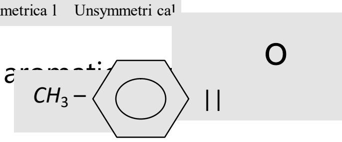
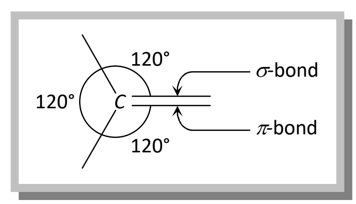
Classification, Structure, Nomenclature and Isomerism.

(1) **Classification**

Aldehydic group is always terminal. Aldehydes can be classified into three categories, (i) **Aliphatic aldehydes :** $R-\overset{O}{\overset{\|}{C}}-H$ (ii) **Aromatic aldehydes:** $Ar-\overset{O}{\overset{\|}{C}}-H$ (iii) **Unsymmetrical aldehydes :** All aldehydes except formaldehyde are unsymmetrical. Both substituents are different $\underset{\text{Formaldehyde}}{H-\overset{O}{\overset{\|}{C}}-H}$ $R-\overset{O}{\overset{\|}{C}}-H$	Ketonic group is never terminal. Ketones can be classified into three categories, (i) **Aliphatic ketones :** $\underset{\text{Symmetrical}}{R-\overset{O}{\overset{\|}{C}}-R}$ $\underset{\text{Unsymmetrical}}{R-\overset{O}{\overset{\|}{C}}-R'}$ (ii) **Aromatic ketones:** In aromati substituents are aryl  $C_6H_6-\overset{O}{\overset{\|}{C}}-C_6H_5$, Aryl group Alkyl group (iii) **Mixed ketones:** In mixed ketones one substituent is aryl and other is alkyl. $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$

(2) **Structure:**Carbonyl carbon atom is joined to three atoms by sigma bonds. Since these bonds utilise sp^2-orbitals, they lie in the same plane and are 120° apart. The carbon-oxygen double bond is different than carbon-carbon double bond. Since, Oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge making the bond polar. The high values of dipole moment,



$$\overset{\delta+}{C}=\overset{\delta-}{O}$$

(2.3 - 2.8D) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group is a resonance hybrid of the following two structures.

$$C=O \longleftrightarrow \overset{+}{C}-\overset{-}{O}$$

(3) **Nomenclature**

(i) **Aldehyde:** There are two systems of naming aldehydes,

(a) Common system: In the common system, aldehydes are named according to the name of the corresponding acid which they form on oxidation. The suffix **–ic acid** the name of the acid is replaced by aldehyde. For example, CH_3CHO derived from acetic acid (CH_3COOH) is named as **acetaldehyde**.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{+ aldehyde}]{-ic \text{ acid}} \underset{\text{Acetaldehyde}}{CH_3 - \overset{\overset{H}{|}}{C} = O}$$ Acetic acid + aldehyde = acetaldehyde

Branching in the aldehyde chain, if any, is indicated by the Greek letters α, β, γ, δ etc. The carbon attached to the $-CHO$ group is α as:

For example, $-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-CHO$ $\qquad$ $\underset{\alpha-\text{Methyl butyraldehyde}}{CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCHO}$

(b) IUPAC system: In the **IUPAC system**, the aldehydes are known as **alkanals**. The name of aldehyde is derived by replacing the terminal **–e** of the name of corresponding alkane by **al**.

For example, $\underset{\text{Methanal}}{HCHO}$ $\underset{\text{Ethanal}}{CH_3CHO}$ $\underset{\text{Propanal}}{C_2H_5CHO}$ Alkane –e + al = Alkanal

(ii) **Ketone:** There are two systems of naming ketone,

(a) Common system: In the common system, ketones are named by using the names of alkyl group present in the molecule. For example,

$\underset{\text{Dimethyl ketone}}{CH_3COCH_3}$ $\qquad$ $\underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$ $\qquad$ $\underset{\text{Diethyl ketone}}{CH_3CH_2COCH_2CH_3}$

$\underset{\text{Methyl } n-\text{propylketone}}{CH_3COCH_2CH_2CH_3}$ $\qquad$ $\underset{\text{Methyl isopropyl ketone}}{CH_3COCH(CH_3)_2}$ $\qquad$ $\underset{\text{Benzyl methyl ketone}}{C_6H_5CH_2COCH_3}$

Some of the ketones are known by their old popular names as well. For example, dimethyl ketone, CH_3COCH_3 is still popularly known as acetone.

(b) IUPAC system: In this system, longest chain containing the ketonic group is taken as the parent chain. In naming the ketone corresponding to the chain, the following procedure is adopted.

Root word + ane –e + one i.e., Alkanone

The positions of the ketonic group and the substituents are indicated by the locants.

CH_3COCH_3	Propanone
$CH_3COCH_2CH_3$	Butanone-2
$CH_3CH_2COCH_2CH_3$	Pantanone-3
$CH_3-\underset{\underset{CH_3}{\mid}}{C}HCOCH_2CH_2CH_3$	2-Methylhexanone-3

(4) **Isomerism:** Aldehydes show **chain** and **functional** isomerism.

Chain isomers: $\underset{n-\text{Butanal}}{CH_3CH_2CH_2CHO}$ $\quad$ $\underset{\text{2-Methylpropanal } (iso-\text{Butanal})}{(CH_3)_2CHCHO}$

(i) **Functional isomers:** $\underset{\text{Propanal}}{CH_3CH_2CHO}$; $\underset{\text{Acetone}}{CH_3COCH_3}$; $\underset{\text{Allylalcohol}}{CH_2 = CHCH_2OH}$; $\underset{\alpha,\beta-\text{Propylene oxide}}{CH_3\ CH - CH_2 \ (\text{bridged by } O)}$;

$\underset{\text{Methyl vinyl ether}}{CH_2 = CH.O.CH_3}$

Ketones show **chain, functional and metamerism.** Examples of functional isomerism is given above in aldehydes.

(ii) **Chain isomers:** $\underset{\text{Methylpropyl ketone}}{CH_3CH_2CH_2 - \overset{\overset{O}{\|}}{C} - CH_3}$; $\underset{\text{Methylisopropyl ketone}}{(CH_3)_2CH - \overset{\overset{O}{\|}}{C} - CH_3}$

(iii) **Metamers:** $\underset{\text{Methylpropyl ketone}}{CH_3CH_2CH_2 - \overset{\overset{O}{\|}}{C} - CH_3}$; $\underset{\text{Diethyl ketone}}{CH_3CH_2 - \overset{\overset{O}{\|}}{C} - CH_2CH_3}$