

NEET Revision Notes

Chemistry

Aldehyde, ketone and Carboxylic acid

Aldehydes and ketones are carbonyl compounds, which means they are organic substances. The general formula for aldehydes is RCHO , while the general formula for ketones is RCOR' . C=O is the common group for carbonyl compounds.



Image: Structure of carbonyl group

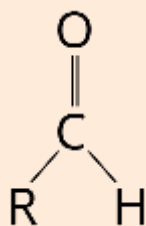


Image: Structure of carbonyl group in aldehyde

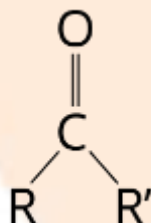


Image: Structure of carbonyl group in ketone

Ketones and aldehydes are employed as solvents, starting materials, and reagents in the chemical industry to synthesize other products.

Ketones dissolve a wide range of organic materials, have convenient boiling points for easy distillation, and have low toxicities. Formaldehyde is well known as the formalin solution used to preserve biological specimens and is also used in the formation of several important polymers such as Bakelite.

Many other ketones and aldehydes are utilized in foods, pharmaceuticals, and other items as flavorings and additives.

Almond extract is primarily made up of benzaldehyde, and carvone provides spearmint chewing gum with its minty flavor.

Physical properties

Through coplanar sigma bonds aligned about 120 degrees apart, the carbonyl carbon atom is sp^2 hybridized and connected to three additional atoms. To form a pi bond, the unhybridized p orbital coincides with an oxygen "p" orbital.

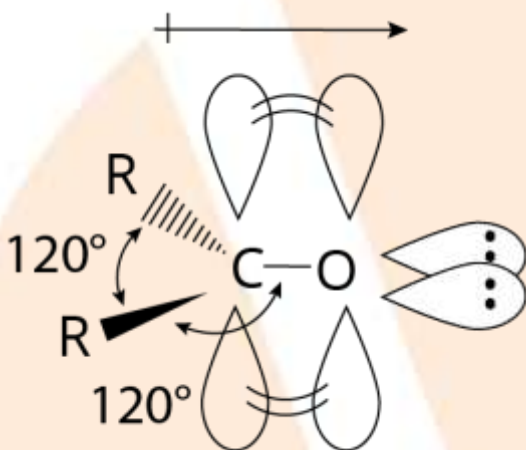


Image: Structure of carbonyl group

Functional Group	Length	Energy
Ketone C=O bond	1.23 \AA	745 kJ/mol
Alkene C=O bond	1.34 \AA	611 kJ/mol

1. Dipole moment

Since oxygen is more electronegative than carbon and the bonding electrons are not shared equally, the carbonyl group's double bond has a significant dipole moment. Ketones and aldehydes have greater dipole moments than most alkyl halides and ethers because the less firmly bound π electrons are drawn more strongly toward the oxygen atom. We can use resonance forms to represent the unequal distribution of π electrons.

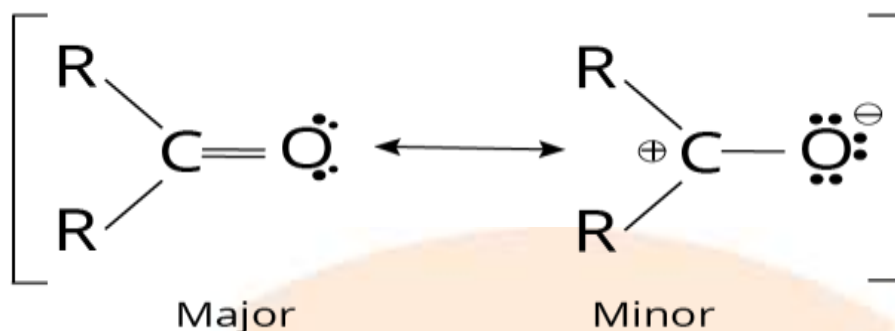


Image: Resonance forms of carbonyl group

Because it involves more bonds and less charge separation, the first resonance form is more critical. The significant dipole moments of the ketones and aldehydes are illustrated here to demonstrate the contribution of the second structure.

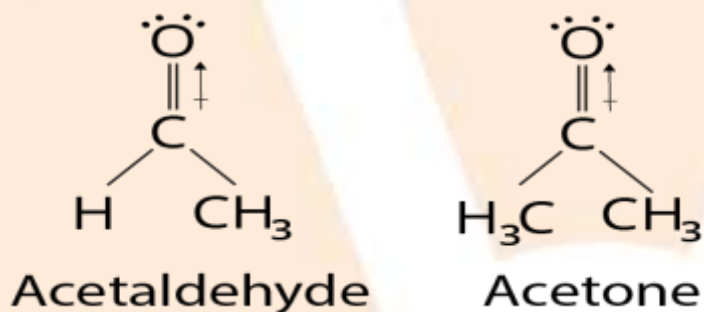


Image: Structure of acetaldehyde and acetone

Lewis acid is formed when a positively polarised carbon atom works as an electrophile and negatively polarised oxygen acts as a nucleophile (Lewis base)

2. Boiling Point

Ketones and aldehydes lack O-H and N-H bonds, they are unable to create hydrogen bonds with one another. As a result, their boiling points are lower than those of similar molecular weight alcohols.

The ketone and aldehyde are more polar and have a higher boiling point than the ether and alkane, but are less polar and have a lower boiling point than the hydrogen-bonded alcohol.

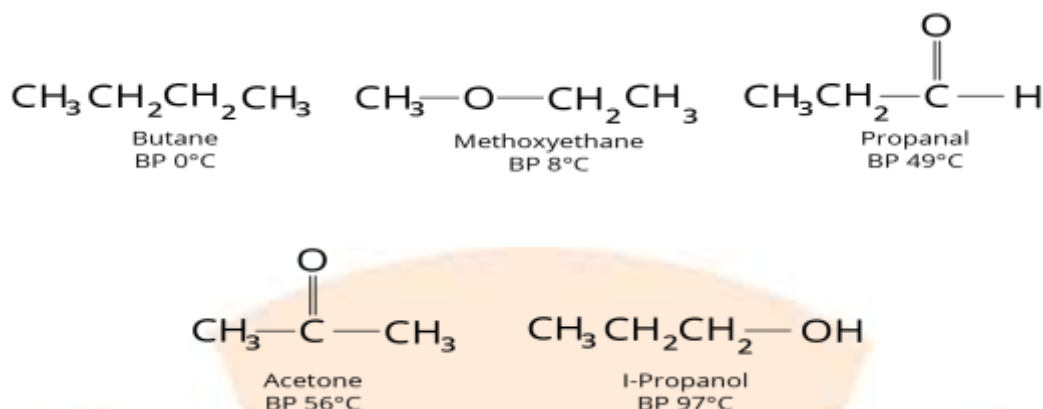


Image: Boiling point of ketone and aldehyde

3. Solubility

Although pure ketones and aldehydes are unable to form hydrogen bonds with one another, they do have lone pairs of electrons and can act as hydrogen bond acceptors for other compounds that have O-H or N-H bonds. The unshared electrons on a carbonyl oxygen atom can establish a hydrogen bond with the -OH hydrogen of water or alcohol, for example.

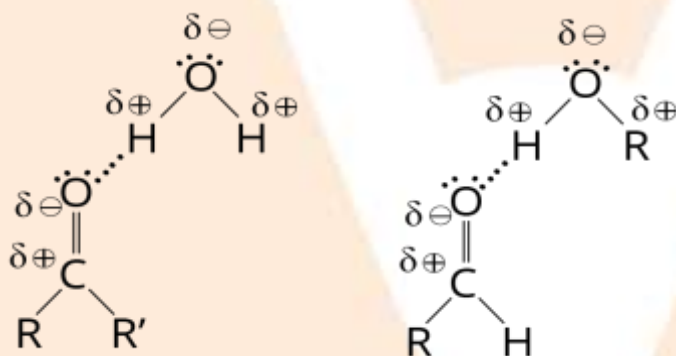


Image: Linkage of ketone and aldehyde with water

Ketones and aldehydes are good solvents for polar hydroxylic compounds like alcohols because of this hydrogen bonding. They're also highly water-soluble. Acetaldehyde and acetone are miscible with water (that is, they are soluble in any concentrations). Water is soluble in other ketones and aldehydes with up to four carbon atoms. These qualities of solubility are comparable to those of ethers and alcohols, which form hydrogen bonds with water as well.

Preparation of carbonyl compound

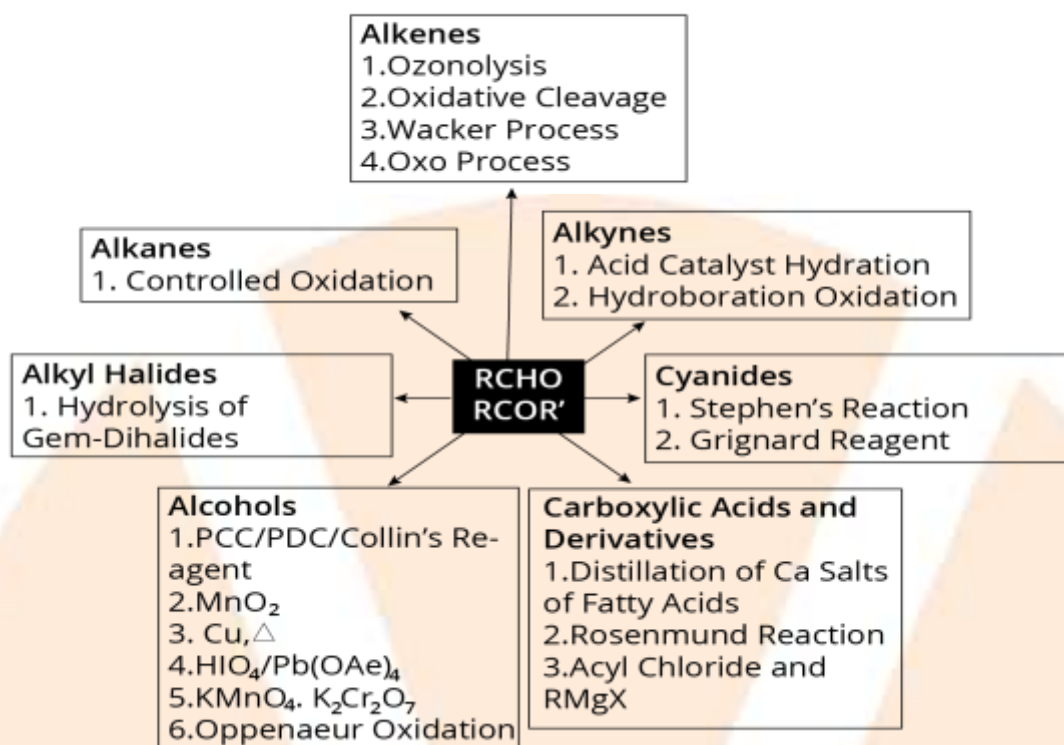


Image: Preparation of carbonyl group

1. Alkanes

Carbonyl compounds are formed through the controlled oxidation of alkanes at high temperatures and pressures in the presence of a catalyst.

Example:



Image: Oxidation of alkane

2. Alkenes

Ozonolysis

If alkenes are generated using O_3 and then reduced with $\text{Zn}/\text{H}_2\text{O}$, they can be oxidized to aldehydes and ketones. The aldehyde produced cannot be separated if a reducing agent is not applied since it is further oxidized to carboxylic acids.

Example:

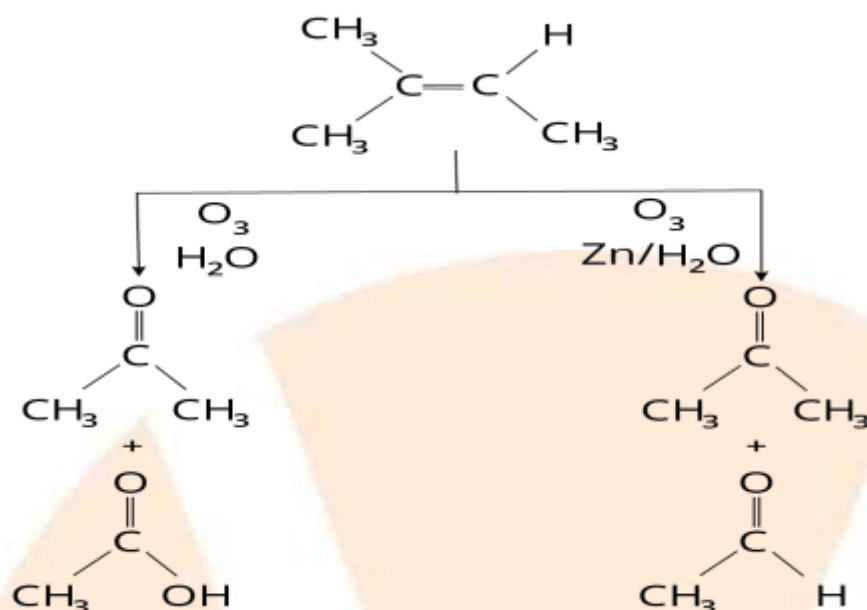


Image: Ozonolysis of alkene

Oxidative Cleavage

Strong oxidizing agents, such as acidic $K_2Cr_2O_7$ or alkaline $KMnO_4$, promote double bond oxidation, resulting in ketones and carboxylic acids.

Example:

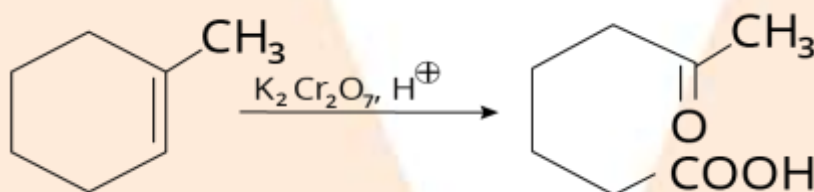


Image: Oxidation cleavage

Wacker Process

It's how acetaldehyde is made in the industry.

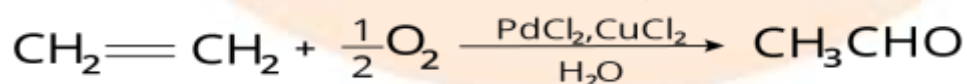


Image: Wacker process

Oxo Process

Hydroformylation is another name for this process. Under pressure, carbon monoxide and hydrogen are passed over a catalyst.

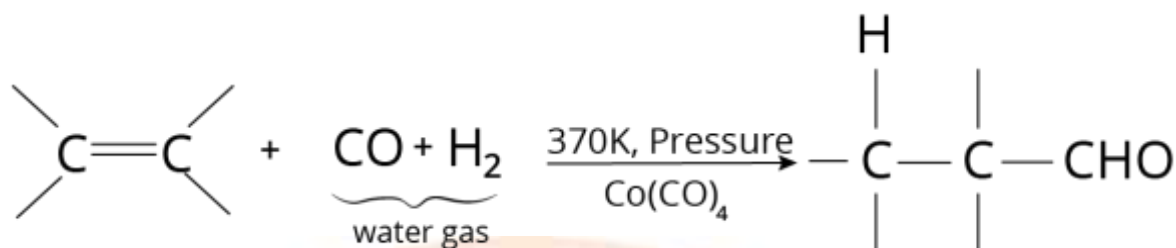


Image: Hydroformylation reaction

The resulting product is a mixture of isomeric and branched-chain aldehydes.

3. Alkynes

Acid Catalysed hydration in presence of Mercuric salt

This reaction occurs after the Markovnikov addition.

Example:

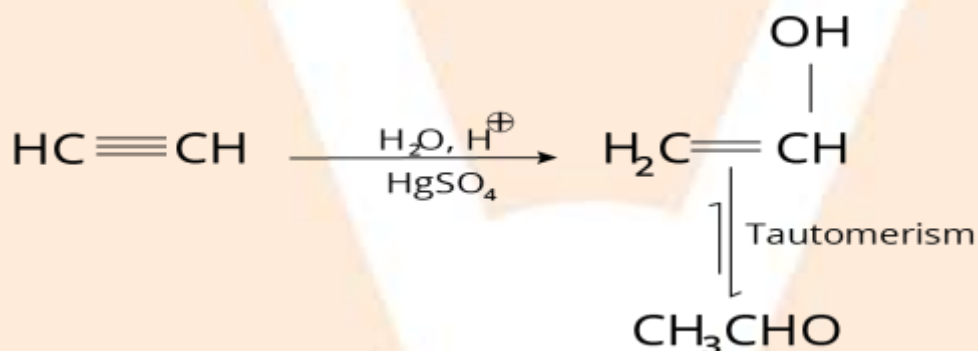


Image: Reaction of alkynes with mercuric salt

4. Alkyl Halides

Carbonyl compounds are formed when geminal dihalides are hydrolyzed.

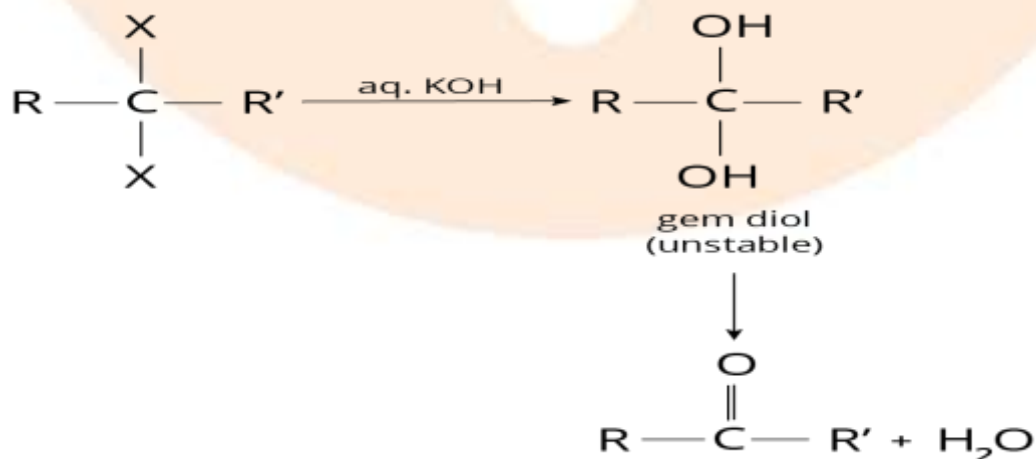


Image: Reaction of alkyl halide

5. Alkyl Cyanides

Reduction of Cyanides

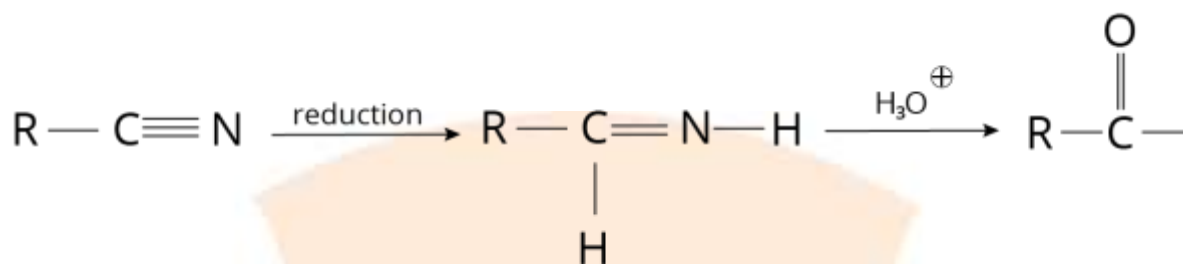


Image: Reaction of cyanides

1. The reaction is known as Stephan's Reduction when it is carried out with $\text{SnCl}_2, \text{HCl}$.
2. DIBAL-H can also be used for the reduction (Di-Isobutyl Aluminium Hydride)
3. This approach produces only aldehydes.

6. Alcohols

Using proper reagents, primary alcohols (1°) are oxidized to aldehydes, whereas secondary alcohols (2°) are oxidized to ketones. The following procedures will not oxidize tertiary alcohols (3°).

Manganese dioxide or MnO_2

MnO_2 oxidizes allylic, benzylic, and propargylic alcohol to aldehydes and ketones.

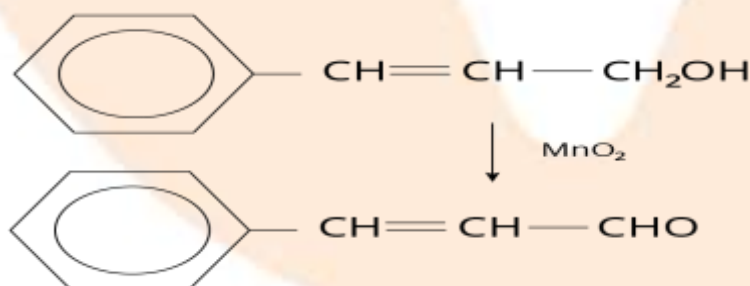


Image: Oxidation of alcohols

7. Carboxylic Acids and Derivates

Decarboxylation of Ca Salts

Heating a calcium salt of monocarboxylic acids produces ketone. The result is an aldehyde when heated with the calcium salt of formic acid.

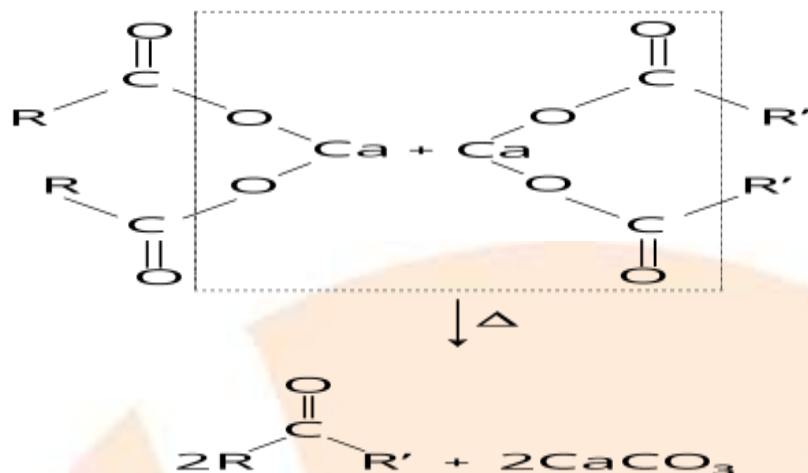


Image: Decarboxylation reaction

Rosemund's Reaction

Palladium catalyst supported on barium sulphate is used to reduce acid chloride in boiling xylene. For intense poisoning, small amounts of quinoline and sulphur are also added. Acid chloride can also be converted to the aldehyde using lithium t-butoxyaluminium hydride.

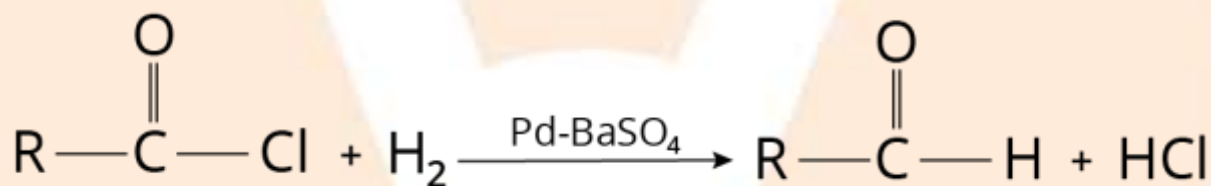


Image: Rosemund's reaction

Reactions of Carbonyl Compounds

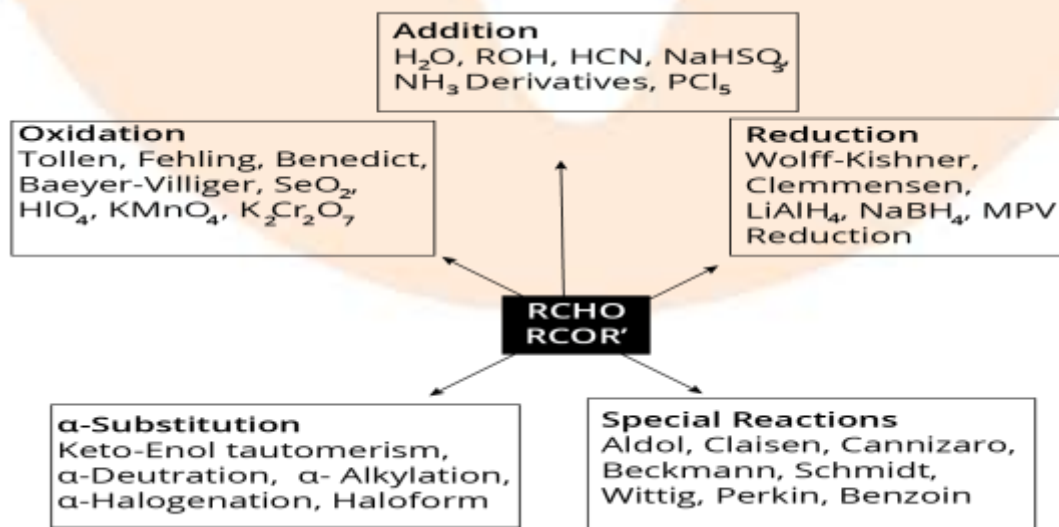


Image: Reactions of carbonyl compounds

1. Addition Reactions

General Mechanism

A tetrahedral carbonyl compound is formed from a trigonal carbonyl compound. The electronic and steric factors indicate that aldehyde is more reactive than ketone.

Addition of H_2O - Hydrate Formation

Hydrate is a geminal diol that is usually unstable, which is why it can't be separated from the water. The equilibrium constant, which indicates the stability of the corresponding hydrate, affects formation.

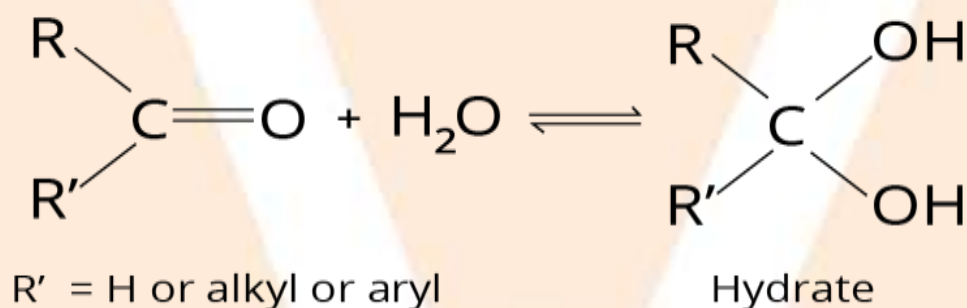


Image: Addition reaction

The hydrate is stabilized by electron-withdrawing groups.

2. Reduction Reactions

Reduction to Alkanes

(A) Wolff-Kishner Reduction

When hydrazone or semicarbazone is heated to 180°C with sodium ethoxide, nitrogen and hydrocarbon are released.

(B) Clemmensen Reduction

With an excess of the amalgamated zinc (Zn-Hg) and HCl , aldehydes and ketones that are not acid sensitive give rise to the corresponding alkanes.

3. Oxidation Reactions

Aldehydes are powerful reducing agents because they are easily oxidised. Fehling's solution (an alkaline solution of Cu^{2+} with tartaric acid) is reduced to the red cuprous oxide by aldehydes, while Tollen's reagent (ammoniacal silver

nitrate) is reduced to metallic silver by aldehydes. Cu^{2+} salt is not reduced by benzaldehyde (Fehling solution). Ketones do not decrease Tollen's reagent or the Fehling solution (except α -hydroxy ketones).

Tollen's test is positive when benzaldehyde is present. Permanganate, acid dichromates, and other oxidizing agents oxidize all aldehydes and ketones. These powerful oxidizers oxidize nearby carbon atoms in ketonic carbonyls, leaving the carbonyl group primarily with smaller alkyl groups (Popoff's rule).

4. Alpha substitutions

A hydrogen atom at the alpha carbon atom (the carbon adjacent to the carbonyl group) is replaced by another group in alpha replacements. Because the 'enolate ion that arises from its removal is resonance-stabilized, with the negative charge delocalized over the alpha carbon atom and the carbonyl oxygen atom, the alpha hydrogen is more acidic.

Haloform Reaction

Methyl ketones are cleaved in the presence of a base when they react with excess halogen. A trihalomethane (haloform) and a carboxylate salt are the end products. The rate has been found to be independent of bromine concentration in aqueous sodium hydroxide. The reaction is used to determine the structure of things. In most cases, the positive iodoform (bright yellow ppt) confirms as part.

5. Special Reactions

Aldol Condensation

(A) Self- Aldol Condensation

(At or below room temperature) dimerizes and produces aldol.

The reaction includes the nucleophilic addition of an enolate ion to the carbonyl group., α, β unsaturated aldehyde or ketone is the result of the subsequent dehydration. Aldehydes are better than ketones for aldol condensation.

(B) Cross- Aldol Condensation (Claisen – Schmidt Reaction)

The most suited is a mixed aldol condensation, specifically the condensation of aromatic aldehyde (or aldehyde without α -Hs) with an enolizable aldehyde and ketone.

(C) Intramolecular Aldol Condensation

This reaction occurs when dicarbonyl compounds undergo cyclization; the product generated is dependent on the size of the ring (usually 5 or 6 membered rings are formed).

Analysis of Aldehydes and Ketones

The addition of nucleophilic reagents to the carbonyl group of aldehydes and ketones, particularly ammonia derivatives, is used to describe them. For example, an aldehyde or ketone reacts with 2, 4-nitrophenylhydrazine to produce an insoluble yellow or red solid.

Aldehydes are distinguished from ketones by their ease of oxidation: aldehydes pass the Tollens' reagent test, but ketones do not. Some phenols and amines also provide positive Tollen's tests; however, these compounds do not give positive tests with 2, 4-dinitrophenylhydrazine.

The Schiff test is an extremely sensitive aldehyde test. The fuchsin-aldehyde reagent combines with an aldehyde to produce a distinctive magenta color.

In CCl_4 , aliphatic aldehydes and ketones containing an α -hydrogen react with Br_2 . This reaction is too slow to be mistaken with an unsaturation test, and it also liberates HBr .

The melting points of derivatives such as 2, 4-dinitrophenylhydrazones, 'oximes, and semicarbazones are used to identify aldehydes and ketones.

The iodoform test is used to identify methyl ketones.

1. Iodoform Test

The iodoform test determines whether a ketone is a methyl ketone. A ketone of the structure is treated with iodine and sodium hydroxide (sodium hypoiodite, NaOI).

2. Periodic Acid Oxidation

Compounds having $-\text{OH}$ groups connected to adjacent carbon atoms undergo oxidation with the breaking of carbon-carbon bonds when exposed to periodic acid, HIO_4 .

Uses of aldehyde

- Bakelite is a chemical created when phenol and formaldehyde combine. Plastics, coatings, and adhesives all use bakelite in some capacity.

- The chemical formaldehyde is necessary for various industrial processes, including embalming, making glue, tanning, and creating polymeric products.
- It functions as a fungicide, an insecticide, and a germicide.
- Drug testing is aided by formaldehyde. Photography also makes use of it.
- The substance "acetaldehyde" can be used to make acetic acid and pyridine derivatives.
- For the creation of perfumes, cosmetics, and colors, benzaldehyde (aldehyde) is a necessary ingredient. It is included to give certain food products an almond flavor. It serves as a bee deterrent as well.

Uses of ketone

- For several types of plastics and synthetic fibers, ketone functions as an effective solvent.
- Acetone can be used to remove nail polish and thin out the paint.
- Additionally, it is employed medically to cure acne and perform chemical peeling procedures.
- One of the often used solvents is butanone, also referred to as methyl ethyl ketone. It is employed in the manufacture of textiles, varnishes, paint removers, paraffin wax, and plastics, among other things.
- Cyclohexanone, a crucial ingredient in the manufacture of nylon, is another significant ketone.

Carboxylic acid and derivatives

Introduction

Compounds with the carboxyl functional group are known as carboxylic acids.

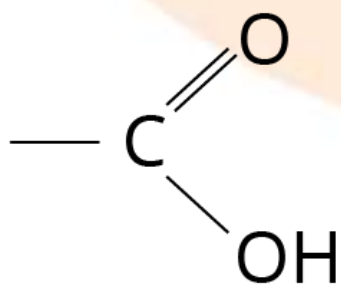


Image: Structure of carboxylic acid

Depending on whether the COOH group is connected to an aliphatic alkyl chain or an aryl group, the carboxylic acids can be aliphatic (R-COOH) or aromatic (Ar-COOH).

Polymers, medicines, solvents, and food additives are all made with carboxylic acids. Acetic acid (a component of vinegar and a precursor to solvents and coatings), acrylic and methacrylic acids (precursors to polymers and adhesives), adipic acid (polymers), citric acid (beverages), ethylenediaminetetraacetic acid (chelating agent), fatty acids (coatings), maleic acid (polymers), propionic acid (food preservatives), terephthalic acid (food preservatives). The major components of lipids are fatty acid esters, whereas the main components of proteins are polyamides of amino carboxylic acids.

Physical properties and Acidic Character

1. Boiling Point

Carboxylic acids boil at far greater temperatures than similar molecular weight alcohols, ketones, or aldehydes.

2. Melting Point and Physical State

At normal temperature, aliphatic acids with up to nine carbon atoms are colorless liquids with foul odors. Because of their low volatility, the higher acids are 'wax-like solids' and are nearly odorless. In aprotic and non-polar solvents, they exist as dimers.

Unbranched acids with an even number of carbon atoms have a greater melting point than homologs with an odd number of carbon atoms. The differences in intermolecular attractive forces in the crystalline state explain the fluctuating behavior of the melting point.

3. Solubility

Carboxylic acids create hydrogen bonds with water, and lower-molecular-weight carboxylic acids (up to four carbon atoms) are water-miscible. Water solubility reduces as the length of the hydrocarbon chain rises until acids with more than 10 carbon atoms are essentially insoluble in water.

4. Acidity of Carboxylic Acids

Carboxylate ions have two equivalent canonical structures A and B. Because carboxylate ions are more stable, the carboxylic acid is acidic in nature because the chemical equilibrium favors the creation of stable ions.

Preparation of Carboxylic Acids

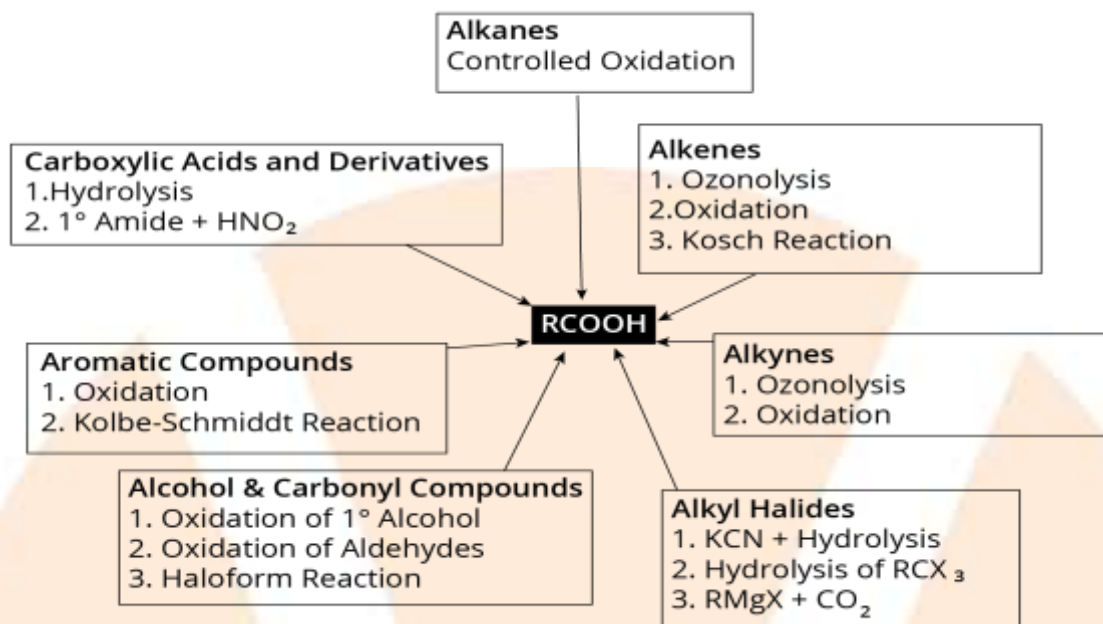


Image: Preparation of carboxylic acid

1. Alkanes

At 120°C, long-chain alkanes are oxidized by air in the presence of a manganese acetate or manganous stearate catalyst.

2. Alkenes

Ozonolysis

On oxidative ozonolysis, monosubstituted alkenes produce carboxylic acid.

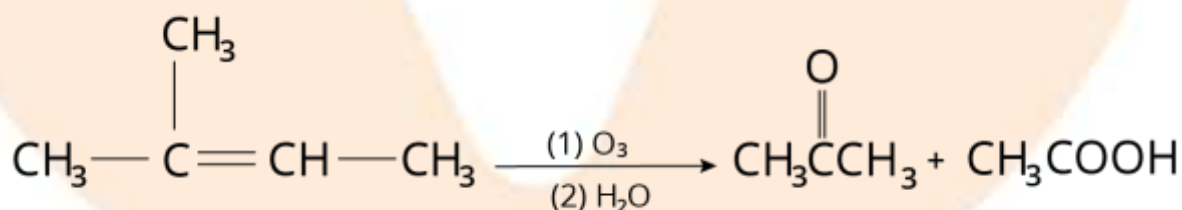


Image: Ozonolysis reaction

3. Alkynes

Ozonolysis

On ozonolysis, alkynes produce carboxylic acids.

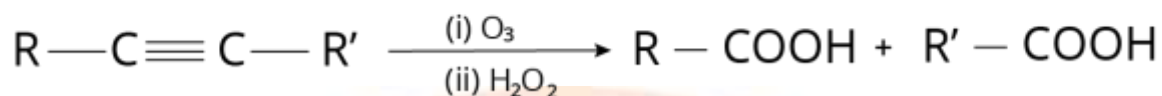
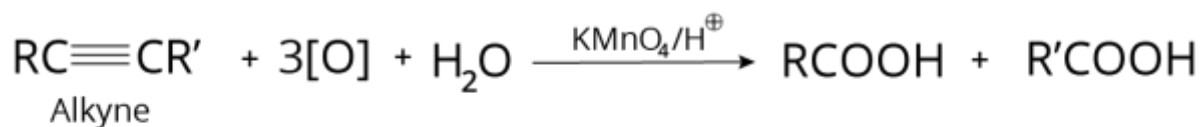


Image: Reaction with alkynes

4. Alkyl Halides

Hydrolysis of terminal tri-halogen derivatives of Alkanes

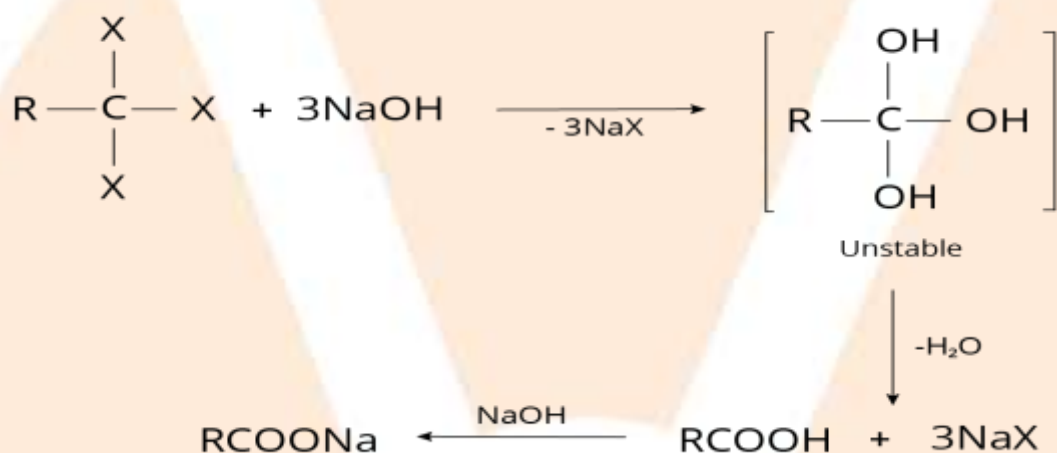


Image: Reaction of alkyl halide

5. Alcohols

Carboxylic acids are formed when primary alcohols are oxidized.

Example:

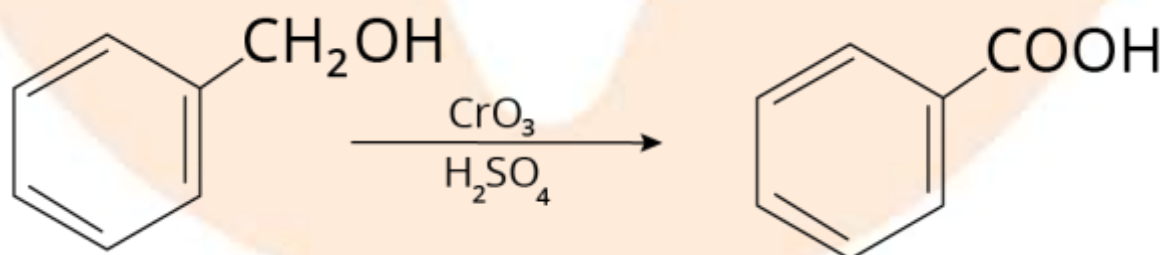


Image: Reaction of alcohols

6. Aldehydes and Ketones Oxidation

Under aggressive circumstances, such as heated $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$, ketones oxidize to produce a mixture of acids.

7. Carboxylic Acids Derivatives

On acidic or basic hydrolysis, carboxylic acids are formed from acyl halide, carboxylic ester, anhydride, and amide.

Reactions of carboxylic Acid

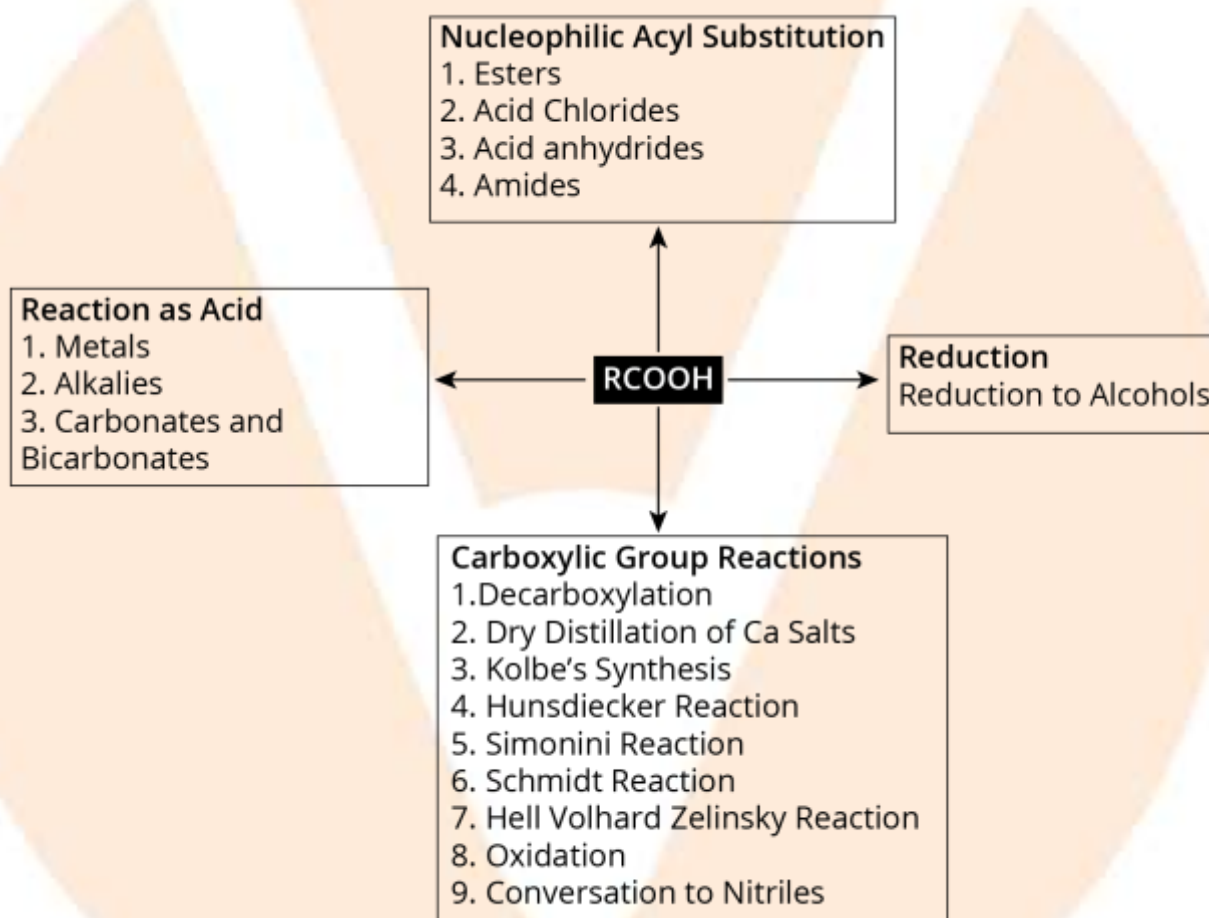
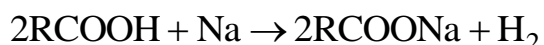


Image: Reactions of carboxylic Acid

1. Reactions as an Acid

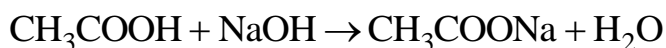
Reactions with strongly Electropositive Metals

Monocarboxylic acids react with strong electropositive metals (such as Na, K, Zn, and others) to produce hydrogen and salts (acidic character).

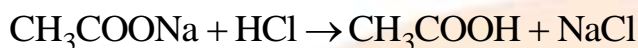


Reaction with Alkali

Monocarboxylic acids react with strong electropositive metals (such as Na, K, Zn, and others) to produce hydrogen and salts (acidic character).

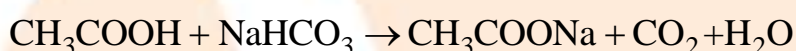
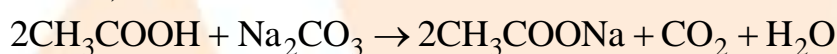


When these salts are exposed to dilute mineral acids, they regenerate carboxylic acids.'



Reaction with Carbonates and Bicarbonates

Due to CO effervescence, this reaction is a laboratory test of carboxylic group (-COOH).



2. Nucleophilic Acyl Substitution

Formation of Esters

Esterification is the name for this reaction, which is catalysed by a little amount of inorganic acids.

The C-OH bond of the acid and the O-H bond of the alcohol are broken during esterification.

Lactones are cyclic esters formed by the intramolecular esterification of hydroxy acids.

3. Reduction

Reduction to Alcohols

LiAlH_4 in ether solution or with H_2 in the presence of a copper chromite CuCr_2O_4 catalyst or BH_3 , THF (diborane or B_2H_6)

4. Carboxyl group Reactions

Decarboxylation

When a carboxylic acid's anhydrous alkali salt is heated with soda lime ($\text{NaOH}:\text{CaO}$ in a 3: 1 ratio), an alkane is produced.

Carbanion intermediate is used in the reaction. The rate of decarboxylation is proportional to the stability of the carbanion.

Uses of carboxylic acid

- Higher fatty acids are required for soap production. Most commonly, higher fatty acids like stearic acid are salts of sodium or potassium in soaps.
- Numerous organic acids are employed by the food sector in the production of soft drinks, culinary items, etc. For instance, vinegar is made using acetic acid. Preservatives use sodium salts of organic acids.
- Numerous medicatisons in the pharmaceutical business use organic acids.
- When making rubber, acetic acids are frequently employed as a coagulant.
- Organic acids are widely used in the production of rayon, fragrances, and dyes.

Solved Examples:

1. The correct order of increasing acidic strength is _____.

A: Phenol < Ethanol < Chloroacetic acid < Acetic acid

B: Ethanol < Phenol < Chloroacetic acid < Acetic acid

C: Ethanol < Phenol < Acetic acid < Chloroacetic acid

D: Chloroacetic acid < Acetic acid < Phenol < Ethanol

Correct Option: (C)

Explanation:

When it comes to ethanol, the obtained cation is not stabilized by resonance. The phenoxide ion obtained is stabilized by resonance, phenol is more acidic than ethanol. Chloroacetic acid has a higher acidity than acetic acid. Carboxylic acids are acidic in comparison to alcohols and phenols. Thus, option (C) is correct.

2. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution?

A: Butan-1-ol

B: Butan-2-ol

C: Both

D: None of these

Correct Option: (B)

Explanation:

Primary alcohol like Butan-1-ol on reaction with a strong oxidizing agent like KMnO_4 gives carboxylic acid, whereas Secondary alcohol like Butan-2-ol gives ketone on oxidizing under the pressure of KMnO_4 . Thus, option B is correct.