Carbonyl Compounds: Aldehydes & Ketones, Class XII

Organic compounds containing carbon-oxygen double bond (C=O), i.e. carbonyl group, are known as carbonyl compounds. Carbonyl compounds are of two types, Aldehydes and ketones. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones it is bonded to two carbon atoms.

STRUCTURE AND NOTATION OF CARBONYL GROUP

The carbonyl carbon atom is sp2 hybridized and forms three sigma bonds. The fourth valence electron of carbon is in a p-orbital which forms a pi bond with oxygen by overlap with p-orbital of an oxygen. In addition, the oxygen atom also has two lone pairs of electrons. The carbonyl group is planar and the bond angles present in it is 120 degree and the bond lengths are different from other bonds in the plane. The bond angles are approximately 120°, as expected of a trigonal coplanar structure.

The electronegativity of oxygen is much higher than that of carbon, thus the carbon-oxygen double bond is polar. Therefore the C-O bond is polar in nature and carbonyl compounds possess dipole moment in the 2.3-3.0D.

Nomenclature of Carbonyl compounds:

1. Common names:

In the IUPAC system, common names of most aldehydes are derived from the common name of the corresponding carboxylic acid by replacing the ending -ic or acid with aldehyde. At the same time, the names reflect the Latin or Greek name for the original source of the acid or aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc. The carbon bearing the -ene directly linked to the aldehyde group. (Ketone the next, and so on. For example:

2. IUPAC Name :

(a) Aldehydes: The suffix "al" of alkane is replaced by the suffix "al" i.e. -ane → al

IUPAC Method:
Count the longest chain including the aldehyde carbon.

(b) Ketones: The suffix "e" of corresponding alkane is replaced by "-one", e.g.
$H_3C-COCH_3$ - Propanone.

NOMENCLATURE IN ALDEHYDES :

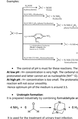
1. Trivial Nomenclature (Common Name)
2. Nomenclature Trivial
3. Functional Nomenclature
4. Functional Nomenclature

Functional Groups: The Little Recognized Synonym

Tautomerism:

Tautomers are structural isomers of chemical compounds that readily interconvert. The chemical reaction interconverting the two is called tautomerism. In addition to interconversion, tautomers are the molecules of hydrogen atoms within the compound.

The most common type of tautomerism is that involving carbonyl, or keto, compounds interconverting with their enol forms. In the keto form, a carbon-oxygen bond is the site of a hydrogen atom between atoms of carbon and oxygen, with the rearrangement of bonds as indicated



Tautomerism

Tautomers are structural isomers of chemical compounds that readily interconvert. The chemical reaction interconverting the two is called tautomerism. In addition to interconversion, tautomers are the molecules of hydrogen atoms within the compound.

The most common type of tautomerism is that involving carbonyl, or keto, compounds interconverting with their enol forms. In the keto form, a carbon-oxygen bond is the site of a hydrogen atom between atoms of carbon and oxygen, with the rearrangement of bonds as indicated

Preparation of Aldehydes and Ketones

By Oxidation of alcohols

Oxidation of primary alcohols gives aldehydes and secondary alcohol gives a ketone. Oxidation agents used are $KMnO_4$, $K_2Cr_2O_7$, CrO_3, PCC are used in oxidation. Oxidation using PCC yields aldehyde.

(b) Dehydrogenation of alcohol:

(c) Dehydration of Alcohol:

Reduction conversion of chlorine gives aldehyde and ketones. Alkenes react with oxygen to form ozonide which on reduction with zinc dust and water yields aldehyde and ketones. Zinc dust removes H_2O_2 formed, which otherwise can oxidize aldehyde/ketone.

(d) Hydration of Alkynes:

Hydration of alkynes in presence of 40% dilute sulphuric acid and 1% $HgSO_4$ to give the corresponding aldehyde/ketone.

(e) Hydration of acetylene yields acetaldehyde

(f) Hydration of alkynes, other than acetylene gives ketones

(g) From Calcium Salts of Carboxylic Acids:

Aldehydes and ketones may be prepared by the dry distillation of calcium salts of carboxylic acids.

Aldehyde is obtained when the mixture of calcium salt of carboxylic acid and calcium formate is subjected to dry distillation.

(h) Hydration of Alkynes:

Hydration of alkynes in presence of 40% dilute sulphuric acid and 1% $HgSO_4$ to give the corresponding aldehyde/ketone.

(i) Hydration of acetylene yields acetaldehyde

(j) Hydration of alkynes, other than acetylene gives ketones

(k) From Calcium Salts of Carboxylic Acids:

Aldehydes and ketones may be prepared by the dry distillation of calcium salts of carboxylic acids.

Aldehyde is obtained when the mixture of calcium salt of carboxylic acid and calcium formate is subjected to dry distillation.

(l) Experimental Ketones can be obtained by dry distillation of the mixture of calcium salt of carboxylic acid (except formic acid).

Formaldehyde cannot be prepared by this method because HCOO- is decomposed by the calcium ion present in the reaction mixture.

(m) Stephen's Reduction of Nitriles

Nitriles on treating with stannous chloride and HCl(aq). Imines are formed, which on hydrolysis gives corresponding aldehyde.

$R-C\equiv N \xrightarrow{SnCl_2/HCl} R-CH=NH \xrightarrow{H_2O} R-CHO + NH_3$

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

This reagent does not affect double bond.

$CH_3-CH=CH-CH_2-CH_2-C\equiv N \xrightarrow{DIBAL-H} CH_3-CH=CH-CH_2-CH_2-CHO$

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

(n) From hydrazones:

(o) By Friedel-Crafts reaction (Formyl chloride solution):

(p) Oxidation by chromic oxide (CrO_3):

(q) Manufacture of Benzaldehyde from Toluene:

(r) Gattermann – Koch Reaction:

(s) Wolker's process:

(t) Oxo process:

$R-CH=CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-CHO$

(u) From Grignard's reagent :

$RX \xrightarrow{Mg} R-X \xrightarrow{Mg} RMgX + HCl \rightarrow RH$

(v) $RMgCl + H-C\equiv N \rightarrow R-C\equiv N \xrightarrow{H_2O} R-CHO + NH_3$

(vi) Hydrolysis of Gemini halides:

$R-CHCl_2 \xrightarrow{H_2O} R-CH(OH)_2 \rightarrow R-CHO + H_2O$

(vii) From Glycols :

$R-CH(OH) \xrightarrow{HIO_4} 2R-CHO + H_2O$

C. Preparation of Ketones:

(i) From acyl chlorides:

Ketones from acyl chlorides with diethylcadmium, prepared by the reaction of anhydrous cadmium with Grignard reagent gives ketones.

$2R-MgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl$

$R_2Cd + 2R'-C(=O)-Cl \rightarrow 2R'-C(=O)-R + CdCl_2$

If we use R-Mg-X directly, then being more reactive, it will react with ketone to give tert. alcohol.

(ii) By Friedel – Craft Acylation:

benzoylbenzene

(iii) Wolker's process:

(iv) Oxo process:

$R-CH=CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-CHO$

(v) From Grignard's reagent :

$RX \xrightarrow{Mg} R-X \xrightarrow{Mg} RMgX + HCl \rightarrow RH$

(vi) $RMgCl + H-C\equiv N \rightarrow R-C\equiv N \xrightarrow{H_2O} R-CHO + NH_3$

(vii) Hydrolysis of Gemini halides:

$R-CHCl_2 \xrightarrow{H_2O} R-CH(OH)_2 \rightarrow R-CHO + H_2O$

(viii) From Glycols :

$R-CH(OH) \xrightarrow{HIO_4} 2R-CHO + H_2O$

C. Preparation of Ketones:

(i) From acyl chlorides:

Ketones from acyl chlorides with diethylcadmium, prepared by the reaction of anhydrous cadmium with Grignard reagent gives ketones.

$2R-MgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl$

$R_2Cd + 2R'-C(=O)-Cl \rightarrow 2R'-C(=O)-R + CdCl_2$

If we use R-Mg-X directly, then being more reactive, it will react with ketone to give tert. alcohol.

(ii) By Friedel – Craft Acylation:

benzoylbenzene

(iii) From Grignard's reagent :

benzophenone

benzoylbenzene

(iii) From Grignard's reagent :

benzophenone

benzoylbenzene

Physical Properties of Aldehydes and Ketones:

Boiling point: The boiling points of aldehydes and ketones increases with an increase in molecular mass. Polarity of the molecule has a significant impact on the strength of the intermolecular forces.

- **Vander Waals dispersion forces:** As the molecules get longer and the number of electrons increases, which results in the increase in the magnitude of van der Waal forces. Therefore, for this reason, the boiling point of aldehydes and ketones increases with the increase in the number of carbon atoms.
- **Vander Waals dipole-dipole attraction:** Because of the presence of polarity in the carbonyl group, aldehydes and ketones are polar in nature. Thus, there will be an attraction between permanent dipoles present in aldehydes and ketones as well as the molecules which are polar in nature. This attraction is stronger than the dispersion forces, giving higher than similar hydrocarbons.
- The boiling point of aldehydes and ketones is higher than that of non-polar compounds but lower than that of alcohols and carboxylic acids. Aldehydes and carboxylic acids do aldehydes and ketones do not form H-bonds with themselves.

Solubility: Aldehydes and ketones are soluble in water but their solubility decreases with an increase in the length of the chain. Methanol, ethanol and propanone are miscible in water. Aldehydes and ketones are also soluble in alcohols with water in almost all proportions.

Aldehydes and ketones cannot form hydrogen bonds with themselves. Thus, they are unable to form H-bonds with water and the H-bonding between the H-bond acceptor of aldehyde and ketones and water.

The higher members do not dissolve in water because the hydrocarbon part is large and it resists the formation of hydrogen bonds with water molecules.

Chemical Properties:

1. Nucleophilic addition reactions:

Nucleophilic addition reaction occurs observed in alkenes. An aldehyde and ketones undergo nucleophilic addition reaction.

Addition of Hydrogen cyanide reaction: A nucleophile attacks the electrophilic carbon atom of the carbonyl group and then a protonation mechanism produces the alcohol product. Methanol solution of cyanide catalyst. The addition of cyanide catalyst changes the pH to the pH of the solution.

(a) Wolker's process:

(b) Oxo process:

$R-CH=CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-CHO$

(c) From Grignard's reagent :

$RX \xrightarrow{Mg} R-X \xrightarrow{Mg} RMgX + HCl \rightarrow RH$

(d) $RMgCl + H-C\equiv N \rightarrow R-C\equiv N \rightarrow R-CHO$

(e) Hydrolysis of Gemini halides:

$R-CHCl_2 \xrightarrow{H_2O} R-CH(OH)_2 \rightarrow R-CHO + H_2O$

(f) From Glycols :

$R-CH(OH) \xrightarrow{HIO_4} 2R-CHO + H_2O$

C. Preparation of Ketones:

(i) From acyl chlorides:

Ketones from acyl chlorides with diethylcadmium, prepared by the reaction of anhydrous cadmium with Grignard reagent gives ketones.

$2R-MgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl$

$R_2Cd + 2R'-C(=O)-Cl \rightarrow 2R'-C(=O)-R + CdCl_2$

If we use R-Mg-X directly, then being more reactive, it will react with ketone to give tert. alcohol.

(ii) By Friedel – Craft Acylation:

benzoylbenzene

(iii) From Grignard's reagent :

benzophenone

benzoylbenzene

(iii) From Grignard's reagent :

benzophenone

benzoylbenzene

Physical Properties of Aldehydes and Ketones:

Boiling point: The boiling points of aldehydes and ketones increases with an increase in molecular mass. Polarity of the molecule has a significant impact on the strength of the intermolecular forces.

- **Vander Waals dispersion forces:** As the molecules get longer and the number of electrons increases, which results in the increase in the magnitude of van der Waal forces. Therefore, for this reason, the boiling point of aldehydes and ketones increases with the increase in the number of carbon atoms.
- **Vander Waals dipole-dipole attraction:** Because of the presence of polarity in the carbonyl group, aldehydes and ketones are polar in nature. Thus, there will be an attraction between permanent dipoles present in aldehydes and ketones as well as the molecules which are polar in nature. This attraction is stronger than the dispersion forces, giving higher than similar hydrocarbons.
- The boiling point of aldehydes and ketones is higher than that of non-polar compounds but lower than that of alcohols and carboxylic acids. Aldehydes and carboxylic acids do aldehydes and ketones do not form H-bonds with themselves.

Solubility: Aldehydes and ketones are soluble in water but their solubility decreases with an increase in the length of the chain. Methanol, ethanol and propanone are miscible in water. Aldehydes and ketones are also soluble in alcohols with water in almost all proportions.

Aldehydes and ketones cannot form hydrogen bonds with themselves. Thus, they are unable to form H-bonds with water and the H-bonding between the H-bond acceptor of aldehyde and ketones and water.

The higher members do not dissolve in water because the hydrocarbon part is large and resists the formation of hydrogen bonds with water molecules.

Chemical Properties:

1. Nucleophilic addition reactions:

Nucleophilic addition reaction occurs observed in alkenes. An aldehyde and ketones undergo nucleophilic addition reaction.

Addition of Hydrogen cyanide reaction: A nucleophile attacks the electrophilic carbon atom of the carbonyl group and then a protonation mechanism produces the alcohol product. Methanol solution of cyanide catalyst. The addition of cyanide catalyst changes the pH to the pH of the solution.

and a tetrahedral alcoholic intermediate is produced. This intermediate captures a proton from the solvent to give the final product, cyanohydrin. The rate-and-equilibrium of the reaction. Strong alkaline reagent stabilizes the cyanide ion.

Relative reactivity of aldehyde and ketones towards nucleophilic addition:

- Aldehyde are more reactive than ketones towards nucleophilic addition because due to steric and electronic reasons.
- Sterically, the approach of a nucleophile to the carbonyl compound is more in aldehyde than ketone because the presence of two alkyl groups in ketones hinders the approach of a nucleophile to the carbonyl group. Electronically, the alkyl groups in ketones reduce the electrophilicity of the carbonyl carbon more effectively than in aldehyde because the inductive effect of two alkyl groups in ketones is more than that of one alkyl group in aldehyde.

Examples of Nucleophilic addition:

Ultraviolet addition reaction, reversal elimination of water molecule.

Acetaldehyde ammonia

Acetaldehyde ammonia

Acetaldehyde ammonia