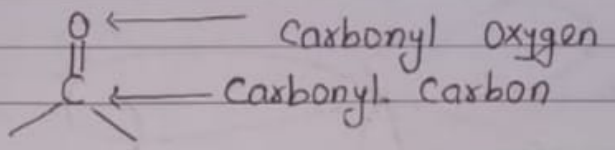
ORGANIC CHEMISTRY

DEGREE I
PAPER – II
GROUP – B

B.Sc. (Honours) :- CHAPTER No. 5.
B.Sc. (Subsidiary) :- CHAPTER No. 3.
⇓ GROUP – C

ALDEHYDES And KETONES

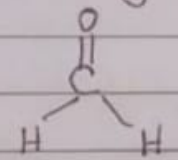
(Lecture - 1)



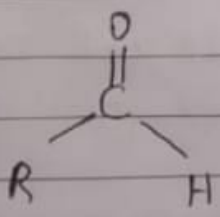
Carbonyl Group

* Aldehydes and ketones are collectively called Carbonyl Compound.

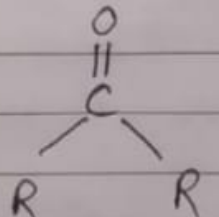
* In aldehydes, the carbonyl carbon is bonded to one hydrogen and one alkyl group.

* In Formaldehyde  , the carbonyl carbon is bonded to two hydrogen atoms.

* In ketones, the carbonyl carbon is bonded to two alkyl groups.
These alkyl groups may be same or differe

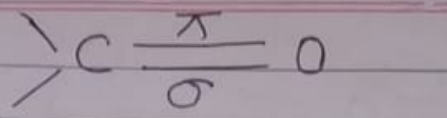


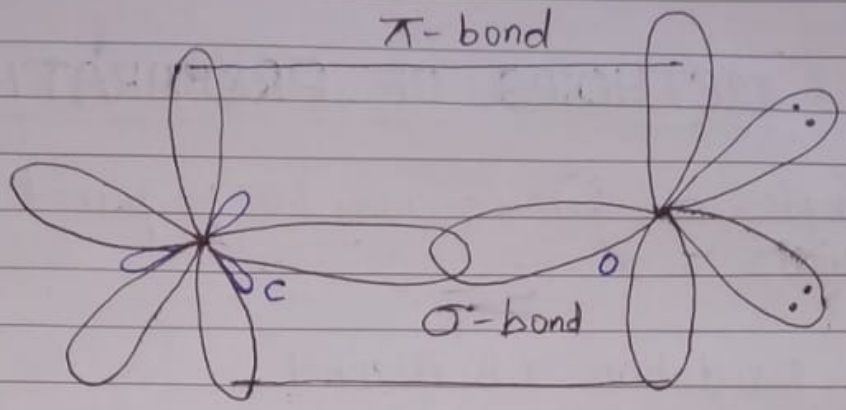
Aldehyde



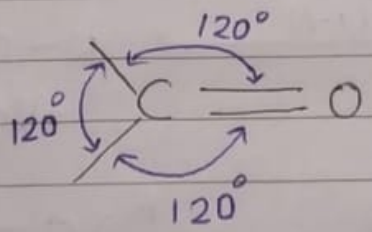
Ketone

Structure of the carbonyl group

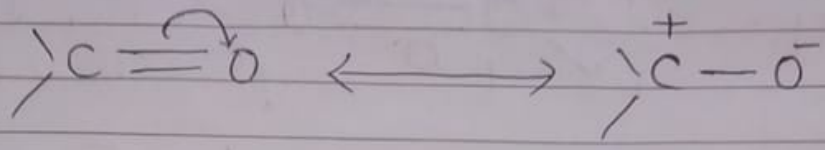




* Both the carbon and oxygen are sp^2 hybridised.
* σ- bond is formed by the overlap of an sp^2 orbital of carbon and an sp^2 orbital of oxygen.
* π- bond is formed by the overlap of unhybridised p- orbital of the two atoms.
* The two unshared electron pairs of oxygen occupy the sp^2 hybrid orbitals of oxygen.
* Because of the carbonyl carbon is sp^2 hybridised, the three atoms attached to it lie in the same plane.
* The bond angles between the attached atoms are approximately 120° c.



Resonating structure of Carbonyl group



METHODS OF PREPARATION

Aldehyde and ketones may be prepared by the following methods :- -

1. By Oxidation Of Alcohol

Oxidising agent used for oxidation are:- -

a) Alkaline potassium permangnate : $KMnO_4/OH^-$

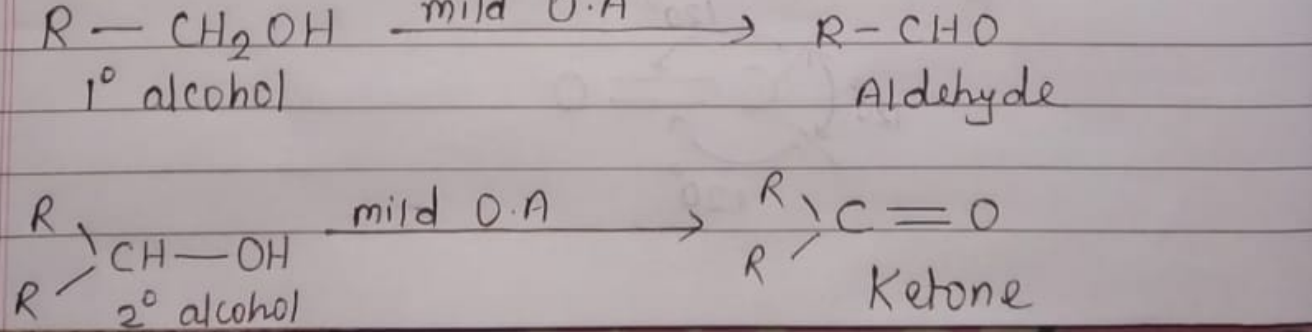
b) Chromic acid : $H_2Cr_2O_7$

* This reagent is prepared in situ from CrO_3 or $Na_2Cr_2O_7$ with dilute sulphuric acid.

c) Pyridinium chlorochromate (PCC), $C_5H_6NCrO_3Cl$ in dichloromethane solvent.

* PCC in dichloromethane is used to convert 1° alcohol to aldehydes.

This reagent does not oxidise aldehydes to carboxylic acid.



Mild O·A $\Longrightarrow$ PCC in dichloromethane

eg; $CH_3^{4}-CH_2^{3}-CH_2^{2}-CH_2^{1}-OH \xrightarrow[CH_2Cl_2]{PCC} H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

Butan-1-ol → Butanal

Aldehydes and Ketones can be prepared by the controlled oxidation of primary and secondary alcohols using an acidified solution of $K_2Cr_2O_7$ (Potassium dichromate) or $KMnO_4$ (Potassium permanganate).

$$R-\overset{H}{\underset{H}{C}}-O-H + [O] \xrightarrow[H^+]{K_2Cr_2O_7} R-\overset{}{\underset{H}{C}}=O + H_2O$$

1° alcohol → Aldehyde

eg; $H_3C-CH_2-OH + [O] \xrightarrow[H^+]{K_2Cr_2O_7} \boxed{H_3C-\underset{H}{C}=O} + H_2O$

Ethanol → Acetaldehyde

* The aldehyde formed in the above reaction are very easily oxidised to carboxylic acid if allowed to remain in the reaction mixture.

$$R-\overset{H}{C}=O + [O] \xrightarrow[H^+]{K_2Cr_2O_7} \boxed{R-\overset{O-H}{C}=O} + H_2O$$

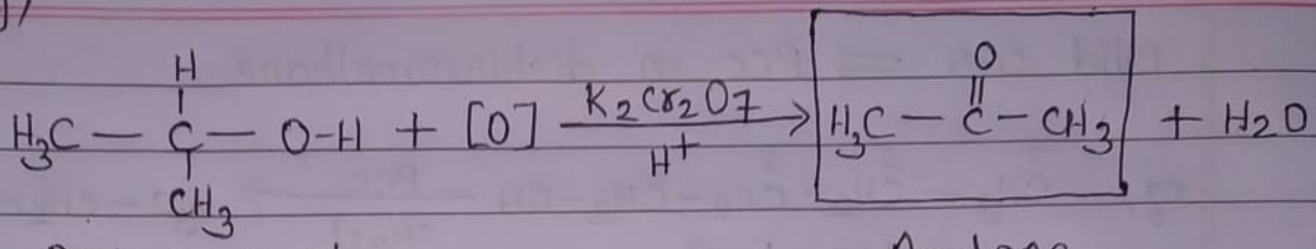
Carboxylic Acid

* Ketones are prepared by the oxidation of secondary alcohols

$$R-\overset{H}{\underset{R'}{C}}-O-H + [O] \xrightarrow[H^+]{K_2Cr_2O_7} \boxed{R-\underset{R'}{C}=O} + H_2O$$

2° alcohol → Ketone

eg;

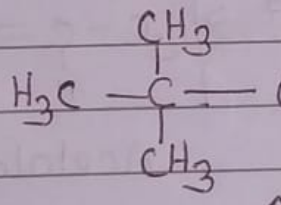


Propan-2-ol Acetone

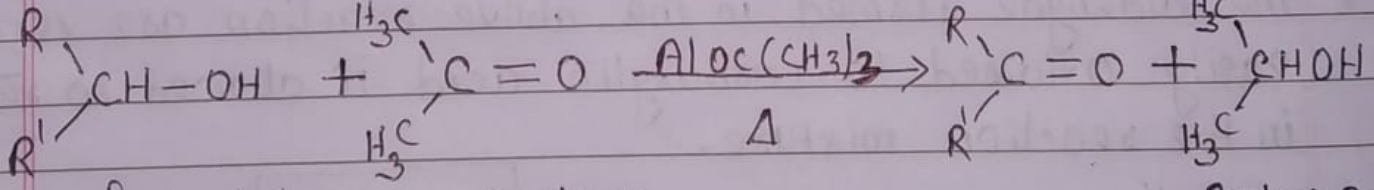
* Ketones are not easily oxidised further and can be obtained in high yield by this method.

* Ketone can be obtained from secondary alcohols by OPPENAUER OXIDATION.

In this process the secondary alcohol is refluxed with excess of acetone in the presence of aluminium tertiary-butoxide ($Al[OC(CH_3)_3]_3$); catalyst.



Aluminium tert. butoxide



2° alcohol Acetone Propan-2-ol

To be continued in next lecture...