□ Introduction :

Organic Compounds having >C=O group are called carbonyl compounds and >C=O group is known as carbonyl or oxo group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3.....) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is -C - H (also known as formyl group). It is a monovalent group

- (b) Ketones : The carbonyl group (>C=O) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.
- Ketones are further classified as :
 - (i) Simple or Symmetrical ketones : Having two similar alkyl groups.
 - (ii) Mixed or unsymmetrical ketones : Having two different alkyl groups. $\stackrel{R}{\xrightarrow{}}C=O$

Example : (Ketones) : Symmetrical

 CH_{3} C=0

Unsymmetrical

 $\sum_{\mathbf{D}}^{\mathbf{N}} C = O$

 $\xrightarrow[C+]{C+O} C=O$

(Acetone or Dimethyl ketone) 2–Propanone (Ethyl methyl ketone) 2-Butanone

Special Point :

$$\begin{array}{c} O & O & O \\ \parallel & \parallel & \parallel \\ -C - \ddot{O}H, -C - \ddot{X}, -C - \ddot{N}H_2, -C - \ddot{O}R \end{array}$$

In all the compounds given above, lone pair of electrons and double bond are conjugate.

 $\begin{bmatrix} \bigcirc & \bigcirc \\ -C & \neg \\$

• Structure :

C = O

In C=O compounds C-atom is sp² hybridised which forms two σ bonds with C and H-atom respectively and one σ bond with oxygen atom. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen atom give the π bond in C=O group.

$$\begin{bmatrix} C_{sp^2} \\ C^{\frac{\sigma}{\pi}} \end{bmatrix}$$
 The C–C–O and H–C–O bond angles are of 120°.

Due to electro-negativity difference in C & O atoms, the C=O group is polar.

Hence aldehydes and Ketones posses dipole moment.

General Methods of Preparation :

(A) For both Aldehydes and Ketones :

- (1) By Oxidation of Alcohols :
 - (a) By $K_2Cr_2O_7 / H_2SO_4$:

Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones. Here, $(K_2Cr_2O_7 / H_2SO_4)$ is a strong oxidising agent.

Aldehydes are quite susceptible to further oxidation to acids -

 $RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$

Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

Note : Aldehydes can be prepared from 1° alcohol, secondary alcohols can be oxidized to ketones, by oxidation with pyridinium chlorchromate (PCC) in CH₂Cl₂ solvent, pyridinium dichromate (PDC) and with Jones reagent(CrO₃+H₂SO₄) in acetone.

(b) Oppenaur Oxidation :

The oxidation of secondary alcohols to ketones by heating them with specific reagent : $[(CH_3)_3CO]_3Al$ (Aluminium-t-butoxide) in presence of acetone. Primary alcohols may also be oxidized to aldehydes if ketones is replaced by a better hydrogen acceptor, e.g. p-benzoquinone. The equilibrium can be controlled by the amount of acetone, an excess of which favours the oxidation of the alcohol.

◆ Note : The reaction is the reverse of Meerwein-Ponndorf -verley reduction.

(c) Mild Oxidising Agent :

- $\begin{array}{cccc} 1^{^{o}} \text{ alcohols will get oxidised with } CrO_{3} \ / \ Pyridine, \ \textbf{collin's reagent} & Ag/O_{2} \ \text{at } 250^{^{o}}C \\ RCH_{2}OH \ + \ [O] & \longrightarrow & RCHO \ + \ H_{2}O \end{array}$
- By this reaction, good yield of aldehyde is possible.
- (2) Dehydrogenation of alcohols :

$$\begin{array}{ccc} CH_{3}CH_{2}OH & \xrightarrow{Cu}{300^{\circ}C} & CH_{3}CHO & (Acetaldehyde) \\ \\ CH_{3}-CHCH_{3} & \xrightarrow{Cu}{300^{\circ}C} & CH_{3}-C-CH_{3} & (Acetone) \\ \\ OH & OH & OH & OH \end{array}$$

$$\begin{array}{ccc} CH_{3} & & CH_{2} \\ H_{3} - C - OH & - \frac{Cu}{300^{\circ}C} \rightarrow & CH_{3} - \frac{H_{2}}{C} + H_{2}O \text{ (Isobutylene)} \\ H_{3} & & CH_{3} - \frac{H_{3}}{C} + H_{3}O \text{ (Isobutylene)} \end{array}$$

(3) By Hydrolysis of gem dihalides :

Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal dihalides give ketone.



(4) By Oxidation of diols :

With periodic acid (HIO_4) & lead tetra acetate $(CH_3COO)_4$ Pb vicinal diols gets oxidised to form carbonyl compounds

$$\begin{array}{cccc} R & -CH - CH - R + HIO_4 & \longrightarrow RCHO + R'CHO + HIO_3 + H_2O \\ & & OH & OH \\ R & -C - C - R + HIO_4 & \longrightarrow R - C - R + R - C - R + HIO_3 + H_2O \\ & & OH & OH \end{array}$$

(5) By Ozonolysis of alkenes :

This reaction is used to determine the position of double bond in alkene.



Unbranched alkene	ØØÈ	aldehyde
Branched alkene	ØØÈ	ketone

(6) From Alkyne :

(a) Hydration : With dil $H_2SO_4 \& 1\% HgSO_4$ at 60-80°C.

$$CH \equiv CH + H_2O \longrightarrow [CH_2 = CHOH] \Longrightarrow CH_3 - \overset{\parallel}{C} - H$$

(Tautomerisation)

Ö

Other alkynes give ketone :

$$\begin{array}{c} C = C + H_2O \longrightarrow C + GH_3 - C = C + J_2 & \longleftrightarrow & H_3 - C - C + J_3 \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

(b) Hydroboration : Reaction with B_2H_6 , $2BH_3$ or R_2BH give dialkyl borane.

(7) By Nef's reaction :

(8)

Nitro alkanes are used in this reaction. The $\alpha\text{-}H$ of nitro alkane shows acidic nature.

$$R-CH_{2}-N_{0}^{O} \longrightarrow R-CH=N_{0}^{O} \xrightarrow{H_{0}OH}_{N+OH} R-CH=N_{0}^{O} \xrightarrow{H_{0}O^{0}}_{H=0}^{H} R-CHO + N_{2}O + H_{2}O + N_{3}OH$$
(Nitro form) (Aci form) (Aldehyde)
1° nitro alkane

$$R_{1}^{O} CH-N_{0}^{O} \longrightarrow R_{1}^{O} C=N_{0}^{O} \xrightarrow{H_{1}OH}_{R}^{O} C=N_{0}^{O} \xrightarrow{I_{1}O^{0}}_{R}^{H} \xrightarrow{R_{1}^{O}}_{R}^{O} C=O + N_{2}O + H_{2}O + N_{3}OH$$
(Nitro form) (Aci form) (Ketone)
2° nitro alkane

$$R_{1}^{O} C-N_{0}^{O} \xrightarrow{N_{3}OH}_{N} No \text{ Reaction}$$
(3° nitro alkane)
By hydrolysis of carbonyl derivatives :

$$R-CH=N-OH \xrightarrow{H_{2}O/H^{0}}_{(Aldehyde)} (R-CHO + NH_{2}-OH (Aldehyde)) (Hydroxyl amine)$$

$$R_{1}^{O} C=N-OH \xrightarrow{H_{2}O/H^{0}}_{R} R_{1}^{O} C=O + NH_{2}-OH (Ketone)$$
(Ketoxime) (Ketone)

$$R_{1}^{O} C=N-OH \xrightarrow{H_{2}O/H^{0}}_{R} R_{1}^{O} C=O + 2ROH (Aldehyde) (Alcohol)$$

(Acetal) (Aldehyde) (Alcohol

$$\begin{array}{c} R \\ R \end{array} \xrightarrow{OR} OR \\ (Ketal) \end{array} \xrightarrow{H_2O/H^{\oplus}} \begin{array}{c} R \\ R \end{array} \xrightarrow{C=O+2ROH} \\ (Ketone) (Alcohol) \end{array}$$

(9) By oxidation of alkyl halides:

Oxidation takes place by $(CH_3)_2S=0$ dimethyl sulphoxide (DMSO).

$$R - CH_2 - X + (CH_3)_2 S = O \longrightarrow RCHO + (CH_3)_2 S + HX$$

Alkyl halide (Aldehyde) (Dimethyl thio ether)



- (10) From Grignard reagents :
 - (a) By Cyanides :

$$RMgX + R - C = N - MgX \xrightarrow{H_2O/H^{\oplus}} R - C - R + NH_3 + Mg \begin{pmatrix} OH \\ X \\ R \\ O \\ (Ketone) \end{pmatrix}$$

(b) By Esters : HCHO can't be prepared by this method.





(c) By acid chlorides :



(11) From s-keto acids

The decarboxylation reaction takes place via formation of six membered ring transition state.

(a) HCOCH₂COOH $\xrightarrow{\Lambda}_{110^{\circ}C}$ CH₃CHO+CO₂

(b)
$$CH_3 = \overset{\beta}{\underset{\basel{constraint}}{\overset{\basel{const}}{\overset{\basel{constraint}}{\overset{\basel{}}{\overset{\basel{}}{\overset{\base$$

- (B) For Aldehydes only :
- (1) Reduction of acyl halides, esters and nitriles :
 - (a) Acyl chlorides can be reduced to aldehydes by treating them with lithium-tri-tert-butoxyaluminium hydride, LiAIH[OC(CH₃)₃], at -78° C.

$$R \xrightarrow[(i]{} O]{} (i)LAH(t-BuO)_{3},-78^{\circ}C} \xrightarrow[(i]{} O]{} R \xrightarrow[(i]{} H_2O]{} (i)H_2O} \xrightarrow[(i]{} A \xrightarrow[(i]{} H_2O]{} (i)H_2O]{} (i)H_2O \xrightarrow[(i]{} H_2O]{} (i)H_2O \xrightarrow[(i]{} H_2O \xrightarrow[(i]{} H_$$

(b) Both esters and nitriles can be reduced to aldehydes by DIBAL-H. Reduction must be carried out at low temperatures. Hydrolysis of the intermediates gives the aldehyde.



(2) Rosenmund's reduction :

Quinoline or sulphur act as a poisoned catalyst, controls the further reduction of aldehyde to alcohols.

$$\begin{array}{l} \text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd}/\text{BaSO}_4} \text{RCHO} + \text{HCl} \\ \\ \text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd}} \text{RCHO} \longrightarrow \text{RCH}_2\text{OH} \end{array}$$

Formaldehyde can not be prepared by this method.

Example : $C_2H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_2H_5CHO + HCl$ Propionyl Chloride Propanal

(3) Stephen's reduction :

Alkyl cyanides are reduced by SnCl₂ and HCl.

$$R \longrightarrow C \equiv N \xrightarrow{SnCl_2/HCl} R \longrightarrow CH = NH \xrightarrow{H_3O^+} RCHO + NH_3$$
$$C_2H_5 \longrightarrow C \equiv N \xrightarrow{SnCl_2/HCl} C_2H_5CH = NH \xrightarrow{H_3O^+} C_2H_5CHO + NH_3$$

(4) Oxo reaction or hydroformylation :

In this reaction symmetrical alkene gives 1^0 aldehyde while unsymmetrical alkene gives isomeric aldehyde (Chain isomers).

$$\begin{array}{cccc} \mathrm{CH}_{2} = \mathrm{CH}_{2} + & \underset{Water \, \mathrm{gas}}{\mathrm{CO}} & & \\ \mathrm{CH}_{3} - \mathrm{CH} = \mathrm{CH}_{2} + \mathrm{CO} + \mathrm{H}_{2} & & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{Co} \\ 150^{\circ}\mathrm{C}} & & \\ \mathrm{CH}_{3} - \mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{CHO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{Co} \\ 150^{\circ}\mathrm{C}} & & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{Ch} \\ \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{CHO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{Ch} \\ \mathrm{CH}_{3}-\mathrm{CHO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{Ch} \\ \mathrm{CHO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array}} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array}} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array}} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array} \xrightarrow{\begin{array}{c} \mathrm{ChO} + & \\ \end{array}} \xrightarrow{\begin{array}{c} \mathrm{ChO} + &$$

- (C) For Ketones only :
- (1) From Grignard's reagent :





(2) From dialkyl Cadmium :

RCdR' (dialkyl Cadmium) is a organometallic compound.

$$RCOCI + RCdR' \longrightarrow RCOR' + RCdCI$$

This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.

- (3) From R_2CuLi : $R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$
- (4) By hydrolysis of Aceto Acetic Ester (AAE) :

$$\begin{array}{cccc} CH_{3}-C-CH_{2}-C-CC_{2}H_{3} & \xrightarrow{H_{3}O^{\oplus}} \\ O & O \\ O &$$



- Other methods for aldehyde and ketone :
- (1) By dry distillation of Ca-salts of carboxylic acid :



Calcium salts of acids other then formic acid on heating together gives ketone



To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :

$$\begin{array}{ccc} & & & & & & \\ CH_{3} - & & & \\ CH_{3} - & & \\ Calcium Acetate & Calcium propionate \end{array} \xrightarrow{O} \begin{array}{c} & & & \\ CH_{2} - & & \\ CH_{2} - & \\ CH_{2} - & \\ CH_{2} - & \\ CH_{2} - & \\ CH_{3} -$$

(2) By Thermal decomposition of carboxylic acids :

Vapour of carboxylic acids when passed over MnO/300°C give carbonyl compounds

$$2 \text{ HCOOH } \xrightarrow{\text{MnO}} \text{HCHO} + \text{H}_2\text{O} + \text{CO}_2$$

$$2 \text{ CH}_3\text{COOH} \xrightarrow{\text{MnO}} \overrightarrow{300^\circ\text{C}} \xrightarrow{\text{CH}_3} \overrightarrow{\text{C}=O+CO_2+H_2O}$$

$$R\text{COOH} + \text{HCOOH} \xrightarrow{\text{MnO}} \overrightarrow{300^\circ\text{C}} \xrightarrow{\text{RCHO} + \text{CO}_2 + H_2O}$$

$$R\text{COOH} + \text{R'COOH} \xrightarrow{\text{MnO}} \overrightarrow{300^\circ\text{C}} \xrightarrow{\text{RCOR'} + \text{CO}_2 + H_2O}$$

(3) Wacker process :

In this reaction double bond is not cleaved so same C-atom aldehyde and ketones are formed.

$$CH_2 = CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + HCl$$

All other alkenes gives ketone.

$$RCH = CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} R \xrightarrow{O} R \xrightarrow{O} R + Pd + HO$$

D Physical Properties :

♦ State :

Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

♦ Odour :

Lower aldehydes give unpleasant smell, higher aldehydes and all ketones have pleasant smell.

Solubility :

 C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $\sum_{k=0}^{\delta_+} C_{k=0}^{\delta_-}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.

H-bonding

◆ Boiling point : Boiling point ∝ Molecular weight

Boiling point order is - Alcohol > Carbonyl compounds > Alkane

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole vander waal force of attraction is present. Alkanes are non polar.

- **Density** : Density of carbonyl compounds is lower than water.
- □ Chemical Properties :

Reactions of both aldehydes and ketones :

Due to strong electronegativity of oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons.

$$c = 0 \longrightarrow c = 0$$

Carbon is thus readily attacked by $\dot{N}u$. The negatively charged oxygen is attacked by electron deficient (electrophile) E⁺.

C = O bond in carbonyl group is stronger than C = C bond in alkanes.

$$\begin{cases} C-O & Bond energy is 84.0 \text{ KCals} \\ C=O & Bond energy is 178 \text{ KCals} \end{cases}$$

$$\begin{cases} C-C & Bond energy is 83.1 \text{ KCals} \\ C=C & Bond energy is 146 \text{ KCals} \end{cases}$$

Reactivity of carbonyl group 11 Magnitude of +ve charge I - I group I - I group I + I group

Ex : Why carbonyl compound gives nucleophilic addition reaction (NAR) ?



Ex. Arrange the following for reactivity in decreasing order

(I) (i)
$$\underset{H}{H} C=O$$
 (ii) $\underset{H}{C}=O$ (iii) $\underset{H}{C}=O$ (iii) $\underset{H}{C}=O$ (iii) $\underset{H}{C}=O$
(II) (i) CICH₂CHO (ii) NO₂CH₂CHO (iii) CH₃CHO (iv) CH₃CH₂CHO
(III) (i) CH₃CHO (ii) CICH₂CHO (iii) HCCl₂CHO (iv) CCl₃CHO
(IV) (i) $\underset{H}{C}=O$ (i) $\underset{H}{C}=O$ (ii) $\underset{H}{C}=O$ (iii) $\underset{H}{C}=O$ (iv) $\underset{H}{C}=O$
Sol. (A) I > II > III (B) II > I > III > IV (C) IV > III > II > I (D) IV > I > II > II > II
[Hint : CH₃— is +I group, decreases the intensity of +ve charge on C-atom of $>C=O$ group.]

Ex. In
$$\begin{array}{c} O (-1) \\ (-1) \\ C \\ (-1) \\ (-1$$

Sol. I is more reactive than II.

□ Chemical Reactions :

Carbonyl compounds in general under goes neucleophilic addition reaction :

- (A) Nucleophilic addition reactions :
- (1) Addition of HCN :



(2) Addition of NaHSO₃:

This reaction is utilized for the separation of carbonyl compounds from non - carbonyl compounds.



Reaction with ammonia derivatives : (3)

These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$$\begin{array}{ccc} NH_{3} & \longrightarrow & NH_{2}Z \text{ (Ammonia derivative)} \\ C = O + H_{2}N - Z & \xrightarrow{-H} & C = N - Z + H_{2}O \end{array}$$

Addition - elimination (Condensation)

Mechanism :

NIC

- Ammonia derivatives (NH_2Z) : ٠
 - = $OH \longrightarrow NH_2OH$ (Hydroxyl amine) Ζ
 - $Z = NH_2 \longrightarrow NH_2NH_2 \text{ (hydrazine)}$
 - = $\text{NHC}_6\text{H}_5 \longrightarrow \text{NH}_2\text{NHC}_6\text{H}_5$ (Phenyl hydrazine) Ζ

$$Z = NH - O NO_2 - NH_2 - NH - O NO_2$$

2, 4-Dinitro phenyl hydrazine (DNP) Brady's reagent.

$$Z = NHCONH_2 \longrightarrow NH_2NHCONH_2$$

Semi Carbazide.

$$\begin{array}{c} R \\ H \end{array} C = O + H_2 NOH \longrightarrow \begin{array}{c} R \\ H \end{array} C = NOH$$
 (Aldoxime)

Ketal

Tri ethoxy methane $[HC(OC_2H_5)_3]$ remove the water formed during the reaction and so the reaction proceeds in forward direction.



(5) Reaction with glycol (group protection) :

(4)



(neutral)

Cyclic acetal / ketal

(6) Reaction with sodium alkynide :



(7) Reaction with Grignard reagent :

$$\begin{array}{c} H \\ H \\ H \end{array} C = O + CH_3 Mgl \longrightarrow H \\ H \\ H \\ C = OMgl \xrightarrow{H_2O} CH_3 CH_2OH + Mg \\ OH \\ OH \end{array}$$

Ethanol (1° alcohol)

$$CH_{3}CHO + CH_{3}MgI \longrightarrow CH_{3} - C - H \xrightarrow{H_{2}O} CH_{3} - C - H + Mg \begin{pmatrix} OH \\ I \\ I \\ OH \end{pmatrix}$$

2-Propanol (2° alcohol)

$$\begin{array}{c} CH_{s} \\ CH_{s} \\ CH_{s} \end{array} C = O + CH_{s} + Mg \\ H_{s} \end{array} \longrightarrow \begin{array}{c} CH_{s} - C \\ -C \\ H_{s} \end{array} \xrightarrow{H_{s}O} CH_{s} - C \\ H_{s} \\ CH_{s} \end{array} \xrightarrow{OH} CH_{s} - Mg \\ H_{s} \\ CH_{s} \end{array} \xrightarrow{OH} CH_{s} + Mg \\ H_{s} \\ CH_{s} \\ CH_{s} \end{array} \xrightarrow{OH} CH_{s} \xrightarrow{OH} CH_{s} + Mg \\ H_{s} \\ CH_{s} \\ CH_$$

2-Methyl-2-propanol (3° alcohol)

(8) **Reaction with H_2O :** It is a reversible reaction.

$$C = O + H_2O \qquad \xrightarrow{Weak acid} \qquad C < OH \\ \xrightarrow{OH} OH$$

(neutral)

unstable hydrate

Ex : Which compound form more stable hydrate with H_2O ?(A) HCHO(B) CH_3CHO (C) CH_3COCH_3

(D) CH₃COC₂H₅

[Hint : HCHO since it is more reactive towards this reaction.]

Ans. (A)

Ex : Which carbonyl compound not gives reversible reaction with water ?

Sol. Chloral hydrate.



(Chloral)

(Chloral hydrate)

Stable by intra molecular hydrogen bonding.

(B) Other Reactions :

(1) Wittig Reaction :

Wittig reaction affords an important and useful method for the synthesis of alkenes by the treatment of aldehydes or kentones with alkylidenetriphenylphosphorane ($Ph_3P = CR_2$) or simply known as phosphorane



The wittig reagent, alkylidenetriphenylphosphorane (ylide), is prepared by treating trialkyl or triarylphosphine usually the latter with an alkyl halide in either soultion. The resulting phosphonium salt is treated with strong base (such as C_6H_5Li , BuLi, NaNH₂, NaH, C_2H_5ONa , etc.)



(2) Cannizaro's reaction :

Those aldehydes which do not contain α -H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol.

In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called disproportionation reaction. (Redox reaction)

HCHO + HCHO
$$\xrightarrow{Conc.}$$
 HCOONa + CH₃OH

Mechanism : (Cannizaro reaction)

(a) Rapid reversible addition of $\overline{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion H to second molecule of HCHO



$$\begin{array}{cccc} H & & & H \\ & & & \\$$

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldelyde is reduced.

2, 2-Dihydroxy methyl -1, 3-propane diol.(Penta erythritol)

(3) Tischenko reaction :

It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_3Al$, to form ester.

$$2\text{RCHO} \xrightarrow{(\text{R'O})_{3}\text{Al}}_{\Delta} \xrightarrow{\text{RCH}_{2} - \text{O} - \text{C} - \text{R}}_{\text{Ester}}$$
Example : $\text{CH}_{3}\text{CHO} + \text{CH}_{3}\text{CHO} \xrightarrow{(C_{2}\text{H}_{5}\text{O})_{3}\text{Al}} \xrightarrow{\text{CH}_{3}\text{COOH} + \text{CH}_{3}\text{CH}_{2}\text{OH}}_{\text{Esterification}} \xrightarrow{\text{CH}_{3} - \text{COOCH}_{2}\text{CH}_{3}} \xrightarrow{\text{CHyl}}_{\text{CHyl}}$

(4) Reaction With Halogen :

(a) Replacement of r-H atoms :

This reaction is not shown by formaldehyde (HCHO), since α -H atoms are absent, as enolisation does not takes place in HCHO.



Example :
$$CH_3 - CH_2 - C - CH_2 - CH_3 + 2Cl_2 \xrightarrow{-2HCl} CH_3 - CH_2 - C - CCl_2 - CH_3$$

 0
 O
 O

(b) Replacement of O-atom of C=O group : It takes place by PCl₅ or SOCl₂.

$$>C=O + PCl_5 \longrightarrow >C < O + POCl_3$$

Phosphorus penta chloride

$$C = O + SOCl_2 \longrightarrow C = O + SOCl_2 + SO_2$$

Thionyl chloride

(c) Haloform reactions :

Chlorine or bromine replaces one or more α -hydrogen atoms in aldehydes and ketones, e.g., acetone may be brominated in glacial acetic acid to give monobromoacetone :

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr (43-44\%)$$

The halogenation of carbonyl compounds is catalysed by acids and bases. Let us consider the case of acetone. In alkaline solution, tribromoacetone and bromoform are isolated. Thus, the introduction of a second and a third bromine atom is more rapid than the first. In aqueous sodium hydroxide, the rate has been shown to be independent of the bromine concentration, but first order with respect to both acetone and base i.e.,

Rate = k [acetone] $[OH^1]$

$$CH_{3}COCH_{3} + OH^{2} \xrightarrow{Slow} H_{2}O + CH_{3} \xrightarrow{O} COCH_{2}^{2} \longleftrightarrow CH_{3}C \xrightarrow{Br_{2}} CH_{3}COCH_{2}Br + Br^{2}$$

(5) Aldol Condensation :

Two molecules of an aldehyde or a ketone undergo condensation in the presence of a base to yield a β -hydroxyaldehyde or a β -hydroxyketone. This reaction is called the aldol condensation. In general Carbonyl compounds which contain α -H atoms undergo aldol condensation with dil. NaOH. Aldol contains both alcoholic and carbonyl group.

□ Mechanism of aldol condensation : It takes place in the following two stages :

- (a) Formation of Carbanion
- (b) Combination of carbanion with other aldehyde molecule.
- (a) Formation of Carbanion :

 α -H atom of C=O group are quite acidic which can be removed easily as proton, by a base.

$$\overline{O}H + \overset{\delta_{+}}{H} - \overset{\delta_{-}}{O}H_{2} - C - H \Longrightarrow \overline{O}H_{2} - C - H + H_{2}O$$

Base Acetaldehyde Carbanion Carbanion thus formed is stable because of resonance -

$$\begin{array}{c} & & \\$$



Aldol condensation is possible between :

- 1. Two aldehyde (Same or different)
- 2. Two ketones (Same or different)
- 3. One aldehyde and one ketone

Identical carbonyl compounds	→ Simple or self aldol condensation.
Different carbonyl compounds	\longrightarrow Mixed or crossed aldol condensation.

Simple or Self condensation :

$$\begin{array}{c} CH_{3}-CH+HCH_{2}CHO \xrightarrow{dl} N_{aOH} \\ \parallel \\ O \end{array} \xrightarrow{dl} OH_{3}-CH-CHO \xrightarrow{\Delta} -H_{3}-CH-CHO \xrightarrow{\Delta} -H_{3}-CH-CHO \\ \parallel \\ OH_{1} \\ H \end{array} \xrightarrow{l} Crotonaldehyde$$



diacetone alcohol

Mesityl oxide or 4-Methyl-3-pentene-2-one



Mixed or Crossed aldol Condensation :

$$\begin{array}{c} CH_{3}-CH_{4}+\overset{\alpha}{CH_{2}}-COOH_{3}-\overset{\alpha}{H^{2}} \\ |\\ OH_{4} \\ H \\ \end{array} \xrightarrow{(H_{2}-COOH_{3}-CH_{4}-CH_{4}-COOH_{3}-CH_{4}-CH_{4}-COOH_{3}-CH_{4}-CH_{4}-COOH_{4} \\ |\\ OH_{4} \\ (Aldol) \end{array}$$

Ex : $CH_3CHO + CH_3CH_2CHO \xrightarrow{1_{OH}} Total 4 products. Write structure of products ?$

Sol.
$$CH_3 \xrightarrow{\alpha} CH_1 + CH_2 CHO \xrightarrow{1} CH \rightarrow (Aldol) \xrightarrow{\Delta} CH_3 - CH = CH - CHO$$

$$\begin{array}{ccc} & & & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

$$\begin{array}{c} CH_{3} \\ CH_{3} - CH_{2} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{2} - CH_{2} - CH_{3} - CH_{2} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{2} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{2} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{2} - CH_{3} \\ H \\ CH_{3} - CH_{3} - CH_{3} - CH_{3} \\ H \\ CH_{3} - CH_{3} - CH_{3} \\ CH_{3} - CH_{3} - CH_{3} \\ CH_{$$

□ Intramolecular aldol condensation :



 $(\alpha,\beta$ – Unsaturated Ketone) (Aldol) Here 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

Note :

 If in crossed aldol condensation reaction, only one carbonyl compound have α–H than total two product formed.

$$CH_{3}CHO + C_{6}H_{5}CHO \xrightarrow{1}_{OH} Total 2 \text{ product.}$$

$$CH_{3}-CH + \overset{\alpha}{O}H_{2}-CHO \xrightarrow{1}_{OH} (Aldol) \xrightarrow{\Delta} CH_{3}-CH = CH-CHO$$

$$\overset{\parallel}{\bigcup} \overset{\parallel}{H} \overset{\parallel}{H}$$

(Crotonaldehyde)

$$\begin{array}{ccc} C_{6}H_{5} & \xrightarrow{-}CH + \overset{\alpha}{O}H_{2} & \xrightarrow{-}CHO & \xrightarrow{-}DHO & \xrightarrow{-}DHO & \xrightarrow{-}H_{2}O & \xrightarrow{-}C_{6}H_{5} & \xrightarrow{-}CH = CH - CHO \\ & & & & \\ O & & & H & \end{array}$$
(Aldol) $\xrightarrow{-}{-}H_{2}O & \xrightarrow{-}C_{6}H_{5} - CH = CH - CHO$

(6) Claisen condensation :

(Cinnamaldehyde)

When two molecules of ester undergo a condensation reaction, the reaction is called Claisen condensation. The product of the claisen condensation is a β -keto ester.



After nucleophilic attack, the aldol addition and the Claisen condensation differ. In the claisen condensation, the negatively charged oxygen reforms the carbon oxygen π -bond and eliminates the OR group.

□ Mixed claisen condensation :



(7) Intramolecular claisen condensation :

Dieckmann condensation : The addition of base to a 1,6-diester causes the diester to undergo intramolecular claisen condensation, thereby forming a five membered ring β -keto ester. An intramolecular claisen condensation is called a Dieckmann condensation.



(8) Perkin reaction :

In perkin reaction, condensation has been effected between aromatic aldehydes and aliphatic acid anhydride in the presence of sodium or potassium salt of the acid corresponding to the anhydride, to yield α , β -unsaturated aromatic acids.

The acid anhydride should have at least two α -H.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{AcONa}{170-180^{\circ}C} C_6H_5 - CH = CH - COOH$$



(9) Knoevenagel Reaction :

Condensation of aldehydes and ketones with compounds having active methylene group in the presence of basic catalyst to form a, b-unsaturated compounds is called Knoevenagel Reaction. The basic catalyst may be ammonia or its derivative. Thus 1°, 2°, 3° amines i.e., aniline, di-or tri - alkyl amines, pyridine or piperidine are used.



(10) Reformatsky Reaction :

A similar reaction like the addition of organometallic compounds on carbonyl compounds that involves the addition of an organozinc reagent to the carbonyl group of an aldehyde or ketone. This reaction, called Reformatsky reaction, extends the carbon skeleton of an aldehyde or ketone and yileds b-hydroxy esters. It involves treating an aldehyde or ketone with an α -bromo ester in the presence of zinc metal; the solvent most often used is benzene. The initial product is a zinc alkoxide, which must be hydrolysed to yield the β -hydroxy ester.



(11) Schmidt Reaction :

This is the reaction between a carbonyl compound and hydrazoic acid in the presence of a strong acid concentrated sulphuric acid. Aldehydes give a mixture of cyanide and formyl derivatives of primary amines, whereas ketones give amides :

RCHO + $HN_3 \xrightarrow{H_2SO_4} RCN + RNHCHO + N_2$

 $RCOR + HN_3 \xrightarrow{H_2SO_4} RCONHR + N_2$

Reaction with primary amine : $C = O + H_2 NR \longrightarrow C = NR + H_2O$

Schiff's Base

(12) Benzoin condensation :

The benzoin condensation is essentially a dimerisation of two aromatic aldehydes under the catalytic influence of cyanide ions to give benzoin (I).



The hydrogen atom attached to the carbonyl group of aldehyde is not active enough to be removed easily but the addition of the cyanide ion to the carbonyl carbon places this hydrogen in the alpha position of the nitrile thus rendering it relatively acidic. The carbanion, thus generated, attacks the carbonyl carbon of the second aldehyde molecule in a rate-determining step forming an unstable cyanohydrin of benzoin which immediately breaks down into benzoin and hydrogen cyanide.





The addition of a strong base to a carbonyl group results in the formation of an anion. The reversal of the anionic charge may cause expulsion of the attached group X, e.g.



However, in a 1, 2-diketone the group X may migrate to the adjacent electron-deficient carbonyl carbon forming α -hydroxy acid.

Thus, benzil on treatment with a strong base forms benzilic acid (salt), hence the name benzilic acid rearrangement.



benzil

sodium salt of benzilic acid

(14) The Beckmann rearrangenment :

The acid catalysed transformation of a ketoxime to an N-substituted amide is known as the Beckmann rearrangement.



The rearrangement is catalysed by a variety of acidic reagents such as H_3PO_2 , H_2SO_4 , $SOCl_2$, PCl_5 , etc.

(C) Oxidation Reactions :

(a) By $K_2Cr_2O_7/H_2SO_4$:

On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same C-atom. While, 2⁰ alcohol on oxidation gives ketone which on further oxidation gives acid with less C-atom.

 $R-CH_2OH \xrightarrow{[0]} R-CH=O \xrightarrow{[0]} R-COOH$

 $(1^{\circ} alcohol)$

$$\begin{array}{c} CH_{3}CH_{2}CH_{2}-C-CH_{3} \xrightarrow{[0]} CH_{3}CH_{2}COOH+CH_{3}COOH\\ \\ \\ \\ OH \\ (2^{\circ} \text{ alcohol}) \end{array} \xrightarrow{[0]} CH_{3}CH_{2}COOH+CH_{3}COOH \\ \\ \\ OH \\ C \end{array}$$

- (i) 3° alcohol is not oxidised within 2 or 3 minutes.
- (ii) 1° and 2° alcohol converts orange colour of $K_2 Cr_2 O_7$ to green in 2-3 minutes.

(b) SeO_2 (Selenium Oxide) :

Ketones or aldehydes on oxidation with SeO_2 gives dicarbonyl compounds. This reaction is possible only in compounds containing α -carbon.

HCHO doesn't show this reaction.

(c) Baeyer's Villiger oxidation :

Both aldehyde and ketones are oxidized by peroxy acids. This reaction, called the Baeyer-villiger oxidation, is especially useful with Ketones, because it converts them to carboxylic esters. For example, treating acetophenone with a peroxy acid converts it to the ester phenyl acetate.



Mechanism :



The product of this reaction show that a phenyl group has a greater tendency to migrate then a methyl group. Had this not been the case, the product would have been $C_6H_5COOCH_3$ and not $CH_3COOC_6H_5$. This tendency of a group to migrate is called is migratory aptitude. Studies of the Baeyer-villiger oxidation and other reaction have shown that the migratory aptitude of groups $H > phenyl > 3^{\circ}$ alkyl > 2° alkyl 1° alkyl > methyl. In all cases, this order is for groups migrating with their electron pairs, that is, as anions.

Ex.
$$CH_3 - C - C_2H_3 \xrightarrow{Per acid} ?$$

Sol.
$$CH_3 - C - OC_2H_5$$

Ex.
$$CH_3$$

 \downarrow
 $C-C-C-CH_3$
 \downarrow
 H_3O
 $Per acid \rightarrow ?$



(D) Reduction :

(a) The wolf kishner reduction :

When a ketone or an aldehyde is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group this process is called Deoxygenation because an oxygen is removed from the reactant. The reaction is known as the Wolf-kishner Reduction.



(b) Clemmensen Reduction :

The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction.



The nature of product depends upon the reducing agent used. It can be summarized as.

(i)
$$\rangle C = O \longrightarrow$$

Reducing agents are

- ◆ Red P/HI at 150°C
- ◆ Zn-Hg/HCl [Clemensen's reduction]
- ◆ NH₂—NH₂/C₂H₅OH,OH¹ [Wolff Kischner's reduction]

(ii) $\rangle C = O \longrightarrow \rangle C + OH$

Reducing agents are

- $LiAlH_4$ (Nicetron brown)
- ♦ Na/C₂H₅OH (Bouvalt blank)
- NaH/Benzene (Darzen reaction)
- ◆ [(CH₃)₂CHO]₃Al (Aluminium isopropoxide)
- ♦ (CH₃)₂ CHOH (Isopropyl alcohol)

Reduction with aluminium isoproposide is excess of isopropanol is called MPV (Meerwein Ponndroff Verley) reduction. Other reducible groups are not attacked like $-NO_2$, $-CH=CH_2$, $-C\equiv C-$.

Example : $CH_3 \rightarrow C=O$ $MPV Reduction \rightarrow CH_2=CH$

 CH_2

$$(H_3)$$
 CHOH $(H_2=CH)$

- (E) Reactions given by only aldehydes :
- (1) Polymerisation : It is a reversible process.Formaldehyde :
 - (a) nHCHO = France and the france of the constant of the con

Paraformaldehyde is a linear polymer which show reducing character with Tollen's reagent, Fehling solution etc.

(b) nHCHO
$$H_{2O}$$
 (CH₂O)_n H₂O

Poly oxy methylene n > 100

(c) 3HCHO
$$\xrightarrow{\text{Allowed to stand}}$$
 (CH₂O)₃

Meta formaldehyde (Trioxane) Cyclic polymer (Trioxy methylene) Cyclic polymer doesn't show reducing character with Tollen's reagent etc.

(d) 6HCHO
$$\xrightarrow{\text{Ca(OH)}_2}$$
 $C_6H_{12}O_6$

Formose sugar A linear polymer (α -acrose)

Acetaldehyde :

(a)
$$3CH_3CHO \xrightarrow{Conc. H_2SO_4} (CH_3CHO)_3$$

 $\xrightarrow{\text{conc. }H_2SO_4} (CH_3CHO)_4$

Para acetaldehyde Paraldehyde (cyclic polymer) Pleasent smelling liquid Hypnotic compound



Meta aldehyde White crystalline solid. Cydic polymer Used as solid fuel or killing snails

(4) Reaction with ammonia :

4CH₃CHO

(b)

Except formaldehyde, all other aldehydes give addition reactions (HCHO give addition elimination i.e. condensation reaction)

$$6CH_{2}O + 4NH_{3} \xrightarrow{Condensation} (CH_{2})_{6}N_{4} + 6H_{2}O$$
Urotropine (Hexamine)
White crystalline solid
Used in preparation of explosive
Used in treatment of urine infection diseases

$$CH_{3}-CH + NH_{2} \xrightarrow{Addition} CH_{3}-CH-NH_{2}$$

$$Ch_{3}-CH = NH$$

$$Acetaldehyde annonia$$

$$Ch_{3}-CH = NH$$

$$\frac{3H_{2}O}{Trimerisation}$$

$$\frac{CO}{Trimerisation}$$

$$\frac{CO}{Trimer$$

(5) Reducing character :

Aldehydes are easily oxidised so they are strong reducing agents.

(a) Tollen's reagent :

It oxidises aldehydes. Tollen's reagent is ammonical silver nitrate solution

 $\begin{array}{cccc} (\mathrm{AgNO}_3 + \mathrm{NH}_4\mathrm{OH}) & \longrightarrow & [\mathrm{Ag}(\mathrm{NH}_3)_2]\mathrm{OH} \\ \mathrm{RCHO} + [\mathrm{Ag}(\mathrm{NH}_3)_2]\mathrm{OH} & \longrightarrow & \mathrm{RCOOH} + \mathrm{Ag} + \mathrm{H}_2\mathrm{O} \\ & & & & & \\ & & & & & \\ \mathrm{Silver\ mirror} \\ \mathrm{AgNO}_3 + \mathrm{NH}_4\mathrm{OH} & \longrightarrow & \mathrm{AgOH} \longrightarrow \mathrm{Ag}_2\mathrm{O} \\ \mathrm{RCHO} + \mathrm{Ag}_2\mathrm{O} & \longrightarrow & \mathrm{RCOOH} + \mathrm{Ag} \downarrow (\mathrm{Silver\ mirror}) \end{array}$

(b) Fehling's solution :

It is a mixture of CuSO₄, NaOH and sodium potassium tartrate.

Fehling solution A- (aq.) solution of CuSO₄

Fehling solution B- Roschelle salt (Sodium potassium tartrate + NaOH)

Fehling solution A + Fehlings solution B(Dark blue colour of cupric tartrate)

$$RCHO + Cu^{+2} + OH^{-} \longrightarrow RCOOH + Cu_{2}O$$

(Cuprous oxide-Red ppt.)

 $Cu^{2+} \longrightarrow Cu^{+}$

(Cupric - Blue)

e) (Cuprous - Red ppt.)

(c) Benedict's solution :

It is a mixture of $CuSO_4$ + sodium citrate + Na_2CO_3 . It provides Cu^{+2} . It is reduced by aldehyde to give red ppt of cuprous oxide.

Cu₂O

 $RCHO + Cu^{2+} + OH^{-} \longrightarrow RCOOH +$

(Cuprous oxide-Red ppt.)

(d) Mercuric chloride :

 $HgCl_2$ is a corrosive sublimate. It is reduced by aldehyde to give white ppt of mercurous chloride (Calonal) which further react with aldehyde to give black ppt of Hg.

 $\begin{array}{cccc} \text{RCHO} + \text{HgCl}_2 + \text{H}_2\text{O} & \longrightarrow \text{RCOOH} + \text{Hg}_2\text{Cl}_2 + \text{HCl} \\ & & (\text{calomal}) \\ \\ \text{RCHO} + \text{Hg}_2\text{Cl}_2 + \text{H}_2\text{O} & \longrightarrow \text{RCOOH} + \text{Hg} + \text{HCl} \\ & & (\text{black ppt}) \end{array}$

(e) Reaction with schiff's reagent :

Schiff's reagent is dil solution of p-roseniline hydrochloride or magenta dye. Its pink colour is discharged by passing SO_2 gas and the colourless solution is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

- (F) Reaction of only ketones :
- (1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



Pinacol

(2) Reaction with chloroform :



(3) Reaction with HNO_2 :

$$\begin{array}{c} O \\ \parallel \\ CH_{3} - C - CH_{3} + O = N - OH \xrightarrow{-H_{2}O} CH_{3} - C - CH = N - OH \end{array}$$

Oximino acetone

(4) Oxidation reaction : According to popoff's rule C=O group stays with smaller alkyl group.

$$CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{3}COOH + CH_{3}COOH$$

(5) Condensation reaction :

(a) In presence of dry HCl - aldol condensation takes place

$$\begin{array}{ccc} CH_{3} & O & CH_{3} & O \\ | & & \parallel \\ CH_{3}-C=O+CH_{3}-C-CH_{3} \xrightarrow{-H_{2}O} CH_{3}-C=CH-C-CH_{3} \end{array}$$

$$\begin{array}{ccc} H_{3} & O & \parallel \\ H_{3}-C=C+C-CH_{3} & \parallel \\ Mesityl \text{ oxide} \end{array}$$

$$\begin{array}{cccc} CH_{3} & CH_{3} & O & CH_{3} \\ \downarrow \\ C=C=CH-COCH_{3}+O=C-CH_{3} \xrightarrow{-H_{2}O} CH_{3}-C=CH-C-CH_{3} \\ \end{array} \\ (Phorone) \text{ or } 2,6-Dimethyl-2,5-hepta diene-4-one \\ \end{array}$$

(b) In presence of $conc.H_2SO_4$



(6) Reaction with ammonia :



(7) Pyrolysis :

CH2-	$-C=O^{\Delta}$	$\rightarrow CH_2 = C = O + CH_4$	$\left(\text{HCHO} \xrightarrow{\Delta} \text{CO} + \text{H}_2 \right)$
Ĥ	ĊH ₃	Ketene	
	Acetone		$\left(CH_{3}CHO \longrightarrow CH_{4} + CO\right)$

TEST FOR HCHO, CH₃CHO, CH₃COCH₃

S.No.	Test	НСНО	CH ₃ CHO	CH ₃ COCH ₃
1.	Legel's test :Na [Fe(NO)(CN) ₃] sodium nitroprusite (alk.)	_	Red	Red
	Only methyl >C=O			
2.	compound gives this test Iodoform test	_	_	_
	(I ₂ + NaOH)	_	yellow ppt	yellow ppt
3.	OH Pyragallol OH OH	white ppt.	_	-
4.	Orthonitro benzaldehyde	-	-	Blue
5.	Tollen's reagent -	Silver mirror	Silver mirror	-
	Fehling's reagent -	Red ppt	Red ppt	-
	Mercuric chloride -	Black ppt	Black ppt	_
	Schiff's reagent -	Pink colour	Pink colour	-
6.	DNP	Orange	Orange	Orange
		colour	colour	colour

BENZALDEHYDE (C_6H_5 CHO) Oil of bitter almonds

General Method of Preparation :



Chemical properties :

CHCH(OH)CN	(Similar) HCN	$\begin{array}{c} (\text{different}) \\ \hline 170^{\circ}/\text{C}_2 \end{array} \rightarrow \text{C}_6\text{H}_2\text{COCl}$
C,H,CH,OH,SO,Na	< ^{NaHSO} 3	$\xrightarrow{2NH_3} C_{c}H_{-}C_{H} \xrightarrow{-} N \xrightarrow{-} C_{c}H_{-}C_{H}$
C₅HįCI+EN−Z	NH₂−Z	2C,H,CHO alc.KCN C,H,−C−C,H, Benzoin
C'H'UH'	$\mathbf{A}^{\operatorname{Red} P + H\mathbf{I}}$	
CH COOH	 ■ Oxidation 	Hat No.
C ₆ H ₂ CHO ₂	← C ₆ H ₅ CHO	→ C ₆ H ₅ -CH=CH=NO ₂ Nitrostyrene Br
Silver mirror <i>test</i>	 ■ Tollen reagent 	(i) Zn+CH_2000C_2H (ii) H_2O Reformatsky reaction
C6H3COONa + C6H3CH2—OH Cannizaro reaction	▲ NaOH	HNO_3/H_2SO_4 m-nitrobenzaldehyde
CcH,CH==N−Ar Schiff's base	← Ar-NH ₂	Furring H ₂ SO ₄ m-formul benzene
Pink colour	Schiffs reagent	G ₂ /FeG ₃ → Chloro benzaldehyde
C,H,COOCH,C,H, Tischenko reachion OH	$ AlO_3 AlOR_3 $	СӉ <u>-</u> С–СӉ
GH−GH-CH	< <u>C₆H₆M₃Br</u> H ₂ O	CGHGH=GH−C−GH3 GH

SOLVED EXAMPLES

Ex 1. What is A in the following reaction ?







Ex 2.

is the final product obtained when one of the following is reacted with base : $C\!H_{\!s}$









 $\begin{array}{ccc} CH_{3} & C & C & C \\ CH_{3} & C & C & C & C \\ CH_{3} & C & H & \stackrel{H^{+}}{\longrightarrow} (A) \end{array}$

The product (A) in the given reaction would be :











Ex 4. End product of the following sequence of reactions is :



- ∴ (B)
- Ex 5. In which of the following substrates, rate of Benzoin condensation will be maximum ?



Benzoin condensation is due to stability of intermediate (III) when negative charge on C extensively delocalised in benzene ring, nitro and C=N group. In all other cases, such dispersal is not extensively possible. On the other hand, NO_2^- is also creating a positive charge center on carbonyl carbon, making it more susceptible to nucleophilic attack of CN^- .

Ex 6. This intermediate is converted into product in the wittig reaction :

$$Ph_{3}P - O$$

$$R - C - C - R_{1} \rightarrow O = P - Ph_{3} + R - C = C - R_{1}$$

$$R_{1} - R_{2} - R_{1} - R_{2}$$

Out of following which statements are correct ?

- (A) C-O bond is weaker as compared to P-O bond
- (B) Lone pair of oxygen atom participate in $p\pi$ -d π bonding with phosphorous atom
- (C) C-P bond is weaker as compare to C-C bond
- (D) C-C bond is weaker as compare to C-O bond

Ex 7. Consider the following sequence :



Ex 10. 3HCHO + CH₃CHO $\xrightarrow{\text{NaOH}}$ A. A found can

- (A) Reduce Tollen's reagent
- (C) React with Na

- (B) Give Cannizaro reaction
- (D) Give green colour with $\rm Cr_2O_7^{2-}/H^+$

Sol. A is by aldol condensation

 \therefore (A), (B), (C) and (D)

Ex 11. $2CH_3 - C - CH_3 \xrightarrow[H^+]{H^+} Product, product in the reaction is :$

Sol. (A)
$$2CH_3 - CO - CH_3 \xrightarrow{M_3/H_3} H_3C \xrightarrow{H_3} H_$$

Ex 12. Benzaldehyde on reaction with acetophenone in the presence of sodium hydroxide solution gives : (A) $C_6H_5CH = CHCOC_6H_5$ (B) $C_6H_5COCH_2C_6H_5$ (C) $C_6H_5CH = CHC_6H_5$ (D) $C_6H_5CH(OH)COC_6H_5$ Sol. (A) $C_6H_5CHO + CH_3COC_6H_5 \xrightarrow{NaOH} -H_2O} C_6H_5 - CH = CH - C - C_6H_5$ Ex 12. Product in following reaction is

Ex 13. Product in following reaction is : $CH_3MgI + HCHO \rightarrow Product$ (A) CH_3CHO (B) CH_3OH (C) C_2H_5OH (D) $CH_3 - O - CH_3$ Sol. (C) $H - CHO + CH_3MgI \rightarrow CH_3 - CH_2 - OH + Mg < OH$