

Class XII Chemistry UNIT 12 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1. Aldehydes and ketones, are commonly called as carbonyl compounds. In aldehydes, the carbonyl group (C=O) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms
2. The carbon and oxygen of the carbonyl group are sp^2 hybridised and the carbonyl double bond contains one σ -bond and one π -bond. The electronegativity of oxygen is much higher than that of the carbon, so there electron cloud is shifted towards the oxygen. Therefore, C-O bond is polar in nature.
3. In Rosemund's reduction, poisoning of Pd with $BaSO_4$ prevent reduction of $R - CHO$ to $R - CH_2OH$.
4. In the reaction of toluene with CrO_3 , acetic anhydride is used to protect benzaldehyde by forming benzylidene diacetate to avoid its oxidation to benzoic acid.
5. Order of reactivity of aldehydes and ketones towards nucleophilic addition is:
 - (i) $HCHO > CH_3CHO > CH_3CH_2CHO$.
 - (ii) $HCHO > RCHO > RCO R$.
 - (iii) $ArCHO > ArCOR > ArCO Ar$.
6. Benzaldehyde does not reduce Fehling's reagent.
7. Aldehydes and ketones with atleast one α -H atom get condensed in presence of a base. This is known as Aldol condensation.
8. Aldol condensation involves carbanion as intermediate.
9. Aldehydes with no α -H atoms under Cannizzaro's reaction.
10. Ketones react with dihydric alcohols to form cyclic ketals.
11. Monocarboxylic acids having (C_{12} - C_{18}) carbon atoms, are called fatty acids.
12. Boiling points of carboxylic acids is greater than corresponding alcohols.
13. Presence of EWGs enhances the acidic character of carboxylic acids.
14. $-COOH$ group is *m*-directing in electrophilic substitution reactions.
15. Compounds containing $-CHO$ group are named as carbaldehydes if –

CHO groups are three or more.

16. Isomerism: Chain, position and functional.

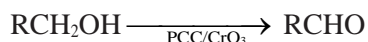


17. Structure of $-\text{CHO}$ group sp^2 hybridized.



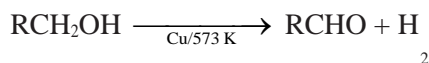
18. General Methods of Preparation:

(i) Controlled oxidation of 1° alcohols:

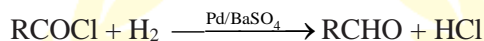


(Collin's reagent)

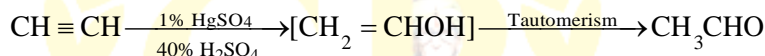
(ii) Dehydrogenation of 1° alcohols:



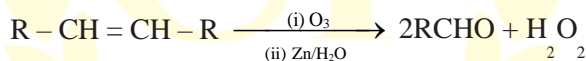
(iii) From Rosenmund reaction/reduction:



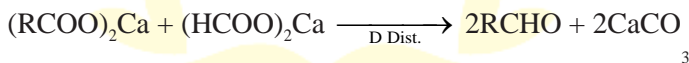
(iv) Hydration of alkynes:



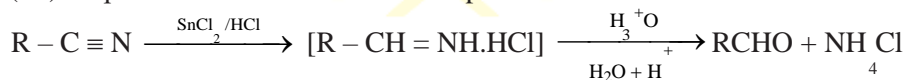
(v) Reductive ozonolysis of alkenes:



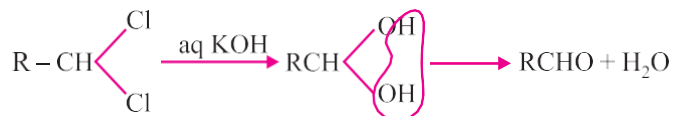
(vi) From salts of fatty acids:



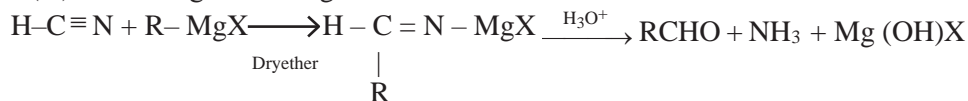
(vii) Stephen's reduction of nitrile compounds:



(viii) Hydrolysis of geminal halides:

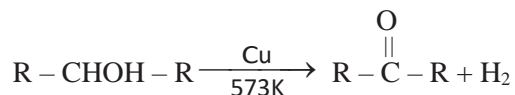


(ix) From Grignard's reagent:

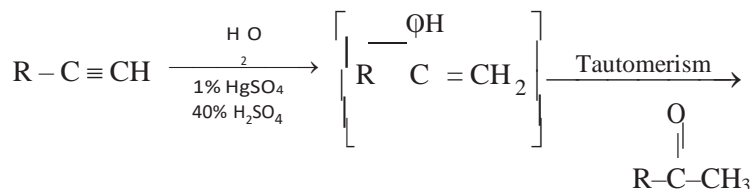


General Methods of Preparation of Ketones only

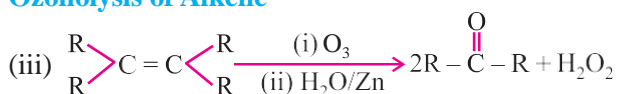
(i) Dehydrogenation of 2° alcohols:



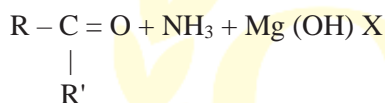
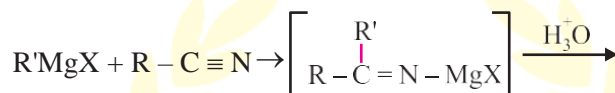
(ii) Hydration of alkynes:



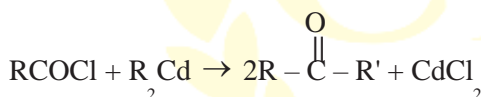
Ozonolysis of Alkene



(iv) From Grignard's reagents:



(iv) From acid chlorides:



Physical Properties:

- HCHO is a gas at normal temperature. Formalin is 40% as solution of HCHO. Due to polarity, they have high values of boiling point. Solubility in water is only for lower members.
- The boiling point of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
- The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.

Reactivity:

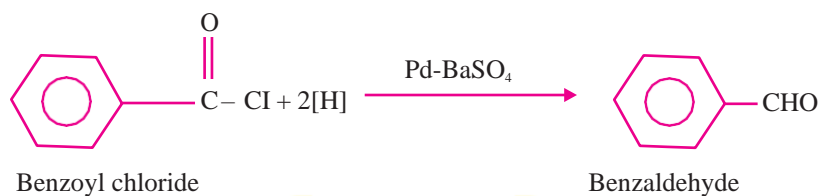
(i) +I effect of alkyl groups decreases the +ve charge on carbonyl carbon.

(ii) Steric hindrance: Bulky group hinders approach of nucleophile.

(iii) α -hydrogen atom is acidic due to resonance.

1. ROSENMUND REDUCTION:

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes



2. STEPHEN REACTION

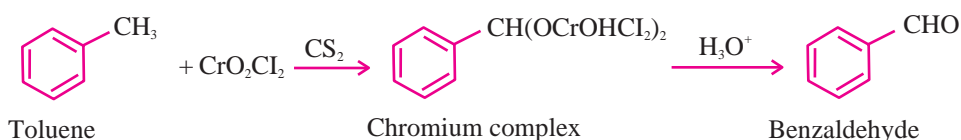
Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.



3. ETARD REACTION

On treating toluene with chromyl chloride CrO_2Cl_2 , the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

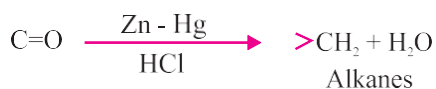
OR



This reaction is called Etard reaction

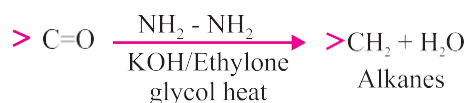
4. CLEMMENSEN REDUCTION

The carbonyl group of aldehydes and ketone is reduced to $-\text{CH}_2$ group on treatment with zinc amalgam and conc. Hydrochloric acid.



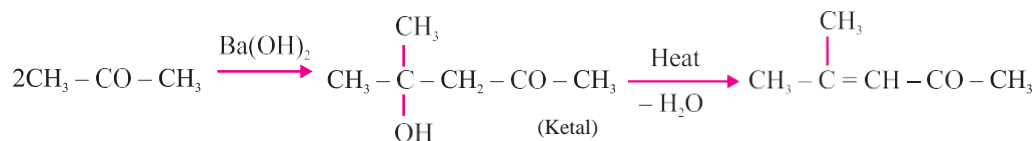
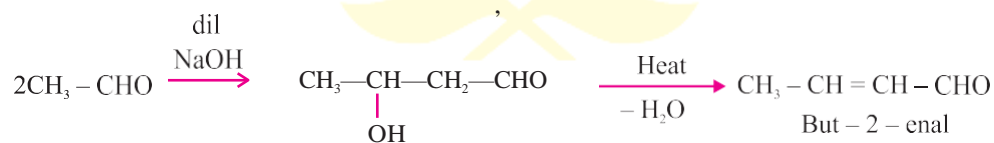
5. WOLFF- KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol



6. ALDOL CONDENSATION

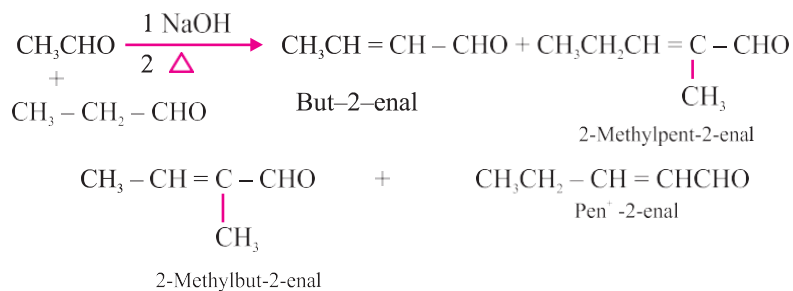
Aldehydes and ketones having at least one α -hydrogen condense in the presence of dilute alkali as catalyst to form α -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol).



4-Methyl pent-3-en-2-one

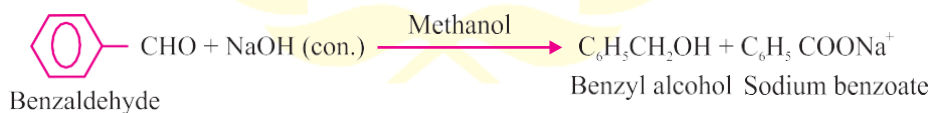
7. CROSS-ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



8. CANNIZZARO REACTION

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.



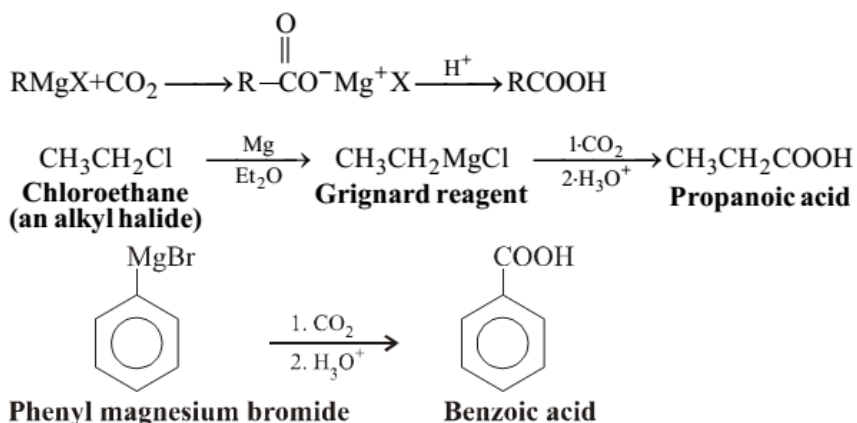
CARBOXYLIC ACID

Methods of Preparation of Carboxylic Acids

The preparation of carboxylic acids can be done using various methods. Some of them are listed below-

1. Preparation of Carboxylic Acid From the Grignard Reagent:

The preparation of carboxylic acid can be done using Grignard reagents chemical reaction. It can be simply done by first reacting to Grignard reagent with dry ice (crushed) or solid CO_2 . In this step, salts of carboxylic acids are formed, after that, acidification of these salts with mineral acids gives corresponding carboxylic acids.



2. Preparation of Carboxylic Acid From Alcohol:

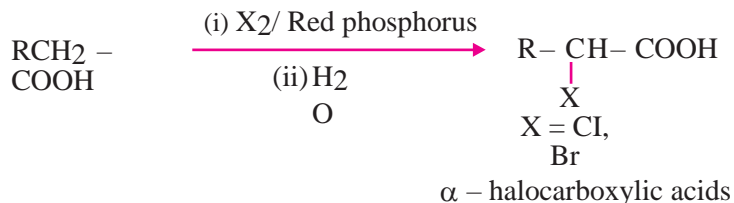
It is very easy to prepare carboxylic acids from alcohol. Alcohols easily undergo oxidation reactions using oxidizing agents such as potassium permanganate (KMnO_4), chromium trioxide ($\text{CrO}_3\text{-H}_2\text{SO}_4$), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). These strong oxidizing agents make alcohol undergo an oxidation reaction twice and convert alcohol into carboxylic acids directly.

3. Preparation of Carboxylic Acid From Ester:

When ester undergoes acid hydrolysis, it leads to the formation of carboxylic acids. In the first step of basic hydrolysis of ester, it produces carboxylates. On further acidification, it gives corresponding carboxylic acids. Also, it is necessary to carry out hydrolysis of esters with mineral acids or alkali to produce a carboxylic acid.

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)

Carboxylic acids having an α - hydrogen is 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.



2. ESTERIFICATION

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc. H_2SO_4 as catalyst to form esters.



18. Vinegar is 8 to 10% solution of CH_3COOH .
19. α -hydrogen atoms in carboxylic acid are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.
21. Relative acid strength of $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3$. It is because a strong acid has weak conjugate base.
22. Some dicarboxylic acids bearing general formula $\text{HOOC} - (\text{CH}_2)_n - \text{COOH}$ where $n = 0, 1, 2, \dots$ etc.
 - $\text{HOOC} - \text{COOH}$ Oxalic acid 1, 2 ethanedioic acid
 - $\text{HOOC} - \text{CH}_2 - \text{COOH}$ Malonic acid 1, 3 propanedioic acid
 - $\text{HOOC} - (\text{CH}_2)_2 - \text{COOH}$ Succinic acid 1, 4 butanedioic acid
 - $\text{HOOC} - (\text{CH}_2)_3 - \text{COOH}$ Glutonic acid 1, 5 pentamdioic acid
 - $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ Adipic acid 1, 6 hexanedioic acid
23. Melting points: Higher: Even carbon atoms than next lower or higher homologues containing even number of carbon atoms due to symmetry and closer packing of molecules in the crystal lattice.

