liquids while those with high molecular mass are wax like solids at room temperature.
- Lower carboxylic acids are soluble in water due to formation of hydrogen bonds. Solubility in water decreases with increase in molecular mass due to increases in non-polar hydrocarbon chain. All the carboxylic acids are soluble in organic solvents.



- Boiling point of carboxylic acids are higher than that of alcohol of similar molecular weight.This is because of the greater extent of intermolecular hydrogen bonding in carboxylic acid than in alcohol.



Reactions Involving Cleavage of O–H Bond

Acidity

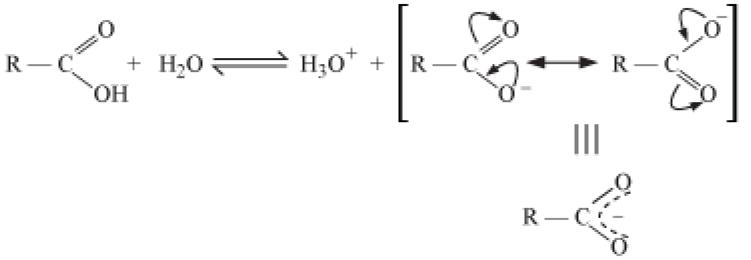
- Reactions with metals and alkalies:

$$2R-COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2RCOONa} + H_2$$

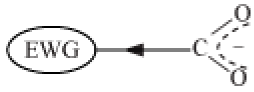
$$R-COOH + NaOH \longrightarrow R-COONa + H_2O$$

$$R-COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

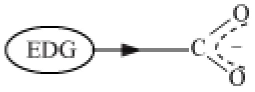
- Dissociate in water to give resonance-stabilised carboxylate anions and hydronium ion



- Effects of substituents on the acidity of carboxylic acids



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



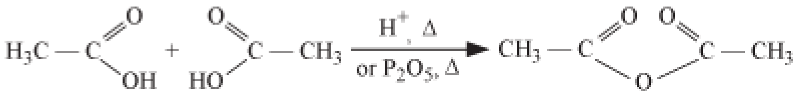
Electron-donating group (EDG) destabilises the carboxylate anion and weakens the acid

- The order of the effect of the groups in increasing acidity is

  Ph < I < Br < Cl < F < CN < NO_2 < CF_3

Reactions Involving Cleavage of C–OH Bond

- **Formation of anhydride**



Ethanoic acid

Ethanoic anhydride

- **Esterification**

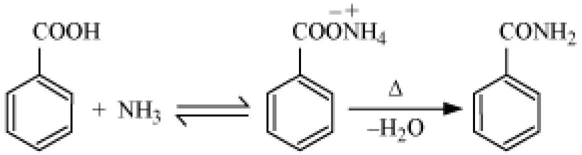
$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xleftrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + \underset{\text{Water}}{H_2O}$$

- **Reactions with PCl5, PCl3, and SOCl2**

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

- **Reaction with ammonia**

$$CH_3COOH + NH_3 \longleftrightarrow \underset{\text{Ammonium acetate}}{CH_3CO\overset{-}{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$



Ammonium benzoate

Benzamide

Reactions Involving –COOH group

- **Reduction**

$$R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i)} LiAlH_4\text{/Ether or } B_2H_6} \underset{\text{(Alcohol)}}{R-CH_2-OH}$$

- **Decarboxylation**

$$R-COONa \xrightarrow[\text{Heat}]{\text{NaOH}-\text{CaO}} \underset{\text{(Alkane)}}{R-H} + Na_2CO_3$$

-

- Kolbe’s electrolysis – On electrolysis of an aqueous solution of alkali metal salts of carboxylic acids, the salts undergo decarboxylation, forming hydrocarbons containing twice the number of carbon atoms present in the alkyl group of the acid.

Substitution reactions in the hydrocarbon part

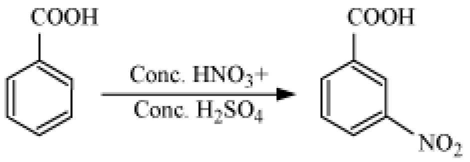
- Halogenation (Hell-Volhard-Zelinsky reaction)

$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Phosphorus}} R-\underset{\substack{| \\ X}}{CH}-COOH$$

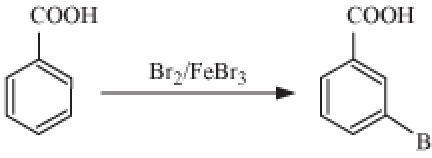
X = Cl, Br

α-Halocarboxylic acid

- **Ring substitution**
- Undergo electrophilic substitution reactions (except Friedel-Craft reaction)



m-Nitrobenzoic acid



m-Bromobenzoic acid

Uses of Carboxylic Acids

- Methanoic acid – In rubber, textile, dyeing, leather and electroplating industries
- Ethanolic acid – As a solvent and as a vinegar in food industry
- Hexanoic acid – In the manufacture of nylon-6, 6
- Higher fatty acids – For the manufacture of soaps and detergents

- Esters of benzoic acid – In perfumery
- Sodium benzoate – As a food preservative