11

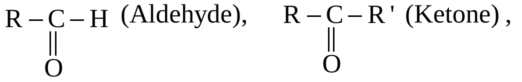
ALDEHYDES, KETONES & CARBOXYLIC ACID

CARBONYL COMPOUNDS

INTRODUCTION

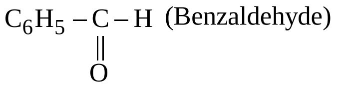
1. A divalent group in which a double bond (=) is present between carbon and oxygen atoms, is called a "Carbonyl Group" [C=O]
2. Aldehydes and ketones are collectively known as carbonyl compounds.
3. When oxygen is attached to a primary carbon atom, the compound is known as an aldehyde and if it is attached to a secondary carbon, the compound is known as a ketone.

Ex.



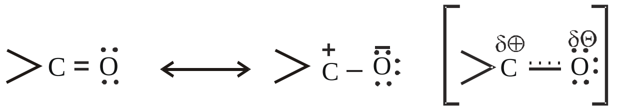
$$R-\underset{\underset{O}{\parallel}}{C}-H \text{ (Aldehyde)}, \quad R-\underset{\underset{O}{\parallel}}{C}-R' \text{ (Ketone)},$$

(Where R is hydrocarbon radical)



$$C_6H_5-\underset{\underset{O}{\parallel}}{C}-H \text{ (Benzaldehyde)}$$

4. If the radicals R & R' attached to the ketonic group are identical (R = R), then ketones are called simple or sym or symmetrical ketones and if nonidentical (R ≠ R'), they are called mixed or unsym or unsymmetrical ketone.
5 General formula of these compound is $C_nH_{2n}O$.
6. Hybridisation state of carbon in carbonyl group is sp^2 and sp^2 orbital overlaps with p–orbital of oxygen and forms C–O, sp^2–p, σ–bond.
7. The carbonyl group is polar in nature. The π–bond cloud is unsymmetrical because of the greater negativity of oxygen (3.5) than the carbon (2.5).
8. The C=O bond length is 1.23 Å and bond energy is 178 Kcal
9. Resonance hybrid structure of carbonyl group can be indicated by



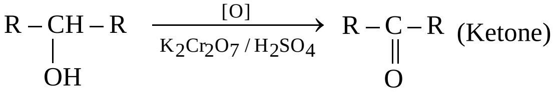
(Canonical structures) Resonance hybrid structure

GENERAL METHODS OF PREPARATION

By Oxidation of Alcohol (by $K_2Cr_2O_7/H_2SO_4$) :

(a) Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketons

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4\text{(dil.)}]{[O]} \underset{\text{(Aldehyde)}}{RCHO}$$



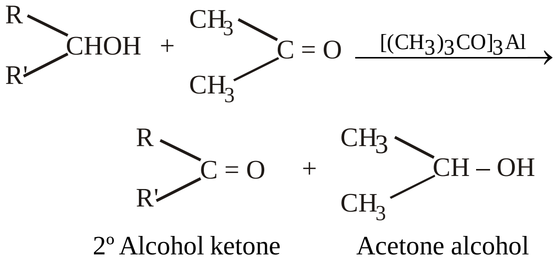
$$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} R-\underset{\underset{O}{\parallel}}{C}-R \text{ (Ketone)}$$

($K_2Cr_2O_7/H_2SO_4$) is a strong oxidising agent.
Aldehydes are quite susceptible to further oxidation to acids.

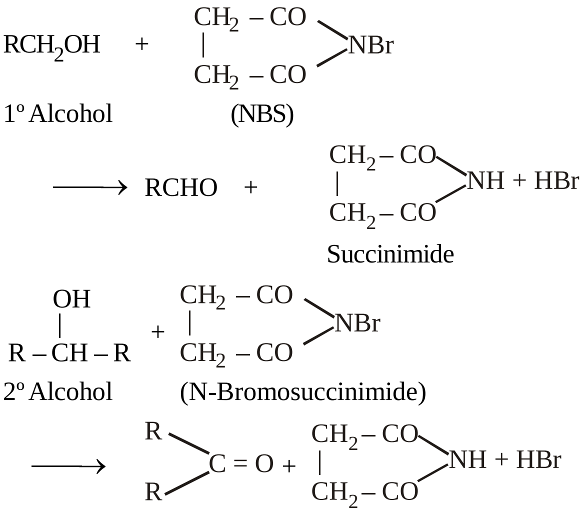
$$RCH_2OH \xrightarrow{[O]} R\text{–}CHO \xrightarrow{[O]} R\text{–}COOH$$

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

(b) **Oppenaure Oxidation :** The oxidation of sec. alcohols to ketones by heating them with specific reagent.
$[(CH_3)_3CO]_3Al$:Aluminium-t-butoxide in presence of acetone.



(c) **By N-Bromo Succinamide (NBS) :**

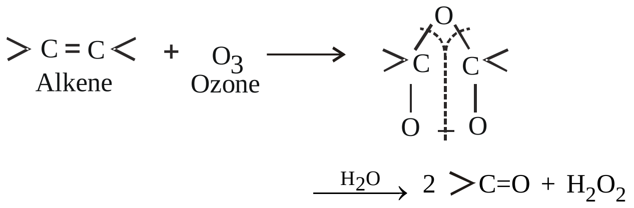


(d) **Mild Oxidising Agent :**
Only 1° alcohol will get oxidised with CrO_3 / Pyridine (Collin's reagent), Ag/O_2 at 250°C

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

By this reaction, good yield of aldehyde is possible. Ketones can not be prepared by this method.

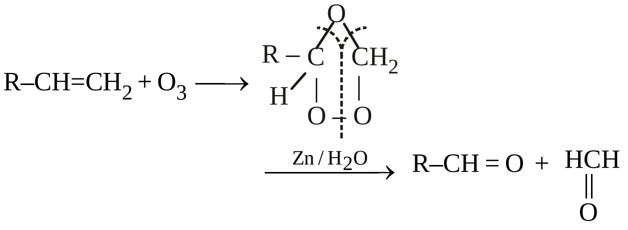
By ozonolysis of Alkene :



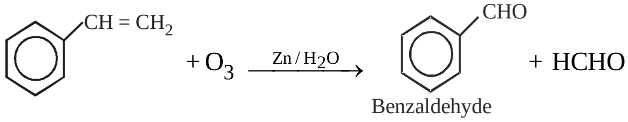
$$>C=C< + O_3 \longrightarrow \text{ozonide} \xrightarrow{H_2O} 2\ >C=O + H_2O_2$$

Note : To prevent further oxidation of carbonyl compound by H_2O_2, we add zinc in the reaction to destroy H_2O_2

$$Zn + H_2O_2 \rightarrow ZnO + H_2O$$



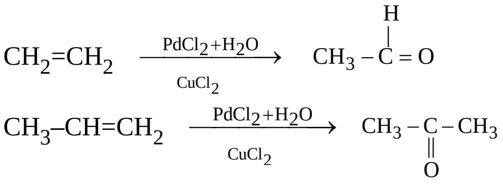
$$R\text{–}CH=CH_2 + O_3 \longrightarrow \text{ozonide} \xrightarrow{Zn/H_2O} R\text{–}CH=O + HCHO$$



$$C_6H_5CH=CH_2 + O_3 \xrightarrow{Zn/H_2O} C_6H_5CHO + HCHO$$

By Wacker's process :

Reagent : Acidified aqueous solution of $PdCl_2$ and $CuCl_2$



$$CH_2=CH_2 \xrightarrow[CuCl_2]{PdCl_2+H_2O} CH_3-\overset{H}{\overset{|}{C}}=O$$

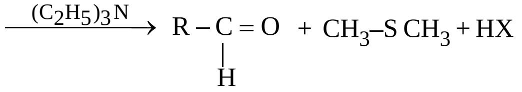
$$CH_3\text{–}CH=CH_2 \xrightarrow[CuCl_2]{PdCl_2+H_2O} CH_3-\underset{O}{\underset{||}{C}}-CH_3$$

By oxidation of Alkyl halide :

1° Alkyl halides $\xrightarrow{\text{Oxidation}}$ Aldehydes

2° Alkyl halides $\xrightarrow{\text{Oxidation}}$ Ketones.

$R\text{–}CH_2\text{–}X + CH_3\text{–}SO\text{–}CH_3$



$$\xrightarrow{(C_2H_5)_3N} R-\underset{H}{\underset{|}{C}}=O + CH_3\text{–}S\,CH_3 + HX$$

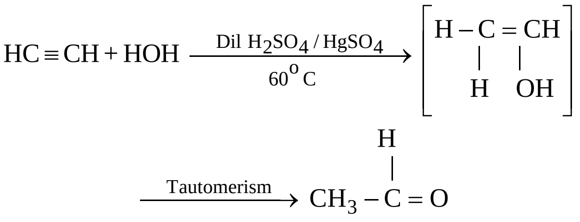
Dimethyl sulphoxide

$>CH\text{–}X + CH_3\text{–}SO\text{–}CH_3$

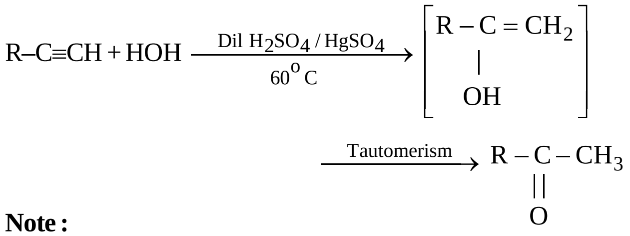
$$\xrightarrow{(C_2H_5)_3N} >C=O + CH_3\text{–}S\text{–}CH_3 + HX$$

By Hydration of Alkyne :

Catalytic acidic hydration : Acetaldehyde is formed on passing acetylene in 40% aqueous solution of H_2SO_4 at 60°C in the presence of 1% $HgSO_4$. The reaction is called "Kucherov Reaction."



$$HC\equiv CH + HOH \xrightarrow[60^{o}C]{Dil\ H_2SO_4/HgSO_4} \left[\begin{array}{c} H-C=CH \\ \ \ |\qquad | \\ \ \ H\quad OH \end{array}\right] \xrightarrow{\text{Tautomerism}} CH_3-\overset{H}{\overset{|}{C}}=O$$



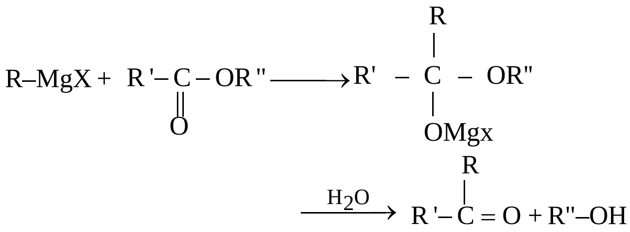
$$R\text{–}C\equiv CH + HOH \xrightarrow[60^{o}C]{Dil\ H_2SO_4/HgSO_4} \left[\begin{array}{c} R-C=CH_2 \\ | \\ OH \end{array}\right] \xrightarrow{\text{Tautomerism}} R-\underset{O}{\underset{||}{C}}-CH_3$$

Note :

(i) Formaldehyde can't be prepared by this method

(ii) Only ethyne gives acetaldehyde while other alkynes give ketones.

From Grignard's reagent : Ketones are obtained from acetic and higher esters -



$$R\text{–}MgX + R'-\underset{O}{\underset{||}{C}}-OR'' \longrightarrow R'-\underset{OMgx}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OR'' \xrightarrow{H_2O} R'-\overset{R}{\overset{|}{C}}=O + R''\text{–}OH$$

Note : Acid chloride and amides can be taken in place of ester.

$C_6H_5\text{–}MgBr + HCOOC_2H_5$ (Ethyl formate)

$$\longrightarrow C_6H_5CHO + MgBr(OC_2H_5)$$

Benzaldehyde

Oxidation of Nitroalkane (NEF reaction) :

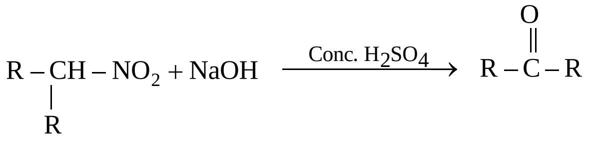
Primary Nitroalkane → Aldehyde
Secondary Nitroalkane → Ketone

Nitro alkanes are used in this reaction The α-hydrogen in nitroalkane shows acidic character.

$$CH_3NO_2 + NaOH \xrightarrow{-H_2O} [CH_2=NO_2]^{-}Na^{+}$$

$$\xrightarrow{Conc.\ H_2SO_4} HCHO + N_2O + Na_2SO_4 + H_2O$$

$$RCH_2NO_2 + NaOH \xrightarrow{Conc.\ H_2SO_4} RCHO$$

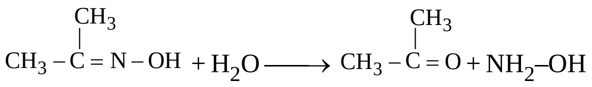


$$R-\underset{R}{\underset{|}{C}H}-NO_2 + NaOH \xrightarrow{Conc.\ H_2SO_4} R-\overset{O}{\overset{||}{C}}-R$$

By hydrolysis of oximes :

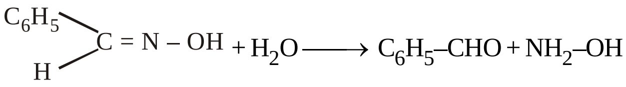
$$CH_3\text{–}CH=NOH + H_2O \longrightarrow CH_3CHO + NH_2OH$$

Acetaldoxime



$$CH_3-\overset{CH_3}{\overset{|}{C}}=N-OH + H_2O \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=O + NH_2\text{–}OH$$

Acetoneoxime



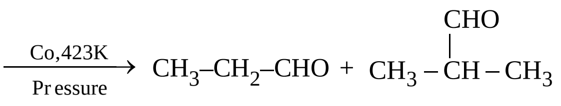
$$C_6H_5(H)C=N-OH + H_2O \longrightarrow C_6H_5\text{–}CHO + NH_2\text{–}OH$$

Benzaldoxime Banzaldehyde

METHODS OF PREPARATION OF ONLY ALDEHYDE

By hydroformylation of alkene (Oxo reaction) :

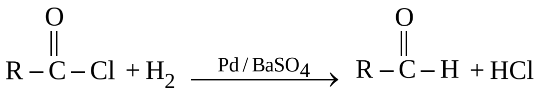
$2CH_3-CH=CH_2 + CO + 2H_2O$



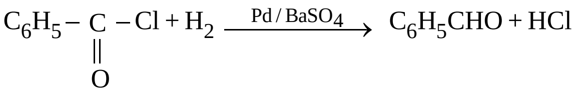
$$\xrightarrow[\text{Pressure}]{\text{Co,423K}} CH_3-CH_2-CHO + CH_3-\overset{CHO}{\overset{|}{CH}}-CH_3$$

Rosenmund's Reaction :

Reduction of an acid chloride by Pd-$BaSO_4$ in boiling xylene.



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$$



$$C_6H_5-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

Note :

(i) Formaldehyde can not be prepared by this method because, the corresponding acid chloride (HCOCl) is unstable.

(ii) In the above reaction $BaSO_4$ acts as catalyst poison and decreases the catalytic efficiency of Pd, due to which further reduction of aldehyde to alcohol can't take place.

By reduction of alkyl cyanide (Stephen's reaction) :

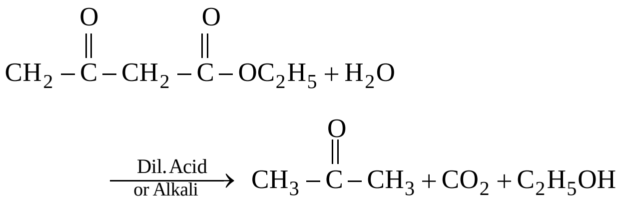
Reagent : ($SnCl_2$/HCl)

Alkyl cyanides are reduced by $SnCl_2$ and HCl.

$$R-C\equiv N + 2H \xrightarrow{SnCl_2/HCl} R-CH=NH.HCl$$
$$\xrightarrow{H_2O} RCHO + NH_4Cl$$
$$R-C\equiv N \xrightarrow{+2H} R-CH=NH.HCl$$
$$\xrightarrow{HOH} R-CH=O + NH_4Cl$$
$$C_6H_5-C\equiv N \xrightarrow{SnCl_2/HCl} C_6H_5-CH=NH.HCl$$
$$\xrightarrow{H_3O^+} C_6H_5CHO + NH_4Cl$$

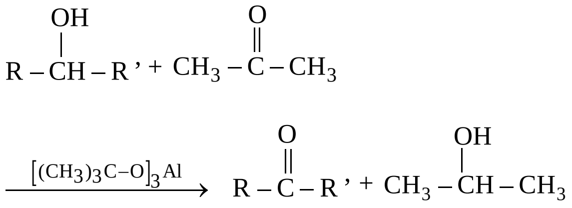
METHODS OF PREPARATION OF ONLY KETONE

By alkaline hydrolysis of acetoaceticester or its Alkyl derivative :



$$CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O \xrightarrow[\text{or Alkali}]{\text{Dil. Acid}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2 + C_2H_5OH$$

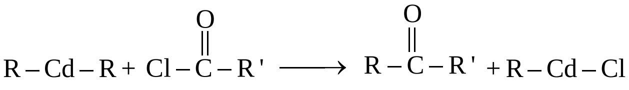
By Oppenauer oxidation :



$$R-\overset{OH}{\overset{|}{CH}}-R' + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{[(CH_3)_3C-O]_3Al} R-\overset{O}{\overset{\|}{C}}-R' + CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$$

Note : The reverse of this reaction is called Meerwein Ponndorf Verley reduction.

From dialkyl cadmium :



$$R-Cd-R + Cl-\overset{O}{\overset{\|}{C}}-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + R-Cd-Cl$$

Dialkyl cadmium can be obtained by

$$2R-Mg-Cl + Cd\,Cl_2 \longrightarrow R-Cd-R + 2MgCl_2$$

This method is very important for synthesis of Ketone.

PHYSICAL PROPERTIES

(a) **Physical state :** Formaldehyde is a gas. All other aldehydes and ketones upto C_{11} are colourless volatile liquids. Higher members are solids at room temperature.

(b) **Odour :** Lower aldehydes have an unpleasant odour. Higher aldehydes and ketones have a pleasant odour.

(c) **Solubility :** Lower carbonyl compounds are soluble in water but solubility decreases with increase in molecular weight.

(d) **Boiling point :**

Boiling point and Melting point $\propto$ Molecular weight

$\propto$ 1/(Branching)

Boiling points of carbonyl compounds are less than the corresponding alcohols of comparable molecular weight but are higher than corresponding alkanes.

(e) Reactivity : Reactivity depends on the nature of alkyl group attached to it. Smaller the alkyl group, the more reactive is the compound.

Reactivity $\propto$ Magnitude of +ve charge on carbon atom of the carbonyl group.

(f) 40% aqueous solution of HCHO (4–6% CH_3OH) is called formalin. It is used as a disinfectant and antiseptic. It is also used for preserving biological specimen.

(g) HCHO + Lactose = Formamint used for throat infection.

(h)

Carbonyl compound	HCHO	CH_3CHO	CH_3COCH_3
Boiling point	–21°C	+ 21° C	56° C

CHEMICAL PROPERTIES

Aldehydes and Ketones show following types of reactions.

1. **Nucleophilic addition reactions :**

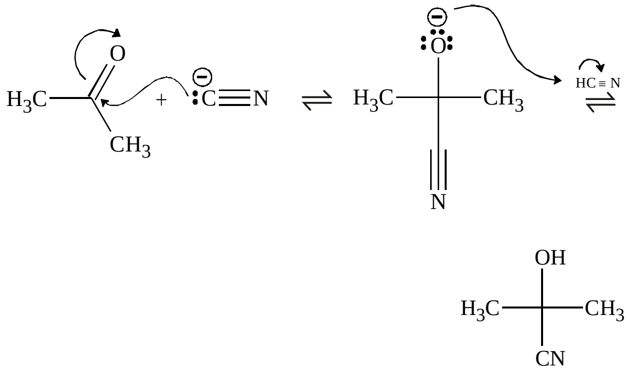
* Aldehydes undergo nucleophilic addition reactions faster than ketones. Thus, among the compounds HCHO, CH_3COCH_3, and CH_3CHO, the order of reactivity to nucleophilic addition will be

$$HCHO > CH_3CHO > CH_3COCH_3.$$

* Ketones with small alkyl groups bonded to the carbonyl carbon are more reactive than ketone with large alkyl groups.

* Aldehydes and ketones are less reactive than acyl halides and acid anhydrides but are more reactive than esters, carboxylic acids, and amides.

(a) **Reaction With hydrogen cyanide (HCN) :** HCN adds to aldehydes and ketones to form cyanohydrins. This reaction increases the number of carbon atoms in the reactant by one. In the first step of the reaction, the cyanide ion attacks the carbonyl carbon. The oxyanion then accepts a proton from an undissociated molecule of hydrogen cyanide.

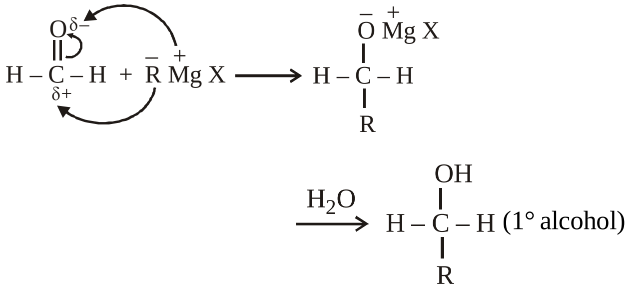


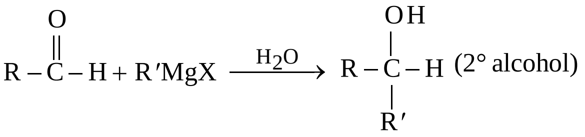
Cyanohydrin

Note :

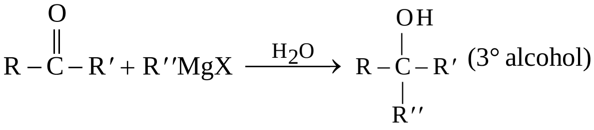
- * Reaction takes place in presence of mild base which abstract H^+ from HCN and produce CN^- ion which acts as nucleophile.
- * If R = H then product will be formaldehyde cyanohydrin.

(b) Reaction with Grignard reagent :





$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H+R'MgX\xrightarrow{H_2O}R-\overset{OH}{\underset{R'}{C}}-H\ \text{(2° alcohol)}$$

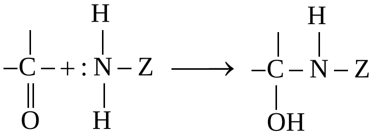


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'+R''MgX\xrightarrow{H_2O}R-\overset{OH}{\underset{R''}{C}}-R'\ \text{(3° alcohol)}$$

Formaldehyde yields primary alochols, higher aldehydes produce secondary alcohols, and ketones produce tertiary alcohols with Grignard reagents.

(c) Reaction with ammonia derivatives :

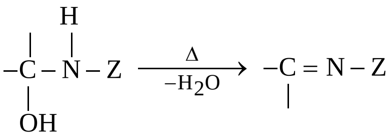
Addition of nitrogenous nucleophile on carbonyl group takes place according to the following mechanism :



$$-\underset{\underset{\displaystyle O}{\|}}{C}-+:\overset{H}{\underset{H}{N}}-Z\longrightarrow-\underset{OH}{C}-\overset{H}{N}-Z$$

Adduct

The end product is formed by elimination of water from the adduct under appropriate energy condition.



$$-\underset{OH}{C}-\overset{H}{N}-Z\xrightarrow[-H_2O]{\Delta}-C=N-Z$$

In the above two steps, it appears that an unsaturated condensation product is formed by liberation of the water molecule from carbonyl group and nitrogenous nucleophile.

$$-C=O+H_2N-Z\xrightarrow[-H_2O]{\Delta}-C=N-Z$$

(i) With hydroxylamine :

$$>C=O+H_2NOH\xrightarrow[-H_2O]{\Delta}>C=NOH$$

Oxime

(ii) With hydrazine :

$$>C=O+H_2NNH_2\xrightarrow[-H_2O]{\Delta}>C=NNH_2$$

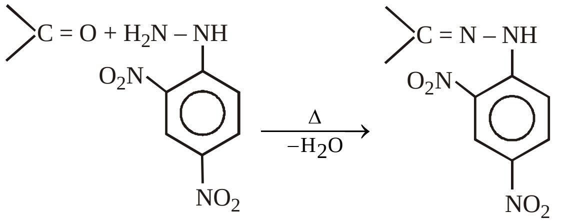
Hydrazone

(iii) With Phenylhydrazine :

$$>C=O+H_2NNHC_6H_5\xrightarrow[-H_2O]{\Delta}>C=NNHC_6H_5$$

Phenylhydrazone

(iv) With 2,4-Dinitrophenylhydrazine :



2,4-Dinitrophyenyhydrazone
yellow ppt

(v) With Semicarbazide :

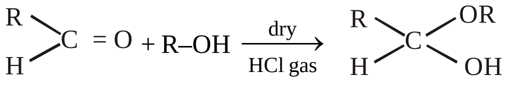
$$>C=O+H_2NNHCONH_2\xrightarrow[-H_2O]{\Delta}>C=NNHCONH_2$$

Semicarbazone

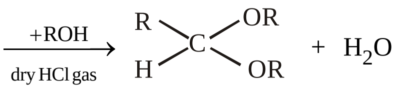
On reacting a carbonyl compound with 2,4-dinitropnenyl hydrazine, a yellow precipitate of 2-4-dinitrophenylhydrazone derivatives is obtained. White precipitate is obtained by the reaction with hydroxylamine, hydrazine phenylhydrazine and semicarbazide. The pure parent carbonyl compound can be obtained by hydrolysis of the above five derivatives.

$$>C=N-Z+HOH\longrightarrow>C=O+H_2N\text{–}Z$$

(d) Reaction with alcohol :

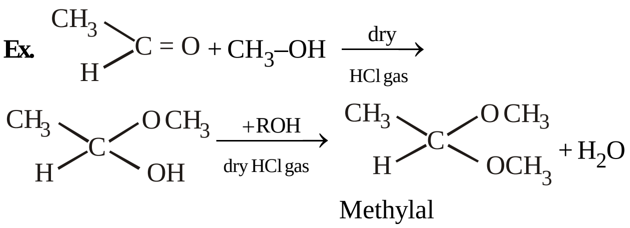


Acetal



Semiacetal

Ex.



$$\begin{matrix}CH_3\\H\end{matrix}\!>\!C=O + CH_3-OH \xrightarrow[\text{HCl gas}]{\text{dry}}$$

$$\begin{matrix}CH_3\\H\end{matrix}\!>\!C\!<\!\begin{matrix}OCH_3\\OH\end{matrix} \xrightarrow[\text{dry HCl gas}]{+ROH} \begin{matrix}CH_3\\H\end{matrix}\!>\!C\!<\!\begin{matrix}OCH_3\\OCH_3\end{matrix} + H_2O$$

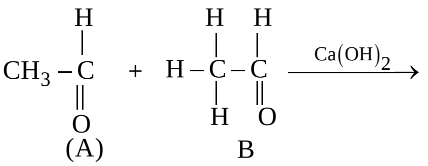
Methylal

Note :

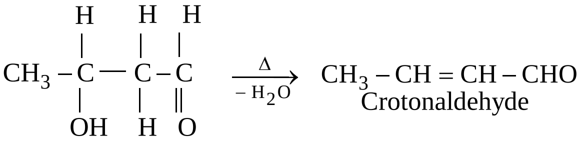
(i) Ketones don't react with alcohols. They form cyclic acetal when reacted with glycol.

(ii) Acetal can be decomposed by dilute mineral acids to give back the original aldehyde.

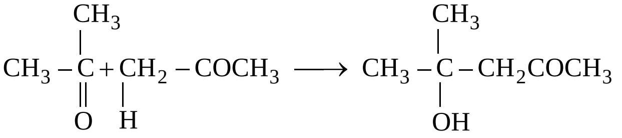
(e) Aldol Condensation : Addition of an α hydrogen atom of a carbonyl compound to the carbonyl group of another carbonyl compound forming a β-hydroxyaldehyde or a β-hydroxyketone is termed as aldol condensation. Carbonyl compound containing at least one α-hydrogen atom undergo aldol condensation in the presence of a weak base like $Ba(OH)_2$, $Ca(OH)_2$, K_2CO_3, Na_2CO_3, etc.



$$\underset{(A)}{CH_3-\overset{H}{\underset{\underset{O}{\|}}{C}}} + \underset{B}{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\underset{O}{\|}}{C}}} \xrightarrow{Ca(OH)_2}$$

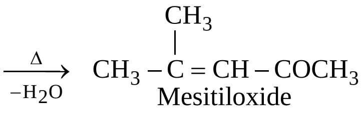


$$CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\underset{O}{\|}}{C}} \xrightarrow[-H_2O]{\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO}$$



$$CH_3-\overset{CH_3}{\underset{\underset{O}{\|}}{C}}+\underset{H}{CH_2}-COCH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2COCH_3$$

2,6-Dimethyl-2,5-heptadiene-4-on (foron)



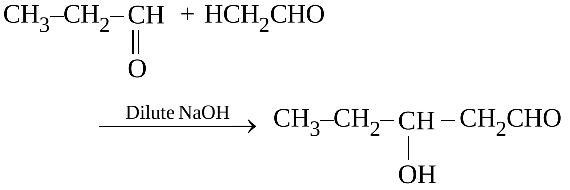
$$\xrightarrow[-H_2O]{\Delta} CH_3-\overset{CH_3}{C}=CH-COCH_3$$

Mesitiloxide

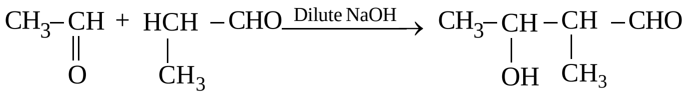
Simple aldol condensation :

When both carbonyl compounds are similar.

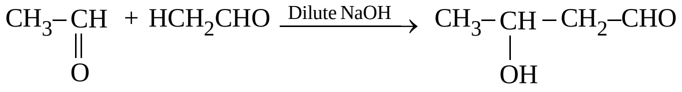
Mixed aldol condensation : When two different aldehydes are used (which have α-Hydrogen atom), a mixture of four aldols is obtained. For example, a mixture of CH_3CHO and CH_3CH_2CHO gives the following aldols. The reaction is then known as mixed aldol condensation.



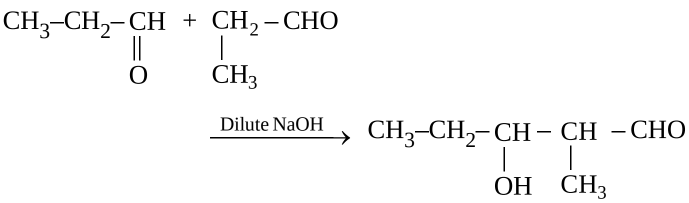
$$CH_3-CH_2-\underset{\underset{O}{\|}}{CH} + HCH_2CHO \xrightarrow{\text{Dilute NaOH}} CH_3-CH_2-\underset{OH}{CH}-CH_2CHO$$



$$CH_3-\underset{\underset{O}{\|}}{CH} + H\underset{CH_3}{CH}-CHO \xrightarrow{\text{Dilute NaOH}} CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO$$



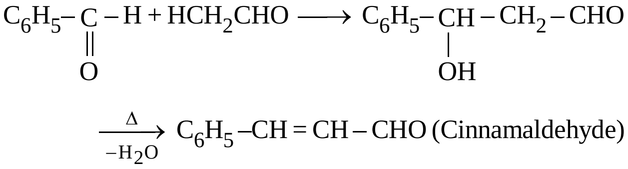
$$CH_3-\underset{\underset{O}{\|}}{CH} + HCH_2CHO \xrightarrow{\text{Dilute NaOH}} CH_3-\underset{OH}{CH}-CH_2-CHO$$



$$CH_3-CH_2-\underset{\underset{O}{\|}}{CH} + \underset{CH_3}{CH_2}-CHO$$

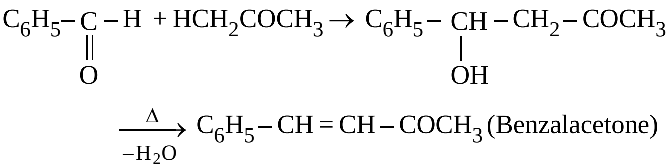
$$\xrightarrow{\text{Dilute NaOH}} CH_3-CH_2-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO$$

Cross aldol condensation : When two different aldehydes are used, (one aldehyde have α-hydrogen but other aldehyde does not have α-hydrogen) gives crossed aldol condensation.



$$C_6H_5-\underset{\underset{O}{\|}}{C}-H + HCH_2CHO \longrightarrow C_6H_5-\underset{OH}{CH}-CH_2-CHO$$

$$\xrightarrow[-H_2O]{\Delta} C_6H_5-CH=CH-CHO \text{ (Cinnamaldehyde)}$$



$$C_6H_5-\underset{\underset{O}{\|}}{C}-H + HCH_2COCH_3 \rightarrow C_6H_5-\underset{OH}{CH}-CH_2-COCH_3$$

$$\xrightarrow[-H_2O]{\Delta} C_6H_5-CH=CH-COCH_3 \text{ (Benzalacetone)}$$

(f) Halogenation, Oxidation, Reduction reactions :

Halogenation :

(i) With halogen : Carbonyl compounds containing α–hydrogen atom undergo halogenation in presence of an acid or base

$CH_3-CO-CH_3 + Cl_2 \xrightarrow{CH_3COOH} ClCH_2-CO-CH_3 + HCl$

$CH_3-CHO + Cl_2 \xrightarrow{SbCl_3} CCl_3CHO + 3HCl$

$CH_3-CHO + Cl_2 \xrightarrow{\text{Strong Base}} CHCl_3$

$CH_3-CO-CH_3 + Cl_2 \xrightarrow{h\nu} CCl_3COCCl_3 + 6HCl$

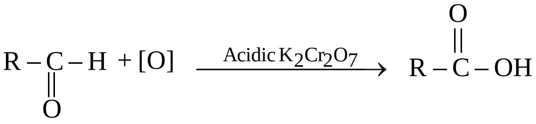
(ii) With Phosphorus pentachloride :

$C_6H_5CHO + PCl_5 \longrightarrow C_6H_5CHCl_2 + POCl_3$

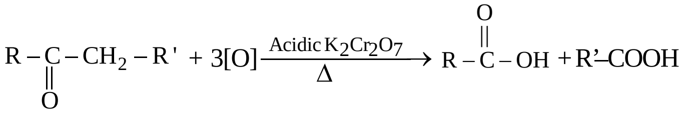
Oxidation :

Aldehyde : Get easily oxidised and give acid of same carbon atom

Ketone : Oxidisation is difficult and give mixture of acids, having lesser number of carbon atoms than the ketone.



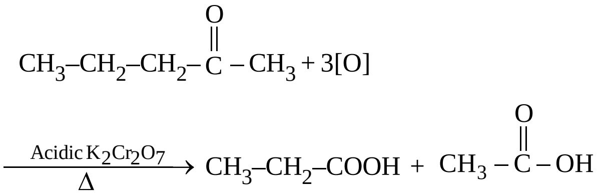
$$R-\underset{\underset{O}{\|}}{C}-H + [O] \xrightarrow{\text{Acidic } K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-OH$$



$$R-\underset{\underset{O}{\|}}{C}-CH_2-R' + 3[O] \xrightarrow[\Delta]{\text{Acidic } K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-OH + R'-COOH$$

$$C_6H_5CHO \xrightarrow{\text{alk.}KMnO_4} C_6H_5COOH \text{ (Benzoic acid)}$$

In case of mixed ketone, the carbonyl group (>C=O) remains with the smaller alkyl group during oxidation. This is known as **"Popott's Rule".**

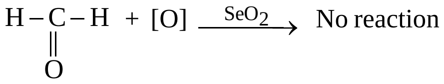


$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + 3[O]$$

$$\xrightarrow[\Delta]{\text{Acidic } K_2Cr_2O_7} CH_3-CH_2-COOH + CH_3-\overset{\overset{O}{\|}}{C}-OH$$

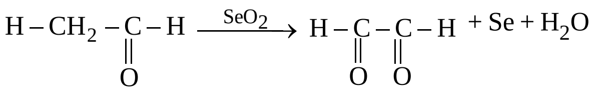
Note :

(i) If oxidant is SeO_2, the α-CH_2 (Methylene) group gets converted to >C=O group at room temperature.



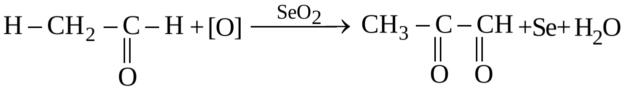
$$H-\underset{\underset{O}{\|}}{C}-H + [O] \xrightarrow{SeO_2} \text{No reaction}$$

(α-CH_2 group is absent)



$$H-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow{SeO_2} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H + Se + H_2O$$

Glyoxal



$$H-CH_2-\underset{\underset{O}{\|}}{C}-H + [O] \xrightarrow{SeO_2} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{CH} + Se + H_2O$$

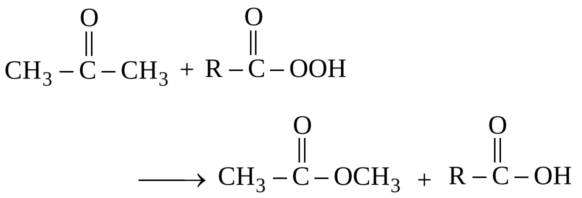
Methylglyoxal

(ii) If oxidant is peracid then

Aldehydes ⟶ Acid

Ketones ⟶ Acid + Ester

The reaction is called Baeyer–Villiger reaction



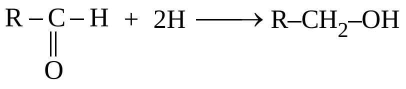
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + R-\overset{\overset{O}{\|}}{C}-OOH$$

$$\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + R-\overset{\overset{O}{\|}}{C}-OH$$

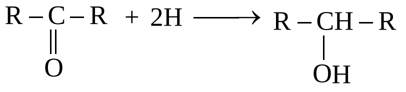
Reduction :

Aldehyde ⟶ Primary alcohol

Ketone ⟶ Secondary alcohol



$$R-\underset{\underset{O}{\|}}{C}-H + 2H \longrightarrow R-CH_2-OH$$



$$R-\underset{\underset{O}{\|}}{C}-R + 2H \longrightarrow R-\underset{\underset{OH}{|}}{CH}-R$$

Note :

(i) Reduction with amalgamated Zinc and conc. HCl gives alkane **(Clemmensen's reaction)**

(ii) With Red P + HI it gives alkane.

(iii) With $LiAlH_4$ or NaH it gives alcohol **(Darzen's Reduction)**

(iv) With $[(CH_3)_2CH-O]_3Al$ gives alcohol **[Merwin-Ponndorf-Verley reduction]**

(v) With basic solution of hydrazine gives alkane **[Wolf-Kishner reduction]**

(vi) With basic solution of ethylene glycol gives alkane in excess **[Huang–Minlon reduction]**

$$C_6H_5CHO + 2H \xrightarrow[Na-Hg/HCl]{Zn+HCl} C_6H_5CH_2OH$$

Benzylalcohol

Pyrolysis, Polymerisation :

Pyrolysis : $HCHO \xrightarrow{\Delta\ (\geq 600°C)} H_2 + CO$ [Water gas]

$$CH_3CHO \xrightarrow{\Delta\ (\geq 600°C)} CH_4 + CO$$

$$CH_3-CO-CH_3 \xrightarrow[(\geq 600°C)]{\Delta} CH_4 + CH_2=C=O \text{ (Ketene)}$$

Polymerisation : Types of polymerisation

(A) Addition polymerisation

(B) Condensation Polymerisation

Aldehydes show addition and condensation polymerization while ketones show only condensation polymerization.

(A) Addition Polymerisation reaction of Formaldehyde

(a) Formalin (aqueous solution of formaldehyde) gives white crystalline solid paraformaldehyde on evaporation.

$$nHCHO \xrightarrow{\text{Evaporation}} [-CH_2-O-]_n \ (n = 6 \text{ to } 100)$$

On depolymerisation of paraformaldehyde, its monomer HCHO gas is liberated out.

$$[-CH_2-O]_n \xrightarrow[\text{Dil. Base}]{\Delta} nHCHO\uparrow$$

(b) A cyclic trimer metaformaldehyde is formed by trimerisation on leaving formaldehyde at room temperature with concentrated H_2SO_4. Trioxane is anhydrous form of formaldehyde.

(c) When formalin is treated with a mild alkali such as slaked lime $[Ca(OH)_2]$ or barita water $[Ba(OH)_2]$ and allowed to stand for a few days, a mixture of sugars (hexoses) is formed. This mixture is called formos or α–acrose. Formation of hexose is an example of hexamerisation.

$$6HCHO \xrightarrow{Ca(OH)_2} (HCHO)_6 \text{ or } C_6H_{12}O_6$$

Formose

(B) Condensation polymerisation reactions of Formaldehyde :

(a) **With ammonia :** Formaldehyde forms white crystalline compound, hexamethylene tetramine or urotropine, or aminoform or hexamine

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

(b) **With Phenol :** Formaldehyde condenses with phenol in presence of a catalyst to form bakelite

Addition polymerisation reactions of Acetaldehyde :

(a) On adding a few drops of conc. H_2SO_4 to acetaldehyde and leaving it at room temp^r, a cyclic trimer called paraldehyde is formed.

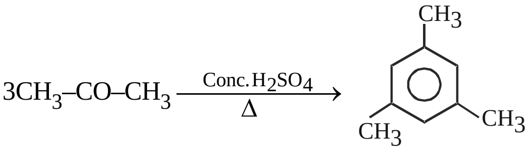
$$3CH_3CHO \xrightarrow[H_2SO_4]{conc.} \underset{\text{Paraldehyde}}{(CH_3CHO)_3}$$

Paraldehyde is used as mild hypnotic.

(b) Addition tetramerisation of acetaldehyde takes place at 0° C in the presence of concentrated H_2SO_4 or at –20°C with dry HCl gas metaldehyde is formed. Metaldehyde regenerates acetaldehyde when distilled with dil. H_2SO_4. It is used as a solid fuel

Polymerisation reaction of Acetone (Only condensation) :

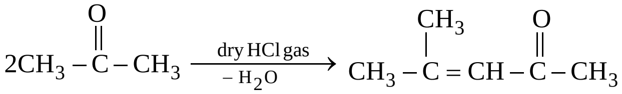
(a) On heating with conc. H_2SO_4, mesitylene is formed



(Mesitylene)

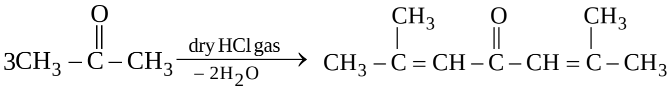
Note : It is an important reaction in which conversion of non aromatic compound into an aromatic compound takes place, it is called aromatization.

(b) In presence of dry HCl gas, two molecule of acetone give mesityl oxide while it's three molecule give phorone.



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{\text{dry HCl gas}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(Mesityloxide)



$$3CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[-2H_2O]{\text{dry HCl gas}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3$$

REACTIONS OF ALDEHYDE ONLY

Reducing properties : Aldehydes readily undergo oxidation, therefore they are strong reducing agents. They reduce Fehling's solution, Benedict's solution, Tollen's reagent and mercuric chloride solution.

With Fehling's solution :

Fehling solution is a mixture of two solutions.

(a) Fehling solution A → Aqueous solution $CuSO_4$ (Blue)

(b) Fehling solution B → Alkaline solution of sodium potassium tartarate[$C_4H_4O_6NaK$]

(Rochelle's salt) → (Colour less)

Fehling solution A + Fehling solution B = A dark blue solution

$$R-CHO + \underbrace{Cu^{2+}+OH^-}_{\text{From Fehling's soution}} \longrightarrow RCOOH + Cu_2O\downarrow \text{ (Red ppt.)}$$

Note : Reacting species of Fehling solution is CuO. In this reaction Cu^{+2} changes to Cu^+ Benzaldehyde does not reduces Fehling's solutions

With Benedict's solution :

Bendict solution ⇒ $CuSO_4 + Na_2CO_3$ + Sodiumcitrate

$R–CHO + Cu^{+2} + OH^- \rightarrow RCOOH + Cu_2O\downarrow$

(Red PPt.)

With Tollen's Reagent : Tollen's reagent is a solution of ammoniacal silver nitrate ($AgNO_3 + NH_4OH$)

$AgNO_3 + NH_4OH \rightarrow AgOH + NH_4NO_3$

$2AgOH \rightarrow Ag_2O + H_2O$

$R-CHO + Ag_2O \rightarrow RCOOH + 2Ag\downarrow$ (Silver mirror)

$$R-CHO + 2Ag^+(NH_3)_2 + 3OH \rightarrow RCOOH + 4NH_3 + 2H_2O + 2Ag$$

Note :

(i) Reacting species of Tollen's reagent is $Ag^+(NH_3)_2$

(ii) In this reaction Ag^+ changes to Ag

With mercuric chloride solution :

$$\text{Mercuric chloride} \xrightarrow{\text{Aldehyde}} \underset{\text{(White ppt.)}}{\text{Mercurous chloride}}$$

$$\xrightarrow{\text{Aldehyde}} \text{Mercury}\downarrow \text{(Grey or Black ppt.)}$$

$R–CHO+2HgCl_2 + H_2O \rightarrow R–COOH + 2HCl + Hg_2Cl_2\downarrow$

(White ppt.)

$R–CHO + 2Hg_2Cl_2 + H_2O \rightarrow R–COOH + 2HCl + Hg\downarrow$

(Black or grey ppt.)

With Schiff's reagent :

Schiff's reagent is a solution of the magneta dye (rosaniline hydrochloride or fuchsine) decolourised by passing SO_2.

Cold dilute Schiff's reagent (colour less) + Aldehyde

→ Pink coloured solution

Cannizzaro's reaction :

Those aldehydes, which do not contain α–hydrogen atoms give this reaction with conc. alkali like conc. NaOH or KOH. In this reaction two molecule of aldehyde react in such a way that one molecule gets oxidised and the other gets reduced. This type of reaction is called disproportionation reaction.

* Aldehydes not containing α–hydrogen are :

HCHO, C_6H_5CHO, CCl_3CHO, $(CH_3)_3C–CHO$, etc.

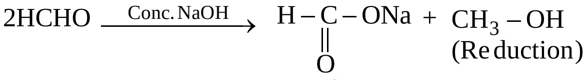
* When two molecules in a reaction are same it is called simple Cannizzaro reaction. In case of different molecules it is a mixed Cannizzaro reaction.

* In mixed Cannizzaro reaction

More reactive aldehyde ⟶ Gets oxidised

Less reactive aldehyde ⟶ Gets reduced

* In this reaction transfer of hydride ion (H^-) takes place

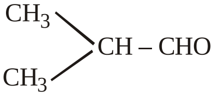


$$2HCHO \xrightarrow{\text{Conc. NaOH}} \underset{\text{(Oxidation)}}{H-\underset{\underset{\displaystyle O}{\|}}{C}-ONa} + \underset{\text{(Reduction)}}{CH_3-OH}$$

$$2C_6H_5-CHO + NaOH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2–OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

$$HCHO + C_6H_5CHO \xrightarrow{\text{Conc. NaOH}} \underset{\text{(Oxidation)}}{HCOONa} + \underset{\text{(Reduction)}}{C_6H_5CH_2OH}$$

NOTE

(i)  gives cannizaro reactions although it has one α-H.

(ii) CCl_3-CHO does not give cannizaro reaction while it has no α-H. It gives haloform reaction.

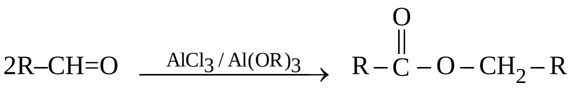
(iii) Cannizaro reaction is an example of disproportionation reaction and it is also an example of redox reaction.

Cross Cannizaro reaction : If two different aldehydes (α-hydrogen less) are used then one of the aldehyde under goes oxidation while other aldehyde under goes reduction.

$$Ph-CHO + HCHO \xrightarrow{\text{Conc. NaOH}/\Delta} H-COO^{-}Na^{+} + Ph-CH_2OH$$

Note : α-hydrogen less aldehyde having more electron deficient carbonyl carbon under goes oxidation.

Tischenko reaction :



$$2R-CH=O \xrightarrow{AlCl_3/Al(OR)_3} R-\overset{\overset{O}{\|}}{C}-O-CH_2-R$$

Aldehyde (2 Mole) Ester (One mole)

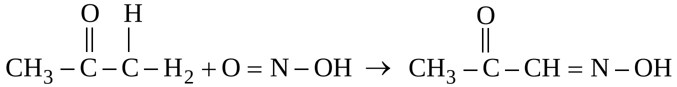
$$2C_6H_5-CHO \xrightarrow{AlCl_3/Al(OR)_3} C_6H_5COOCH_2C_6H_5$$

Benzyl benzoate

Note : The reaction is modified Cannizzaro reaction.

REACTIONS OF KETONES ONLY

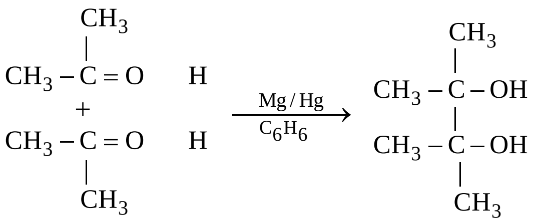
With Nitrous acid :



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}-H_2 + O=N-OH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH=N-OH$$

Oximino acetone

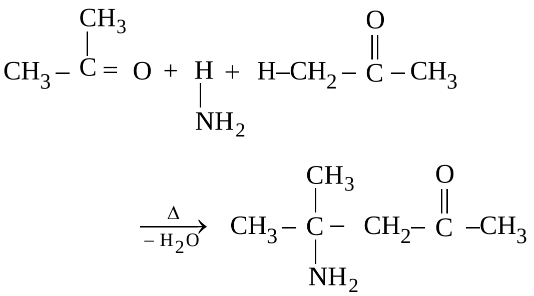
Bimolecular reduction :



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C=O \\ + \\ CH_3-C=O \\ | \\ CH_3 \end{array} \quad \begin{array}{c} H \\ \\ \\ \\ H \end{array} \xrightarrow[C_6H_6]{Mg/Hg} \begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$$

Pinacol

With ammonia :



$$CH_3-\overset{\overset{CH_3}{|}}{C}=O + \underset{\underset{NH_2}{|}}{H} + H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{NH_2}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Diacetoneamine

Note : A cyclic condensation product, triacetone amine is obtained on heating acetone and ammonia for some more time.

TESTS FOR ACETONE

1. No reaction takes place with Schiff's reagent. Tollen's reagent, Fehling's solution, Benedict's solution and mercuric chloride solution (distinction from aldehyde), but reacts with HCN, $NaHSO_3$, NH_2OH, NH_2NH_2, $NH_2NHC_6H_5$ and $NH_2NHCONH_2$ (Similarity with ketone.)

2. **Iodoform Test :** Gives a yellow precipitate of iodoform on heating with iodine and alkali (Similarity with acetaldehyde and all methyl ketone, but distinction from other carbonyl compound).

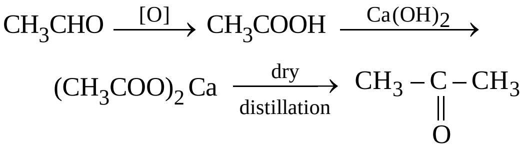
3. **Legal's Test :** When sodium nitroprusside is added to acetone and basified with dilute NaOH, a red-violet colour is obtained. This test is also given by other methyl ketone.

DISTINCTION OF FORMALDEHYDE AND ACETALDEHYDE :

1. **Odour :** Formaldehyde has a characteristic pungent odour, but the pungent odour of acetaldehyde is not characteristic.
2. **Iodoform test :** Acetaldehyde gives iodoform test, but formaldehyde does not.
3. **Fehling's solution :** Acetaldehyde gives red precipitate of Cu_2O, whereas formaldehyde gives red-brown precipitate of Cu.
4. **Benedict's solution :** Acetaldehyde gives red precipitate of Cu_2O, whereas formaldehyde gives red-brown precipitate of Cu.

INTERCONVERSIONS

Acetaldehyde to acetone :



$$CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{Ca(OH)_2}$$

$$(CH_3COO)_2Ca \xrightarrow[\text{distillation}]{\text{dry}} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Acetaldehyde to formaldehyde :

$$CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow[CaO]{NaOH} CH_4 \xrightarrow{Cl_2}$$

$$CH_3Cl \xrightarrow{(aq.)KOH} CH_3OH \xrightarrow{[O]} HCHO$$

Formaldehyde to acetaldehyde :

$$HCHO \xrightarrow{+2H} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN}$$

$$CH_3CN \xrightarrow{+4H} CH_3CH_2NH_2$$

$$\xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{O} CH_3-CHO$$

Acetaldehyde to acetone :

$$CH_3CHO \xrightarrow{CH_3MgBr+H_3O^{+}} (CH_3)_2CHOH$$

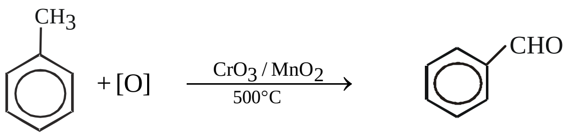
$$\xrightarrow{[O]} (CH_3)_2C=O$$

BENZALDEHYDE

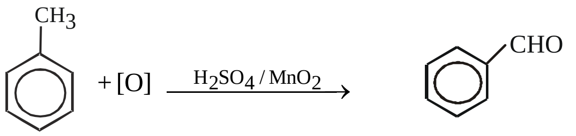
Benzaldehyde is also called "oil of bitter almonds".

Remaining Methods of Preparation :

(a) **By Oxidation of Toluene :**



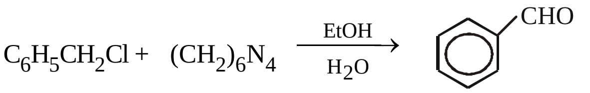
vapour state Benzaldehyde



Liquid state Benzaldehyde

Note : If oxidation is done through alkaline $KMnO_4$ then benzoic acid is formed.

(b) **By Sommelet's reaction :** Benzyl chloride reacts with hexamethylene tetramine (urotropine) in aq. ethanolic solution then benzaldehyde is formed.



Urotropine Benzaldehyde (60–70%)

(c) **By Etard reaction :** This is oxidation of toluene. In this chromyl chloride is used as an oxidant.

$$C_6H_5CH_3 + 2CrO_2Cl_2 \longrightarrow C_6H_5CH_3.2CrO_2Cl_2$$

$$\xrightarrow{H_2O} C_6H_5CHO\ (80\%)$$

(d) **By Gattermann Aldehyde synthesis :**

When benzene reacts with mixture of hydrogen cyanide and hydrogen chloride in the presence of $ZnCl_2$ catalyst intermediate benzaldimine is formed which on hydrolysis gives benzaldehyde.

$$HCl + HCN \xrightarrow{ZnCl_2} ClCH{=}NH$$

$$C_6H_6 + ClCH{=}NH \rightarrow C_6H_5CH{=}NH.HCl$$

$$C_6H_5CH{=}NH.HCl \xrightarrow{\overset{\oplus}{H_3O}} C_6H_5CHO + NH_4Cl$$

(e) **By Gattermann Koch reaction :** When benzene reacts with carbon monoxide and hydrogen chloride mixture, in the presence of anhydrous $AlCl_3$, then benzaldehyde is formed.

$$CO + HCl \longrightarrow HCOCl$$

$$C_6H_6 + HCOCl \xrightarrow[-HCl]{AlCl_3} C_6H_5CHO\ (\text{Benzaldehyde})$$

(f) **With Benzoic acid :**

$$C_6H_5-COOH \xrightarrow[300°C]{HCOOH,\ MnO\ or\ TiO_2} C_6H_5{-}CHO$$

Benzaldehyde

Physical Properties :

(i) It is a colourless liquid with a smell of bitter almonds.
(ii) It is insoluble in water and soluble in organic solvents.
(iii) It's boling point is 179°C.
(iv) It is poisonous in nature.

Chemical Properties :

(i) **Claisen condensation :**

(a) **With acetaldehyde :** $C_6H_5CHO + CH_3CHO$

$$\xrightarrow[-H_2O]{dil.\ NaOH,\Delta} C_6H_5CH=CH-CHO+H_2O$$

Cinnamaldehyde

(b) **With acetone :**

$$C_6H_5CHO + CH_3COCH_3$$

$$\xrightarrow[-H_2O]{dil.\ NaOH} C_6H_5CH=CH-COCH_3$$

Benzylidene acetone

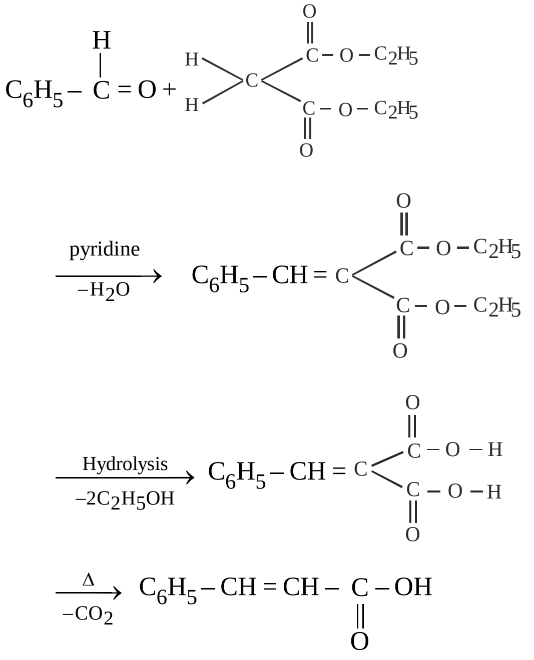
$$2C_6H_5CHO + CH_3COCH_3$$

$$\xrightarrow[-2H_2O]{ethanolic\ NaOH} C_6H_5-CH=CH-CO-CH=CH-C_6H_5$$

(ii) **Perkin reaction :** $C_6H_5CHO + (CH_3CO)_2O$

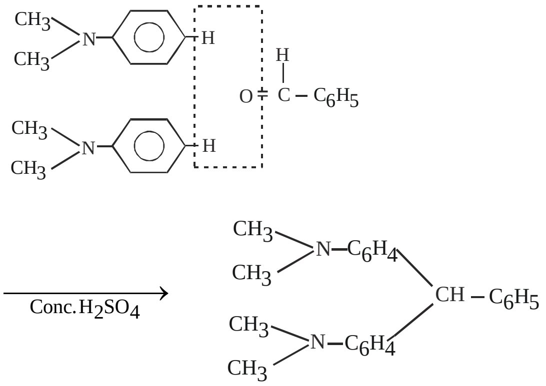
$$\xrightarrow[-CH_3COOH]{CH_3COONa} C_6H_5CH=CHCOOH(\text{Cinnamic acid})$$

(iii) **Knoevenagel reaction :** It is the reaction of benzaldehyde with malonic acid or ester and finally cinnamic acid is formed.



Cinnamic acid

(iv) **Reaction with N, N-dimethyl aniline :**

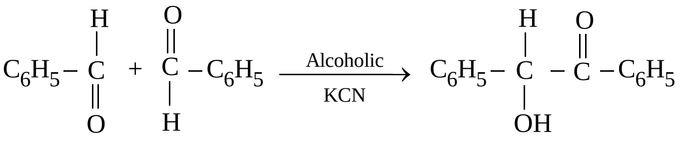


malachite green

(v) Reaction with Nitromethane :

$C_6H_5-CH=O+H_2-CH-NO_2 \rightarrow C_6H_5-CH=CH-NO_2$ Nitrostyrene

(vi) Benzoin condensation :



$$C_6H_5-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + \underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-C_6H_5 \xrightarrow[\text{KCN}]{\text{Alcoholic}} C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

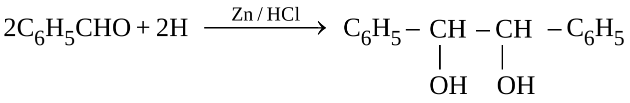
Benzoin

Note%

(a) Due to resonance and m-directing nature of – CHO group, benzaldehyde gives meta products.

(b) Like nitrobenzene, benzaldehyde does not show Friedel Craft reaction.

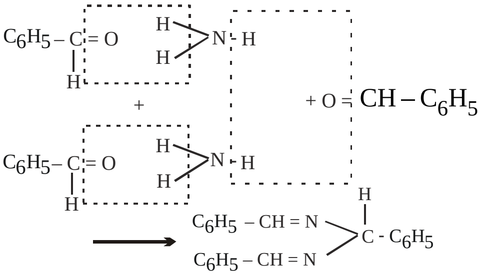
(vii) Bimolecular reduction :



$$2C_6H_5CHO+2H \xrightarrow{Zn/HCl} C_6H_5-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C_6H_5$$

Hydrobenzoin

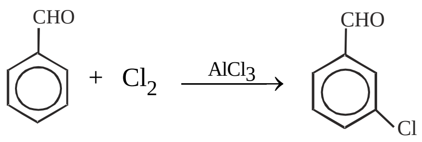
(viii) With ammonia :



Hydrobenzamide (amide without $-CONH_2$ group)

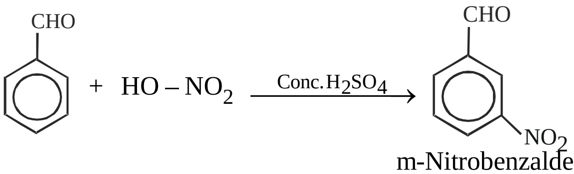
Reactions of benzene ring :

(a) Halogenation :



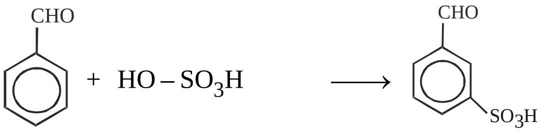
m-Clorobenzaldehyde

(b) Nitration :



m-Nitrobenzaldehyde

(c) Sulphonation :



USES :

(i) As a solvent for oil, resin, cellulose, nitrate etc.

(ii) In manufacturing perfuming agent.

(iii) In preparation of cinnamaldehyde, cinnamic acid, benzoic acid etc.

TRY IT YOURSELF-1

Q.1 Grignard reagents do not give carbonyl compounds with

(A) CO_2 (B) RCOCl

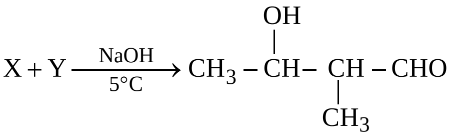
(C) RCN (D) RCOOR

Q.2 Gem dihalide on hydrolysis gives –

(A) Vic diol (B) Gem diol

(C) Carbonyl compound (D) Carboxylic acid

Q.3 In the given reaction :



$$X+Y \xrightarrow[5°C]{NaOH} CH_3-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CHO$$

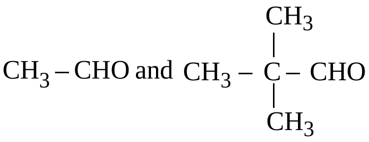
(X) and (Y) will respectively be –

(A) CH_3-CH_2-CHO and CH_3-CH_2-CHO

(B) CH_3-CHO and CH_3-CH_2-CHO

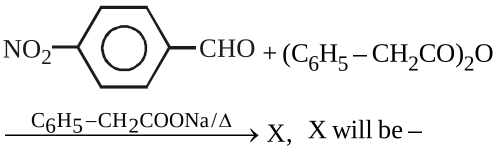
(C) CH_3-CHO and CH_3-CHO

(D)



CH_3-CHO and $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO$

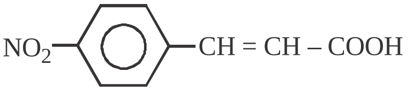
Q.4 The Product of the reaction :



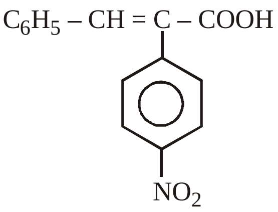
X will be –

(A) $C_6H_5-CH=CH-COOH$

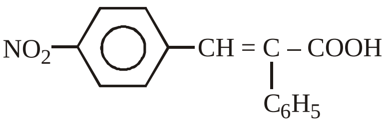
(B)



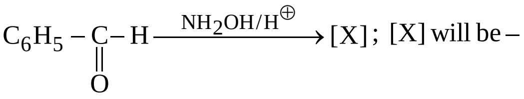
(C)



(D)



Q.5 In the given reaction,



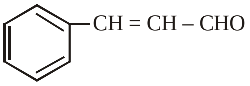
$$C_6H_5-\underset{\underset{O}{\|}}{C}-H \xrightarrow{NH_2OH/H^{\oplus}} [X];$$ [X] will be –

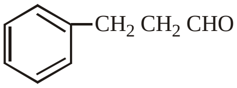
(A) Only syn oxime

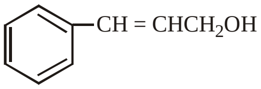
(B) Only anti oxime

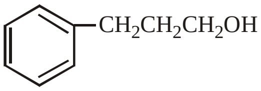
(C) mixture of syn and anti oxime

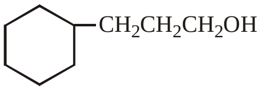
(D) secondary amide

Q.6  $\xrightarrow{LiAlH_4}$ Product is

(A) 

(B) 

(C) 

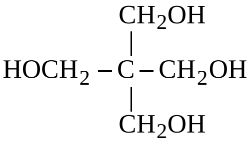
(D) 

Q.7 Cyanohydrin of which compound on hydrolysis will give lactic acid ?

(A) C_6H_5CHO (B) $HCHO$

(C) CH_3CHO (D) CH_3-CH_2-CHO

Q.8 Acetaldehyde can be converted into



$$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$$

by which reagent ?

(A) KOH

(B) KOH followed by LAH

(C) excess of HCHO and KOH

(D) KCN followed by SBH

Q.9 Schiff's base is prepared from –

(A) Carbonyl compound and primary amine

(B) Carbonyl compound and secondary amine

(C) Carbonyl compound and tertiary amine

(D) All of these

Q.10 Which will give silver mirror test with Tollens reagent

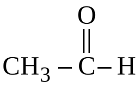
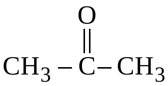
(A) C_6H_5CHO (B) CH_3-CHO

(C) HCOOH (D) All of these

Q.11 Acetaldehyde cannot give –

(A) Iodoform test (B) Lucas test

(C) Benedict test (D) Tollens test

Q.12  $CH_3-\overset{O}{\overset{\|}{C}}-H$ and  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ is differentiated by –

(A) Tollen's reagent (B) Lucas test

(C) Iodoform (D) $NaHSO_3$

Q.13 Acetaldehyde is obtained by ozonolysis of –

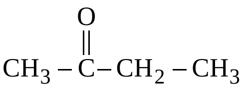
(A) Toluene (B) 1-phenylpropene

(C) o-xylene (D) All of these

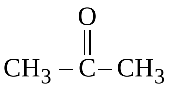
Q.14 $CH_3-COCl \xrightarrow{H_2/Pd-BaSO_4} A \xrightarrow{PCl_5} B$

$\xrightarrow[ether]{Zn} C \xrightarrow{dil.\ H_2SO_4} D \xrightarrow{PCC} D$

(A) CH_3-CHO

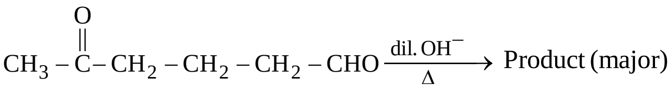
(B)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

(C) $CH_3-CH_2-CH_2-CHO$

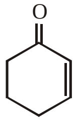
(D)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

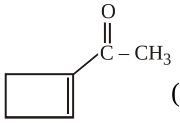
Q.15 When benzaldehyde is treated with propanoic anhydride in presence of sodium propionate, it gives

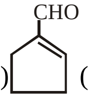
Q.16 In the given reaction,

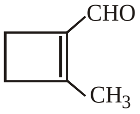


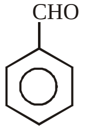
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CHO \xrightarrow[\Delta]{dil.\ OH^-} \text{Product (major)}$$

(A) 

(B) 

(C) 

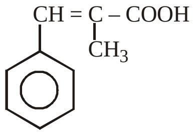
(D) 

Q.17  $\xrightarrow{PCl_5} A \xrightarrow[FeCl_3]{Cl_2} B \xrightarrow{aq.\ KOH} C$

The major product (C) is

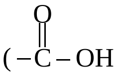
ANSWERS

(1) (A)	**(2)** (C)	**(3)** (B)
(4) (D)	**(5)** (C)	**(6)** (C)
(7) (C)	**(8)** (C)	**(9)** (A)
(10) (D)	**(11)** (B)	**(12)** (A)
(13) (B)	**(14)** (D)	

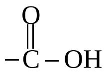
(15)  **(16)** (A) **(17)** 

CARBOXYLIC ACID & THEIR DERIVATIVES

INTRODUCTION

1. Organic compounds containing carboxyl ( $-\overset{O}{\overset{\|}{C}}-OH$) group are known as carboxylic acids and the term 'Carboxylic' was firstly proposed by scientist 'Bayer'.

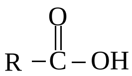
2. Carboxyl group is made up of carbonyl and hydroxyl groups

i.e. $>C=O$ – $O-H$ $\longrightarrow$  $-\overset{O}{\overset{\|}{C}}-OH$

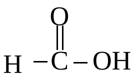
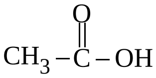
(Carboxyl) (Hydroxyl) (Carboxyl group)

3. **Classification :**

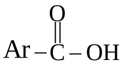
On the basis of the group to which –COOH group is attached.

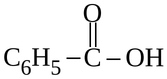
(a) Aliphatic carboxylic acid $\Rightarrow$  $R-\overset{O}{\overset{\|}{C}}-OH$

(R $\Rightarrow$ H atom or alkyl group).

 $H-\overset{O}{\overset{\|}{C}}-OH$,  $CH_3-\overset{O}{\overset{\|}{C}}-OH$

Formic acid, Acetic acid

(b) Aromatic carboxylic acid $\Rightarrow$  $Ar-\overset{O}{\overset{\|}{C}}-OH$ (Ar $\Rightarrow$ Aryl group)

 $C_6H_5-\overset{O}{\overset{\|}{C}}-OH$

Benzoic acid

4. On the basis of number of –COOH groups in their molecule.

	No. of –COOH group
(a) Mono carboxylic acid	1
(b) Dicarboxylic acid	2
(c) Tricarboxylic acid	3

5. General formula is $C_nH_{2n}O_2$ or C_nH_{2n+1} COOH

6. Saturated and unsaturated mono carboxylic acid are also called fatty acid, because higher acid like palmitic acid, steric acid, oleic acid, etc. were obtained by hydrolysis of fat and oil.

7. Hybridisation state of C in the carboxyl group is sp^2

METHODS OF PREPARATION

1. By the oxidation of alcohol, aldehyde and ketone :

(a) 1° Alcohol $\xrightarrow{[O]}$ corresponding carboxylic acid.

$$R-CH_2-OH+[O]\xrightarrow[K_2Cr_2O_7]{KMnO_4\text{ or}} R\text{–}CHO \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$$

Ex. $$CH_3-CH_2-OH+[O]\xrightarrow[K_2Cr_2O_7]{KMnO_4\text{ or}} CH_3\text{–}CHO \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$C_6H_5-CH_2-OH+[O]\xrightarrow[K_2Cr_2O_7]{KMnO_4\text{ or}} C_6H_5\text{–}CHO \xrightarrow{[O]} C_6H_5-\overset{O}{\overset{\|}{C}}-OH$$

(b) Aldehyde $\xrightarrow{[O]}$ corresponding acid

$$R\text{–}CH{=}O+[O]\xrightarrow{\text{Acidic }K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-OH$$

Ex. $$CH_3-CH{=}O+[O]\xrightarrow{\text{Acidic }K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$C_6H_5\text{–}CH{=}O+[O]\xrightarrow{\text{Acidic }K_2Cr_2O_7} C_6H_5-\overset{O}{\overset{\|}{C}}-OH$$

(c) Ketone $\xrightarrow{[O]}$ mixture of acids of lesser number of carbon atoms than the ketone.

$$R-\overset{O}{\overset{\|}{C}}-CH_2-R'+[O]\xrightarrow[\Delta]{\text{Acidic }K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-OH+R'\text{–}COOH$$

Ex. $$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+3[O] \xrightarrow[\Delta]{\text{Acidic }K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH+CO_2+H_2O$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3+3[O]\xrightarrow[\Delta]{\text{Acidic }K_2Cr_2O_7} C_6H_5-\overset{O}{\overset{\|}{C}}-OH+CO_2+H_2O$$

2. By hydrolyses of Cyanide (nitrile) :

Cyanide on complete hydrolysis in presence of dilute HCl forms carboxylic acid.

$$R-C\equiv N\xrightarrow{\text{Complete hydrolysis}} R-\overset{O}{\overset{\|}{C}}-OH+NH_3$$

Ex. $$CH_3-C\equiv N\xrightarrow{\text{Complete hydrolysis}} CH_3-\overset{O}{\overset{\|}{C}}-OH+NH_3$$

$$C_6H_5-C\equiv N\xrightarrow{\text{Complete hydrolysis}} C_6H_5-\overset{O}{\overset{\|}{C}}-OH+NH_3$$

3. From hydrolysis of acid derivatives :

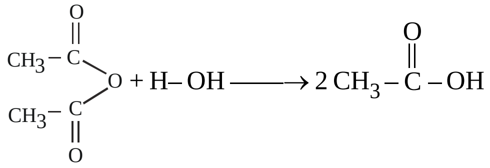
$$Ar/R-\overset{O}{\overset{\|}{C}}-Z+H-OH\longrightarrow Ar/R-\overset{O}{\overset{\|}{C}}-OH+HZ$$

(a) From acyl halides :

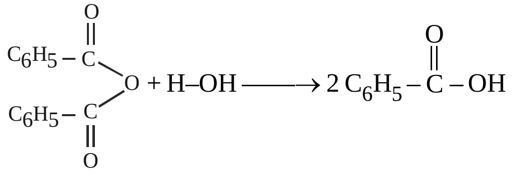
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+H-OH\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH+HCl$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl+H-OH\longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OH+HCl$$

(b) From acid anhydrides :



$$(CH_3-\overset{O}{\overset{\|}{C}})_2O+H-OH\longrightarrow 2\,CH_3-\overset{O}{\overset{\|}{C}}-OH$$



$$(C_6H_5-\overset{O}{\overset{\|}{C}})_2O+H-OH\longrightarrow 2\,C_6H_5-\overset{O}{\overset{\|}{C}}-OH$$

Note : Formic acid cannot be prepared by these two methods (a & b) because it's corresponding formyl chloride and formic anhydride are unstable compounds.

(c) From carboxylic esters :

$$C_2H_5-\overset{O}{\overset{\|}{C}}-OCH_3+HOH\longrightarrow C_2H_5-\overset{O}{\overset{\|}{C}}-OH+CH_3-OH$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-OCH_3+HOH\longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OH+CH_3-OH$$

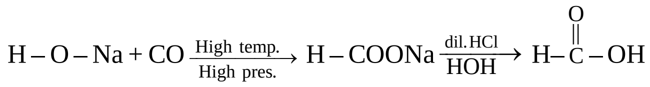
(d) From acid amides :

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2+HOH\xrightarrow{\text{dil. HCl}} CH_3-\overset{O}{\overset{\|}{C}}-OH+NH_4Cl$$

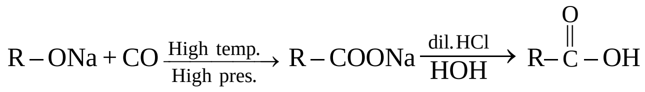
$$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2+HOH\xrightarrow{\text{dil. HCl}} C_6H_5-\overset{O}{\overset{\|}{C}}-OH+NH_4Cl$$

Carbonylation of :

(a) Sodium alkoxide or sodium hydroxide :

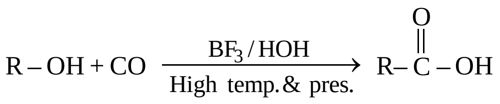


$$H-O-Na + CO \xrightarrow[\text{High pres.}]{\text{High temp.}} H-COONa \xrightarrow[\text{HOH}]{\text{dil.HCl}} H-\overset{\overset{\large O}{||}}{C}-OH$$

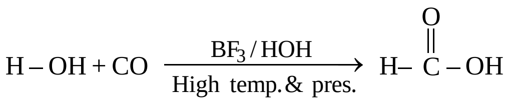


$$R-ONa + CO \xrightarrow[\text{High pres.}]{\text{High temp.}} R-COONa \xrightarrow[\text{HOH}]{\text{dil.HCl}} R-\overset{\overset{\large O}{||}}{C}-OH$$

(b) From Alcohol :



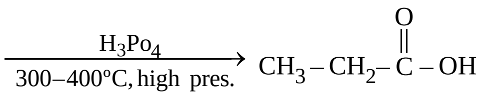
$$R-OH + CO \xrightarrow[\text{High temp.\& pres.}]{BF_3/HOH} R-\overset{\overset{\large O}{||}}{C}-OH$$



$$H-OH + CO \xrightarrow[\text{High temp.\& pres.}]{BF_3/HOH} H-\overset{\overset{\large O}{||}}{C}-OH$$

(c) Alkene (Koch Reaction) :

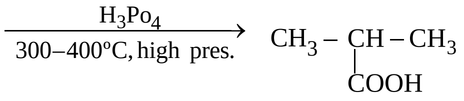
$CH_2 = CH_2 + CO + H_2O$



$$\xrightarrow[300-400^\circ C,\text{ high pres.}]{H_3Po_4} CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-OH$$

Propanoic acid

$CH_3-CH=CH_3 + CO + H_2O$

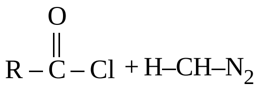


$$\xrightarrow[300-400^\circ C,\text{ high pres.}]{H_3Po_4} CH_3-\underset{\underset{COOH}{|}}{CH}-CH_3$$

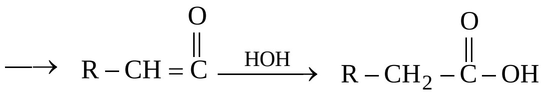
2-Methylpropanoic acid

Note : Formic acid and acetic acid can not be prepared by this method.

Arndt - Eistert reaction :



$$R-\overset{\overset{\large O}{||}}{C}-Cl + H-CH-N_2$$



$$\longrightarrow R-CH=\overset{\overset{\large O}{||}}{C} \xrightarrow{HOH} R-CH_2-\overset{\overset{\large O}{||}}{C}-OH$$

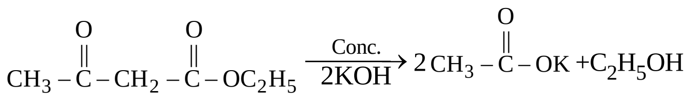
(Acyl diazomethane) (Ketene)

Note :

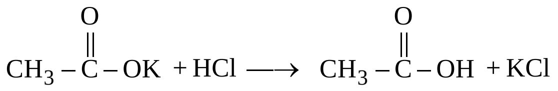
(i) The method can be used to ascend a homologous series.

(ii) The method can be used only for synthesis of carboxylic acids having three or more carbon atoms. HCOOH or CH_3COOH are not prepared by this reaction.

From acetoacetic ester :



$$CH_3-\overset{\overset{\large O}{||}}{C}-CH_2-\overset{\overset{\large O}{||}}{C}-OC_2H_5 \xrightarrow[\text{2KOH}]{\text{Conc.}} 2\,CH_3-\overset{\overset{\large O}{||}}{C}-OK + C_2H_5OH$$



$$CH_3-\overset{\overset{\large O}{||}}{C}-OK + HCl \longrightarrow CH_3-\overset{\overset{\large O}{||}}{C}-OH + KCl$$

PHYSICAL PROPERTIES

1. Physical State :

C_1 to C_3 = Colourless pungent smelling liquids

C_4 to C_9 = Oily liquids having goat's butter like smell.

$C_{10}+$ = Colourless & odourless waxy solids.

2. Solubility : Upto C_4 = Highly soluble in water

Solubility $\propto$ (1/Molecular weight)

Solubility of lower members of carboxylic acid family is due to the formation of hydrogen bond between –COOH group and water molecules.

As the alkyl group increases in size in acid, water repelling (hydrophobic) tendency of the hydrocarbon chain increases and it outweighs the effect of hydrogen bonding. This is the reason why solubility decreases in higher members.

3. Boiling point (B.P.) : Boiling point $\propto$ Molecular weight, Boiling point of acid > Boiling point of alcohol.

Because, a carboxylic acid molecule can form hydrogen bonding at two different points. This leads to the formation of cyclic dimers in acid. This is the reason why lower acids occur as dimers in solution.

4. Melting point (M.P.) : Melting point of carboxylic acid do not vary smoothly from one molecule to another

For first ten members

M.P. of C_{2n} > M.P. of C_{2n+1}

$(n = 1, 2, 3, 4, 5)$ $(n = 0, 1, 2, 3, 4)$

Reason : In acids of even number of carbon atoms terminal $-CH_3$ and –COOH groups lie on the opposite sides on the carbon chain. Provides more effective packing of the molecules in the lattice. While in acids of odd number of carbon atoms they lie on the same sides on the carbon chain.

$$\text{Acidic strength} \propto -\text{I effect} \propto \frac{1}{+\text{I effect}}$$

CHEMICAL PROPERTES

Acidity : Carboxylic acids are acidic in nature. These are more acidic than water, alcohols, and phenols, but less acidic than mineral acids, (HCl, HNO_3, H_2SO_4, etc.). In general, the acidic nature of certain organic compounds follows the order.

Alkynes < Alcohols < Water < Phenols < Carboxylic acids < mineral acids

——— Acidic nature/strength increases ————→

When an acid is dissolved in water, it ionises to give ions in accordance with the reaction,

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

At equilibrium, the concentrations of the acid and the ions are related by the expression, $K_a = \dfrac{[RCOO^-][H_3O^+]}{[RCOOH]}$

The equilibrium constant, K_a is called the ionisation constant of the acid. K_a is also commonly called as dissociation constant of the acid. The extent of ionisation, hence the strength of the acid in any solution is thus given by the magnitude of K_a. A large value of K_a means that the reaction is more favourable in the forward direction.

Sometimes a quantity pK_a is also used in describing the strength of an acid. This is given by

$$pK_a = -\log K_a$$

Acid strength decreases as a the size of the alkyl group attached to – COOH group increases.

For example, $HCOOH > CH_3COOH > CH_3CH_2COOH$

Acid strength increases with the electronegativity of the substituent. For example,

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

Acid strength increases with an increase in the number of electron-withdrawing substituent on the carbon next to the – COOH group. For example,

$Cl_3COOH > Cl_2CHCOOH > ClCH_2.COOH > CH_3COOH$

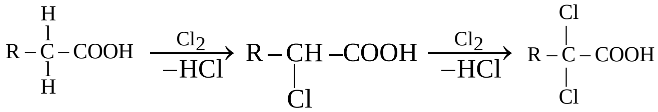
Acid strength decreases with increasing distance of the electron-withdrawing substituent from the – COOH group. For example,

$$CH_3CH_2\underset{Cl}{\underset{|}{CH}}COOH > CH_3\underset{Cl}{\underset{|}{CH}}CH_2COOH > \underset{Cl}{\underset{|}{CH_2}}CH_2CH_2COOH$$

Chemical reactions : Carboxylic acids give the following reactions.

1. Reactions due to alkyl group :

Halogenation : Acids having α–hydrogen atom give this reaction. The α–hydrogen atoms are easily replaced by chlorine or bromine atom, forming halogen derivatives of the acid.



$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-COOH \xrightarrow[-HCl]{Cl_2} R-\underset{\underset{Cl}{|}}{CH}-COOH \xrightarrow[-HCl]{Cl_2} R-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-COOH$$

Note :

(i) Reaction is known as Hell-Volhard-Zelinsky (HVZ) reaction.

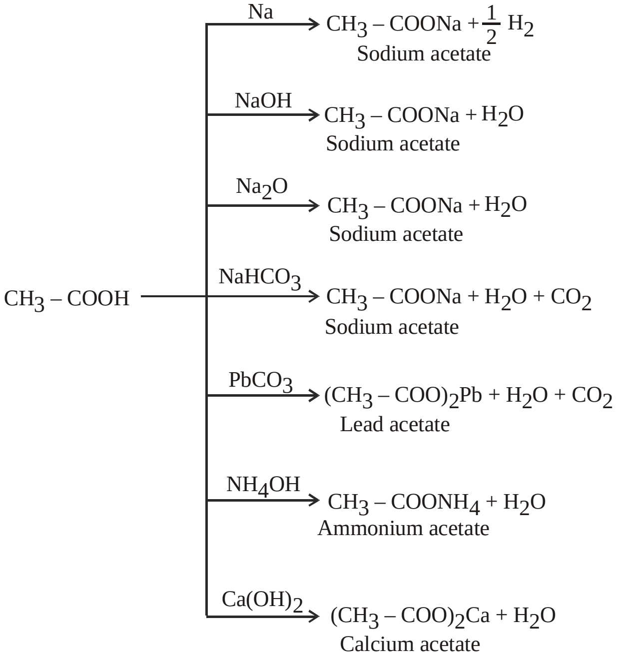
(ii) In presence of phosphorus, monohalo derivative is the main product.

$$R–CH_2–COOH + Br_2 \xrightarrow{P} R–CH(Br)–COOH + HBr.$$

(iii) Formic acid and benzoic acid do not show HVZ reaction due to absence of α –hydrogen atoms.

2. Due to acidic hydrogen :

(a) Salt formation : Carboxylic and Benzoic acids form salt with metals, metal oxides, hydroxides, carbonates, bicarbonates and compounds showing basic nature.



$$CH_3-COOH \xrightarrow{Na} CH_3-COONa + \frac{1}{2}H_2$$
Sodium acetate

$$CH_3-COOH \xrightarrow{NaOH} CH_3-COONa + H_2O$$
Sodium acetate

$$CH_3-COOH \xrightarrow{Na_2O} CH_3-COONa + H_2O$$
Sodium acetate

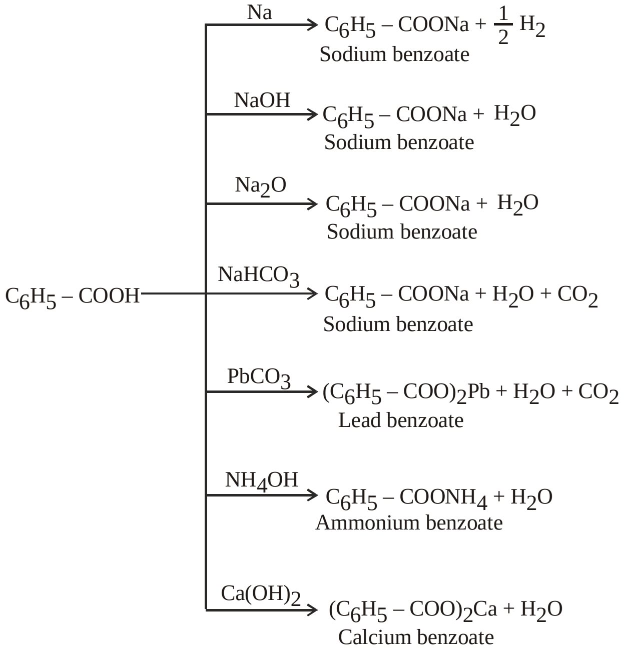
$$CH_3-COOH \xrightarrow{NaHCO_3} CH_3-COONa + H_2O + CO_2$$
Sodium acetate

$$CH_3-COOH \xrightarrow{PbCO_3} (CH_3-COO)_2Pb + H_2O + CO_2$$
Lead acetate

$$CH_3-COOH \xrightarrow{NH_4OH} CH_3-COONH_4 + H_2O$$
Ammonium acetate

$$CH_3-COOH \xrightarrow{Ca(OH)_2} (CH_3-COO)_2Ca + H_2O$$
Calcium acetate

Note : Acids liberate CO_2 with $NaHCO_3$. This reaction is used to distinguish carboxylic acids from phenols which do not react with $NaHCO_3$.



$$C_6H_5-COOH \xrightarrow{Na} C_6H_5-COONa + \frac{1}{2}H_2$$
Sodium benzoate

$$C_6H_5-COOH \xrightarrow{NaOH} C_6H_5-COONa + H_2O$$
Sodium benzoate

$$C_6H_5-COOH \xrightarrow{Na_2O} C_6H_5-COONa + H_2O$$
Sodium benzoate

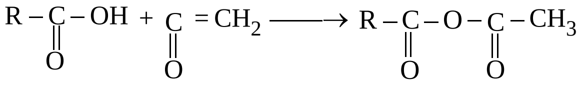
$$C_6H_5-COOH \xrightarrow{NaHCO_3} C_6H_5-COONa + H_2O + CO_2$$
Sodium benzoate

$$C_6H_5-COOH \xrightarrow{PbCO_3} (C_6H_5-COO)_2Pb + H_2O + CO_2$$
Lead benzoate

$$C_6H_5-COOH \xrightarrow{NH_4OH} C_6H_5-COONH_4 + H_2O$$
Ammonium benzoate

$$C_6H_5-COOH \xrightarrow{Ca(OH)_2} (C_6H_5-COO)_2Ca + H_2O$$
Calcium benzoate

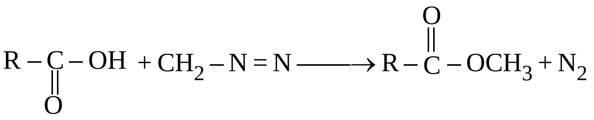
(b) Reaction with ketene :



$$R-\underset{\underset{O}{\|}}{C}-OH + \underset{\underset{O}{\|}}{C}=CH_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3$$

(Anhydride)

(c) Reaction with diazomethane :

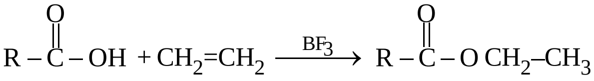


$$R-\underset{\underset{O}{\|}}{C}-OH + CH_2-N=N \longrightarrow R-\overset{\overset{O}{\|}}{C}-OCH_3 + N_2$$

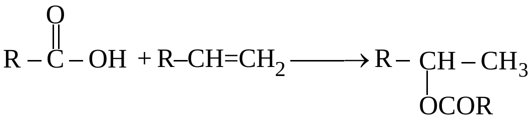
Methyl ester

Note : Diazomethane is a powerful methylating agent. So by using this method methyl ester is prepared.

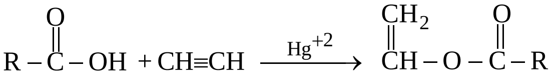
(d) Reaction with alkene and alkyne :



$$R-\overset{\overset{O}{\|}}{C}-OH + CH_2{=}CH_2 \xrightarrow{BF_3} R-\overset{\overset{O}{\|}}{C}-O\,CH_2–CH_3$$



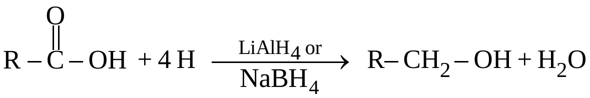
$$R-\overset{\overset{O}{\|}}{C}-OH + R–CH{=}CH_2 \longrightarrow R-\underset{\underset{OCOR}{|}}{CH}-CH_3$$



$$R-\overset{\overset{O}{\|}}{C}-OH + CH{\equiv}CH \xrightarrow{Hg^{+2}} \overset{\overset{CH_2}{\|}}{CH}-O-\overset{\overset{O}{\|}}{C}-R$$

3. Reactions due to (>C=O) group :

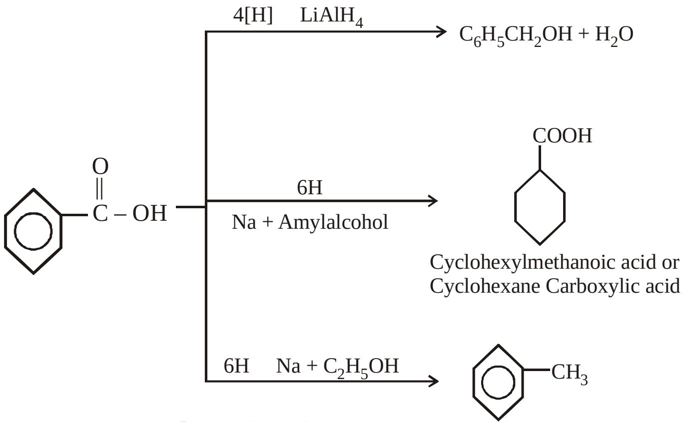
(a)



$$R-\overset{\overset{O}{\|}}{C}-OH + 4\,H \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} R–CH_2-OH + H_2O$$

(b) $$R-\overset{O}{\overset{\|}{C}}-OH + 6HI \xrightarrow[\Delta\,200°C]{Red\,P} R-CH_3 + 2H_2O + 3I_2$$

Ex. $$CH_3-\overset{O}{\overset{\|}{C}}-OH + 4\,H \xrightarrow[NaBH_4]{LiAlH_4\text{ or}} CH_3-CH_2-OH + H_2O$$



Cyclohexylmethanoic acid or Cyclohexane Carboxylic acid

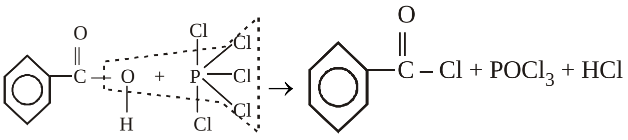
4. Reactions due to (–OH) group :

Reaction with Phosphorus Chloride :

$$3R-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \longrightarrow 3R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + HCl + POCl_3$$

Ex. $$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + POCl_3$$

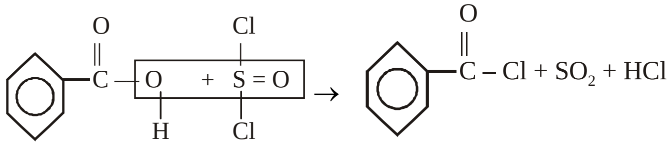


$$3C_6H_5COOH + PCl_3 \longrightarrow 3C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

(d) With Thionylchloride :

$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{Pyridine} R-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2\uparrow$$

Ex. $$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{Pyridine} CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2\uparrow$$



Note : In the reaction SO_2 is gas so escapes out and HCl is an acid, gets absorbed by basic pyridine and pure acyl chloride is left. So it is best method for preparing acyl chloride from acid.

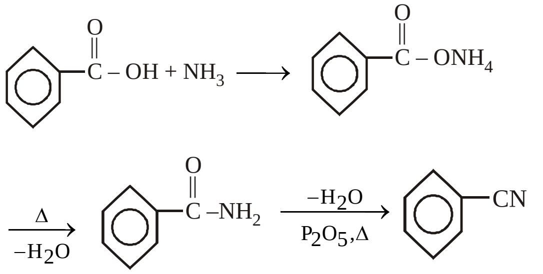
(e) Formation of acidamides and alkanenitrile :

$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-ONH_4$$

$$\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[P_2O_5]{\Delta} R-C\equiv N + H_2O$$

Ex. $$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-ONH_4$$

$$\xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[P_2O_5]{\Delta} CH_3-C\equiv N + H_2O$$



(f) With Hydrazoic acid (Schmidt reaction) :

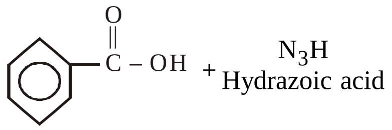
N_3H = Hydrozoic acid

$$R-\overset{O}{\overset{\|}{C}}-OH + HN_3 \xrightarrow{H_2SO_4} R-\overset{O}{\overset{\|}{C}}-N_3 + H_2O$$

$$\longrightarrow R\text{–}NH_2 + CO_2 + N_2$$

The reaction is a modification of "curtius reaction".

Ex. $$CH_3\text{–}COOH + HN_3 \xrightarrow{H_2SO_4} CH_3\text{–}NH_2 + CO_2 + N_2$$



$$\xrightarrow[\Delta]{H_2SO_4} C_6H_5NH_2 + CO_2 + N_2$$

Mechanism :

$$\underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + N_3H \xrightarrow[(-H_2O)]{\Delta}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{-N_2} CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}:$$

$\downarrow$ Rearrangement

$$CH_3-NH_2 \xleftarrow[-CO_2\uparrow]{} CH_3-NH-COOH \xleftarrow{H_2O}$$

Methanamine

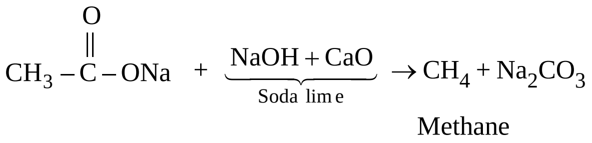
$CH_3-N=C=O$

(Methylisocyanate)

Note : The reaction is useful in stepping down a homologous series.

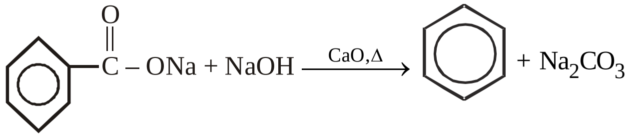
5. Reactions due to (–COOH) group :

(a) Decarboxylation :



$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + \underbrace{NaOH + CaO}_{Soda\ lime} \rightarrow CH_4 + Na_2CO_3$$

Methane



Note : This reaction is useful for stepping down in a homologous series.

(b) Kolbe's electrolytic synthesis :

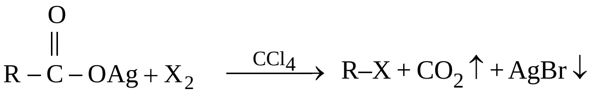
$2RCOOK \Rightarrow 2RCOO^- + 2K^+$

At Anode : $2RCOO^- \longrightarrow R-R + CO_2\uparrow$

At Cathode : $2K^+ + HOH \longrightarrow 2KOH + H_2\uparrow$

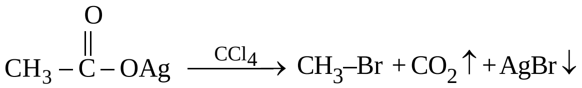
Note : Kolbe synthesis undergoes free radical mechanism.

(c) Hundsdiecker reaction :

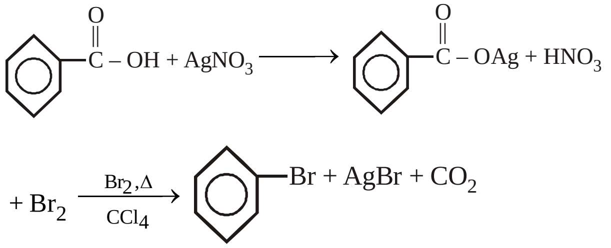


$$R-\overset{\overset{O}{\|}}{C}-OAg + X_2 \xrightarrow{CCl_4} R-X + CO_2\uparrow + AgBr\downarrow$$

$(X = Cl_2 \text{ or } Br_2)$

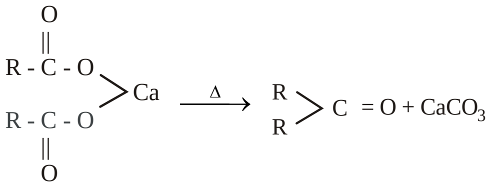
Ex. 

$$CH_3-\overset{\overset{O}{\|}}{C}-OAg \xrightarrow{CCl_4} CH_3-Br + CO_2\uparrow + AgBr\downarrow$$

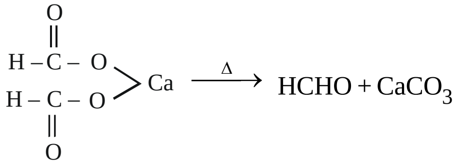


Note : In the reaction decarboxylative halogenation of the acid takes place. The reaction is useful in stepping down a homologous series.

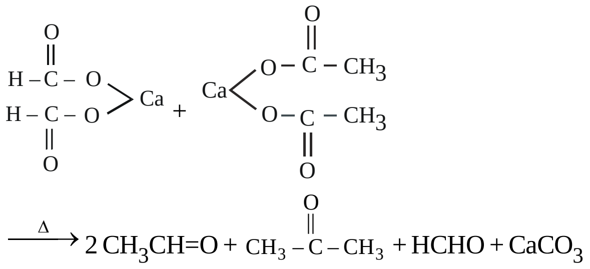
(d) Formation of carbonyl compounds [Dry Distillation of calcium salt] :



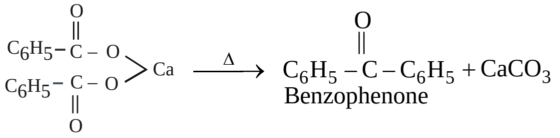
$$\begin{matrix}R-\overset{\overset{O}{\|}}{C}-O\\ R-\underset{\underset{O}{\|}}{C}-O\end{matrix}\!\!>Ca \xrightarrow{\Delta} \begin{matrix}R\\R\end{matrix}\!\!>C=O + CaCO_3$$



$$\begin{matrix}H-\overset{\overset{O}{\|}}{C}-O\\ H-\underset{\underset{O}{\|}}{C}-O\end{matrix}\!\!>Ca \xrightarrow{\Delta} HCHO + CaCO_3$$



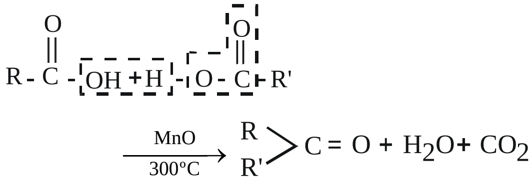
$$\begin{matrix}H-\overset{\overset{O}{\|}}{C}-O\\ H-\underset{\underset{O}{\|}}{C}-O\end{matrix}\!\!>Ca + Ca<\!\!\begin{matrix}O-\overset{\overset{O}{\|}}{C}-CH_3\\ O-\underset{\underset{O}{\|}}{C}-CH_3\end{matrix} \xrightarrow{\Delta} 2\,CH_3CH=O + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + HCHO + CaCO_3$$



$$\begin{matrix}C_6H_5-\overset{\overset{O}{\|}}{C}-O\\ C_6H_5-\underset{\underset{O}{\|}}{C}-O\end{matrix}\!\!>Ca \xrightarrow{\Delta} C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 + CaCO_3$$

Benzophenone

(e) With Manganous oxide :

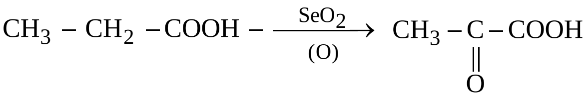


$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH + H}-O-\overset{\overset{O}{\|}}{C}-R' \xrightarrow[300°C]{MnO} \begin{matrix}R\\R'\end{matrix}\!\!>C=O + H_2O + CO_2$$

(Carbonyl compounds)

6. Special reaction of alkanoic acid :

(a) Oxidation : By SeO_2 α keto acid is formed



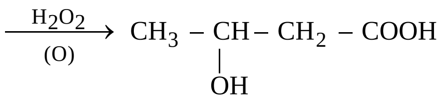
$$CH_3-CH_2-COOH \xrightarrow[(O)]{SeO_2} CH_3-\underset{\underset{O}{\|}}{C}-COOH$$

Pyruvic acid

By H_2O_2 – OH group comes at β – C atom.

$CH_3-CH_2-CH_2-COOH$

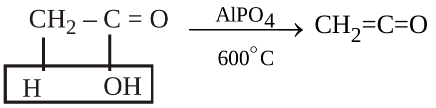
(Butanoic acid)



$$\xrightarrow[(O)]{H_2O_2} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$$

(3-Hydroxy Butanoic acid)

(b) Pyrolysis :

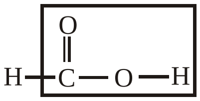


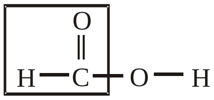
$$\underset{\boxed{H\quad OH}}{CH_2-C=O} \xrightarrow[600^\circ C]{AlPO_4} CH_2=C=O$$

(Ketene)

SPECIAL FEATURES OF FORMIC ACID

(a) Formic acid shows acidic character due to presence of –COOH group as well as shows reducing character due to presence of –CHO group.


– COOH group


– CHO group

(b) It reduces Tollen's reagent and forms silver mirror.

(c) It reduces mercuric chloride and forms black ppt. of mercury.

(d) It decolourises the pink colour of acidic $KMnO_4$

(e) It forms brown ppt. of MnO_2 with basic $KMnO_4$

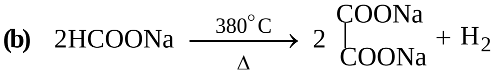
(f) It converts the orange colour of acidic $K_2Cr_2O_7$ into green colour.

(g) It reduces Fehling solution but benzaldehyde cannot reduce Fehling solution.

(h) Dehydration — $HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} H_2O + CO_2$

(i) **Effect of heat :**

(a) $HCOOH \xrightarrow[\Delta]{160^\circ C} CO_2 + H_2$


(b) $2HCOONa \xrightarrow[\Delta]{380^\circ C} 2\begin{matrix}COONa\\|\\COONa\end{matrix} + H_2$

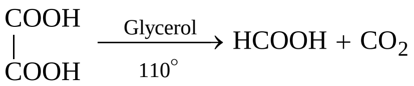
Sodium oxalate

DISTINCTION BETWEEN FORMIC ACID AND ACETIC ACID

S. No.	HCOOH	CH_3COOH
1.	Decomposes on heating to give carbon dioxide and hydrogen.	Stable
2.	With concentrated sulphuric acid gives carbon monoxide and water.	Stable
3.	With halogen, there is not action.	Substituted acid are formed.
4.	Reduces ammonical silver nitrate and Fehling's solution.	No reaction.
5.	Calcium salt on heating gives formaldehyde.	Calcium salt on heating gives acetone.
6.	Sodium salt on heating gives sodium oxalate hydrogen.	No reaction.
7.	Sodium salt + soda lime gives hydrogen on heating.	Methane is produced.
8.	Electrolysis of alkali solution gives hydrogen.	Ethane is obtained.
9.	Decolourises acidified $KMnO_4$ solution.	No reaction.
10.	Dichromate solution turns into green coloured solution.	No reaction.

SPECIAL ABOUT HCOOH

1. **Lab Reaction :**


$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow[110^\circ]{\text{Glycerol}} HCOOH + CO_2$$

Note : Boiling point of HCOOH is 100.5°, for removal of water from formic acid we can use $PbCO_3$ or PbO (Litharze) and H_2S.

$2HCOOH + PbCO_3 \longrightarrow (HCOO)_2Pb + CO_2 + H_2O$

$(HCOO)_2\,Pb + H_2S \xrightarrow{100^\circ C} 2HCOOH + PbS$

(PPT)

2. **Industrial method :** It is prepared on large scale by reaction CO with aqueous sodium hydroxide under pressure 1 atm and 473K.

$$CO + NaOH \xrightarrow[1atm]{473K} HCOONa$$

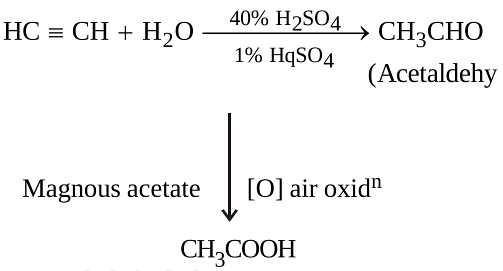
$$\xrightarrow{H_2O} HCOOH + NaOH$$

SPECIAL ABOUT CH_3COOH

1. **Lab reaction :** All general methods can apply.

2. **Industrial methods :**

(a) **From ethyne :**


$$\begin{tikzcd} HC \equiv CH + H_2O \arrow[r, "40\%\ H_2SO_4", "1\%\ HqSO_4"'] & CH_3CHO \arrow[d, "\text{[O] air oxid}^n", "\text{Magnous acetate}"'] \\ & CH_3COOH \end{tikzcd}$$

(Acetaldehy

(b) **From ethyl alcohol**

(i) By dehydrogenation —

$$CH_3CH_2OH \xrightarrow[\substack{300^\circ C\\(-H_2)}]{Cu} CH_3CHO$$

$$\xrightarrow[\text{(Magnous acetate)}]{[O]} CH_3COOH$$

(ii) By fermentation (Quick vinegar process)

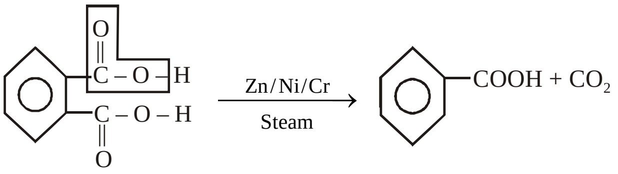
$$CH_3CH_2OH + O_2 \xrightarrow[\text{(Mycoderma acetaii)}]{\text{Acetobector bacteria}} CH_3COOH + H_2O$$

[dilute form 8 – 10% Called VINEGAR]

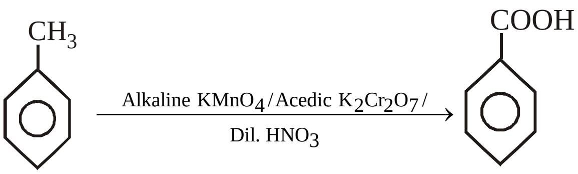
(iii) From $CH_3OH–CH_3OH + CO \xrightarrow[\text{or Rh}]{BF_3} CH_3COOH$

SPECIAL ABOUT C_6H_5COOH :

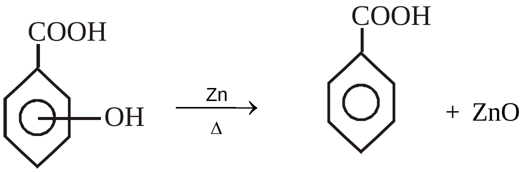
(A) From Phthalic acid (Industrial method) :



(B) By Oxidation of toluene :



(C) From Dehydroxylation of o-,m- or p- Hydroxybenzoic acid :

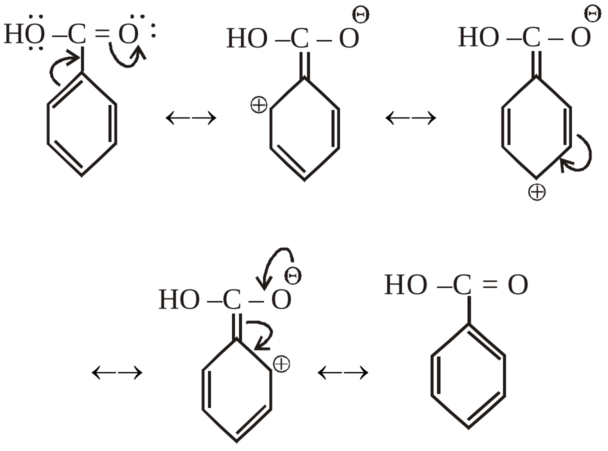


PHYSICAL PROPERTIES :

(i) It is a crystalline solid (M.P. 122°C)

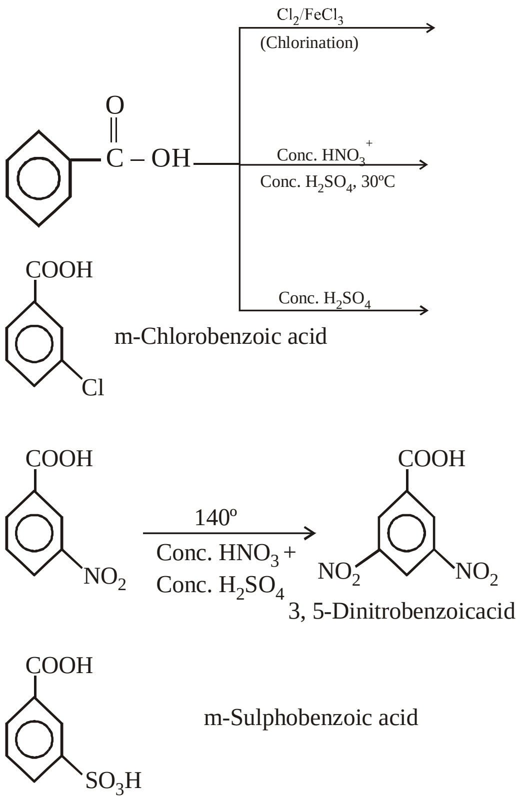
(ii) Sparingly soluble in cold water but rapidly soluble in hot water also,soluble in organic solvents like alcohol,ether, etc.

Resonance in Benzoic Acid :



In Benzoicacid, the carboxyl group shows -m (negative mesomeric) effect.Due to negative mesomeric effect, positive change is produced on the ortho and para positions and therefore attacking electrophile attacks on comparative e^- rich it meta position.

Reactions due to Benzene ring : (meta directing) (Electrophilic substitution reaction)



m-Chlorobenzoic acid

3, 5-Dinitrobenzoicacid

m-Sulphobenzoic acid

Note : It does not give friedel craft reaction because of presence of deactivating m-directing (–COOH) group.

Test : Benzoic acid + Neutral $FeCl_3$ ⟶ Red brown ppt.

USES :

(i) As an antiseptic

(ii) Sodium benzoate as preservation of food products, etc.

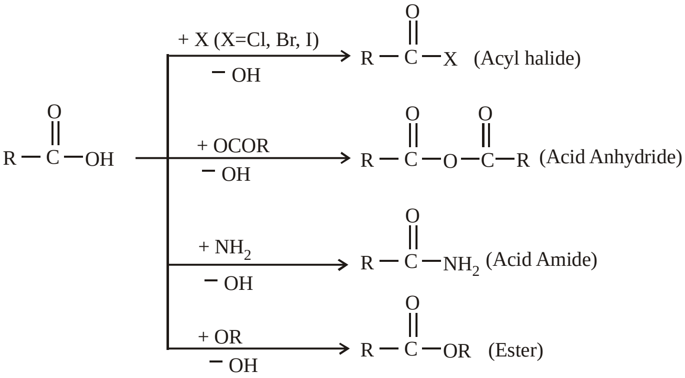
(iii) In manufacturing of many synthetic dyes

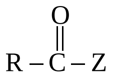
(iv) In the form of ester, benzoic acid is used in perfume industry.

ACID DERIVATIVES

Introduction

1. Replacement of – OH group of the –COOH group in a carboxylic acid by an atom or by any other functional group give rise to certain new families of compounds. These compounds are called acid derivatives.

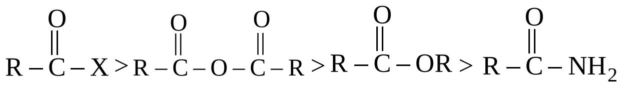


2. Acyl chloride are the most important acid halide. The first member of this family is acetyl chloride because formylchloride (HOCl) is unstable.
3. Similarly Acetic Anhydride is the representative member of acid anhydrides family, because formic anhydride is unstable.
4. The first two members of Acid Amide family are formamide and Acetamide. Acetamide is an important acid amide.
5. Esters have functional group isomerism with acids.
6. 
$R-\overset{\overset{O}{\|}}{C}-Z$ [Where Z = –X, –NH_2, –OCOR, –OR]

Order of basic character of group Z

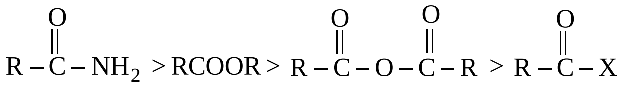
$$X^{\ominus} < \overset{\ominus}{O}COR < \overset{\ominus}{O}R < \overset{\ominus}{N}H_2$$

Reactivity order/Rate of hydrolysis



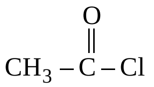
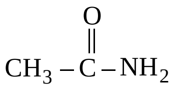
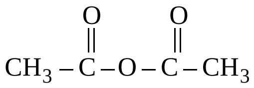
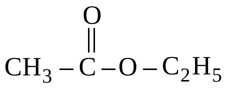
$$R-\overset{\overset{O}{\|}}{C}-X > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R > R-\overset{\overset{O}{\|}}{C}-OR > R-\overset{\overset{O}{\|}}{C}-NH_2$$

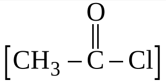
Order of stability :



$$R-\overset{\overset{O}{\|}}{C}-NH_2 > RCOOR > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R > R-\overset{\overset{O}{\|}}{C}-X$$

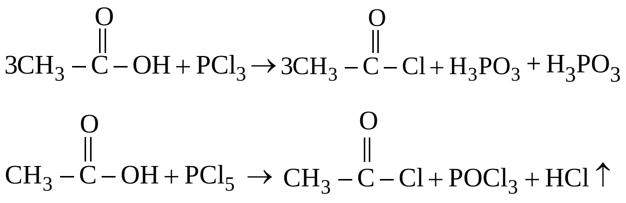
7. Derivatives regenerate the perent derivatives on hydrolysis
8. Four important acid derivative with their common name and IUPAC name.

Acid Derivative	**Common name**	**IUPAC name**
 $CH_3-\overset{\overset{O}{\|}}{C}-Cl$	Acetyl Chloride	Ethyanoyl Chloride
 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$	Acetamide	Ethanamide
 $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$	Acetic anhydride	Ethanoic anhydride
 $CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5$	Ethyl acetate	Ethyl ethanoate

ACETYL CHLORIDE  $[CH_3-\overset{\overset{O}{\|}}{C}-Cl]$

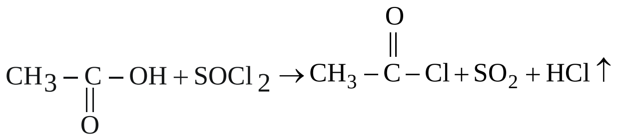
Method of preparation :

1. **Laboratory method :**



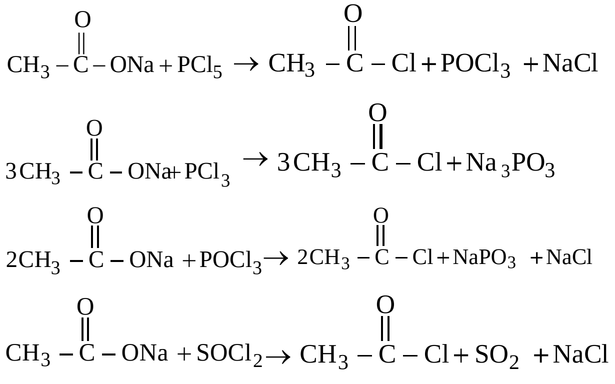
$$3CH_3-\overset{\overset{O}{\|}}{C}-OH + PCl_3 \rightarrow 3CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_3PO_3 + H_3PO_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + PCl_5 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl + POCl_3 + HCl\uparrow$$



$$CH_3-\underset{\underset{O}{\|}}{C}-OH + SOCl_2 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl + SO_2 + HCl\uparrow$$

2. **From sodiumacetate :**



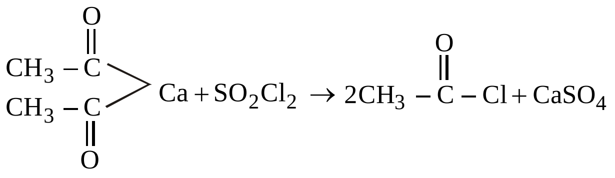
$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + PCl_5 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl + POCl_3 + NaCl$$

$$3CH_3-\overset{\overset{O}{\|}}{C}-ONa + PCl_3 \rightarrow 3CH_3-\overset{\overset{O}{\|}}{C}-Cl + Na_3PO_3$$

$$2CH_3-\overset{\overset{O}{\|}}{C}-ONa + POCl_3 \rightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-Cl + NaPO_3 + NaCl$$

$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + SOCl_2 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl + SO_2 + NaCl$$

3, **By the reaction of sulphuryl chloride on calcium ethanoate:**



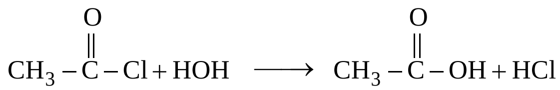
$$\begin{matrix}CH_3-\overset{\overset{O}{\|}}{C}\\ CH_3-\underset{\underset{O}{\|}}{C}\end{matrix}\!\!>Ca + SO_2Cl_2 \rightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-Cl + CaSO_4$$

Physical properties :

(i) Colourless liquid, having pungent odour.
(ii) Slowly soluble in water, Soluble in organic solvents like $CHCl_3$, CCl_4, CH_3–CO–CH_3, etc.
(iii) Fumes strongly in moist air.
(iv) Boiling point is 51°C.
(v) Produces blister on skin and its vapour causes irritation in eyes.

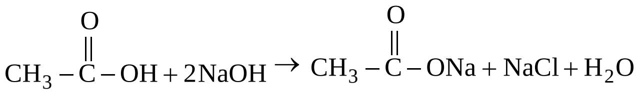
Chemical properties :

1. **Hydrolysis :**



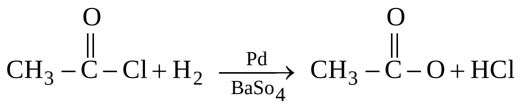
$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + HOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + HCl$$

on alkaline hydrolysis



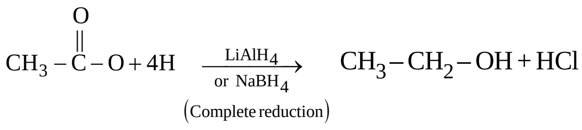
$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 2NaOH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + NaCl + H_2O$$

2. **Reduction :**

(i) 

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[BaSo_4]{Pd} CH_3-\overset{\overset{O}{\|}}{C}-O + HCl$$

(Rosenmund's reduction, partial reduction)

(ii) 

$$CH_3-\overset{\overset{O}{\|}}{C}-O + 4H \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2-OH + HCl$$

(Complete reduction)

3. Curtius Reaction :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+NaN_3 \longrightarrow \underset{\text{Acetazide}}{CH_3-\overset{O}{\overset{\|}{C}}-N_3}$$

$$\xrightarrow{\Delta/HOH} CH_3–NH_2+N_2+CO_2$$

4. Friedel Craft's reaction :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+H-C_6H_5 \xrightarrow[AlCl_3]{\text{Anhyd.}} \underset{\text{Acetophenone}}{CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5+HCl}$$

5. With Grignard's reagent :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+R-MgX \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-R+Mg\begin{matrix}X\\Cl\end{matrix}$$

6. Halogenation :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetylchloride}}{Cl-CH_2-\overset{O}{\overset{\|}{C}}-Cl+HCl}$$

7. With Ether :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+C_2H_5-O-C_2H_5$$

$$\xrightarrow[ZnCl_2]{\text{Anhyd.}} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+C_2H_5Cl$$

8. With Sodium ethoxide :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+NaOC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+NaCl$$

9. With Sodium acetate :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NaO-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+NaCl$$

Acetic anhydride

10. Acetylation of Compounds having reactive hydrogen atom :

$$R-\overset{O}{\overset{\|}{C}}-Cl+H-Z \rightarrow R-\overset{O}{\overset{\|}{C}}-Z+HCl$$

Ex. $H–NH_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ (Acetamide)

$H–NH–CH_3 \rightarrow CH_3–CO–NH–CH_3$ (N–methylacetamide)

$H–N(CH_3)_2 \rightarrow CH_3–CO–N(CH_3)_2$ (N, N-dimethylacetamide)

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H–NH–CO–NH_2$$

$\rightarrow CH_3–CO–NH–CO–NH_2$ (Acetylurea)

$H–NH–OH \rightarrow CH_3–CO–NH–OH$ (Acethydroxamic acid)

$H–NH–NH_2 \rightarrow CH_3–CO–NH–NH_2$ (Acetic hydrazide)

$H–S–CH_3 \rightarrow CH_3–CO–S–CH_3$ (Methylthioacetate)

$H–O–C_6H_4COOH$ (o) $\rightarrow CH_3–COOC_6H_4COOH$

(o) Acetyl salicylic acid or Aspirin

$H–OR \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-OR$ (Alkyl acetate)

11 With Alkene :

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+CH_2=CH_2 \xrightarrow[AlCl_3]{\text{Anhyd.}} \underset{\text{(4-Chlorobutanone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-Cl}$$

$$\xrightarrow{\Delta} \underset{\text{Methylvinylketone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH=CH_2}$$

ACETIC ANHYDRIDE $\left[CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3\right]$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-OH]{OCOCH_3} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Method of preparation :

From Acetyl Chloride : (Laboratory Method)

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+H-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+Na-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+NaCl$$

From Acetic acid :

$$CH_3-\overset{O}{\overset{\|}{C}}-OH+H-O-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\xrightarrow{P_2O_5} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+H_2O$$

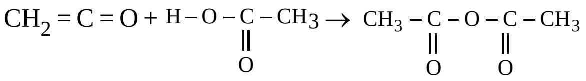
By Passing Chlorine in a mixture of SCl_2 & Sodium acetate:

$8CH_3COONa+SCl_2+2Cl_2$

$$\longrightarrow 4CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+6NaCl+Na_2SO_4$$

From Ketene :

$$\overset{H}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{C}}=O \xrightarrow[600^oC]{AlPO_4} CH_2=C=O\ (\text{ketene})+H_2O$$



$$CH_2=C=O+H-O-\overset{}{\underset{\underset{O}{||}}{C}}-CH_3\rightarrow CH_3-\underset{\underset{O}{||}}{C}-O-\underset{\underset{O}{||}}{C}-CH_3$$

Physical properties :

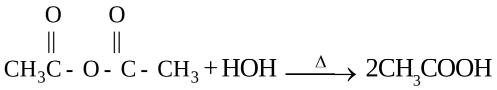
(i) It is a colourless liquid having pungest vinegar like odour.

(ii) Boiling point is 138ºC

(iii) Slowly soluble in cold water, but readily soluble in hot water

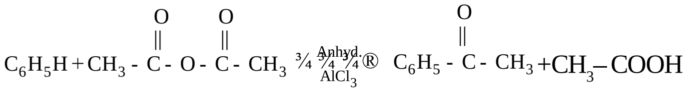
Chemical properties :

Hydrolysis :



$$CH_3\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+HOH\xrightarrow{\Delta}2CH_3COOH$$

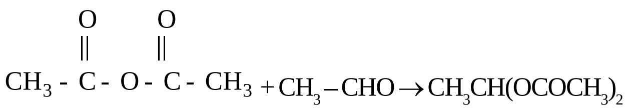
With Benzene [Friedel - Craft's Reaction] :



$$C_6H_5H+CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3\xrightarrow[AlCl_3]{Anhyd.}C_6H_5-\overset{\overset{O}{||}}{C}-CH_3+CH_3-COOH$$

Acetophenone

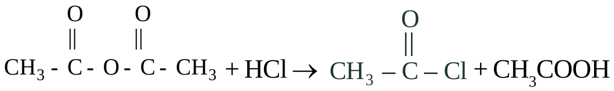
With Acetaldehyde :



$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+CH_3-CHO\rightarrow CH_3CH(OCOCH_3)_2$$

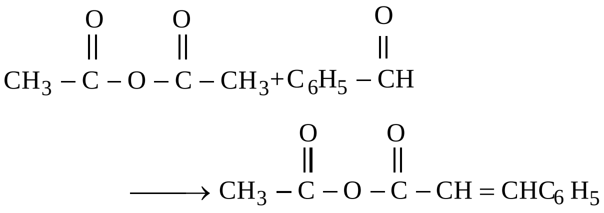
Ethyledene diacetate

With Dry HCl Gas :



$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+HCl\rightarrow CH_3-\overset{\overset{O}{||}}{C}-Cl+CH_3COOH$$

Perkin's Reaction :



$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+C_6H_5-\overset{\overset{O}{||}}{CH}$$

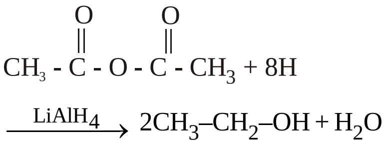
$$\longrightarrow CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH=CHC_6H_5$$

(Benzeldehyde)

C_6H_5–CH=CH-COOH + CH_3COOH

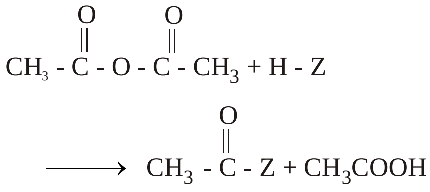
(Cinnamic acid)

Reduction :



$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+8H\xrightarrow{LiAlH_4}2CH_3-CH_2-OH+H_2O$$

With compounds having reactive -H atom :

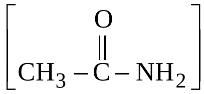


$$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3+H-Z\longrightarrow CH_3-\overset{\overset{O}{||}}{C}-Z+CH_3COOH$$

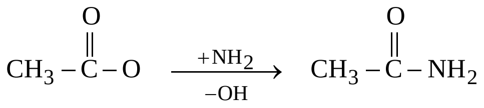
Acetyl derivative

Products are similar as in case of Acetylchloride.

ACETAMIDE



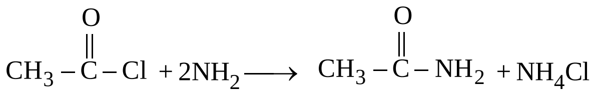
$$\left[CH_3-\overset{\overset{O}{||}}{C}-NH_2\right]$$



$$CH_3-\overset{\overset{O}{||}}{C}-O\xrightarrow[-OH]{+NH_2}CH_3-\overset{\overset{O}{||}}{C}-NH_2$$

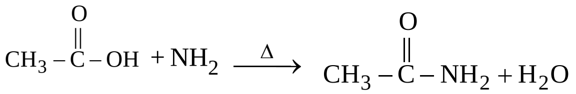
Method of preparation :

1. **From Acetychloroid :**



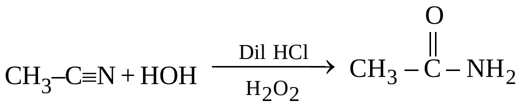
$$CH_3-\overset{\overset{O}{||}}{C}-Cl+2NH_2\longrightarrow CH_3-\overset{\overset{O}{||}}{C}-NH_2+NH_4Cl$$

2. **From Acetic Acid :**



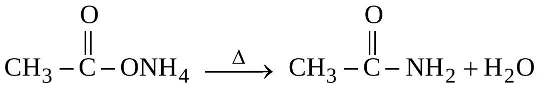
$$CH_3-\overset{\overset{O}{||}}{C}-OH+NH_2\xrightarrow{\Delta}CH_3-\overset{\overset{O}{||}}{C}-NH_2+H_2O$$

3. **Partial hydrolysis of Acetonitrile :**



$$CH_3-C\equiv N+HOH\xrightarrow[H_2O_2]{Dil\ HCl}CH_3-\overset{\overset{O}{||}}{C}-NH_2$$

4. **By thermal decomposition of Ammonium acetate :**



$$CH_3-\overset{\overset{O}{||}}{C}-ONH_4\xrightarrow{\Delta}CH_3-\overset{\overset{O}{||}}{C}-NH_2+H_2O$$

Physical properties :

(i) It is a hygroscopic white crystalline solid.

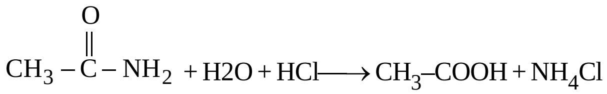
(ii) It has faint smell in pure state, but a rate like smell in impure state.

(iii) It is soluble in water and alcohol, but springly soluble in ether.

(iv) Melting point 82°C and boiling point is 222°C.

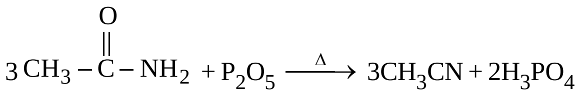
Chemical properties :

Hydrolysis :

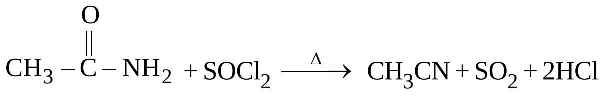


$$CH_3-\overset{\overset{O}{||}}{C}-NH_2+H2O+HCl\longrightarrow CH_3-COOH+NH_4Cl$$

Dehydration :



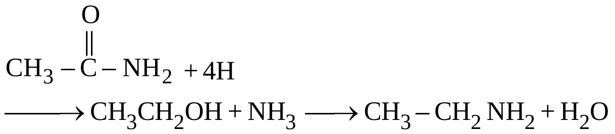
$$3CH_3-\overset{\overset{O}{||}}{C}-NH_2+P_2O_5\xrightarrow{\Delta}3CH_3CN+2H_3PO_4$$



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2+SOCl_2\xrightarrow{\Delta}CH_3CN+SO_2+2HCl$$

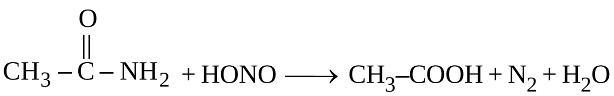
Reduction :

Reducing Agent : Methyl Catalyst + H_2, Na+ Ethanol, $LiAlH_4$, $NaBH_4$, etc.



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2+4H\longrightarrow CH_3CH_2OH+NH_3\longrightarrow CH_3-CH_2NH_2+H_2O$$

With Nitrous Acid :

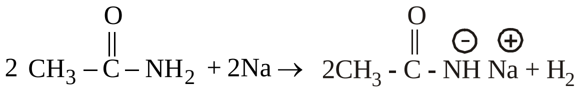


$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + HONO \longrightarrow CH_3\text{–}COOH + N_2 + H_2O$$

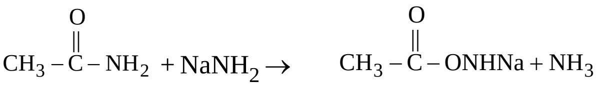
Amphoretic character :

Acetamides forms salts on reacting with strong bases as well as strong acids. Therefore it behaves like a weak base as well as a weak acid. i.e. it shows amphoteric character.

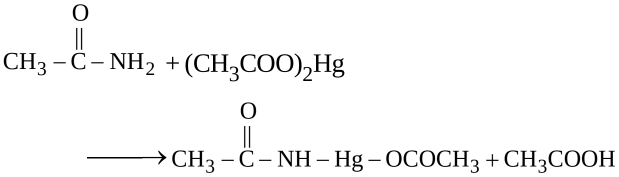
(i) **Weak acidic behaviour :**



$$2\ CH_3-\overset{\overset{O}{||}}{C}-NH_2 + 2Na \rightarrow 2CH_3-\overset{\overset{O}{||}}{C}-\overset{\ominus}{NH}\ \overset{\oplus}{Na} + H_2$$



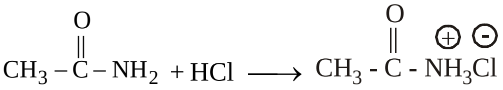
$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + NaNH_2 \rightarrow CH_3-\overset{\overset{O}{||}}{C}-ONHNa + NH_3$$



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + (CH_3COO)_2Hg \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-NH-Hg-OCOCH_3 + CH_3COOH$$

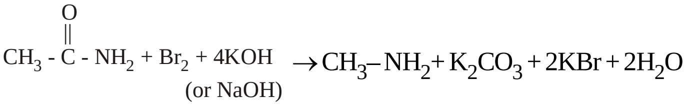
Acitamidomercuriacetate

(ii) **Weak basic behaviour :**



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + HCl \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-\overset{\oplus}{NH_3}\overset{\ominus}{Cl}$$

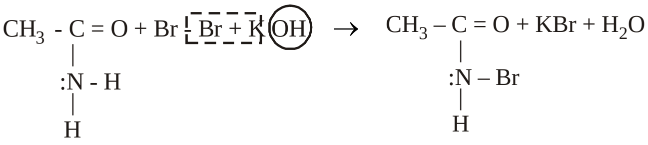
Hofmann Bromamide Reaction or Hypobromite Reaction :



$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + \underset{(\text{or NaOH})}{4KOH} \rightarrow CH_3\text{–}NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Slightly Mechanism :

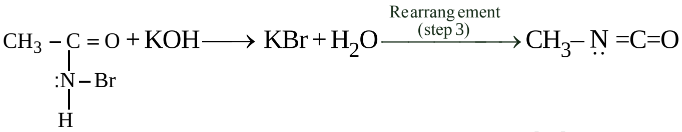
Step-1 : Bromination



$$CH_3-\underset{\underset{\underset{\underset{H}{|}}{:N-H}}{|}}{C}=O + Br\,\boxed{Br + K}\,\bigcirc\!\!\!\!\!\!OH \rightarrow CH_3-\underset{\underset{\underset{\underset{H}{|}}{:N-Br}}{|}}{C}=O + KBr + H_2O$$

Acetobromamide

Step-2 : Dehydrobromination :



$$CH_3-\underset{\underset{\underset{\underset{H}{|}}{:N-Br}}{|}}{C}=O + KOH \longrightarrow KBr + H_2O \xrightarrow[(\text{step }3)]{\text{Rearrangement}} CH_3\text{–}\underset{..}{N}=C=O$$

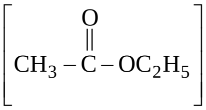
Methylisocyanate

Step-3 : Hydrolysis :

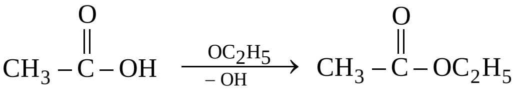
$$CH_3\text{–}N=C=O + 2KOH \longrightarrow \underset{\text{Methylamine}}{CH_3-NH_2} + K_2CO_3$$

Note : In the reaction decrease of one carbon atom takes place. Therefore it can be used in descending down a homologous series and it is also called Hofmann degradation.

ETHYLACETATE AND ACETIC ESTER



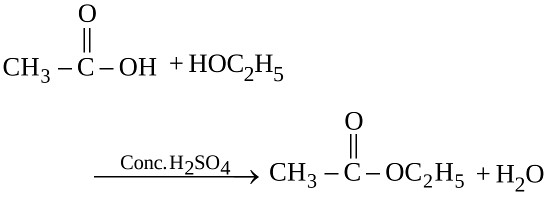
$$\left[CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5\right]$$



$$CH_3-\overset{\overset{O}{||}}{C}-OH \xrightarrow[-\,OH]{OC_2H_5} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5$$

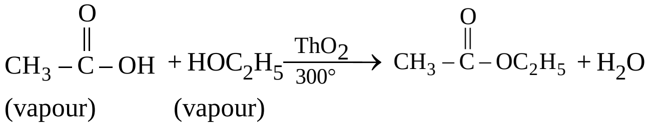
Methods of preparation :

1. **By liquid phase Esterification :**



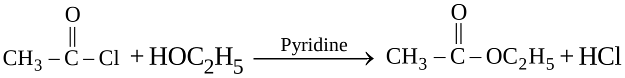
$$CH_3-\overset{\overset{O}{||}}{C}-OH + HOC_2H_5 \xrightarrow{\text{Conc.}H_2SO_4} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + H_2O$$

2. **By vapour phase Esterification :**

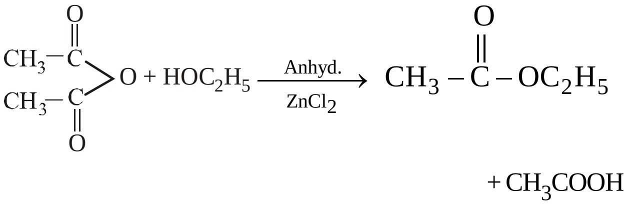


$$\underset{(\text{vapour})}{CH_3-\overset{\overset{O}{||}}{C}-OH} + \underset{(\text{vapour})}{HOC_2H_5} \xrightarrow[300°]{ThO_2} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + H_2O$$

3. **By Acetylation of Ethanol :**

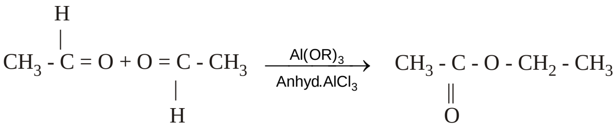


$$CH_3-\overset{\overset{O}{||}}{C}-Cl + HOC_2H_5 \xrightarrow{\text{Pyridine}} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + HCl$$



$$(CH_3CO)_2O + HOC_2H_5 \xrightarrow[ZnCl_2]{\text{Anhyd.}} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + CH_3COOH$$

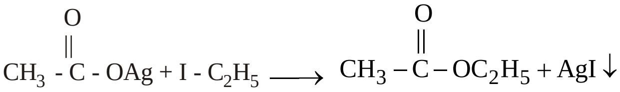
4. **Tischenko Reaction :**



$$CH_3-\overset{\overset{H}{|}}{C}=O + O=\underset{\underset{H}{|}}{C}-CH_3 \xrightarrow[\text{Anhyd.}AlCl_3]{Al(OR)_3} CH_3-\underset{\underset{O}{||}}{C}-O-CH_2-CH_3$$

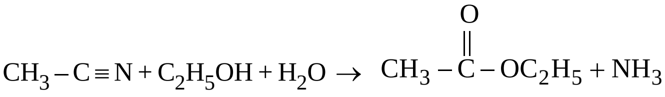
Ethyl acetate

5. **Ethylation of Silver halides :**



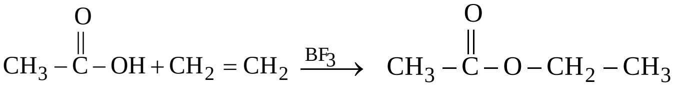
$$CH_3-\overset{\overset{O}{||}}{C}-OAg + I-C_2H_5 \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + AgI\downarrow$$

6. **Ethanolysis of Ethanenitrile :**



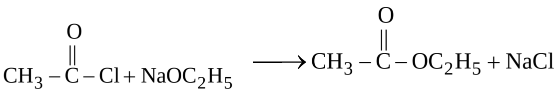
$$CH_3-C\equiv N + C_2H_5OH + H_2O \rightarrow CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + NH_3$$

7. **By addition of Acetic acid on Ethylene :**



$$CH_3-\overset{\overset{O}{||}}{C}-OH + CH_2=CH_2 \xrightarrow{BF_3} CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3$$

8. By reaction of sodium Ethoxide on Acetyl chloride :



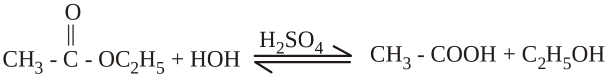
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+NaOC_2H_5\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+NaCl$$

Physical properties :

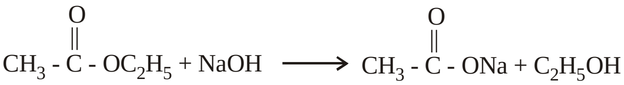
(i) Colourless, sweet smelling stemvolatile, inflammable liquid.
(ii) Very springly soluble in water, but soluble in organic solvents.
(iii) Boiling point 78°

Chemical properties

1. Hydrolysis



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+HOH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3-COOH+C_2H_5OH$$

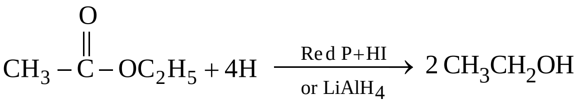


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+NaOH\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa+C_2H_5OH$$

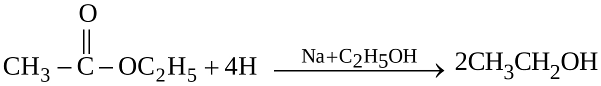
Note : In case of caustic alkalies hydrolysis is rapid and complete.

Alkaline hydrolysis of esters called "Saponification".

2. Reduction :



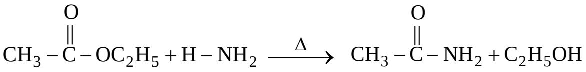
$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+4H\xrightarrow[\text{or LiAlH}_4]{\text{Red P+HI}} 2\,CH_3CH_2OH$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+4H\xrightarrow{Na+C_2H_5OH} 2CH_3CH_2OH$$

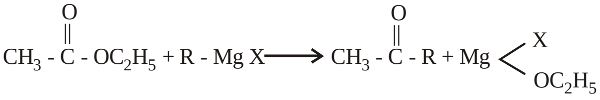
(Bouveault-Blanc reduction)

3. Ammonolysis :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+H-NH_2\xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2+C_2H_5OH$$

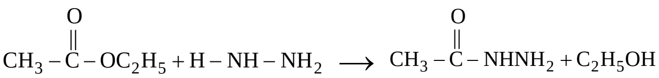
4. With Grignard's Reagent :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+R-Mg\,X\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-R+Mg\begin{matrix}X\\OC_2H_5\end{matrix}$$

Note : The product will be tertiary alcohol when 2 mole of Grignard's reagent are taken.

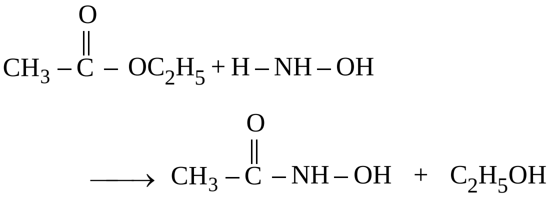
5. With Hydrazine :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+H-NH-NH_2\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NHNH_2+C_2H_5OH$$

Acetyl hydrazine

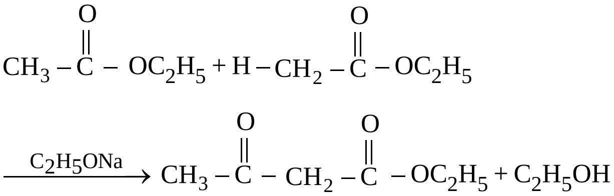
With Hydroxyl Amine :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+H-NH-OH\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-OH+C_2H_5OH$$

Acetyl hydraxomic acid

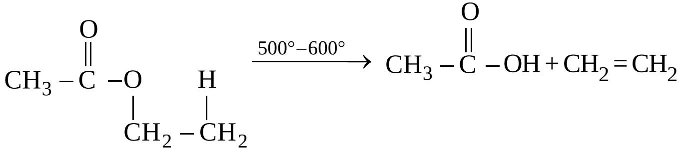
7. Claisen Ester Condensation :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+H-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5\xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5+C_2H_5OH$$

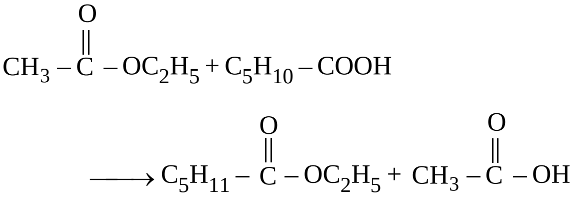
Acetoaceticester

8. Pyrolysis or Thermal decomposition :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-H\xrightarrow{500^\circ-600^\circ} CH_3-\overset{O}{\overset{\|}{C}}-OH+CH_2=CH_2$$

9. Acidolysis :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+C_5H_{10}-COOH\longrightarrow C_5H_{11}-\overset{O}{\overset{\|}{C}}-OC_2H_5+CH_3-\overset{O}{\overset{\|}{C}}-OH$$

TRY IT YOURSELF-2

Q.1 In the given reaction :

$$CH_3CHO\xrightarrow[\text{(ii) }H_2O/H^{\oplus}/\Delta]{\text{(i) NaCN/HCl}}(A)\xrightarrow[\text{reagent}]{\text{Fenton}}(B)$$

(B) will be –

(A) Acetic acid	(B) Oxalic acid
(C) Pyruvic acid	(D) Citric acid

Q.2 Which of the following compounds gives carbondioxide with $NaHCO_3$?

(A) Acetic acid	(B) Hexanol
(C) Phenol	(D) Acetylene

Q.3 In the given reaction :

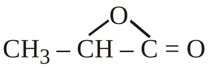
$$CH_3CH_2-COOH\xrightarrow[\text{(ii) }Br_2/\Delta]{\text{(i) }AgNO_3}[X]$$; [X] will be –

(A) Ethyl bromide	(B) Propyl bromide
(C) Propyl propanoate	(D) All of these

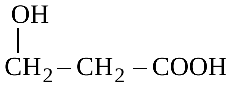
Q.4 In the reaction sequence :

$$CH_3-\underset{OH}{\underset{|}{CH}}-COOH\xrightarrow{\Delta}[Y]$$

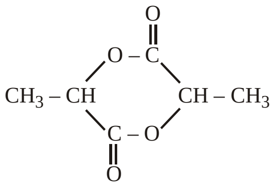
[Y] will be –

(A) 

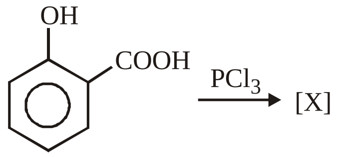
(B) $CH_2=CH-COOH$

(C) 

$$\overset{OH}{\overset{|}{CH_2}}-CH_2-COOH$$

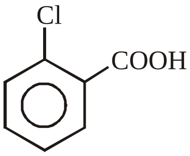
(D) 

Q.5 In the given reaction :

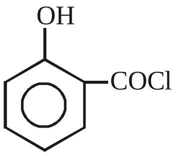


[X] will be –

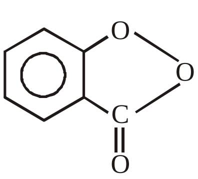
(A)



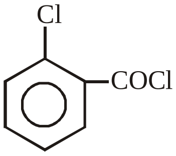
(B)



(C)

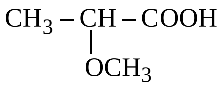


(D)



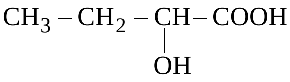
Q.6 Which optically active compound on reduction with $LiAlH_4$ will give optically inactive compound?

(A)



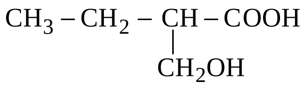
$CH_3-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-COOH$

(B)



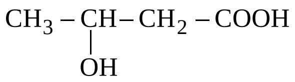
$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$

(C)



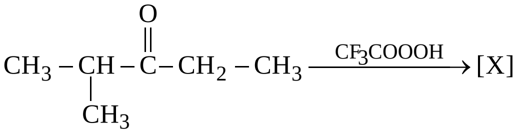
$CH_3-CH_2-\underset{\displaystyle CH_2OH}{\underset{|}{CH}}-COOH$

(D)



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-COOH$

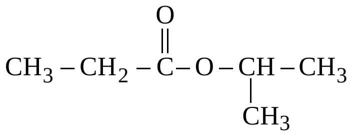
Q.7 In the given reaction



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3 \xrightarrow{CF_3COOOH} [X]$

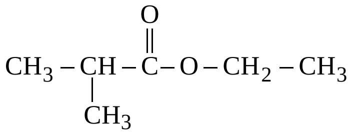
as main product [X] will be –

(A)



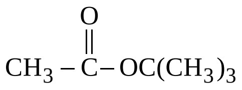
$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(B)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-O-CH_2-CH_3$

(C)



$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-OC(CH_3)_3$

(D) $(CH_3)_3COOCH_3$

Q.8 Acidic anhydride and ammonia gives the product –

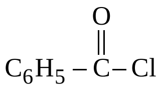
(A) CH_3CONH_2	(B) $CH_3CONHCH_3$
(C) CH_3CN	(D) CH_3COONH_4

Q.9 Two treatment of an open chain ester with $LiAlH_4$ followed by acid hydrolysis produces –

(A) Two aldehyde
(B) One carboxylic acid and one alcohol
(C) Two alcohols
(D) Two acids.

Q.10 Which one of the following compounds gives carboxylic acid with HNO_2 ?

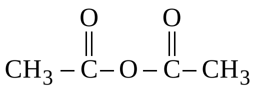
(A)



$C_6H_5-\overset{\displaystyle O}{\overset{||}{C}}-Cl$

(B) $C_6H_5CONH_2$

(C)



$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-O-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$

(D) $CH_3COOC_2H_5$

Q.11 Carboxylic acid is formed by

(A) Hydrolysis of alkyl cyanide
(B) Reaction of Grignard salt with CO_2 followed by hydrolysis.
(C) Reaction of alkene with CO and H_2O in presence of $Co_4(CO)_8$.
(D) All of these.

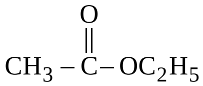
Q.12 $CH_3-COOH \xrightarrow[1\,eq]{Cl_2/P} A \xrightarrow[aq.]{NaCN} B \xrightarrow{H_2O/H^+} C$

Product (C) is –

(A) Malonic acid	(B) Succinic acid
(C) Maleic acid	(D) Oxalic acid

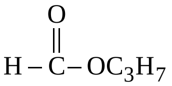
Q.13 An ester having formula $C_4H_8O_2$ gives 4 carbon containing alcohol with excess of CH_3-MgBr/H_2O. Ester will be

(A)



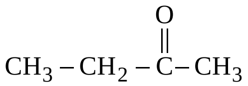
$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-OC_2H_5$

(B)



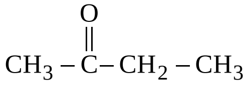
$H-\overset{\displaystyle O}{\overset{||}{C}}-OC_3H_7$

(C)



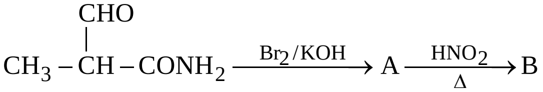
$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$

(D)



$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3$

Q.14



$CH_3-\overset{\displaystyle CHO}{\overset{|}{CH}}-CONH_2 \xrightarrow{Br_2/KOH} A \xrightarrow[\Delta]{HNO_2} B$

$\xrightarrow[\Delta]{H^+} C \xrightarrow{Conc.\ NaOH} D$; Product (D) is –

(A) $CH_2=CH-CHO$	(B) $CH_2=CH-CH_2-OH$
(C) $CH_2=CH-COONa$	(D) Mixture of (B) and (C)

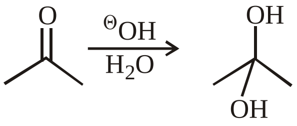
ANSWERS

(1) (C)	**(2)** (A)	**(3)** (A)
(4) (D)	**(5)** (B)	**(6)** (C)
(7) (A)	**(8)** (A)	**(9)** (C)
(10) (B)	**(11)** (D)	**(12)** (A)
(13) (A)	**(14)** (D)	

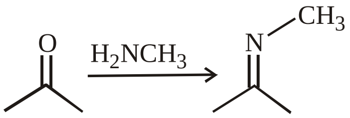
USEFUL TIPS

* The five classes of reactions of nucleophiles with carbonyl groups. Reactions from each class can occur with aldehydes, ketones and carboxylic acid derivaties.

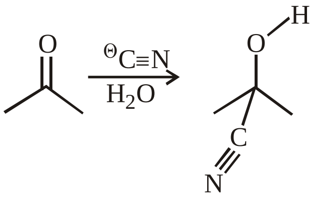
(i) Addition of a heteroatom nucleophile
for example, hydrated formation



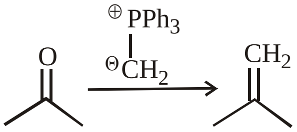
(ii) Substitution by a heteroatom nucleophile
for example, imine formation



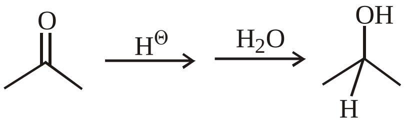
(iii) Addition of a carbon nucleophile
for example, cyanohydrin formation



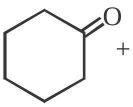
(iv) Substitution by a carbon nucleophile
for example, Wittig reaction



(v) Addition of the equivalent of a hydride ion
for example, reduction to an alcohol

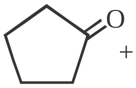


* Ketones and aldehyde react with phenylhydrazines, hydroxylamine, and semicarbazide to form substitution products.

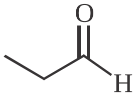


+ 2,4-Dinitrophyenylhydrazine

→ 2,4-Dinitrophyenylhydrazone (2,4-DNP)



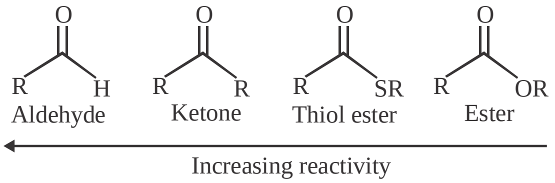
+Hydroxylamine ⟶ An oxime + H_2O

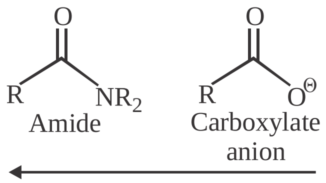


+ Semicarbazide

⟶ A Semicarbazone + H_2O

* Order of reactivity of carbonyl compounds toward nucleophiles.

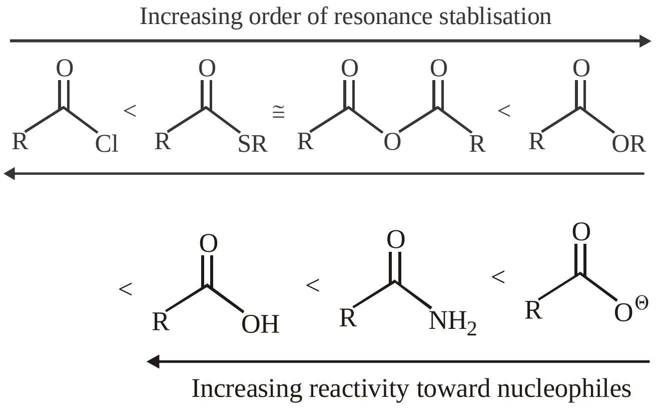


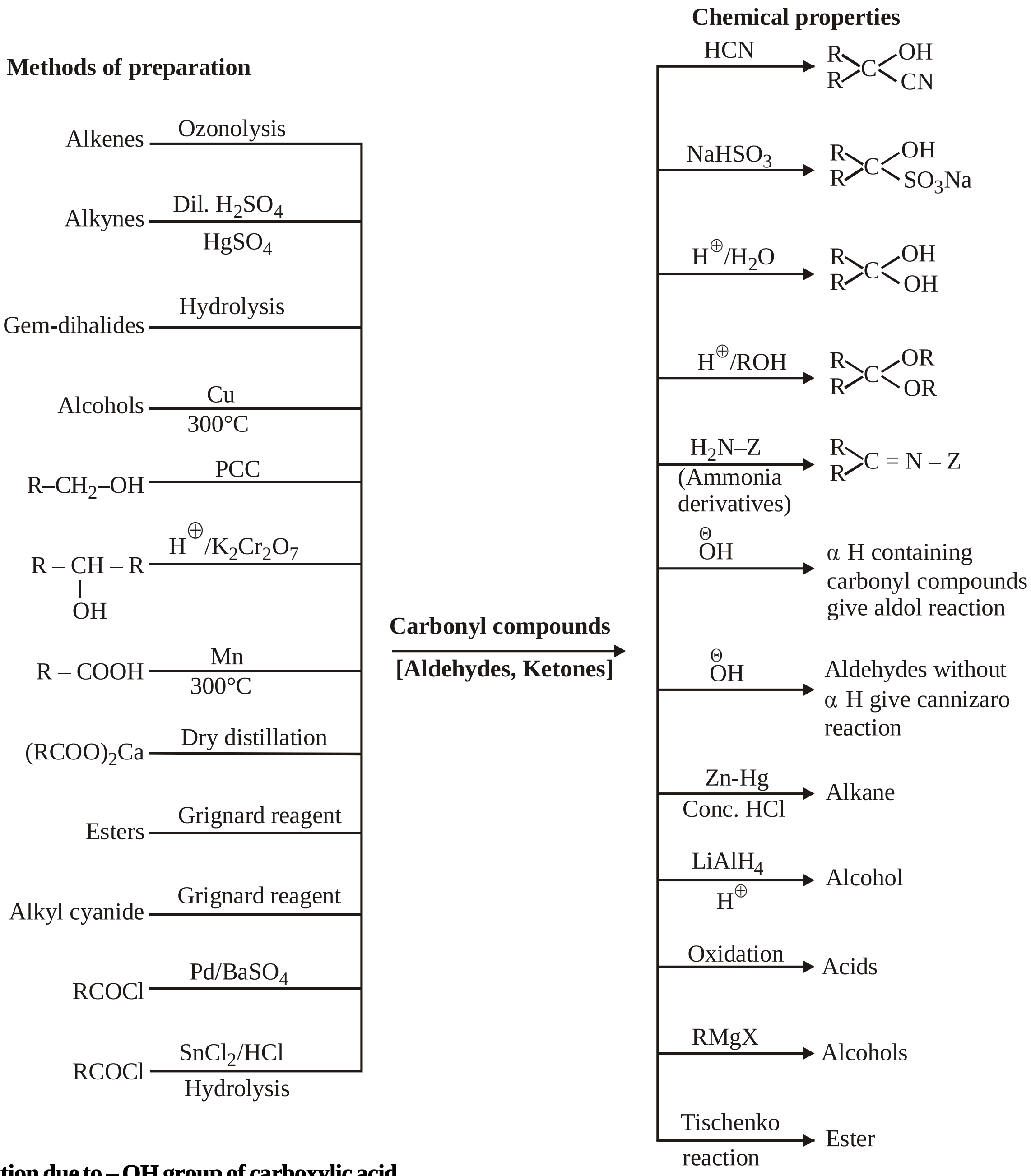


* **Table : Synthetic utility of Grignard reactions**

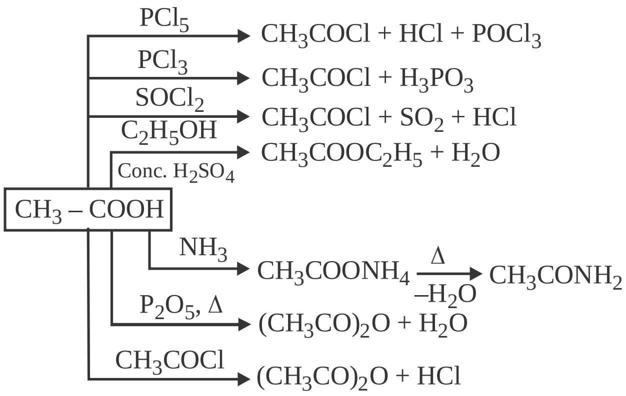
Reactants	Product
R – MgX + Formadehyde	Primary alcohol
R – MgX + Aldehyde	Secondary alcohol (R groups can be the same or different)
R – MgX + Ketone	Tertiary alcohol (R groups can be the same or different)
R – MgX + Ester	Tertiary alcohol (Two of the R groups must be the same)
R – MgX + CO_2	Carboxylic acid
R – MgX + 	Primary alcohol
R – MgX + H_2O	Hydrocarbon

* Order of stability of the various carboxylic acid derivatives.

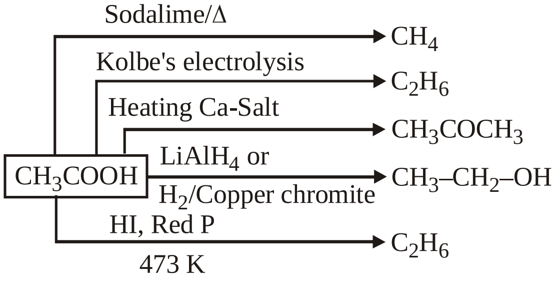




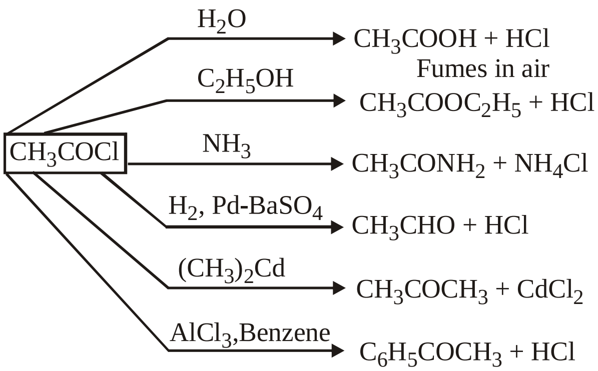
* **Reaction due to – OH group of carboxylic acid**



* **Reaction due to carboxyl group (–COOH)**

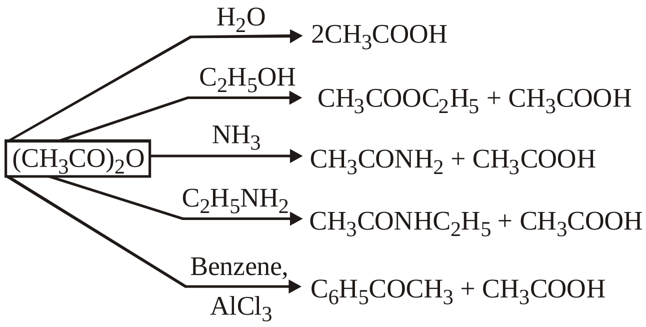


* **Acyl halides**



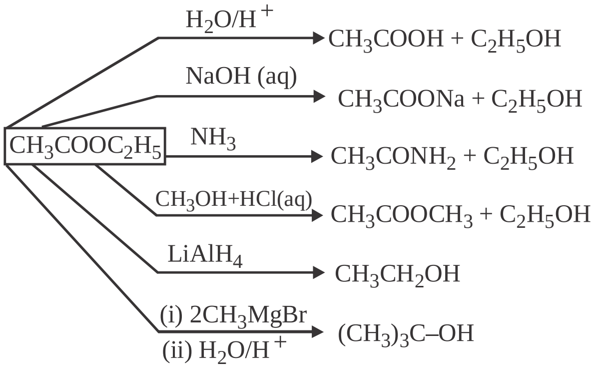
$$CH_3COCl \xrightarrow{H_2O} CH_3COOH + HCl \text{ (Fumes in air)}$$
$$CH_3COCl \xrightarrow{C_2H_5OH} CH_3COOC_2H_5 + HCl$$
$$CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 + NH_4Cl$$
$$CH_3COCl \xrightarrow{H_2,\ Pd\text{-}BaSO_4} CH_3CHO + HCl$$
$$CH_3COCl \xrightarrow{(CH_3)_2Cd} CH_3COCH_3 + CdCl_2$$
$$CH_3COCl \xrightarrow{AlCl_3,Benzene} C_6H_5COCH_3 + HCl$$

* **Acid anhydrides : $(RCO)_2O$**



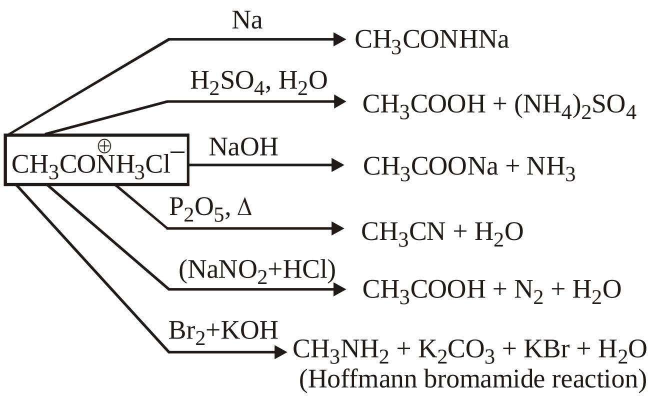
$$(CH_3CO)_2O \xrightarrow{H_2O} 2CH_3COOH$$
$$(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOC_2H_5 + CH_3COOH$$
$$(CH_3CO)_2O \xrightarrow{NH_3} CH_3CONH_2 + CH_3COOH$$
$$(CH_3CO)_2O \xrightarrow{C_2H_5NH_2} CH_3CONHC_2H_5 + CH_3COOH$$
$$(CH_3CO)_2O \xrightarrow[AlCl_3]{Benzene,} C_6H_5COCH_3 + CH_3COOH$$

* **Ester : RCOOR**



$$CH_3COOC_2H_5 \xrightarrow{H_2O/H^+} CH_3COOH + C_2H_5OH$$
$$CH_3COOC_2H_5 \xrightarrow{NaOH\ (aq)} CH_3COONa + C_2H_5OH$$
$$CH_3COOC_2H_5 \xrightarrow{NH_3} CH_3CONH_2 + C_2H_5OH$$
$$CH_3COOC_2H_5 \xrightarrow{CH_3OH+HCl(aq)} CH_3COOCH_3 + C_2H_5OH$$
$$CH_3COOC_2H_5 \xrightarrow{LiAlH_4} CH_3CH_2OH$$
$$CH_3COOC_2H_5 \xrightarrow[(ii)\ H_2O/H^+]{(i)\ 2CH_3MgBr} (CH_3)_3C\text{–}OH$$

* **Acid amides**



$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{Na} CH_3CONHNa$$
$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{H_2SO_4,\ H_2O} CH_3COOH + (NH_4)_2SO_4$$
$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{NaOH} CH_3COONa + NH_3$$
$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{P_2O_5,\ \Delta} CH_3CN + H_2O$$
$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{(NaNO_2+HCl)} CH_3COOH + N_2 + H_2O$$
$$CH_3CO\overset{\oplus}{N}H_3Cl^- \xrightarrow{Br_2+KOH} CH_3NH_2 + K_2CO_3 + KBr + H_2O$$

(Hoffmann bromamide reaction)

* **Comparison of Aldehyde and Ketone**

S.N.	Reactions	CH_3CHO	$CH_3CO\ CH_3$
1.	With Fehling's solution.	gives a red precipitate	does not react.
2.	With Tollen's reagent.	gives silver mirror.	no silver mirror.
3.	Oxidation	gives acetic acid	gives acetic acid with loss of one carbon atom.
4.	Reduction with $NaBH_4$	ethanol (primary alcohol)	isopropyl alcohol (secondary alcohol)
5.	With NH_3	simple addition product is formed.	forms complex ketonic amine.
6.	Iodoform reaction	forms iodoform and formic acid.	forms iodoform and acetic acid.
7.	Polymerisation	forms paraldehyde	forms condensation products.
8.	With Schiff's reagent.	pink colour appears in cold.	no pink colour in cold.
9.	Warming with NaOH	a brown resinons mass.	no resinous mass.

* **Comparison of Aliphatic aldehyde and Aromatic aldehyde**

S.N.	Reactions	CH_3CHO	C_6H_5CHO
1.	Heating with Fehling's solution.	gives a red precipitate	no reaction.
2.	With ammonia	forms simple addition product.	forms complex condensation product.
3.	With caustic soda	undergoes Aldol condensation	undergoes Cannizzaro reaction.
4.	With primary amines	does not form Schiff's base	forms Schiff's base.
5.	With chlorine	does not form acetyl chloride	forms benzoyl chloride.
6.	Polymerisation	undergoes polymerisation.	does not polymerise.
7.	Electrophilic substitution.	does not undergo.	undergoes at the meta position.
8.	With Schiff's reagent.	gives pink colour in cold.	gives pink colour.

* CCl_3 – CHO does not give cannizaro reaction while it has no α-H. It gives haloform reaction.

* 2-Methylpentanal, Cyclohexanone, 1-Phenylpropanone, Phenylacetaldehyde
contains α-hydrogens hence, gives Aldol condensation.

* Methanal, Benzaldehyde, 2, 2-Dimethylbutanal
do not contain α-hydrogen can give Cannizzaro reaction.

QUESTION BANK

CHAPTER 11 : ALDEHYDES, KETONES & CARBOXYLIC ACID

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

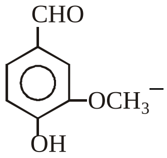
PART 1 : NOMENCLATURE AND STRUCTURE OF ALDEHYDES AND KETONES

Q.1 IUPAC name of CH_3COCH_3 is
(A) Acetone (B) 2-propanone
(C) Dimethyl ketone (D) Propanal

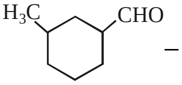
Q.2 IUPAC name of CCl_3CHO is
(A) Chloral (B) Trichloro acetaldehyde
(C) 1, 1, 1-trichloroethanal (D) 2, 2, 2-trichloroethanal

Q.3 The location of substituent on the carbon atoms next to the carbonyl group indicated as
(A) α (B) $\alpha\,\alpha'$
(C) β (D) $\beta\,\beta'$

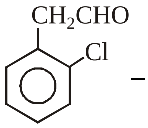
Q.4 Which of the following names of the organic compounds is not correctly written?

(A) 

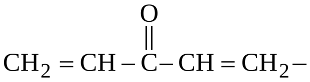
– 4-Hydroxy-3-methoxybenzaldehyde

(B) 

– 5-Methylcyclohexanecarbaldehyde

(C) 

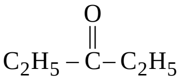
– 2-(2-Chlorophenyl)ethanal

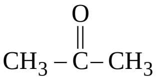
(D) 
$CH_2 = CH - \overset{\overset{O}{||}}{C} - CH = CH_2$ – Penta-1, 4-dien-3-one

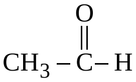
Q.5 When the aldehyde group is attached to a ring, the suffix ____ is added after the full name of the cycloalkane.
(A) aldehyde (B) carbaldehyde
(C) carboxyaldehyde (D) cycloaldehyde

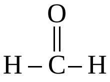
Q.6 Alkylphenyl ketones are named by adding the acyl group as prefix to
(A) benzene (B) phenyl
(C) phenone (D) All of these

Q.7 Which of the following carbonyl compounds is most polar?

(A) 
$C_2H_5 - \overset{\overset{O}{||}}{C} - C_2H_5$

(B) 
$CH_3 - \overset{\overset{O}{||}}{C} - CH_3$

(C) 
$CH_3 - \overset{\overset{O}{||}}{C} - H$

(D) 
$H - \overset{\overset{O}{||}}{C} - H$

PART 2 : PREPARATION OF ALDEHYDES AND KETONES

Q.8 $CH_3COCl \xrightarrow[Pd/BaSO_4]{2H} CH_3CHO + HCl;$

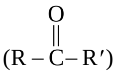
The above reaction is called
(A) Reimer-Tiemann reaction
(B) Cannizzaro reaction
(C) Rosenmund reaction
(D) Reformatsky reaction

Q.9 Ethyne on reaction with water in the presence of $HgSO_4$ and H_2SO_4 gives –
(A) Acetone (B) Acetaldehyde
(C) Acetic acid (D) Ethyl alcohol

Q.10 Choose the correct option –
(A) Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.
(B) Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde.
(C) When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde.
(D) All of these

Q.11 Benzaldehyde can be prepared from benzene by passing vapours of ____ and ____ in its solution in presence of catalyst mixture of aluminium chloride and cuprous chloride. The reaction is known as –
(A) HCl, $SnCl_4$, Rosenmund reduction
(B) CO, HCl, Gattermann-Koch reaction
(C) CO_2, H_2SO_4, Clemmensen reduction
(D) O_3, alcohol, Wolff-Kishner reduction

Q.12 Which of the following reaction(s) is/are correct regarding the preparation of ketone?
(A) Treatment of acyl chlorides with dialkyl cadmium prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.
(B) When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it gives the corresponding ketone. This reaction is known as Friedel-Craft acylation reaction.
(C) Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.
(D) All of the above.

Q.13 Ketones  $(R - \overset{\overset{O}{||}}{C} - R')$ can be obtained in one step by (where R and R' are alkyl groups)
(A) hydrolysis of esters.
(B) oxidation of primary alcohols.
(C) oxidation of secondary alcohols.
(D) reaction of alkyl halides with alcohols.

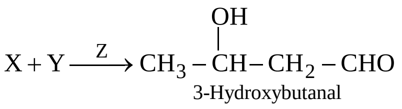
Q.14 Which of the starting material is used for the synthesis of aldehyde by the ozonolysis?
(A) Alkane (B) Alkene
(C) Alkyne (D) All of these

Q.15 Propanone can be prepared from ethyne by
(A) passing a mixture of ethyne and steam over a catalyst, magnesium at 420°C.
(B) passing a mixture of ethyne and ethanol over a catalyst zinc chromite.
(C) boiling ethyne with water and H_2SO_4.
(D) treating ethyne with iodine and NaOH.

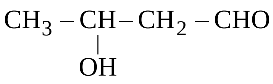
PART 3 : PHYSICAL AND CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Q.16 Which of the following will not give aldol condensation?
(A) Phenyl acetaldehyde (B) 2-Methylpentanal
(C) Benzaldehyde (D) 1-Phenylpropanone

Q.17 Identify (X), (Y) and (Z) in the given reaction.


$$X + Y \xrightarrow{Z} CH_3-\underset{}{\overset{OH}{\overset{|}{CH}}}-CH_2-CHO$$
3-Hydroxybutanal

(A) X-HCHO, Y-CH_3CHO, Z-KOH
(B) X-CH_3CHO, Y-CH_3CHO, Z-NaOH
(C) X-CH_3CH_2OH, Y-HCHO, Z-H_2SO_4
(D) X-CH_3CH_2CHO, Y-HCHO, Z-Dry ether

Q.18 Acetaldehyde when treated with dilute NaOH gives
(A) CH_3CH_2OH (B) CH_3COOH
(C)

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$
(D) CH_3-CH_3

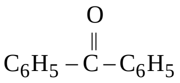
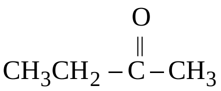
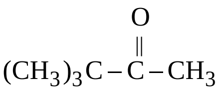
Q.19 Which one of the following reactions is a method for the conversion of a ketone into a hydrocarbon
(A) Aldol condensation
(B) Reimer-Tiemann reaction
(C) Cannizzaro reaction
(D) Wolf-Kishner reduction

Q.20 Identify the product Y in the sequence

$$CH_3CHO + CH_3MgI \xrightarrow{Ether} X \xrightarrow{H_2O/H^+} Y$$

(A) CH_3OH (B) CH_3CH_2OH
(C) $(CH_3)_2CHOH$ (D) $(CH_3)_3CHOH$

Q.21 Which of the aldehyde is most reactive ?
(A) C_6H_5-CHO (B) CH_3CHO
(C) HCHO (D) All the equally reactive

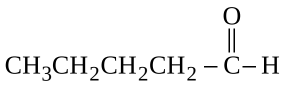
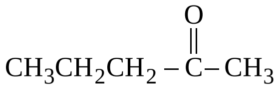
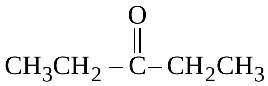
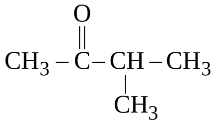
Q.22 Which of the following gives aldol condensation reaction
(A) C_6H_5OH
(B)

$C_6H_5-\overset{O}{\overset{||}{C}}-C_6H_5$
(C)

$CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_3$
(D)

$(CH_3)_3C-\overset{O}{\overset{||}{C}}-CH_3$

Q.23 If formaldehyde and KOH are heated, then we get
(A) Acetylene (B) Methane
(C) Methyl alcohol (D) Ethyl formate

Q.24 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) $C_6H_5CH(OH)COC_6H_5$

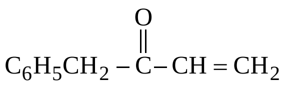
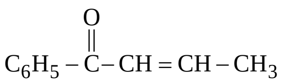
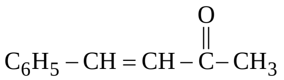
Q.25 Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali?
(A) $CH \equiv C-CHO$ (B) $CH_2 = CHCHO$
(C) C_6H_5CHO (D) CH_3CH_2CHO

Q.26 Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.
Ethanal, Propanal, Propanone, Butanone
(A) Butanone < Propanone < Propanal < Ethanal
(B) Propanone < Butanone < Ethanal > Propanal
(C) Propanal < Ethanal < Propanone < Butanone
(D) Ethanal < Propanal < Propanone < Butanone

Q.27 Which of the following is the most reactive isomer?
(A)

$CH_3CH_2CH_2CH_2-\overset{O}{\overset{||}{C}}-H$
(B)

$CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-CH_3$
(C)

$CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_3$
(D)

$CH_3-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

Q.28 The methanol, ethanal and propanone are miscible with water because they form
(A) van der Waals' forces with water.
(B) hydrogen bond with water.
(C) dipole-dipole bond with water.
(D) ion-dipole bond with water.

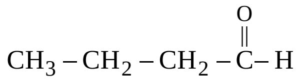
Q.29 Identify the example in which nucleophilic addition and nucleophilic addition elimination reaction both occur respectively in the carbonyl compound.
(A) Reduction to alcohols
(B) Addition of sodium hydrogen sulphite
(C) Tollen's test
(D) Reaction with alcohols

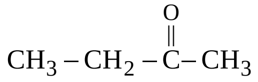
Q.30 The condensation product of benzaldehyde and acetone is
(A) $C_6H_5CH = C(CH_3)_2$
(B)

$C_6H_5CH_2-\overset{O}{\overset{||}{C}}-CH = CH_2$
(C)

$C_6H_5-\overset{O}{\overset{||}{C}}-CH = CH-CH_3$
(D)

$C_6H_5-CH = CH-\overset{O}{\overset{||}{C}}-CH_3$

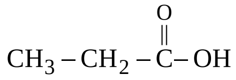
Q.31 Which among the following is most reactive to give nucleophilic addition?
(A) FCH_2CHO (B) $ClCH_2CHO$
(C) $BrCH_2CHO$ (D) ICH_2CHO

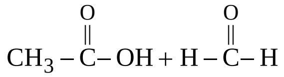
Q.32 Which of the following compounds will undergo Cannizzaro reaction?
(A) CH_3CHO (B) CH_3COCH_3
(C) C_6H_5CHO (D) $C_6H_5CH_2CHO$

Q.33 Addition of water to alkynes occurs in acidic medium in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?

(A) 
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

(B) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(C) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

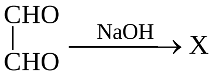
(D) 
$CH_3-\overset{\overset{O}{\|}}{C}-OH+H-\overset{\overset{O}{\|}}{C}-H$

Q.34 There is a large difference in the boiling points of butanal and butan-1-ol due to –
(A) intermolecular hydrogen bonding in butan-1-ol.
(B) intramolecular hydrogen bonding in butanal
(C) higher molecular mass of butan-1-ol
(D) resonance shown by butanal.

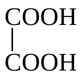
Q.35 Arrange the following compounds in the increasing order of their boiling points.
(I) $CH_3CH_2CH_2CHO$
(II) $CH_3CH_2CH_2CH_2OH$
(III) $H_5C_2O-C_2H_5$
(IV) $CH_3CH_2CH_2CH_2CH_3$
(A) IV < I < II < III (B) IV < III < II < I
(C) IV < III < I < II (D) IV < II < III < I

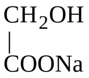
Q.36 Which of the following statement(s) is/are correct about the aldol reaction?
(A) Aldehyde and ketones having at least one β-hydrogen.
(B) The reaction is carried out in the presence of concentrated alkali.
(C) The product formed is β-hydroxy aldehydes (aldol) or β-hydroxy ketone (ketol).
(D) All of the above

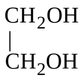
Q.37 Aldehydes that do not undergo aldol condensation are
(1) propanal (2) trichloroethanal
(3) 2-phenylethanal (4) ethanal
(5) benzaldehyde
(A) 3 and 4 only (B) 2 and 5 only
(C) 1, 2 and 3 only (D) 2, 3 and 5 only

Q.38 
$\begin{matrix}CHO\\|\\CHO\end{matrix}\xrightarrow{NaOH}X$. The product (X) will be –

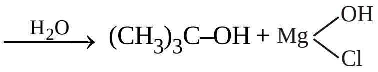
(A) 
$\begin{matrix}CH_2ONa\\|\\COONa\end{matrix}$

(B) 
$\begin{matrix}COOH\\|\\COOH\end{matrix}$

(C) 
$\begin{matrix}CH_2OH\\|\\COONa\end{matrix}$

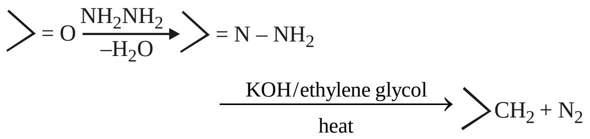
(D) 
$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$

Q.39 Identify reactant (X) in the given reaction sequence.
$CH_3COCH_3+X\rightarrow(CH_3)_3C\text{–}OMg\text{–}Cl$


$\xrightarrow{H_2O}(CH_3)_3C\text{–}OH+Mg\begin{matrix}OH\\Cl\end{matrix}$

(A) CH_3MgCl (B) $CH_3COCl+Mg$
(C) $MgCl_2$ (D) CH_3CH_2MgCl

Q.40 The addition of HCN to carbonyl compounds is an example of –
(A) nucleophilic (B) electrophilic
(C) free radical (D) electromeric

Q.41 

The above reaction is known as
(A) Wolff-Kishner reduction
(B) Clemmensen's reduction
(C) Both (A) and (B)
(D) None of these

Q.42 In the following sequence of reaction, the final product (Z) is

$CH\equiv CH\xrightarrow[H_2SO_4]{Hg^{2+}}X\xrightarrow[H_2O]{CH_3MgX}Y\xrightarrow{[O]}Z$

(A) ethanal (B) propan-2-ol
(C) propanone (D) propan-1-ol

Q.43 Compounds A & C in the following reaction are

$CH_3CHO\xrightarrow[\text{(ii) }H_2O]{\text{(i) }CH_3MgBr}(A)$

$\xrightarrow{H_2SO_4,\,\Delta}(B)\xrightarrow[\text{oxidation}]{\text{Hydroboration}}(C)$

(A) identical (B) positional isomers
(C) functional isomers (D) optical isomers

Q.44 In nucleophilic addition reactions, the reactivity of carbonyl compounds follows the order –
(A) $HCHO > RCHO > ArCHO > R_2CO > Ar_2CO$
(B) $HCHO > R_2CO > Ar_2CO > RCHO > ArCHO$
(C) $Ar_2CO > R_2CO > ArCHO > RCHO > HCHO$
(D) $ArCHO > Ar_2CO > RCHO > R_2CO > HCHO$

Q.45 Which of the following does not undergo Cannizzaro's reaction?
(A) Benzaldehyde (B) 2-Methylpropanal
(C) p-Methoxybenzaldehyde (D) 2,2-Dimethylpropanal

PART 4 : IDENTIFICATION TEST FOR ALDEHYDES AND KETONES

Q.46 C_2H_5CHO and $(CH_3)_2CO$ can be distinguished by testing with
(A) Phenyl hydrazine (B) Hydroxylamine
(C) Fehling solution (D) Sodium bisulphite

Q.47 Dimethyl ketones are usually characterised through
(A) Tollen's reagent (B) Iodoform test
(C) Schiff's test (D) Benedict's reagent

Q.48 Silver mirror is a test for –
(A) Aldehydes (B) Thio alcohols
(C) Amines (D) Ethers

Q.49 Acetaldehyde and acetone can be distinguished by
(A) Molisch test (B) Bromoform test
(C) Solubility in water (D) Tollen's test

Q.50 Acetaldehyde cannot show
(A) Iodoform test (B) Lucas test
(C) Benedict's test (D) Tollen's test

Q.51 Select the reagent used in the haloform reaction.
(A) Sodium sulphate (B) Sodium carbonate
(C) Sodium hypohalite (D) Sodium hyposulphite

Q.52 The reagent with which both aldehyde and acetone react easily is
(A) Fehling's reagent (B) Grignard reagent
(C) Schiff's reagent (D) Tollen's reagent

Q.53 Composition of Fehling solution A and Fehling solution B is
(A) an aqueous copper sulphate and alkaline sodium potassium tartarate (Rochelle salt) respectively.
(B) an alkaline sodium potassium tartarate (Rochelle salt) and aqueous copper sulphate respectively.
(C) an aqueous copper sulphate (Rochelle salt) and acidic sodium potassium tartarate respectively.
(D) an acidic sodium potassium tartarate (Rochelle salt) and aqueous copper sulphate respectively.

Q.54 To differentiate between pentan-2-one and pentan-3-one a test is carried out. Which of the following is the correct answer?
(A) Pentan-2-one will give silver mirror test
(B) Pentan-2-one will give iodoform test.
(C) Pentan-3-one will give iodoform test
(D) None of these

PART 5 : USES OF ALDEHYDES AND KETONES

Q.55 Choose the correct statement –
(A) Acetaldehyde is used as a starting material in the manufacture of acetic acid
(B) Benzaldehyde is used in perfumery and in dye industries.
(C) Both (A) and (B)
(D) None of these

Q.56 Formalin is an aqueous solution of
(A) Formic acid (B) Formaldehyde
(C) Fluorescein (D) Furfuraldehyde

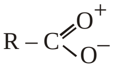
Q.57 Choose the INCORRECT statement –
(A) Acetone and ethyl methyl ketone are common industrial solvents.
(B) Butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.
(C) Both (A) and (B)
(D) None of these

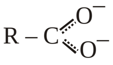
PART 6 : NOMENCLATURE AND STRUCTURE OF CARBOXYLIC ACIDS

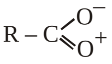
Q.58 The name of the compound having the structure $ClCH_2CH_2COOH$ is –
(A) 3-chloropropanoic acid
(B)2-chloropropanoic acid
(C) 2-chloroethanoic acid
(D) Chlorosuccinic acid

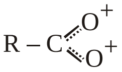
Q.59 IUPAC name of α-acetyl succinic acid is
(A) 2 (1-oxoethyl) butane-1, 4-dioic acid
(B) 3-(2-oxoethyl) butane-1, 4-dioic acid
(C) Hexane-1, 6-dioic acid
(D) Butan-1, 4-dicarboxylic acid

Q.60 The correct structure representation of carboxylate ion is

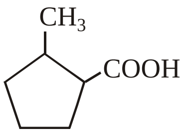
(A) 

(B) 

(C) 

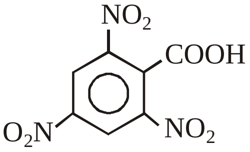
(D) 

Q.61 Which of the following IUPAC names is not correctly matched?

(A) 

3-Cyclopentylpropanoic acid

(B) $(CH_3)_2C = CHCOOH$: 3-Methylbut-2-enoic acid
(C) $PhCH_2CH_2COOH$: 3-Phenylpropanoic acid

(D) 

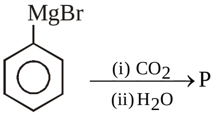
2, 4, 6-Trinitrobenzoic acid

PART 7 : PREPARATION OF CARBOXYLIC ACIDS

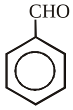
Q.62 α-Hydroxypropanoic acid can be prepared from ethanal by following the steps given in the sequence.
(A) Treat with HCN followed by acidic hydrolysis.
(B) Treat with $NaHSO_3$ followed by reaction with Na_2CO_3.
(C) Treat with H_2SO_4 followed by hydrolysis.
(D) Treat with $K_2Cr_2O_7$ in presence of sulphuric acid.

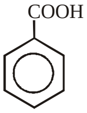
Q.63 Which of the following on hydrolysis forms acetic acid
(A) CH_3CN (B) CH_3OH
(C) C_2H_5OH (D) $C_2H_5NH_2$

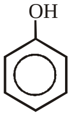
Q.64 When benzyl alcohol is oxidised with $KMnO_4$ the product obtained is –
(A) Benzaldehyde (B) Benzoic acid
(C) CO_2 and H_2O (D) None of these

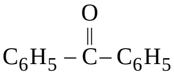
Q.65 

In the reaction, product P is –

(A) 

(B) 

(C) 

(D) 
$C_6H_5-\overset{\overset{\large O}{\|}}{C}-C_6H_5$

Q.66 Acetic acid will be obtained on oxidation of –

(A) Ethanol	(B) Propanal
(C) Methanal	(D) Glyoxal

Q.67 An organic compound (X) with molecular formula $C_9H_{10}O$ gives positive 2,4-DNP and Tollens tests. It undergoes Cannizzaro reaction and on vigorous oxidation it gives 1,4-benzenedi-carboxylic acid. Compound (X) is

(A) benzaldehyde	(B)o-methylbenzaldehyde
(C) p-ethylbenzaldehyde	(D) 2,2-dimethylhexanal

Q.68 The end product (Z) in the given sequence of reaction is

$$CH_3CH=CHCHO \xrightarrow{NaBH_4} X$$

$$\xrightarrow[ZnCl_2]{HCl} Y \xrightarrow[(ii)\ H^+]{(i)\ KCN} Z$$

(A) $CH_3CH=CHCH_2COOH$
(B) $CH_3CH_2CH_2COOH$
(C) $CH_3CH=CHCOOH$
(D) $CH_3CH(Cl)CH_2COOH$

PART 8 : PHYSICAL AND CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

Q.69 Carboxylic acids dimerise due to
(A) high molecular weight
(B) coordinate bonding
(C) intermolecular hydrogen bonding
(D) covalent bonding.

Q.70 Which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide

(A) Acetic acid	(B) n-hexanol
(C) Phenol	(D) Both (A) and (C)

Q.71 A carboxylic acid is converted into its anhydride using

(A) Thionyl chloride	(B) Sulphur chloride
(C) Sulphuric acid	(D)Phosphorus pentoxide

Q.72 Consider the acidity of the carboxylic acids :

(a) PhCOOH	(b) $o-NO_2C_6H_4COOH$
(c) $p-NO_2C_6H_4COOH$	(d) $m-NO_2C_6H_4COOH$

Which of the following order is correct ?

(A) a > b > c > d	(B) b > d > c > a
(C) b > d > a > c	(D) b > c > d > a

Q.73 Higher carboxylic acids are insoluble in water due to
(A) increased hydrophobic interaction of the hydrocarbon part.
(B) decreased hydrophobic interaction of the hydrocarbon part.
(C) Both (A) and (B)
(D) None of the above

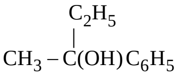
Q.74 Acetic acid can be halogenated in presence of phosphorus and chlorine. Formic acid cannot be halogenated with same way because of
(A) presence of α-H atom in formic acid
(B) presence of α- H atom in acetic acid
(C) absence of α-H atom in CH_3COOH
(D) higher acidic strength of acetic acid than formic acid.

Q.75 Which of the following orders is not correct for the decreasing order of acidic character?
(A) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH > CH_2(Cl)CH_2CH_2COOH > CH_3CH_2CH_2COOH$
(B) $ICH_2COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(C) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$
(D) $HCOOH > CH_3COOH > C_2H_5COOH > (CH_3)_2CHCOOH$

Q.76 In a set of the given reactions, acetic acid yielded a product C.

$$CH_3COOH + PCl_5 \rightarrow A \xrightarrow[\text{anh. } AlCl_3]{C_6H_6} B$$

$\xrightarrow[\text{Ether}]{C_2H_5MgBr} C$. Product C would be

(A) $CH_3CH(OH)C_2H_5$
(B) $CH_3COC_6H_5$
(C) $CH_3CH(OH)C_6H_5$
(D) 
$CH_3-\overset{\overset{\large C_2H_5}{|}}{C}(OH)C_6H_5$

Q.77 Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid because
(A) of greater electronegativity of sp hybridised carbon to which carboxyl carbon attached.
(B) of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached
(C) of ions electronegativity of sp hybridised carbon to which carboxyl carbon is attached.
(D) None of the above

Q.78 – OH group present in alcohols is neutral while it is acidic in carboxylic acid because –
(A) in carboxylic acid – OH group is attached to electron withdrawing carbonyl group.
(B) in alcohols – OH group is attached to alkyl group which is electron withdrawing.
(C) carboxylic group is an electron releasing group.
(D) alcoholic group is an electron withdrawing group.

PART 9 : ACID DERIVATIVES

Q.79 Acetyl chloride is reduced with $LiAlH_4$ the product formed is

(A) Methyl alcohol (B) Ethyl alcohol

(C) Acetaldehyde (D) Acetone

Q.80 Acetamide reacts with P_2O_5 (phosphorus pentaoxide) to give

(A) Methyl cyanide (B) Methyl cyanate

(C) Ethyl cyanide (D) Ethyl isocyanate

Q.81 Which of the reagent(s) is/are used for the conversion of ethanoic acid to ethanoic anhydride?

(A) $SOCl_2, \Delta$ (B) PCl_3, Δ

(C) P_2O_5, Δ (D) All of the above

PART 10 : USES OF CARBOXYLIC ACIDS

Q.82 Which one of the following acid is present in lemon?

(A) Acetic acid (B) Tartaric acid

(C) Citric acid (D) Oxalic acid

Q.83 Vinegar obtained from sugarcane has

(A) CH_3COOH (B) $HCOOH$

(C) C_6H_5COOH (D) CH_3CH_2COOH

Q.84 Which of the following acid is used in rubber, textile, dyeing, leather & electroplating industries?

(A) Hexanedioic acid (B) Ethanoic acid

(C) Methanoic acid (D) Sodium benzoate

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 Compound which gives acetone on ozonolysis

(A) $CH_3-CH=CH-CH_3$ (B) $(CH_3)_2C=C(CH_3)_2$

(C) $C_6H_5CH=CH_2$ (D) $CH_3CH=CH_2$

Q.2 From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide

(A) $HCHO$ (B) CH_3CHO

(C) CH_3COCH_3 (D) CO_2

Q.3 Methyl ethyl ketone is prepared by the oxidation of

(A) 2-propanol (B) 1-butanol

(C) 2-butanol (D) t-butyl alcohol

Q.4 Ketones are prepared by

(A) Clemmensen's reduction (B) Cannizzaro reaction

(C) Rosenmund's reduction (D) Oppenaur's oxidation

Q.5 Acetophenone can be prepared by

(1) Oxidation of 1-phenylethanol.

(2) Reaction of benzalthanol with methyl magnesium bromide.

(3) Friedel Craft's reaction of benzene with acetyl chloride.

(4) Distillation of calcium benzoate.

Correct statements are –

(A) 1 and 2 (B) 1 and 4

(C) 1 and 3 (D) 3 and 4

Q.6 Which one of the following pairs is not correctly matched

(A) $>C=O \xrightarrow{\text{Clemenson's reduction}} >CH_2$

(B) $>C=O \xrightarrow{\text{Wolf -Kishner reduction}} >CHOH$

(C) $-COCl \xrightarrow{\text{Rosenmund's reduction}} CHO$

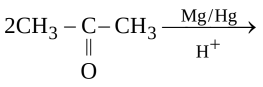
(D) $-C\equiv N \xrightarrow{\text{Stephen reduction}} CHO$

Q.7 $CH_3CH=CHCHO$ is oxidised to

$CH_3CH=CHCOOH$ using –

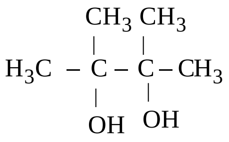
(A) Alkaline $KMnO_4$ (B) Selenium dioxide

(C) Ammoniacal $AgNO_3$ (D) All of these

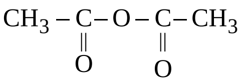
Q.8 

$2CH_3-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[H^+]{Mg/Hg}$ Product,

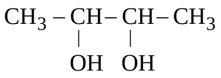
product in the reaction is

(A) 

$H_3C-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

(B) 

$CH_3-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3$

(C) 

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$

(D) None of these

Q.9 The reaction of an aldehyde with hydroxylamine gives a product which is called

(A) Aminohydroxide (B) Hydrazone

(C) Semicarbazone (D) Oxime

Q.10 Which of the following products is obtained by the oxidation of propionaldehyde

(A) Acetic acid

(B) Formic acid and acetic acid

(C) Propanoic acid

(D) n-propyl alcohol

Q.11 Pyrolysis of acetone gives $CH_2=C=O$ called

(A) Methylene oxide (B) Ketene

(C) Methyl carbon monoxide (D) Methone

Q.12 Schiff's reagent gives pink colour with

(A) Aldehydes (B) Ethers

(C) Ketones (D) Carboxylic acid

Q.13 When formic acid reacts with PCl_5 it forms

(A) Formyl chloride (B) Acetyl chloride

(C) Methyl chloride (D) Propionyl chloride

Q.14 Reaction of acetaldehyde with HCN followed by hydrolysis gives a compound which shows –

(A) Optical isomerism (B) Geometrical isomerism

(C) Metamerism (D) Tautomerism

Q.15 $CH_3-CH_2-C\equiv CH \xrightarrow[H_2O]{R}$ Butanone, R is

(A) Hg^{++} (B) $KMnO_4$

(C) $KClO_3$ (D) $K_2Cr_2O_7$

Q.16 Acetophenone is prepared by the reaction of which of the following in the presence of $AlCl_3$ catalyst

(A) Phenol and acetic acid

(B) Benzene and acetone

(C) Benzene and acetyl chloride

(D) Phenol and acetone

Q.17 Acetaldehyde and acetone differ in their reaction with –
(A) Sodium bisulphite (B) Ammonia
(C) Phosphorus pentachloride (D) Phenyl hydrazine

Q.18 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(A) Benzyl alcohol and sodium formate
(B) Sodium benzoate and methyl alcohol
(C) Sodium benzoate and sodium formate
(D) Benzyl alcohol and methyl alcohol

Q.19 Which gives lactic acid on hydrolysis after reacting with HCN
(A) HCHO (B) CH_3CHO
(C) C_6H_5CHO (D) CH_3COCH_3

Q.20 When CH_3COCH_3 reacts with Cl_2 and NaOH, which of the following is formed –
(A) $CHCl_3$ (B) CCl_4
(C) CCl_2H_2 (D) CH_3Cl

Q.21 Benzaldehyde and acetaldehyde can be differentiated by
(A) HCN (B) NH_2OH
(C) Hydrazine (D) NaOH solution

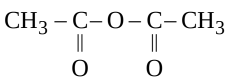
Q.22 Which is not true about acetophenone
(A) Reacts to form 2, 4-dinitorphenyl hydrazine.
(B) Reacts with Tollen's reagent to form silver mirror.
(C) Reacts with I_2/NaOH to form iodoform.
(D) On oxidation with alkaline $KMnO_4$ followed by hydrolysis gives benzoic acid.

Q.23 Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is
(A) MeCOCl (B) MeCHO
(C) MeCOOMe (D) MeCOOCOMe

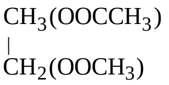
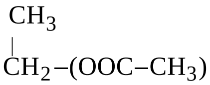
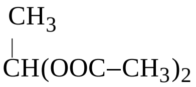
Q.24 The vapour of a carboxylic acid HA when passed over MnO_2 at 573 K yields propanone. The acid HA is
(A) Methanoic acid (B) Ethanoic acid
(C) Propanoic acid (D) Butanoic acid

Q.25 When CH_3COOH reacts with CH_3-Mg-X
(A) CH_3COX is formed (B) Hydrocarbon is formed
(C) Acetone is formed (D) Alcohol is formed

Q.26 Which class of compounds shows H-bonding even more than in alcohols
(A) Phenols (B) Carboxylic acids
(C) Ethers (D) Aldehydes

Q.27 $2CH_3COOH \xrightarrow[300^oC]{MnO} A$, product 'A' in the reaction is
(A) CH_3CH_2CHO (B) CH_3-CH_2-OH
(C) CH_3COCH_3 (D)

$\begin{array}{c} CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \end{array}$

Q.28 RCOOH on treatment with PCl_5 and KCN, is subjected to hydrolysis followed by Clemmensen's reduction, the product obtained is –
(A) RCH_2-COCl (B) RCH_2-COOH
(C) RCOCN (D) RCN

Q.29 CH_3COOH is reacted with $CH\equiv CH$ in presence of Hg^{++} the product is
(A)

$\begin{array}{l} CH_3(OOCCH_3)\\ |\\ CH_2(OOCH_3)\end{array}$
(B)

$\begin{array}{l} CH_3\\ |\\ CH_2-(OOC-CH_3)\end{array}$
(C)

$\begin{array}{l} CH_3\\ |\\ CH(OOC-CH_3)_2\end{array}$
(D) None of these

Q.30 X is heated with soda lime and gives ethane. X is
(A) Ethanoic acid (B) Methanoic acid
(C) Propanoic acid (D) Either (A) or (C)

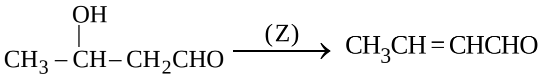
Q.31 Which of the following is an amphoteric acid
(A) Glycine (B) Salicylic acid
(C) Benzoic acid (D) Citric acid

Q.32 Acetaldehyde reacts with Cl_2 (in excess) to give
(A) Chloral (B) Chloroform
(C) Acetic acid (D) Trichloroacetic acid

Q.33 Toluene is converted to ____on treating with chromic oxide in acetic anhydride with aqueous acid.
(A) Benzyl diacetate (B) Benzylideneacetate
(C) Benzylacetate (D) Benzaldehyde

Q.34 Fill in the reagents for the given conversion:

$$CH_3COCl \xrightarrow{(X)} CH_3CHO \xrightarrow{(Y)}$$


$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CHO \xrightarrow{(Z)} CH_3CH=CHCHO$$

(A) X-Pd/$BaSO_4$, Y-dil. NaOH, Z-Heat
(B) X-NaOH, Y-Hydrolysis, Z-heat
(C) X-I_2/NaOH, Y-$LiAlH_4$, Z-H_3O^+
(D) X-CrO_3, Y-Warm, Z-CO_2

Q.35 Aldehydes other than formaldehyde react with Grignard's reagent to give addition products which on hydrolysis give –
(A) tertiary alcohols (B) secondary alcohols
(C) primary alcohols (D) carboxylic acids.

Q.36 The final product (Y) in the following sequence of chemical reaction is

$$CH_3OH \xrightarrow[300°C]{Cu} X \xrightarrow{NaOH} Y + CH_3OH$$

(A) an alkene
(B) a carboxylic acid
(C) an aldehyde
(D) sodium salt of carboxylic acid.

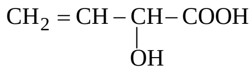
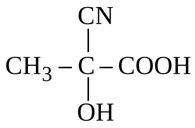
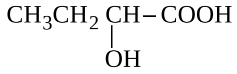
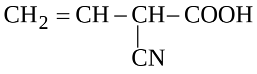
Q.37 Few simple chemical tests are given below to differentiate between the pairs of compounds. Which of the following tests is not correct for differentiation?
(A) Propanal and propanone – Silver mirror test
(B) Acetophenone and benzophenone – Iodoform test
(C) Ethanal and propanal – Fehling's test
(D) Benzoic acid and ethyl benzoate – Sodium bicarbonate test

Q.38 Which of the following compounds does not react with $NaHSO_3$?
(A) HCHO (B) $C_6H_5COCH_3$
(C) CH_3COCH_3 (D) CH_3CHO

Q.39 Which of the following does not answer iodoform test?
(A) n-Butyl alcohol (B) sec-Butyl alcohol
(C) Acetophenone (D) Acetaldehyde

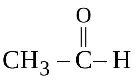
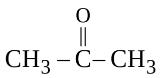
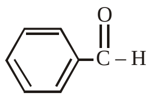
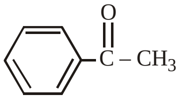
Q.40 Study the following sequence of reactions and identify the product (Y).

$$CH_3CHO + HCHO \xrightarrow[\text{heat}]{\text{dil. NaOH}} X \xrightarrow[H_3O^+]{HCN} Y$$

(A) 
$CH_2=CH-\underset{OH}{\underset{|}{CH}}-COOH$
(B) 
$CH_3-\overset{CN}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-COOH$
(C) 
$CH_3CH_2\underset{OH}{\underset{|}{CH}}-COOH$
(D) 
$CH_2=CH-\underset{CN}{\underset{|}{CH}}-COOH$

Q.41 Propanal on treatment with dilute sodium hydroxide gives
(A) $CH_3CH_2CH_2CH_2CH_2CHO$
(B) $CH_3CH_2CH(OH)CH_2CH_2CHO$
(C) $CH_3CH_2CH(OH)CH(CH_3)CHO$
(D) CH_3CH_2COOH

Q.42 Which of the following compounds is most reactive towards nucleophilic addition reactions?

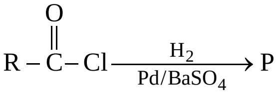
(A) 
$CH_3-\overset{O}{\overset{||}{C}}-H$
(B) 
$CH_3-\overset{O}{\overset{||}{C}}-CH_3$
(C) 
(D) 

Q.43 Identify (X), (Y) and (Z) in the given reaction.

$$CH_3COCH_3 \xrightarrow[\text{Heat}]{I_2+NaOH} X \xrightarrow[\text{Heat}]{Ag} \xrightarrow[\text{Heat}]{H_2SO_4/HgSO_4} Z$$

(A) $X = CHI_3, Y = CH_3CHO, Z = HCHO$
(B) $X = CHI_3, Y = CH_3OH, Z = CH_3CHO$
(C) $X = CHI_3, Y = CH\equiv CH, Z = CH_3CHO$
(D) $X = CH_3COCl_3, Y = CH_2 = CH_2,$
$Z = CH_3CHO$

Q.44 In the following reaction, product (P) is


$R-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} P$

(A) RCHO (B) RCH_3
(C) RCOOH (D) RCH_2OH

Q.45 A compound (X) having molecular formula $C_4H_8O_2$ is hydrolysed by water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). (Z) on oxidation with chromic acid gives (Y). (X), (Y) and (Z) are
(A) X-CH_3COOCH_3, Y-CH_3COOH, Z-CH_3OH
(B) X-$CH_3COOC_2H_5$, Y-CH_3COOH, Z-C_2H_5OH
(C) X-$C_2H_5COOCH_3$, Y-C_2H_5COOH, Z-C_2H_5OH
(D) X-$CH_3COOC_2H_5$ Y-C_2H_5COOH, Z-CH_3OH

Q.46 An organic compound of molecular formula C_3H_6O did not give a silver mirror with Tollens' reagent but give an oxime with hydroxylamine. It may be –
(A) $CH_2=CH–CH_2–OH$ (B) CH_3COCH_3
(C) CH_3CH_2CHO (D) $CH_2=CH–OCH_3$

Q.47 Which of the following statements is correct regarding formic acid?
(A) It is a reducing agent.
(B) It is a weaker acid than acetic acid.
(C) It is an oxidising agent.
(D) When its calcium salt is heated, it forms acetone.

Q.48 Which of the following statements is not correct?
(A) Aldehydes and ketones are functional isomers.
(B) Formaldehyde reacts with ammonia to form hexamethylenetetramine.
(C) $LiAlH_4$ converts ketones into sec-alcohols.
(D) Ethanal and propanal give positive iodoform test.

Q.49 Which of the following statements is incorrect?
(A) $FeCl_3$ is used in the detection of phenols.
(B) Fehling solution is used in the detection of glucose.
(C) Tollens' reagent is used in the detection of unsaturation.
(D) $NaHSO_3$ is used in the detection of carbonyl compounds.

Q.50 What is the product formed when ketones react with ethylene glycol in the presence of dry HCl gas?
(A) Ethylene glycol ketal.
(B) Ethylene glycol hemiketal.
(C) Cyanohydrin.
(D) Oxalic acid.

Q.51 What are the correct steps to convert acetaldehyde to acetone?
(A) CH_3MgBr, H_2O, Oxidation
(B) Oxidation, $Ca(OH)_2$, Heat
(C) Reduction, KCN, Hydrolysis
(D) Oxidation, C_2H_5ONa, Heat

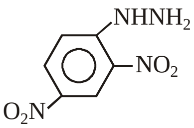
Q.52 Aldehydes and ketones
(A) are insoluble in organic solvents like benzene, ether, methanal, chloroform etc
(B) solubility increases rapidly on increasing the length of the alkyl chain.
(C) are used in the blending of perfumes and flavouring agents.
(D) All of the above

Q.53 Which of the following group(s) is/are identified by the haloform reaction?
(A) CH_3CO group (B) $CH_3CH(OH)$ group
(C) $CH_3 – O$ group (D) Both (A) and (B)

Q.54 The reagent which does not react with both, acetone and benzaldehyde is –
(A) sodium hydrogensulphite (B) phenyl hydrazine
(C) Fehling's solution (D) Grignard reagent

Q.55 The oxidation of toluene to benzaldehyde by chromyl chloride is called –
(A) Etard reaction
(B) Riemer-Tiemann reaction
(C) Wurtz reaction
(D) Cannizzaro's reaction.

Q.56 Which of the following compounds will give a coloured crystalline compound with

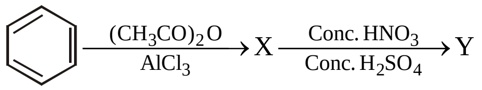


(A) CH_3COCl
(B) $CH_3COOC_2H_5$
(C) CH_3COCH_3
(D) CH_3CONH_2

Q.57 Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?

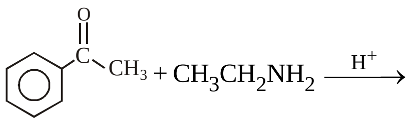
(A) Butan-1-ol
(B) Butan-2-ol
(C) Both of these
(D) None of these

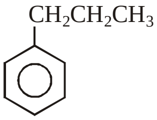
Q.58 Identify the products (X) and (Y) in the given reaction:

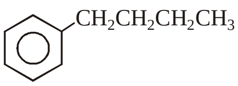


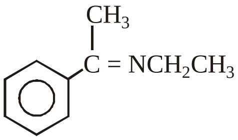
(A) X = Acetophenone, Y = m-Nitroacetophenone
(B) X = Toluene, Y = m-Nitroacetoluene
(C) X = Acetophenone, Y=o and p-Dinitroacetophenone
(D) X = Benzaldehyde, Y = m-Nitrobenzaldehyde

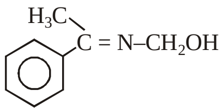
Q.59 Find the product of the given reaction.



(A) 

(B) 

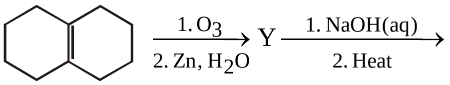
(C) 

(D) 

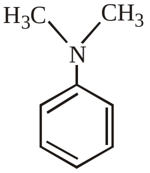
EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

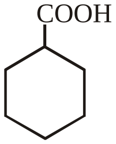
NOTE : The answer to each question is a NUMERICAL VALUE.

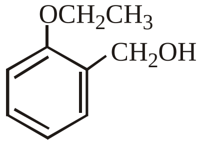
Q.1 In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is:

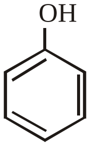


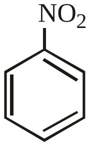
Q.2 Amongst the following, the total number of compounds soluble in aqueous NaOH is :

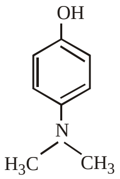


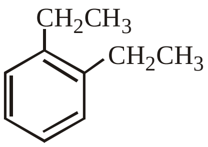


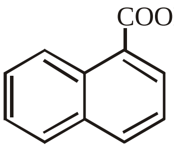




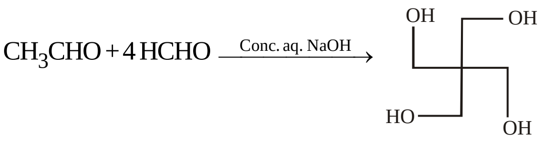




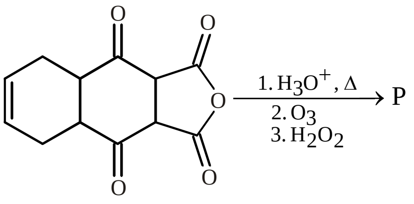




Q.3 The number of aldol reaction(s) that occurs in the given transformation is



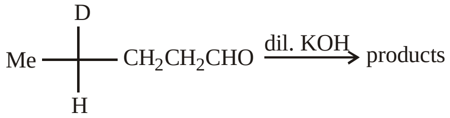
Q.4 The total number of carboxylic acid groups in the product P is :



Q.5 Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$. (NOTE : stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are

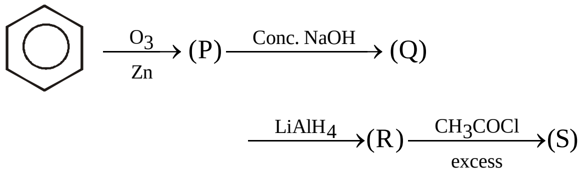
Q.6 $PhCOEt + Mg \xrightarrow{\text{Ether}} ?$

The number of stereoisomers shown by the product of the following reaction would be –

Q.7 

(R) 4-Deutero Pentanal

How many aldol product are formed –

Q.8 

Molecular weight changed from (R) to (S).

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

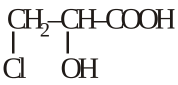
Q.1 End product of the following reaction is –**[AIEEE-2002]**

$CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} \xrightarrow{\text{Alcoholic KOH}}$

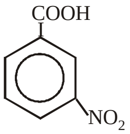
(A) 
$CH_3\underset{OH}{CH}COOH$

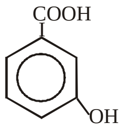
(B) 
$\underset{OH}{CH_2}CH_2COOH$

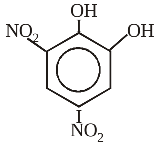
(C) $CH_2=CHCOOH$

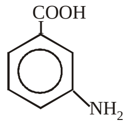
(D) 
$\underset{Cl}{CH_2}-\underset{OH}{CH}-COOH$

Q.2 Picric acid is – **[AIEEE-2002]**

(A) 

(B) 

(C) 

(D) 

Q.3 In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it **[AIEEE-2003]**

(A) The anion $HCOO^-$ has two resonating structures.

(B) The anion is obtained by removal of a proton from the acid molecule.

(C) Electronic orbitals of carbon atom are hybridised.

(D) The C = O bond is weaker than the C – O bond.

Q.4 When $CH_2 = CHCOOH$ is reduced with $LiAlH_4$, the compound obtained is : **[AIEEE-2003]**

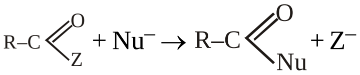
(A) $CH_3CH_2CH_2OH$ (B) CH_3CH_2CHO

(C) CH_3CH_2COOH (D) $CH_2=CHCH_2OH$

Q.5 The general formula $C_nH_{2n}O_2$ could be for open chain : **[AIEEE-2003]**

(A) Diols (B) Dialdehydes

(C) Diketones (D) Carboxylic acid

Q.6 Rate of the reaction : 

is fastest when Z is : **[AIEEE-2004]**

(A) $OCOCH_3$ (B) NH_2

(C) OC_2H_5 (D) Cl

Q.7 Consider the acidity of the carboxylic acids **[AIEEE-2004]**

(1) PhCOOH (2) o-$NO_2C_6H_4COOH$

(3) p-$NO_2C_6H_4COOH$ (4) m-$NO_2C_6H_4COOH$

Which of the following order is correct ? **[AIEEE-2004]**

(A) 2 > 3 > 4 > 1 (B) 2 > 4 > 3 > 1

(C) 2 > 4 > 1 > 3 (D) 1 > 2 > 3 > 4

Q.8 On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[AIEEE-2004]**

(A) $CH_3Cl + C_2H_5COONa$

(B) $CH_3COONa + C_2H_5OH$

(C) $CH_3COCl + C_2H_5OH + NaOH$

(D) $CH_3COOC_2H_5 + NaCl$

Q.9 Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon **[AIEEE-2004]**

(A) Butan-2-one (B) Acetic acid

(C) Acetamide (D) Ethyl acetate

Q.10 Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon **[AIEEE-2004]**

(A) Ethyl acetate (B) Acetic acid

(C) Acetamide (D) Butan-2-one

Q.11 Which one of the following does not have sp^2 hybridized carbon ? **[AIEEE-2004]**

(A) Acetone (B) Acetic acid

(C) Acetonitrile (D) Acetamide

Q.12 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

(a) PhCOOH (b) $o-NO_2C_6H_4COOH$

(c) $p-NO_2C_6H_4COOH$ (d) $m-NO_2C_6H_4COOH$

Which of the following order is correct ?

(A) a > b > c > d (B) b > d > c > a

(C) b > d > a > c (D) b > c > d > a

Q.13 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE-2004]**

(A) Phenol (B) Benzaldehyde

(C) Butanal (D) Benzoic acid

Q.14 The best reagent to convert pent-3-en-2-ol into pent–3-in-2-one is - **[AIEEE-2005]**

(A) Acidic dichromate

(B) Acidic permanganate

(C) Pyridinium chloro–chromate

(D) Chromic anhydride in glacial acetic acid

Q.15 The increasing order of the rate of HCN addition to compounds A – D is - **[AIEEE 2006]**

(a) HCHO (b) CH_3COCH_3

(c) $PhCOCH_3$ (d) $PhCOCH_3$

(A) d < b < c < a (B) d < c < b < a

(C) c < d < b < a (D) a < b < c < d

Q.16 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is – **[AIEEE-2007]**

(A) benzophenone (B) acetophenone

(C) benzoic acid (D) benzyl alcohol

Q.17 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is – **[AIEEE-2007]**

(A) benzophenone (B) acetophenone

(C) benzoic acid (D) benzyl alcohol

Q.18 Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE 2009]**

(A) CH_3COCl (B) CH_3CH_2Cl

(C) CH_2ClCH_2Cl (D) CH_3CHCl_2

Q.19 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : **[AIEEE-2009]**

(A) CH_3OH (B) HCHO

(C) CH_3COCH_3 (D) CH_3COOH

Q.20 In Cannizzaro reaction given below

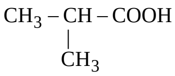
$2PhCHO \xrightarrow{:OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$ the slowest step is – **[AIEEE-2009]**

(A) the deprotonation of $PhCH_2OH$.
(B) the attack of $:OH^{\ominus}$ at the carboxyl group.
(C) the transfer of hydride of the carbonyl group.
(D) the abstraction of proton from the carboxylic group.

Q.21 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of –
(A) two ethylenic double bonds **[AIEEE-2011]**
(B) a vinyl group
(C) an isopropyl group
(D) an acetylenic triple bond

Q.22 Sodiumethoxide has reactedwith ethanoyl chloride. The compound that is produced in the above reaction is : **[AIEEE-2011]**
(A) Diethyl ether (B) 2-Butanone
(C) Ethyl chloride (D) Ethyl ethanoate

Q.23 Silver Mirror test is given by which one of the following compounds ? **[AIEEE-2011]**
(A) Acetaldehyde (B) Acetone
(C) Formaldehyde (D) Benzophenone

Q.24 An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is – **[JEE MAIN 2013]**
(A) CH_3COOH (B) $CH_3CH_2CH_2COOH$
(C) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$
(D) CH_3CH_2COOH

Q.25 In the reaction,

$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_3} B \xrightarrow{Alc.\ KOH} C$

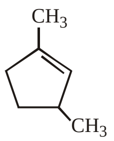
the product C is – **[JEE MAIN 2014]**
(A) Ethylene (B) Acetyl chloride
(C) Acetaldehyde (D) Acetylene

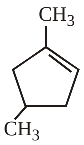
Q.26 In the following sequence of reactions :

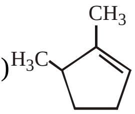
$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C,$

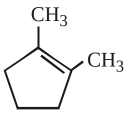
the product C is – **[JEE MAIN 2015]**
(A) $C_6C_5CH_3$ (B) $C_6C_5CH_2OH$
(C) C_6C_5CHO (D) C_6C_5COOH

Q.27 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE MAIN 2015]**

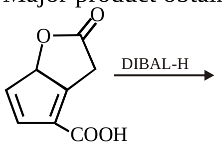
(A) 

(B) 

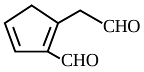
(C) 

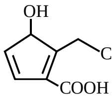
(D) 

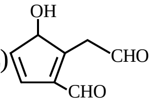
Q.28 Major product obtained in the reaction

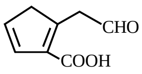


[JEE MAIN 2017]

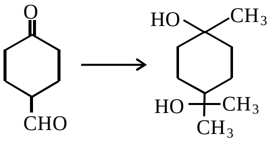
(A) 

(B) 

(C) 

(D) 

Q.29 The correct sequence of reagents for the following conversion will be

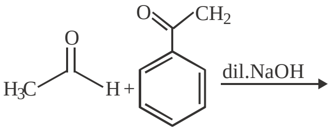


[JEE MAIN 2017]

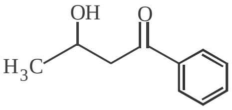
(A) $[Ag(NH_3)_2]^+OH^-$, CH_3MgBr, H^+/CH_3OH
(B) $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH, CH_3MgBr
(C) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+OH^-$
(D) CH_3MgBr, $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH

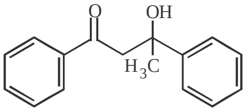
Q.30 The correct decreasing order for acid strength is : **[JEE MAIN 2019 (Jan)]**
(A) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$
(B) $FCH_2COOH > NCCH_2COOH > NO_2CHCOOH > ClCH_2COOH$
(C) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$
(D) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

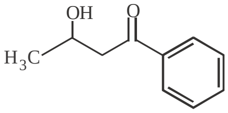
Q.31 The major product formed in the following reaction is:

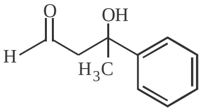


[JEE MAIN 2019 (Jan)]

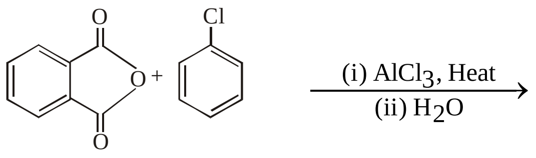
(A) 

(B) 

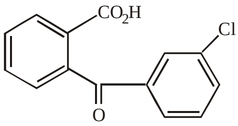
(C) 

(D) 

Q.32 The major product of the following reaction is:



[JEE MAIN 2019 (April)]

(A)


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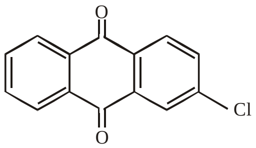

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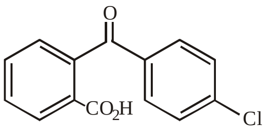
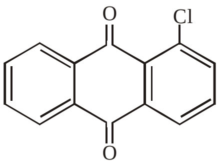


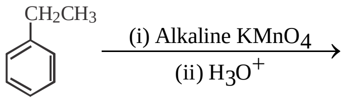
(D)


Q.33 Which of the following compounds will show the maximum enol content? **[JEE MAIN 2019 (APRIL)]**

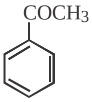
(A) $CH_3COCH_2COCH_3$ (B) CH_3COCH_3

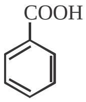
(C) $CH_3COCH_2CONH_2$ (D) $CH_3COCH_2COOC_2H_5$

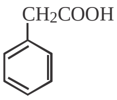
Q.34 The mojor product of the following reaction is :

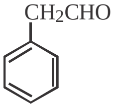


[JEE MAIN 2019 (APRIL)]

(A)


(B)


(C)


(D)


Q.35 In the following reaction

Carbonyl compound + MeOH $\xrightleftharpoons{\text{HCl}}$ Acetal

Rate of the reaction is the highest for :

[JEE MAIN 2019 (APRIL)]

(A) Acetone as substrate and methanol in stoichiometric amount.

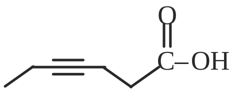
(B) Propanal as substrate and methanol in stoichiometric amount.

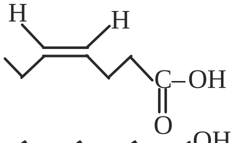
(C) Acetone as substrate and methanol in excess.

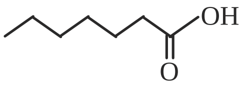
(D) Propanal as substrate and methanol in excess.

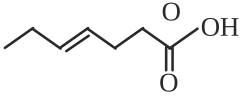
Q.36 What is the product of following reaction ?

Hex-3-ynal $\xrightarrow[\substack{\text{(ii) PBr}_3\\ \text{(iii) Mg/ether}\\ \text{(iv) CO}_2/\text{H}_3\text{O}^+}]{\text{(i) NaBH}_4}$ **[JEE MAIN 2020 (JAN)]**

(A)


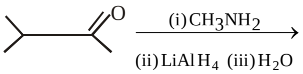
(B)


(C)


(D)


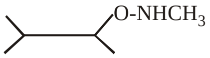
EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 The major organic product formed from the following reaction:

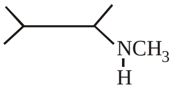


is **[AIPMT 2005]**

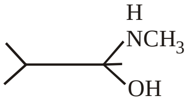
(A)



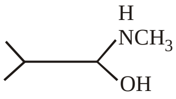
(B)



(C)



(D)

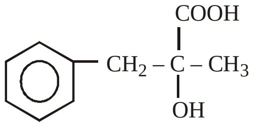


Q.2 In a set of reactions acetic acid yields a product D.

$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhy. }AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of D would be – **[AIPMT 2005]**

(A)



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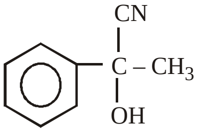
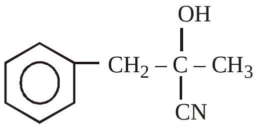
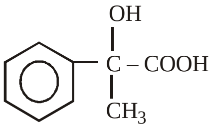


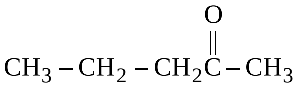
(C)



(D)



Q.3 Nucleophilic addition reaction will be most favoured in:- **[AIPMT 2006]**

(A) 

$CH_3-CH_2-CH_2\overset{\overset{O}{\|}}{C}-CH_3$ (B) $(CH_3)_2C=O$

(C) CH_3CH_2CHO (D) CH_3CHO

Q.4 A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is: **[AIPMT 2006]**

(A) Acetaldehyde (B) Acetone

(C) diethyl ketone (D) Formaldehyde

Q.5 In a set of reactions propionic acid yielded a compound D.

$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[Br_2]{KOH} D$$

The structure of D would be – **[AIPMT 2006]**

(A) $CH_3CH_2CONH_2$ (B) $CH_3CH_2NHCH_3$

(C) $CH_3CH_2NH_2$ (D) $CH_3CH_2CH_2NH_2$

Q.6 Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields – **[AIPMT 2006]**

(A) acetoacetic ester (B) methyl acetoacetate

(C) ethyl propionate (D) ethyl butyrate

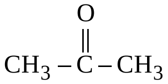
Q.7 Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called **[AIPMT 2007]**

(A) Cope reduction (B) Dow reduction

(C) Wolf-Kishner reduction (D) Clemmensen reduction

Q.8 Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid **[AIPMT 2007]**

(A) C_6H_5CHO (B) $CH_3CH_2CH_2CHO$

(C) 

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (D) $C_6H_5CH_2CHO$

Q.9 The product formed in Aldol condensation is – **[AIPMT 2007]**

(A) a beta-hydroxy aldehyde or a beta-hydroxy ketone.

(B) an alpha-hydroxy aldehyde or ketone.

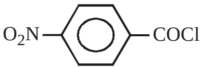
(C) an alpha, beta unsaturated ester

(D) a beta-hydroxy acid

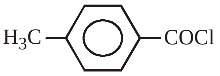
Q.10 Consider the following compounds

(i) C_6H_5COCl

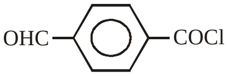
(ii)



(iii)



(iv)



The correct decreasing order of their reactivity towards hydrolysis is – **[AIPMT 2007]**

(A) (i) > (ii) > (iii) > (iv) (B) (iv) > (ii) > (i) > (iii)

(C) (ii) > (iv) > (i) > (iii) (D) (ii) > (iv) > (iii) > (i)

Q.11 Which of the following represents the correct order of the acidity in the given compounds – **[AIPMT 2007]**

(A) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

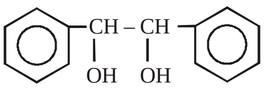
(B) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

(C) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

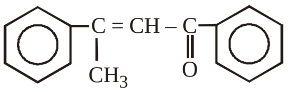
(D) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

Q.12 Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure : **[AIPMT 2008]**

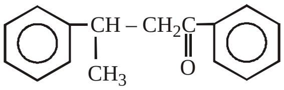
(A)



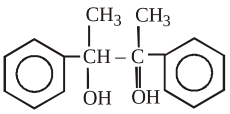
(B)



(C)



(D)



Q.13 A strong base can abstract an α-hydrogen from

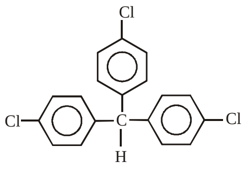
(A) Alkane (B) Alkene **[AIPMT 2008]**

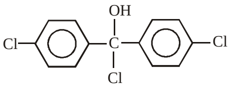
(C) Amine (D) Ketone

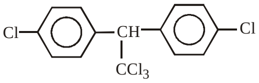
Q.14 The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of **[AIPMT 2008]**

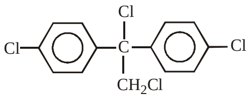
(A) Acyl chloride > Ester > Acid anhydride > Amide
(B) Acyl chloride > Acid anhydride > Ester > Amide
(C) Ester > Acyl chloride > Amide > Acid anhydride
(D) Acid anhydride > Amide > Ester > Acyl chloride

Q.15 Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces: **[AIPMT 2009]**

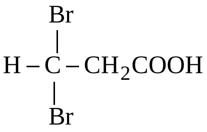
(A) 

(B) 

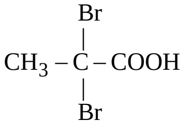
(C) 

(D) 

Q.16 Propionic acid with $Br_2 | P$ yields a dibromo product. Its structure would be **[AIPMT 2009]**

(A) 
$$\mathrm{H-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2COOH}$$

(B) CH_2Br-CH_2-COBr

(C) 
$$\mathrm{CH_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-COOH}$$

(D) $CH_2Br-CHBr-COOH$

Q.17 Which of the following reactions will not result in the formation of carbon-carbon bonds **[AIPMT (PRE) 2010]**

(A) Reimer-Tieman reaction (B) Cannizaro reaction
(C) Wurtz reaction (D) Friedel-Crafts acylation

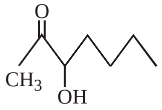
Q.18 Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine **[AIPMT (PRE) 2010]**

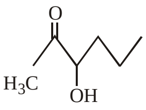
(A) NaOH-Br_2 (B) Sodalime
(C) Hot conc. H_2SO_4 (D) PCl_5

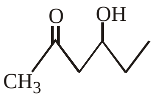
Q.19 Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is **[AIPMT (PRE) 2010]**

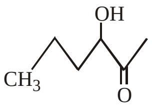
(A) CH_3COOCH_3 (B) CH_3CONH_2
(C) $CH_3COOCOCH_3$ (D) CH_3COCl

Q.20 Which one of the following compounds will be most readily dehydrated? **[AIPMT (MAINS) 2010]**

(A) 

(B) 

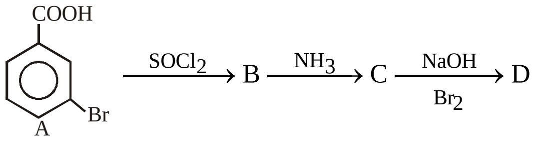
(C) 

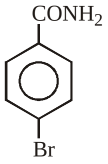
(D) 

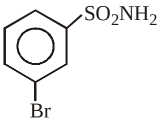
Q.21 Clemmensen reduction of a ketone is carried out in the presence of which of the following? **[AIPMT (PRE) 2011]**

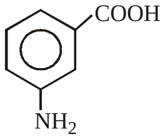
(A) H_2 and Pt as catalyst (B) Glycol with KOH
(C) Zn-Hg with HCl (D) $LiAlH_4$

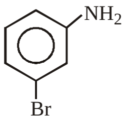
Q.22 In a set of reactions m-bromobenzoic acid gave a product D. Identify the product D. **[AIPMT (PRE) 2011]**



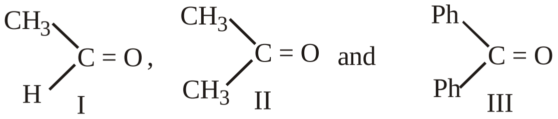
(A) 

(B) 

(C) 

(D) 

Q.23 The order of reactivity of phenylmagnesium bromide (PhMgBr) with the following compounds :

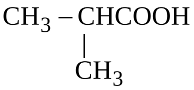


[AIPMT (MAINS) 2011]

(A) III > II > I (B) II > I > III
(C) I > III > II (D) I > II > III

Q.24 An organic compound 'A' on treatment with NH_3 gives B which on heating gives C, C when treated with Br_2 in the presence of KOH produces ethylamine. Compound A is : **[AIPMT (MAINS) 2011]**

(A) CH_3COOH (B) $CH_3CH_2CH_2COOH$

(C) 
$$\mathrm{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}COOH}$$

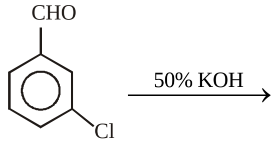
(D) CH_3CH_2COOH

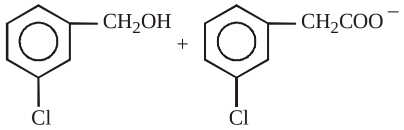
Q.25 Match the compounds given in List-I with List-II and select the suitable option using the code given below : **[AIPMT (MAINS) 2011]**

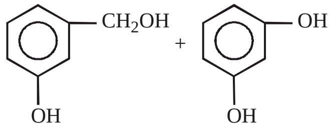
List-I	**List-II**
(a) Benzaldehyde	(i) Phenolphthalein
(b) Phthalic anhydride	(ii) Benzoin condensation
(c) Phenyl benzoate	(iii) Oil of wintergreen
(d) Methyl salicylate	(iv) Fries rearrangement

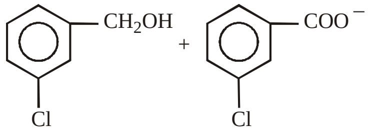
Code :
(A) - (a) - (iv), (b) - (i), (c) - (iii), (d) - (ii)
(B) - (a) - (iv), (b) - (ii), (c) - (iii), (d) - (i)
(C) - (a) - (ii), (b) - (iii), (c) - (iv), (d) - (i)
(D) - (a) - (ii), (b) - (i), (c) - (iv), (d) - (iii)

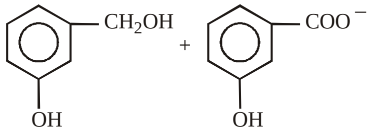
Q.26 Predict the product in the given reaction. **[AIPMT (PRE) 2012]**



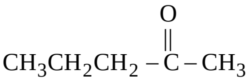
(A) 

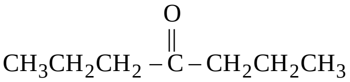
(B) 

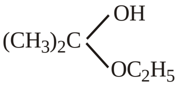
(C) 

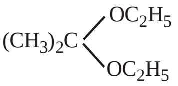
(D) 

Q.27 Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is –

(A)  $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ **[AIPMT (PRE) 2012]**

(B)  $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

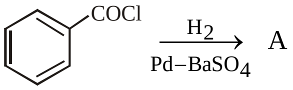
(C) 

(D) 

Q.28 The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is : **[AIPMT (PRE) 2012]**

(A) B > A > D > C
(B) B > D > C > A
(C) A > B > C > D
(D) A > C > B > D

Q.29 Consider the following reaction :



The product 'A' is : **[AIPMT (MAINS) 2012]**

(A) C_6H_5CHO
(B) C_6H_5OH
(C) $C_6H_5COCH_3$
(D) C_6H_5Cl

Q.30 Consider the reaction :

$RCHO + NH_2NH_2 \rightarrow RCH = N - NH_2$

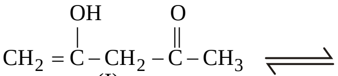
What sort of reaction is it ? **[AIPMT (MAINS) 2012]**

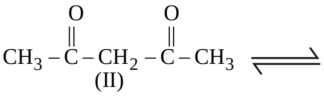
(A) Electrophilic addition - elimination reaction
(B) Free radical addition - elimination reaction
(C) Electrophilic substitution-elimination reaction
(D) Nucleophilic addition- elimination reaction

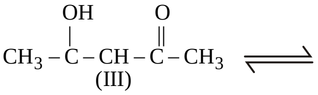
Q.31 Which of the following compounds will give a yellow precipitate with iodine and alkali **[AIPMT (MAINS) 2012]**

(A) Acetophenone
(B) Methyl acetate
(C) Acetamide
(D) 2-Hydroxypropane

Q.32 The order of stability of the following tautomeric compounds is – **[NEET 2013]**

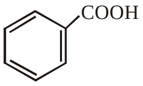

$CH_2=\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$
(I)


$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$
(II)

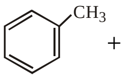

$CH_3-\overset{OH}{\overset{|}{C}}-CH-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$
(III)

(A) II > III > I
(B) I > II > III
(C) III > II > I
(D) II > I > III

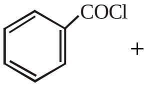
Q.33 Reaction by which Benzaldehyde cannot be prepared – **[NEET 2013]**

(A) 

+ Zn/Hg and conc. HCl

(B) 

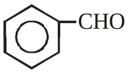
+ CrO_2Cl_2 in CS_2 followed by $H_3O^{\oplus}$

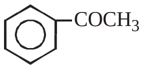
(C) 

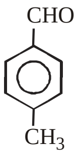
+ H_2 in presence of Pd + $BaSO_4$

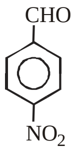
(D)  + CO + HCl in presence of anhydrous $AlCl_3$

Q.34 Which one is most reactive towards Nucleophilic addition reaction? **[AIPMT 2014]**

(A) 

(B) 

(C) 

(D) 

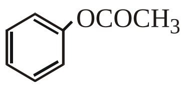
Q.35 An organic compound 'X' having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the Iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be : **[AIPMT 2015]**

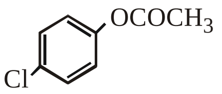
(A) 2-pentanone
(B) 3-pentanone
(C) n-amyl alcohol
(D) pentanal

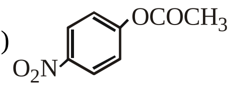
Q.36 The oxidation of benzene by V_2O_5 in the presence of air produces : **[RE-AIPMT 2015]**
(A) benzoic acid (B) benzaldehyde
(C) benzoic anhydride (D) maleic anhydride

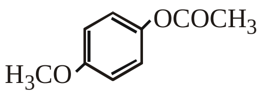
Q.37 Reaction of carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is :
(A) hydrocyanic acid **[RE-AIPMT 2015]**
(B) sodium hydrogen sulphite
(C) a Grignard reagent
(D) hydrazine in presence of feebly acidic solution

Q.38 Which one of the following esters gets hydrolysed most easily under alkaline conditions ? **[RE-AIPMT 2015]**

(A) 

(B) 

(C) 

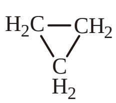
(D) 

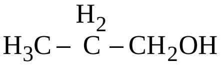
Q.39 Which of the following reagents would distinguish cis-cyclopenta-1, 2-diol from the trans-isomer? **[NEET 2016 PHASE-1]**
(A) Acetone (B) Ozone
(C) MnO_2 (D) Aluminium isopropoxide

Q.40 The product formed by the reaction of an aldehyde with a primary amine is **[NEET 2016 PHASE-1]**
(A) Schiff base (B) Ketone
(C) Carboxylic acid (D) Aromatic acid

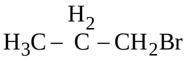
Q.41 The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is – **[NEET 2016 PHASE-1]**
(A) A carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.
(B) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.
(C) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.
(D) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

Q.42 Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?**[NEET 2016 PHASE-2]**

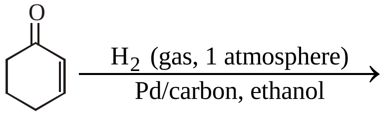
(A) 

(B) 
$H_3C-\overset{H_2}{C}-CH_2OH$

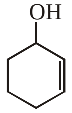
(C) $H_2C=C=O$

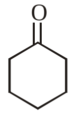
(D) 
$H_3C-\overset{H_2}{C}-CH_2Br$

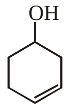
Q.43 The correct structure of the product A formed in the reaction

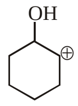


A is **[NEET 2016 PHASE-2]**

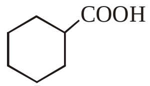
(A) 

(B) 

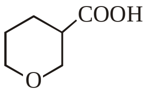
(C) 

(D) 

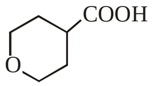
Q.44 The correct order of strengths of the carboxylic acids **[NEET 2016 PHASE-2]**



I



II



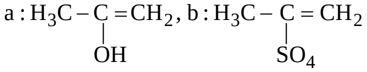
III

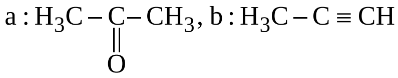
(A) I > II > III (B) II > III > I
(C) III > II > I (D) II > I > III

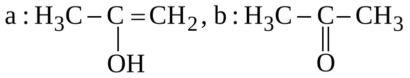
Q.45 Predict the correct intermediate and product in the following reaction : **[NEET 2017]**

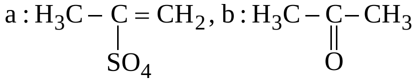
$$H_3C-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_2}$$

$$\underset{(a)}{\text{Intermediate}} \longrightarrow \underset{(b)}{\text{Product}}$$

(A) 
$a : H_3C-\underset{OH}{\underset{|}{C}}=CH_2,\ b : H_3C-\underset{SO_4}{\underset{|}{C}}=CH_2$

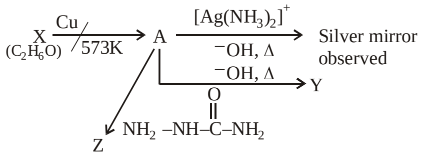
(B) 
$a : H_3C-\underset{O}{\underset{\|}{C}}-CH_3,\ b : H_3C-C\equiv CH$

(C) 
$a : H_3C-\underset{OH}{\underset{|}{C}}=CH_2,\ b : H_3C-\underset{O}{\underset{\|}{C}}-CH_3$

(D) 
$a : H_3C-\underset{SO_4}{\underset{|}{C}}=CH_2,\ b : H_3C-\underset{O}{\underset{\|}{C}}-CH_3$

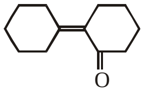
Q.46 Which of the following reactions is appropriate for converting acetamide to methanamine ? **[NEET 2017]**
(A) Hoffmann hypobromamide reaction
(B) Stephens reaction
(C) Gabriels phthalimide synthesis
(D) Carbylamine reaction

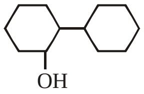
Q.47 Consider the reactions **[NEET 2017]**

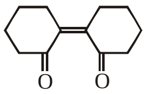


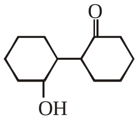
Identify A, X, Y and Z
(A) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.
(B) A-Ethanal, X-Ethanol, Y-But-2-enal, Z-S emicarbazone
(C) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone
(D) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine

Q.48 Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating ? **[NEET 2017]**

(A) 

(B) 

(C) 

(D) 

Q.49 Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their **[NEET 2018]**

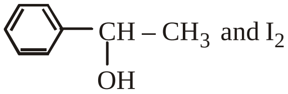
(A) More extensive association of carboxylic acid via vander Waals force of attraction

(B) Formation of carboxylate ion

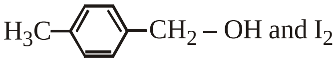
(C) Formation of intramolecular H-bonding

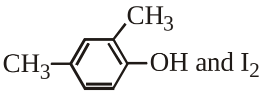
(D) Formation of intermolecular H-bonding

Q.50 Compound A, $C_8H_{10}O$, is found to react with NaOI (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell. A & Y are respectively **[NEET 2018]**

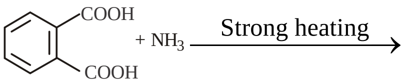
(A) 

(B) 

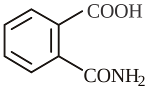
(C) 

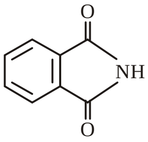
(D) 

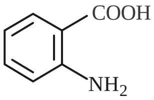
Q.51 The major product of the following reaction is:

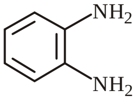


[NEET 2019]

(A) 

(B) 

(C) 

(D) 

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	D	B	B	B	C	D	C	B	D	B	D	C	B	A	C	B	C	D	C	C	C	C	A	D
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	A	A	B	D	D	A	C	B	A	C	C	B	C	A	A	A	C	B	A	B	C	B	A	D	B
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	C	B	A	B	C	B	D	A	A	B	A	A	A	B	B	A	C	A	C	A	D	D	A	B	B
Q	76	77	78	79	80	81	82	83	84																
A	D	B	A	B	A	C	C	A	C																

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	C	C	D	C	B	C	A	D	C	B	A	A	A	A	C	B	A	B	A	D	B	A	B	B
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	B	C	B	C	C	A	A	D	A	B	D	C	B	A	A	C	A	C	A	B	B	A	D	C	A
Q	51	52	53	54	55	56	57	58	59																
A	B	C	D	C	A	C	B	A	C																

EXERCISE - 3

Q	1	2	3	4	5	6	7	8
A	1	5	3	2	5	3	4	84

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	C	A	D	D	D	A	D	A	D	C	D	B	D	B	C	C	D	D	C	B	D	AC	D	A
Q	26	27	28	29	30	31	32	33	34	35	36														
A	C	A	C	B	A	A	C	A	B	D	A														

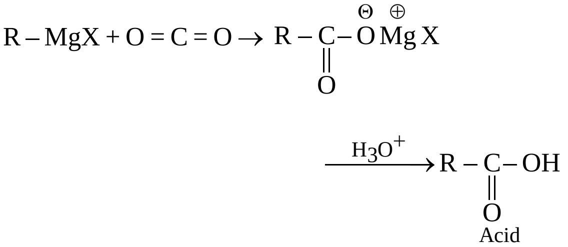
EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	D	D	A	D	A	D	A	A	C	C	B	D	B	C	C	B	A	D	C	C	D	D	D	D
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	D	A	A	D	AD	C	A	D	B	D	D	C	A	A	D	C	B	B	C	A	B	A	D	A
Q	51																								
A	B																								

SOLUTIONS
ALDEHYDES, KETONES & CARBOXYLIC ACID

TRY IT YOURSELF-1

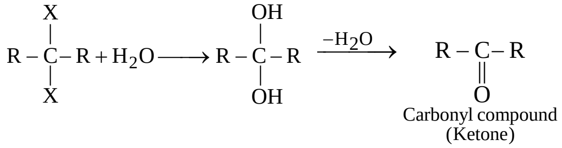
(1) **(A).**



$$R-MgX + O=C=O \rightarrow R-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Mg}X \xrightarrow{H_3O^+} R-\underset{\underset{O}{\|}}{C}-OH$$

Acid

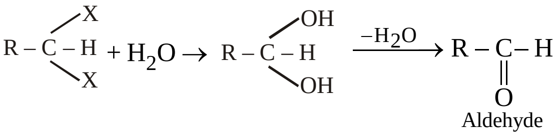
(2) **(C).**



$$R-\underset{X}{\overset{X}{\underset{|}{\overset{|}{C}}}}-R+H_2O \longrightarrow R-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R \xrightarrow{-H_2O} R-\underset{\underset{O}{\|}}{C}-R$$

Carbonyl compound (Ketone)

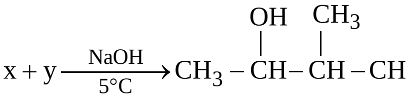
OR



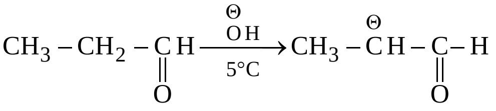
$$R-\underset{X}{\overset{X}{C}}-H + H_2O \rightarrow R-\underset{OH}{\overset{OH}{C}}-H \xrightarrow{-H_2O} R-\underset{\underset{O}{\|}}{C}-H$$

Aldehyde

(3) **(B).** Aldol reaction :

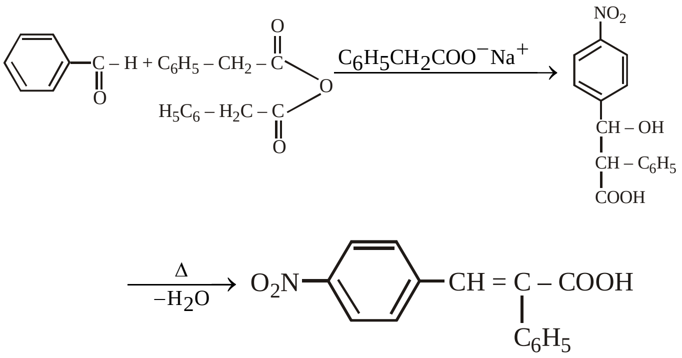


$$x+y \xrightarrow[5^\circ C]{NaOH} CH_3-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH$$



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}H \xrightarrow[5^\circ C]{\overset{\ominus}{O}H} CH_3-\overset{\ominus}{C}H-\underset{\underset{O}{\|}}{C}-H$$

(4) **(D).** Perkin condensation

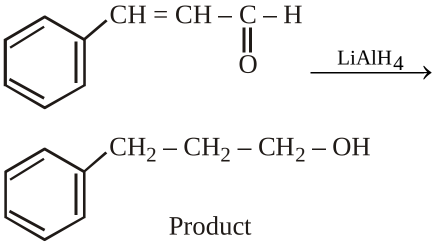


(5) **(C).** $C_6H_5-CH=O+H_2N-OH/H^+$

$$\xrightarrow[-H_2O]{} C_6H_5CH=NOH$$

Oxime
(Mixture of syn & anti)

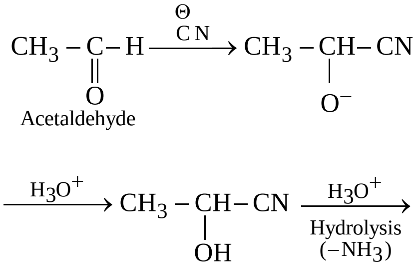
(6) **(C).** $LiAlH_4$ (LAH) ⇒ Strong reducing agent it reduced bond in alkane and $-\underset{\underset{O}{\|}}{C}-H$ group into corresponding alcohol.



Product

Note : $LiAlH_4$ does not reduce double bond of benzene because benzene having extra stability due to aromaticity.

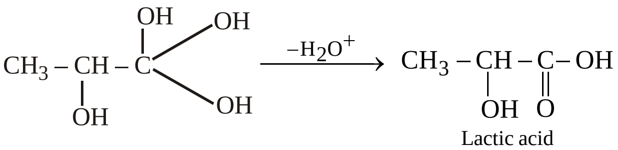
(7) **(C).**



$$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\overset{\ominus}{C}N} CH_3-\underset{O^-}{\underset{|}{CH}}-CN$$

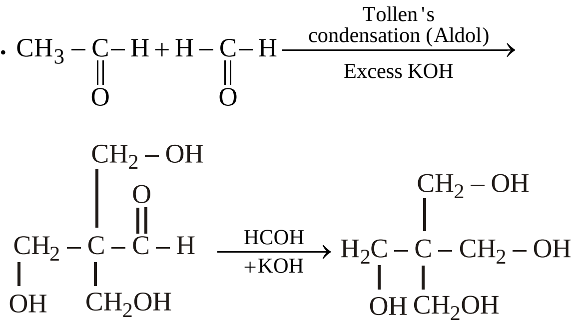
Acetaldehyde

$$\xrightarrow{H_3O^+} CH_3-\underset{OH}{\underset{|}{CH}}-CN \xrightarrow[\text{Hydrolysis } (-NH_3)]{H_3O^+}$$



Lactic acid

(8) **(C).**

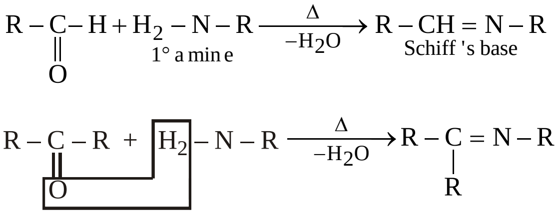


$$CH_3-\underset{\underset{O}{\|}}{C}-H+H-\underset{\underset{O}{\|}}{C}-H \xrightarrow[\text{Excess KOH}]{\text{Tollen's condensation (Aldol)}}$$

$$\underset{OH}{\underset{|}{CH_2}}-\overset{\overset{CH_2-OH}{|}}{\underset{\underset{CH_2OH}{|}}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[+KOH]{HCOH} H_2C-\overset{\overset{CH_2-OH}{|}}{\underset{\underset{CH_2OH}{|}}{C}}-CH_2-OH$$

with OH on H_2C.

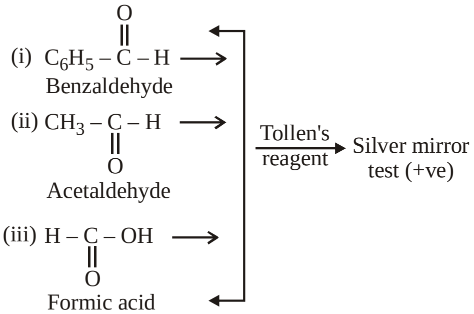
(9) **(A).** When aldehyde & Ketone react with 1° amine so Schiff’s base is formed.



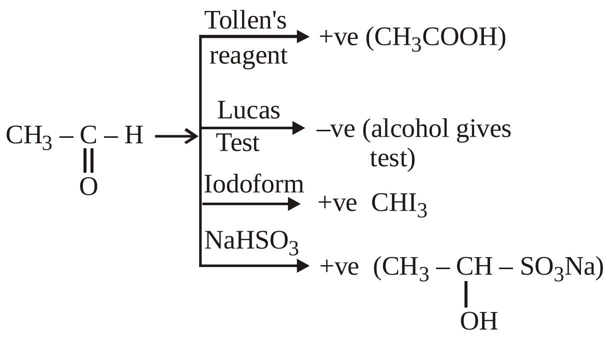
$$R-\underset{\underset{O}{\|}}{C}-H+\underset{1^\circ\text{ amine}}{H_2-N-R} \xrightarrow[-H_2O]{\Delta} \underset{\text{Schiff's base}}{R-CH=N-R}$$

$$R-\underset{\underset{\boxed{O}}{\|}}{C}-R + \boxed{H_2}-N-R \xrightarrow[-H_2O]{\Delta} R-C=N-R$$

(10) **(D).**



(11) **(B).**



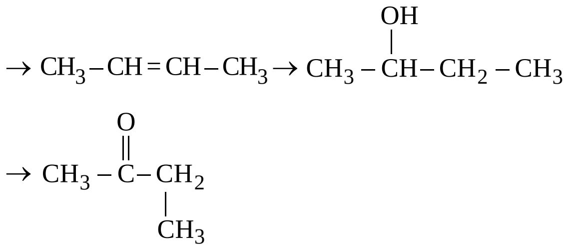
(12) **(A).** Tollen's reagent = Ammonical silver nitrate solution $NH_4OH\,(Ag_2O)$ or $Ag(NH_3)\,OH^-$

* Tollen's reagent reduces aldehyde so by this test we can differentiable ald. to ketone.

(13) **(B).** $CH_3-CH=CH-C_6H_5$

$$\xrightarrow[Zn\text{-}H_2O]{O_3} CH_3-CHO + C_6H_5-CHO$$

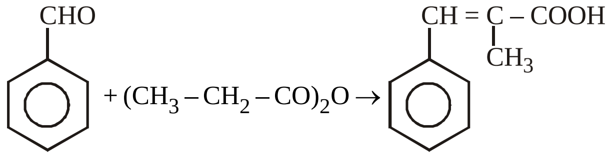
(14) **(B).** $CH_3-COCl \rightarrow CH_3-CHO \rightarrow CH_3-CHCl_2$



$$\rightarrow CH_3-CH=CH-CH_3 \rightarrow CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3$$

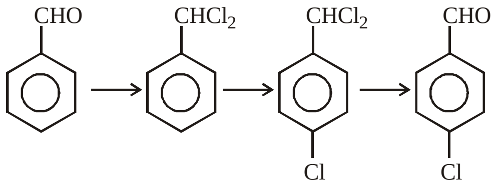
$$\rightarrow CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH_2}$$

(15) Perkin reaction



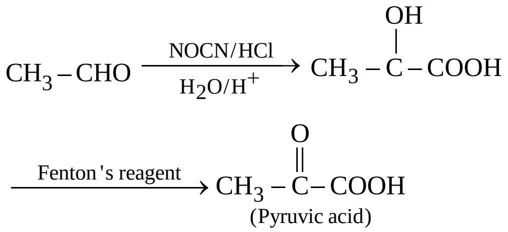
(16) **(A).** Given reaction is Aldol condensation. Six-membered ring is more stable than four-membered ring.

(17)



TRY IT YOURSELF-2

(1) **(C).**



$$CH_3-CHO \xrightarrow[H_2O/H^+]{NOCN/HCl} CH_3-\overset{\overset{OH}{|}}{C}-COOH$$

$$\xrightarrow{\text{Fenton's reagent}} CH_3-\overset{\overset{O}{\|}}{C}-COOH$$

(Pyruvic acid)

(2) **(A).** $NaHCO_3 + CH_3-COOH$

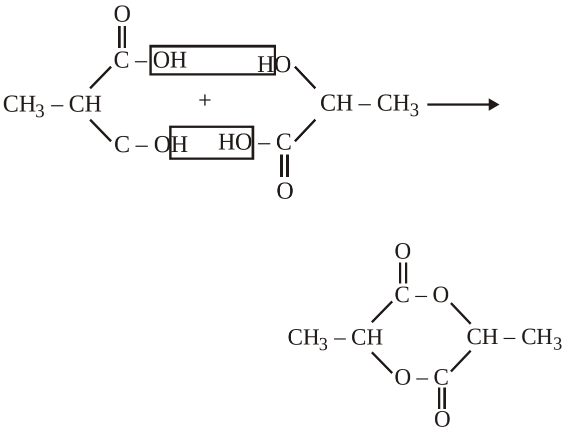
$$\Downarrow$$

$$CH_3-COONa + H_2O + CO_2$$

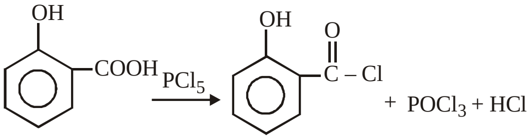
(3) **(A).**

$$CH_3-CH_2-COOH \xrightarrow[(ii)\ Br_2]{(i)\ AgNO_3} CH_3-CH_2-Br$$

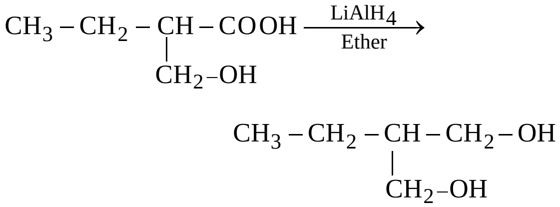
(4) **(D).**



(5) **(B).**



(6) **(C).**

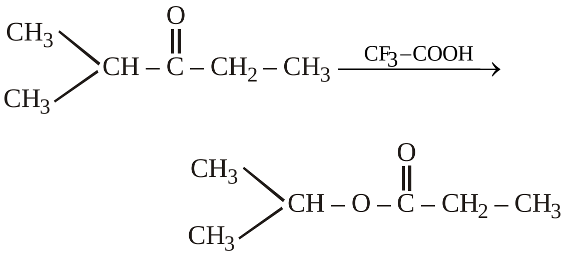


$$CH_3-CH_2-\underset{\underset{CH_2-OH}{|}}{CH}-COOH \xrightarrow[\text{Ether}]{LiAlH_4}$$

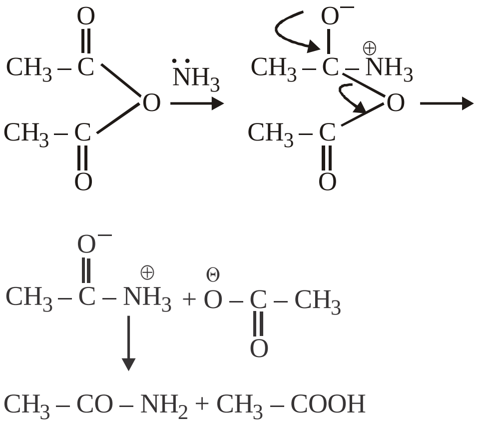
$$CH_3-CH_2-\underset{\underset{CH_2-OH}{|}}{CH}-CH_2-OH$$

in the above reaction chirality is lost.

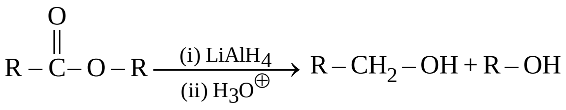
(7) **(A).**



(8) **(A).**

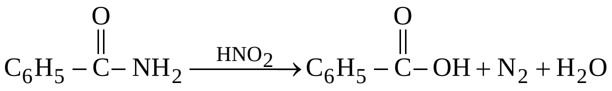


(9) **(C).**



$$R-\overset{O}{\overset{\|}{C}}-O-R \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} R-CH_2-OH+R-OH$$

(10) **(B).**



$$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{HNO_2} C_6H_5-\overset{O}{\overset{\|}{C}}-OH+N_2+H_2O$$

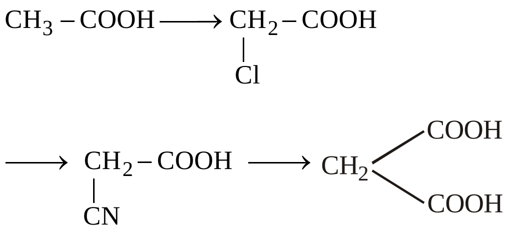
(11) **(D).** $R-CN \xrightarrow[H^+]{H_2O} R-COOH$

$R-MgX \xrightarrow{CO_2} R-COOMgBr$

$\xrightarrow[H^+]{H_2O} R-COOH$

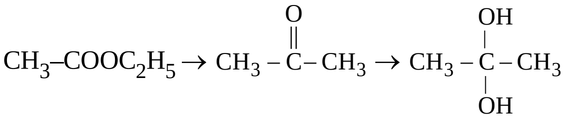
$CH_2=CH_2 \xrightarrow[Co_4(CO)_8]{CO+H_2O} CH_3-CH_2-COOH$

(12) **(A).**



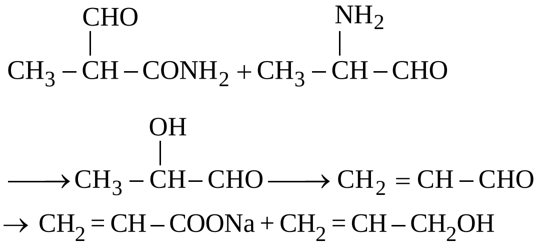
$$CH_3-COOH \longrightarrow \underset{\underset{Cl}{|}}{CH_2}-COOH \longrightarrow \underset{\underset{CN}{|}}{CH_2}-COOH \longrightarrow CH_2<\begin{array}{l}COOH\\COOH\end{array}$$

(13) **(A).**



$$CH_3-COOC_2H_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\underset{\underset{OH}{|}}{\overset{OH}{\overset{|}{C}}}-CH_3$$

(14) **(D).**

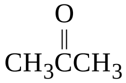


$$CH_3-\overset{CHO}{\overset{|}{CH}}-CONH_2+CH_3-\overset{NH_2}{\overset{|}{CH}}-CHO \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-CHO \longrightarrow CH_2=CH-CHO \rightarrow CH_2=CH-COONa+CH_2=CH-CH_2OH$$

CHAPTER-11 : ALDEHYDES, KETONES AND CARBOXYLIC ACID

EXERCISE-1

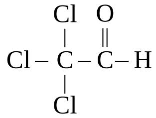
(1) **(B).**



$$CH_3\overset{\overset{O}{\|}}{C}CH_3$$

2 propanone

(2) **(D).**

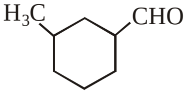


$$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\overset{O}{\|}}{C}-H$$

2, 2, 2, trichloroethanal

(3) **(B).** The locations of substituents are indicated by greek letters $\alpha\,\alpha'$, $\beta\,\beta'$ and so on beginning with the carbon atoms next to the carbonyl group indicated as $\alpha\,\alpha'$.

(4) **(B).**



3-Methylcyclohexanecarbaldehyde

(5) **(B).** When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane.

(6) **(C).** Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.

(7) **(D).** HCHO will be most polar due to lowest electron density on carbon of carbonyl group.

(8) **(C).** $CH_3COCl \xrightarrow[Pd/BaSO_4]{2H} CH_3CHO + HCl$

Rosenmund reaction

(9) **(B).** $HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$

(10) **(D).**

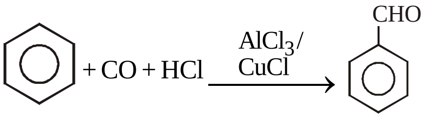
(A) Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

(B) Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde.

(C) When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde.

(11) **(B).** Benzaldehyde can be prepared from benzene by passing vapours of CO and hydrochloric acid in its solution in presence of catalyst mixture of $AlCl_3$/CuCl.

The reaction is known as Gattermann Koch reaction.



(12) **(D).**

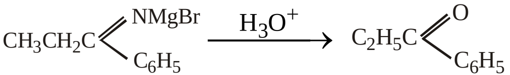
(i) Treatment of acyl chlorides with dialkyl cadmium prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

$2R{-}Mg{-}X + CdCl_2 \rightarrow R_2Cd + 2Mg(X)Cl$

$2R'{-}COCl + R_2Cd \rightarrow 2R'{-}COR + CdCl_2$

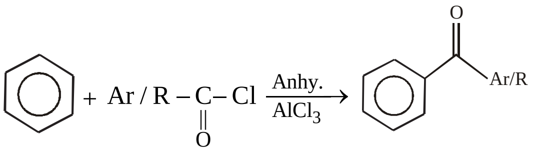
(ii) Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.

$H_3CCH_2CN + C6H5MgBr \xrightarrow{Ether}$

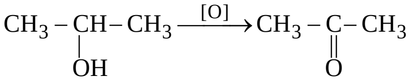


Propiophenone

(iii) When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it gives the corresponding ketone. This reaction is known as Friedel-Craft acylation reaction.



(13) **(C).** Ketones are formed by oxidation of secondary alcohols.



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{[O]} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

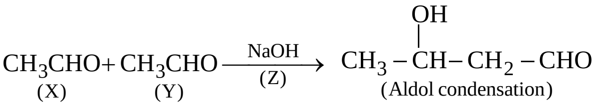
(14) **(B).** Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes and ketones.

(15) **(A).**

$$2CH \equiv CH + 3H_2O \xrightarrow[\substack{Mg\ or\\ Zinc\ vanadate}]{420°C} CH_3COCH_3 + CO_2 + 2H_2$$

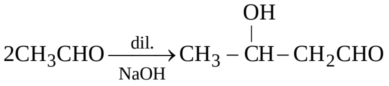
(16) **(C).** Benzaldehyde will not give aldol condensation due to absence of α-H atom.

(17) **(B).**



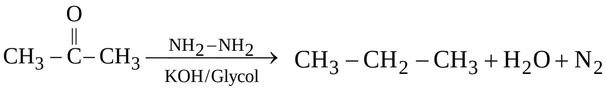
$$\underset{(X)}{CH_3CHO} + \underset{(Y)}{CH_3CHO} \xrightarrow[(Z)]{NaOH} \underset{\text{(Aldol condensation)}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO}$$

(18) **(C).**



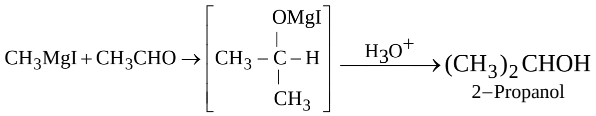
$$2CH_3CHO \xrightarrow[NaOH]{dil.} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2CHO$$

(19) **(D).**



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[KOH/Glycol]{NH_2-NH_2} CH_3-CH_2-CH_3 + H_2O + N_2$$

(20) **(C).**



$$CH_3MgI + CH_3CHO \rightarrow \left[CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgI}{|}}{C}}-H\right] \xrightarrow{H_3O^+} \underset{2-Propanol}{(CH_3)_2CHOH}$$

(21) **(C).** Among Carbonyl Compounds, reactivity decrease with increase in alkyl groups as alkyl groups (+I effect) decrease positive character on C-atom.

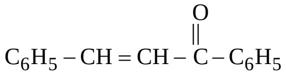
Thus, the correct order of reactivity is

$HCHO > CH_3CHO > C_6H_5CHO$

(22) **(C).** Although both $CH_3CH_2COCH_3$ and $(CH_3)_3CCOCH_3$ contain α-hydrogen, yet $(CH_3)_3CCOCH_3$ does not undergo Aldol condensation due to steric hindrance.

(23) **(C).** $HCHO + HCHO \xrightarrow{KOH} HCOOK + CH_3OH$

(24) **(A).** $C_6H_5CHO + CH_3COC_6H_5 \xrightarrow[-H_2O]{NaOH}$



$C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-C_6H_5$

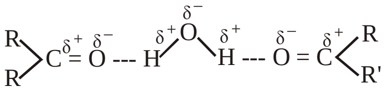
Benzyl acetophenone

(25) **(D).** Since CH_3CH_2CHO has α-hydrogen atom, therefore it will undergo aldol condensation in the presence of cold dilute alkali.

(26) **(A).** Ketones are less reactive than aldehydes.

(27) **(A).** Aldehydes are more reactive than ketones.

(28) **(B).** The lower members of aldehydes and ketones such as methanol, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water.



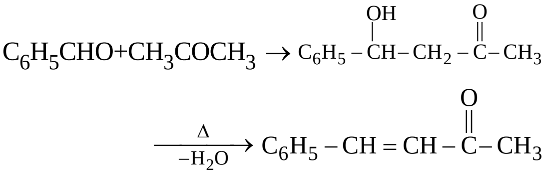
(29) **(D).** Important examples of nucleophilic addition reactions are –

- Addition of hydrogen cyanide (HCN).
- Addition of sodium hydrogen sulphite.
- Addition of Grignard reagents.

Important examples of nucleophilic addition elimination reactions along with nucleophilic addition are –

- Addition of alcohols.
- Addition of ammonia and its derivatives.

(30) **(D).**



$$C_6H_5CHO + CH_3COCH_3 \rightarrow C_6H_5-\overset{\overset{OH}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

$$\xrightarrow[-H_2O]{\Delta} C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

(31) **(A).** FCH_2CHO is most reactive towards nucleophilic addition since presence of most electronegative F withdraws electrons from carbon of carbonyl group making it more polar.

(32) **(C).** Aldehydes with no α-H atom undergo Cannizzaro reaction on heating with cone. alkali solution. Hence, only C_6H_5CHO will undergo the reaction.

(33) **(B).** $CH_3CH_2C \equiv CH \xrightarrow[Hg^{2+}]{H^+/H_2O} CH_3CH_2COCH_3$

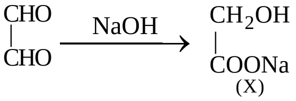
(34) **(A).** Butan-1-ol has higher boiling point due to intermolecular hydrogen bonding.

(35) **(C).** The boiling point of butan-1-ol would be highest, due to extensive intermolecular hydrogen bonding. Butanal is more polar than ethoxyethane. The intermolecular dipole-dipole attraction is stronger in the butanal. n-pentane molecules have only weak van der Waals' forces. The increasing order of boiling point of the given compounds are IV < III < I < II.

(36) **(C).** Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as aldol reaction.

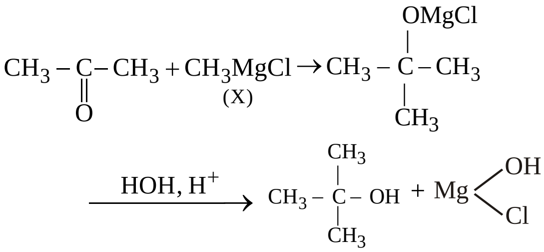
(37) **(B).** The carbonyl compound must contain an α-hydrogen atom, for it to undergo aldol condensation.

(38) **(C).**



$$\underset{CHO}{\overset{CHO}{|}} \xrightarrow{NaOH} \underset{\underset{(X)}{COONa}}{\overset{CH_2OH}{|}}$$

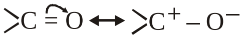
(39) **(A).**



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + \underset{(X)}{CH_3MgCl} \rightarrow CH_3-\overset{\overset{OMgCl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$\xrightarrow{HOH,\ H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + Mg\begin{matrix} OH \\ Cl \end{matrix}$$

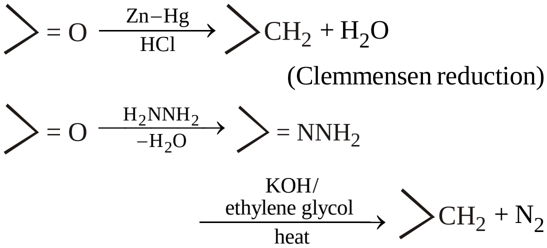
(40) **(A).**



$>C=O \leftrightarrow >C^+-O^-$

Nucleophile attacks at the positive C centre of carbonyl group hence the addition is nucleophilic addition.

(41) **(A).** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and conc. HCl (Clemmensen reduction) or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).



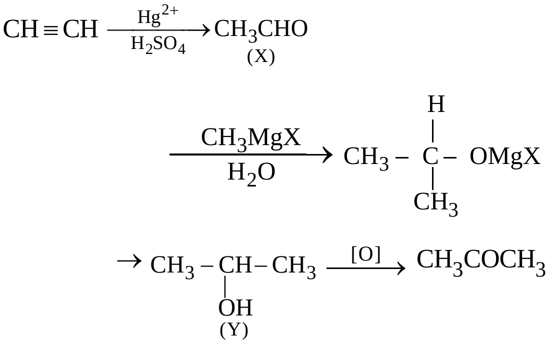
$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

(Clemmensen reduction)

$$>C=O \xrightarrow[-H_2O]{H_2NNH_2} >C=NNH_2 \xrightarrow[heat]{KOH/\ ethylene\ glycol} >CH_2 + N_2$$

(Wolff-Kishner reduction)

(42) **(C).**

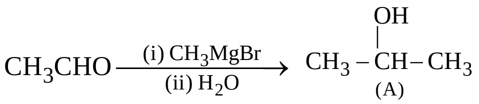


$$CH \equiv CH \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{(X)}{CH_3CHO}$$

$$\xrightarrow[H_2O]{CH_3MgX} CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgX$$

$$\rightarrow \underset{(Y)}{CH_3-\underset{\underset{OH}{|}}{C}H-CH_3} \xrightarrow{[O]} CH_3COCH_3$$

(43) **(B).**



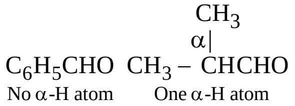
$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} \underset{(A)}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3}$

$\xrightarrow{H_2SO_4,\,\Delta} \underset{(B)}{H_3C-CH=CH_2} \xrightarrow[\text{oxidation}]{\text{Hydroboration}} \underset{(C)}{CH_3CH_2CH_2OH}$

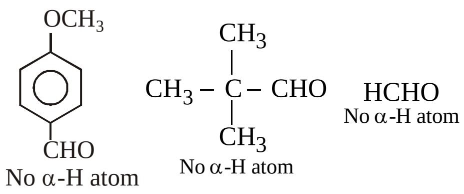
(A) and (C) are the positional isomers.

(44) **(A).** Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Aromatic aldehydes and ketones are less reactive than corresponding aliphatic aldehydes and ketones.

(45) **(B).** Aldehydes containing no α-H atoms on heating with concentrated alkali solution (50%) undergo Cannizzaro's reaction. In this reaction one molecule is oxidised at the expense of other which is reduced to alcohol.



$\underset{\text{No }\alpha\text{-H atom}}{C_6H_5CHO}$ $\underset{\text{One }\alpha\text{-H atom}}{CH_3-\overset{\overset{CH_3}{\alpha|}}{C}HCHO}$



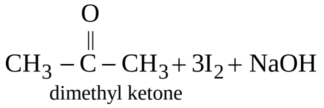
$\underset{\text{No }\alpha\text{-H atom}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO}$ $\underset{\text{No }\alpha\text{-H atom}}{HCHO}$

(46) **(C).** $C_2H_5CHO + 2Cu^{+2} + 5OH^{-}$

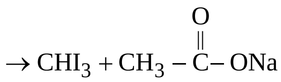
$\rightarrow \underset{\text{Red ppt}}{Cu_2O} + 3H_2O + C_2H_5COO^{-}$

$CH_3COCH_3 + 2Cu^{+2} + 5OH^{-} \rightarrow \text{No reaction}$

(47) **(B).**



$\underset{\text{dimethyl ketone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3} + 3I_2 + NaOH$



$\rightarrow CHI_3 + CH_3-\overset{\overset{O}{||}}{C}-ONa$

(48) **(A).** Silver mirror test is the test of aldehyde.

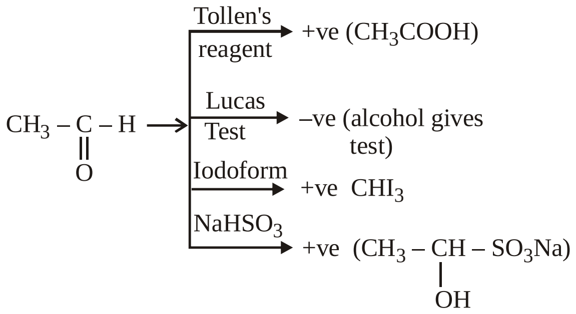
(49) **(D).**

$CH_3CHO \xrightarrow{[Ag(NH_3)_2]} CH_3COOH + Ag_{\downarrow} + NH_3$

Silver mirror test

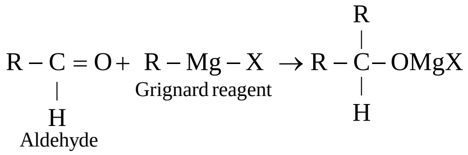
While acetone do not react.

(50) **(B).**

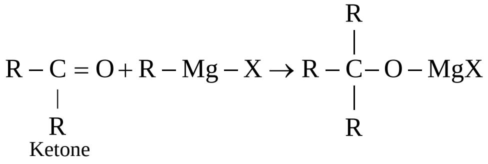


(51) **(C).** Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acid.

(52) **(B).**



$\underset{\text{Aldehyde}}{R-\underset{\underset{H}{|}}{C}=O} + \underset{\text{Grignard reagent}}{R-Mg-X} \rightarrow R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OMgX$



$\underset{\text{Ketone}}{R-\underset{\underset{R}{|}}{C}=O} + R-Mg-X \rightarrow R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-O-MgX$

(53) **(A).** Fehling solution A is aqueous copper sulphate and Fehling B is alkaline sodium potassium tartarate (Rochelle salt).

(54) **(B).** Pentan-2-one will give positive iodoform test while pentan-3-one will not give this test.

$CH_3COCH_2CH_2CH_3 + I_2 + NaOH$

$\rightarrow CHI_3$ (Iodoform) + other products

(55) **(C).** Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs. Benzaldehyde is used in perfumery and in dye industries.

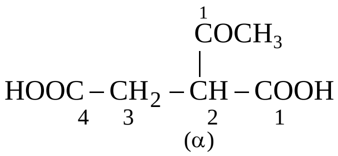
(56) **(B).** Formaline contains 40% HCHO, 8% CH_3OH and 52% water. It is used as biological preservative.

(57) **(D).** Acetone and ethyl methyl ketone are common industrial solvents. Butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

(58) **(A).** $\underset{3}{Cl-CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$

3 chloro propanoic acid

(59) **(A).**

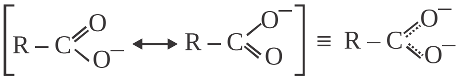


$\underset{4}{HOOC}-\underset{3}{CH_2}-\underset{\underset{(\alpha)}{2}}{\overset{\overset{\overset{1}{COCH_3}}{|}}{CH}}-\underset{1}{COOH}$

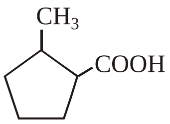
Common name → α-acetylsuccinic acid.
IUPAC name → 2-(1-oxoethyl) butane-1, 4-dioic acid.

(60) **(B).** $R-COOH \xrightarrow{-H^{+}} R-COO^{-}$

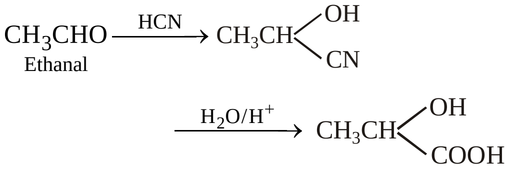
$[R-C\overset{O^{-}}{\underset{O^{-}}{\lessgtr}}]$ is a resonance hybrid of resonating structures.



$\left[R-C\overset{O}{\underset{O^{-}}{\lessgtr}} \longleftrightarrow R-C\overset{O^{-}}{\underset{O}{\lessgtr}}\right] \equiv R-C\overset{O^{-}}{\underset{O^{-}}{\lessgtr}}$

(61) **(A).** 

is 2-methylcyclopentanecarboxylic acid.

(62) **(A).** 

$CH_3CHO \xrightarrow{HCN} CH_3CH(OH)(CN) \xrightarrow{H_2O/H^+} CH_3CH(OH)(COOH)$

Ethanal

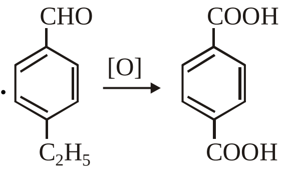
α-Hydroxypropanoic acid

(63) **(A).** $CH_3CN \xrightarrow{H_2O} CH_3COOH + NH_3$

(64) **(B).** $C_6H_5CH_2OH + [O] \xrightarrow{KMnO_4} C_6H_5COOH + H_2O$

(65) **(B).** $\underset{}{C_6H_5MgBr} \xrightarrow[\text{(ii) } H_3\overset{+}{O}]{\text{(i) } CO_2} \underset{(P)}{C_6H_5COOH}$

(66) **(A).** $C_2H_5OH \xrightarrow{[O]} CH_3COOH$

(67) **(C).** 

(X)

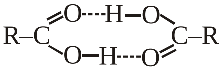
1,4-Benzenedi-carboxylic acid

(68) **(A).**

$CH_3CH = CHCHO \xrightarrow{NaBH_4} CH_3CH = CHCH_2OH\,(X)$

$\xrightarrow{HCl + ZnCl_2} CH_3CH = CHCH_2Cl\,(Y)$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } KCN} CH_3CH = CHCH_2COOH$

(69) **(C).** 

(70) **(A).** $CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

(71) **(D).** $\begin{matrix} RCOOH \\ RCOOH \end{matrix} \xrightarrow{P_2O_5} \begin{matrix} RCO \\ RCO \end{matrix}\rangle O + H_2O$

P_2O_5 acts as a dehydrating agent.

(72) **(D).** Due to ortho effect o – $NO_2C_6H_4COOH$ is the strongest acid.

p-$NO_2C_6H_4COOH$ is more acidic than m-$NO_2C_6H_4COOH$ because the former generates positive charge on carbon bearing –COOH group whereas the latter generates positive charge on the next carbon atoms.

(73) **(A).** Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

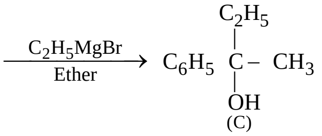
(74) **(B).** HVZ reaction is given by only those carboxylic acids which have α-H atom. CH_3COOH has three α-H atoms but formic acid does not have α-hydrogen atom hence formic acid cannot be halogenated.

(75) **(B).** The correct order of acidity is

$ICH_2COOH < BrCH_2COOH < ClCH_2COOH < FCH_2COOH$

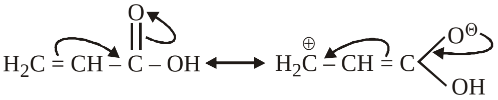
(76) **(D).** $CH_3COOH + PCl_5 \rightarrow CH_3COCl\,(A)$

$\xrightarrow[\text{anh. } AlCl_3]{C_6H_6} C_6H_5COCH_3\,(B)$



$\xrightarrow[\text{Ether}]{C_2H_5MgBr} C_6H_5\overset{C_2H_5}{\underset{OH}{C}}-CH_3$ (C)

(77) **(B).** Direct attachment of group such as phenyl or vinyl to the carboxylic acid, increase the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below.



This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached.

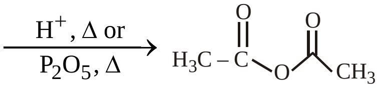
(78) **(A).** In alcohols – OH group is attached to an electron releasing group while in carboxylic acids – OH group is attached to an electron withdrawing group making it more acidic.

(79) **(B).** $CH_3COCl \xrightarrow{LiAlH_4} CH_3CH_2OH + HCl$

(80) **(A).** $CH_3 - CO - NH_2 \xrightarrow{P_2O_5} CH_3 - C \equiv N + H_2O$

(81) **(C).** Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.

H_3C-COOH(ethanoic acid) + CH_3COOH



Ethanoic anhydride

(82) **(C).** Citric acid is present in the lemon which is responsible for its sour taste.

(83) **(A).** Acetic acid is the chief constituent of vinegar and hence its name (Latin : acetum = vinegar).

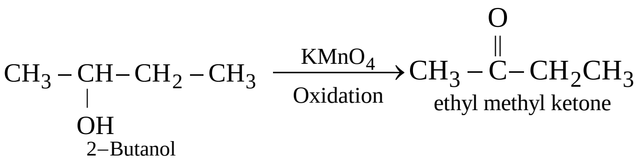
(84) **(C).** Methanoic acid used in rubber, textile, dyeing, leather and electroplating industries.

EXERCISE-2

(1) **(B).** $(CH_3)_2C = C(CH_3)_2 \xrightarrow{O_3} 2CH_3 - CO - CH_3$

(2) **(C).** $\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{CH_3MgI} \underset{\text{tert-Butyl alcohol}}{(CH_3)_3COH}$

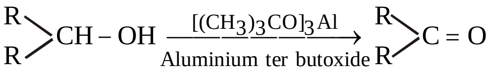
(3) **(C).**



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow[\text{Oxidation}]{KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

2–Butanol; ethyl methyl ketone

(4) **(D).**



$$\begin{matrix}R\\R\end{matrix}\!\!>CH-OH \xrightarrow[\text{Aluminium ter butoxide}]{[(CH_3)_3CO]_3Al} \begin{matrix}R\\R\end{matrix}\!\!>C=O$$

Isopropyl alcohol; Ketone

(5) **(C).** $\underset{\text{1–Phenylethanol}}{C_6H_5CHOHCH_3} \xrightarrow{[O]} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$

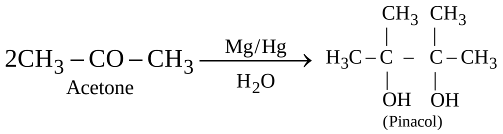
$$C_6H_6+CH_3COCl \xrightarrow[\text{reaction}]{\text{Friedel craft's}} C_6H_5COCH_3+HCl$$

(6) **(B).** Wolf-Kishner reduction does not convert > CO to CHOH but converts it to > CH_2.

(7) **(C).** $CH_3CH=CHCHO+2[Ag(NH_3)_2]^+ \rightarrow$

$$2Ag+4NH_3+CH_3CH=CHCOOH+H_2O$$

(8) **(A).**



$$\underset{\text{Acetone}}{2CH_3-CO-CH_3} \xrightarrow[H_2O]{Mg/Hg} \underset{\text{(Pinacol)}}{H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

(9) **(D).** $R-CHO \xrightarrow{H_2N-OH} \underset{\text{Oxime}}{RCH=N-OH}$

$$CH_3CHO+NH_2OH \rightarrow \underset{\text{Acetaldoxime}}{CH_3-CH=N-OH}+H_2O$$

(10) **(C).** $\underset{\text{Propanal}}{CH_3-CH_2-CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Propanoic acid}}{CH_3CH_2-COOH}$

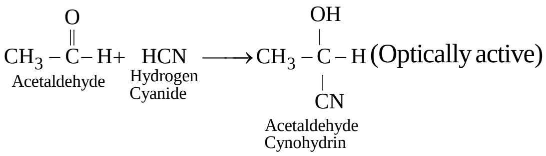
(11) **(B).** $\underset{\text{Acetone}}{CH_3-CO-CH_3} \xrightarrow{\text{Pyrolysis}} \underset{\text{Ketene}}{CH_2=C=O}$

(12) **(A).** Aldehyde + Schiff's reagent → Pink colour
(Colourless)

Ketone do not give this test.

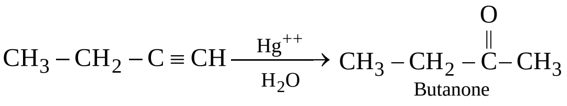
(13) **(A).** $\underset{\text{Formic acid}}{HCOOH+PCl_5} \rightarrow \underset{\text{Formyl chloride}}{HCOCl}+POCl_3+HCl$

(14) **(A).**



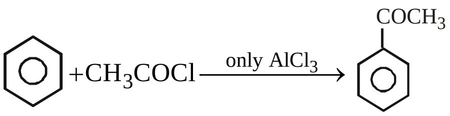
$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H}+\underset{\text{Hydrogen Cyanide}}{HCN} \longrightarrow \underset{\text{Acetaldehyde Cynohydrin}}{CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H}\ \text{(Optically active)}$$

(15) **(A).** It is hydration of alkynes.

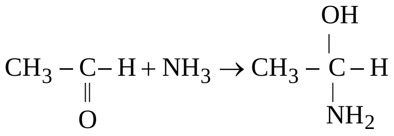


$$CH_3-CH_2-C\equiv CH \xrightarrow[H_2O]{Hg^{++}} \underset{\text{Butanone}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

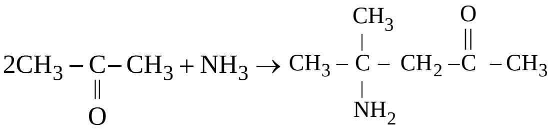
(16) **(C).**



(17) **(B).**



$$CH_3-\underset{\underset{O}{\|}}{C}-H+NH_3 \rightarrow CH_3-\underset{\underset{NH_2}{|}}{\overset{\overset{OH}{|}}{C}}-H$$



$$2CH_3-\underset{\underset{O}{\|}}{C}-CH_3+NH_3 \rightarrow CH_3-\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

(18) **(A).** Crossed aldol reaction gives benzyl alcohol and sodium formate.

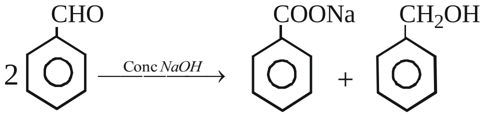
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{NaOH(aq)} \underset{\text{Benzylalcohol}}{C_6H_5CH_2OH}+\underset{\text{Sod.formate}}{HCOONa}$$

(19) **(B).** $CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow{2H_2O/H^+} CH_3CH(OH)COOH$

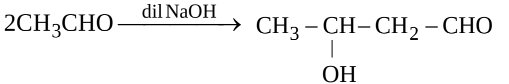
(20) **(A).** $2CH_3COCH_3+Cl_2\ /\ NaOH$

$$\rightarrow 2CHCl_3\ +2CH_3COONa+HCl$$

(21) **(D).** Benzaldehyde gives cannizaro's reaction whereas acetaldehyde gives aldol condensation.



Cannizaro



$$2CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

(Aldol)

(22) **(B).** Acetophenone is a ketone and does not react with Tollen's reagent to give silver mirror.

(23) **(A).** Amongst aldehyde & the acid derivatives, acid chloride are the most susceptible to nucleophilic attack due to strong –I effect & weak +R effect of the Cl-atom as a result of which carbonyl carbon has the highest electron deficiency.
The actual order is
MeCOCl > MeCOOCOMe > MeCOOMe > MeCHO

(24) **(B).** $2CH_3COOH \xrightarrow[573K]{MnO} CH_3COCH_3+CO_2+H_2O$

(25) **(B).** $CH_3COOH+CH_3-Mg-X \rightarrow CH_3-CH_3$

(26) **(B).** Forms H-bonding by means two highly electronegative atoms present in it.

(27) **(C).** $2CH_3COOH \xrightarrow[300^oC]{MnO} \underset{\text{Acetone}}{CH_3COCH_3}+CO_2+H_2O$

(28) **(B).** $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

$$\xrightarrow{KCN} RCOCN + KCl \xrightarrow{2H_2O} RCOCOOH + 2NH_3$$

$$\xrightarrow[\text{Zn-Hg/Conc. HCl}]{\text{Clemenson reduction}} RCH_2COOH + H_2O$$

(29) **(C).** $CH \equiv CH + CH_3COOH \xrightarrow{[Hg^{2+}]}$

$$\underset{\text{Vinyl acetate}}{H_2C = CH - OCOCH_3} \xrightarrow{CH_3COOH}$$

$$\underset{\text{Ethylidene acetate}}{CH_3 - CH(O - COCH_3)_2}$$

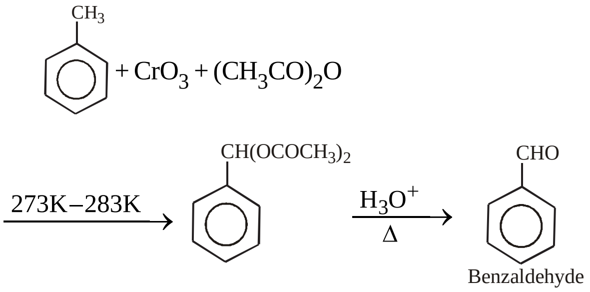
(30) **(C).** $X \xrightarrow{NaOH/CaO} C_2H_6$

$$\underset{\text{propionic acid}}{C_2H_5COOH} \xrightarrow{NaOH/CaO} \underset{\text{ethane}}{C_2H_6}$$

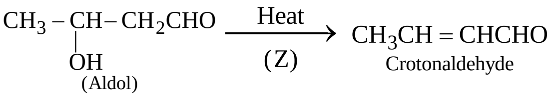
(31) **(A).** Glycine is a amphoteric acid as it contains both acidic as well as basic groups.

(32) **(A).** $CH_3CHO \xrightarrow{Cl_2} \underset{\text{(Choral)}}{CCl_3CHO} + 3HCl$

(33) **(D).** Toluene is converted to benzylidenedi-acetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.

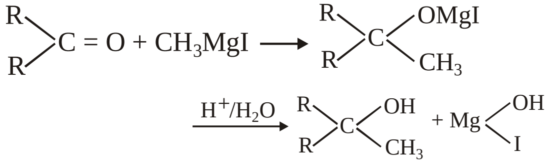


(34) **(A).** $CH_3COCl \xrightarrow[(X)]{Pd/BaSO_4} CH_3CHO \xrightarrow[(Y)]{\text{dil. NaOH}}$



$$\underset{\text{(Aldol)}}{CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2CHO} \xrightarrow[(Z)]{Heat} \underset{\text{Crotonaldehyde}}{CH_3CH = CHCHO}$$

(35) **(B).** Formaldehyde forms primary alcohol while all other aldehydes form secondary alcohols on reaction with Grignard's reagent followed by hydrolysis.



(36) **(D).** $CH_3OH \xrightarrow[300^\circ C]{Cu} \underset{(X)}{HCHO} \xrightarrow{NaOH} \underset{(Y)}{HCOONa} + CH_3OH$

(37) **(C).** Both ethanal and propanal will give silver mirror test and red precipitate with Fehling's solution. They can be differentiated by iodoform test.

(38) **(B).** Aromatic ketones are less reactive than aliphatic ketones which in turn are less reactive than aldehydes. Acetophenone does not react with $NaHSO_3$.

(39) **(A).** Iodoform test is given by the compounds containing CH_3CO group or CH_3CHOH group (which is oxidised to CH_3CO group). Sample is heated with I_2 and NaOH, the existence of yellow ppt. indicates the presence of CH_3CO group or CH_3CHOH group.

e.g., $CH_3CHO + 3I_2 + 4NaOH$

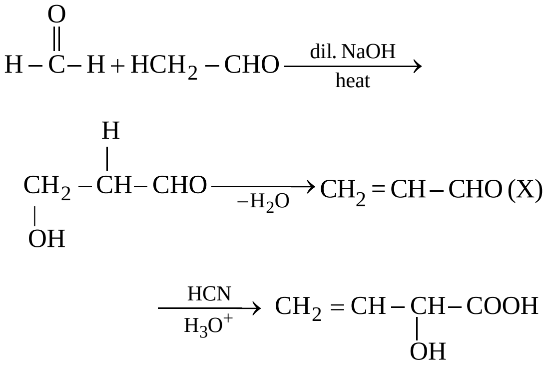
$$\rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

Iodoform (yellow ppt.)

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow[NaOH]{I_2} CHI_3$$

∴ n-butyl alcohol ($CH_3CH_2CH_2CH_2OH$) does not give iodoform test as it does not possess the CH_3CHO or CH_3CHOH group.

(40) **(A).**

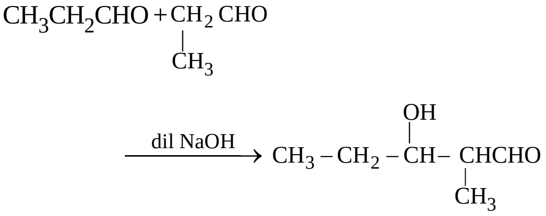


$$H - \overset{\overset{O}{\|}}{C} - H + HCH_2 - CHO \xrightarrow[heat]{\text{dil. NaOH}}$$

$$\underset{\underset{OH}{|}}{CH_2} - \overset{\overset{H}{|}}{CH} - CHO \xrightarrow[-H_2O]{} CH_2 = CH - CHO\,(X)$$

$$\xrightarrow[H_3O^+]{HCN} CH_2 = CH - \underset{\underset{OH}{|}}{CH} - COOH$$

(41) **(C).**



$$CH_3CH_2CHO + \underset{\underset{CH_3}{|}}{CH_2}\,CHO$$

$$\xrightarrow{\text{dil NaOH}} CH_3 - CH_2 - \overset{\overset{OH}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH}CHO$$

(42) **(A).** CH_3CHO is most reactive towards nucleophilic addition reactions.

(43) **(C).** $CH_3COCH_3 \xrightarrow[Heat]{I_2 + NaOH} \underset{(X)}{CHI_3}$

$$\xrightarrow[Heat]{Ag} CH \equiv CH\,(Y) \xrightarrow[Heat]{H_2SO_4/HgSO_4} CH_3CHO\,(Z)$$

(44) **(A).** Acid chlorides are reduced to aldehydes on reaction with $BaSO_4$ and Pd.The reaction is called Rosenmund reduction.

$$RCOCl \xrightarrow[Pd/BaSO_4]{H_2} RCHO + HCl$$

(45) **(B).** $\underset{\substack{\text{Ethyl ethanoate}\\(X)}}{CH_3COOC_2H_5} \xrightarrow{H_2O/H^+} \underset{(Y)}{CH_3COOH} + \underset{(Z)}{C_2H_5OH}$

$$\downarrow CrO_3$$

$$\underset{(Y)}{CH_3COOH}$$

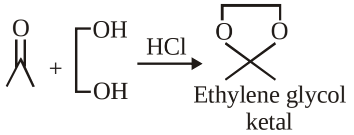
(46) **(B).** Aldehydes give silver mirror test with Tollens' reagent while ketones form oximes with hydroxylamine. Hence the compound is a ketone. Alcohol and ethers do not give this test.

(47) **(A).** Formic acid acts as a reducing agent it reduces Fehling's and Tollen's reagent.

(48) **(D).** Ethanal gives iodoform test while propanal does not give iodoform test.

(49) **(C).** Tollens' reagent is used to detect aldehyde group.

(50) **(A).** Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycols ketals.



(51) **(B).** $$CH_3CHO \xrightarrow[\text{[O]}]{K_2Cr_2O_7/H^+} CH_3COOH$$

$$\xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Heat}} CH_3COCH_3$$

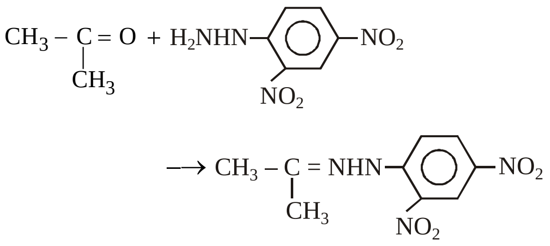
(52) **(C).** The solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform etc. In fact many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

(53) **(D).** Iodoform reaction with sodium hypoiodite is also used for the detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.

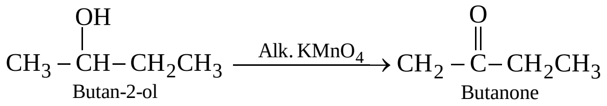
(54) **(C).** Fehling's test is given by aliphatic aldehydes only.

(55) **(A).** The oxidation of toluene ($C_6H_5CH_3$) with chromyl chloride (CrO_2Cl_2) in CCl_4 or CS_2 to give benzaldehyde is called Etard reaction. In this reaction, the chromyl chloride first forms a brown complex, which is separated and then decomposed with H_2O to give benzaldehyde (C_6H_5CHO).

(56) **(C).**



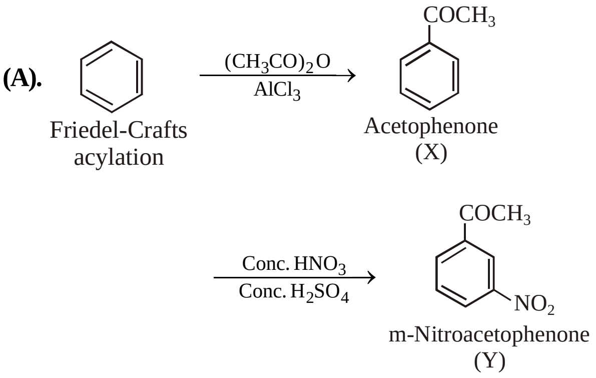
(57) **(B).**



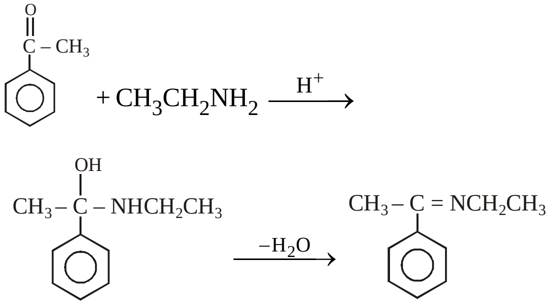
$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CH_3 \xrightarrow{\text{Alk. KMnO}_4} CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

Butan-2-ol Butanone

(58) **(A).**

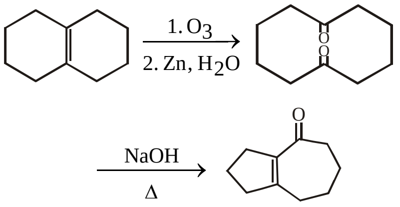


(60) **(C).**

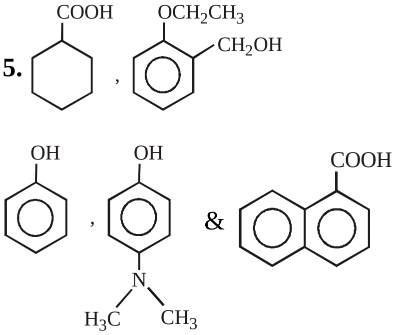


EXERCISE-3

(1) **1.**

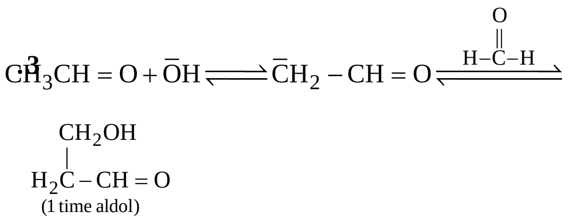


(2) **5.**



are soluble in aqueous NaOH.

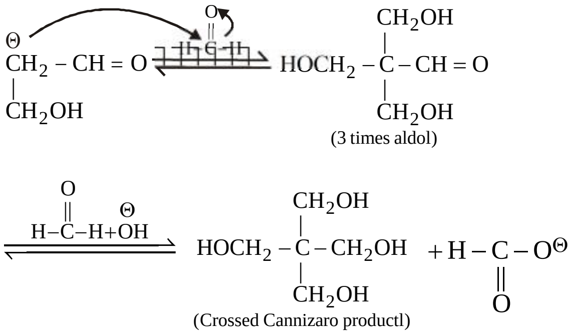
(3)



$$\overset{\cdot}{C}H_3CH = O + \bar{O}H \rightleftharpoons \bar{C}H_2 - CH = O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H}$$

$$H_2\overset{CH_2OH}{\overset{|}{C}}-CH = O$$

(1 time aldol)

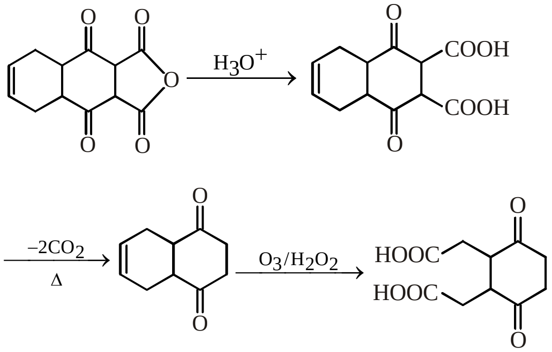


(3 times aldol)

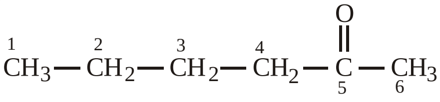
(Crossed Cannizzaro productl)

the carboxyl functional group $(-\underset{\underset{O}{\|}}{C}-OH)$ s present in.

(4) 2.

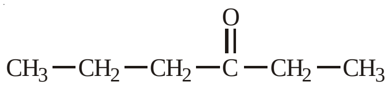


(5) 5. (I)



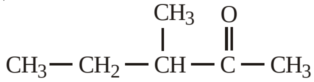
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\underset{5}{\overset{\overset{O}{\|}}{C}}-\underset{6}{CH_3}$$

(II)



$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

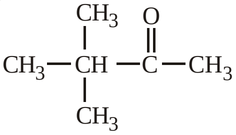
(III)



$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_3$$

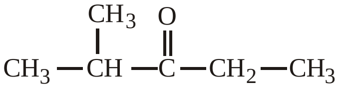
It has chiral centre

(IV)



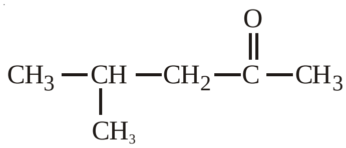
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-\overset{\overset{O}{\|}}{C}-CH_3$$

(V)



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

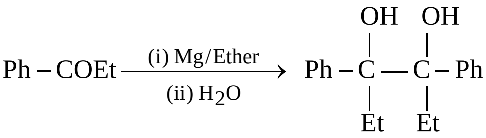
(VI)



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Only (III) form diastereomers on addition reaction so, desired ketones as per addition reaction is 5.

(6) 3.



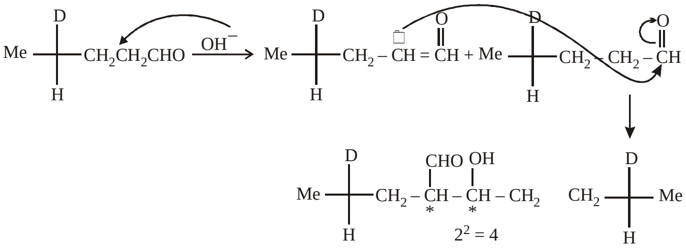
$$Ph-COEt\xrightarrow[\text{(ii) }H_2O]{\text{(i) Mg/Ether}}Ph-\underset{\underset{Et}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{Et}{|}}{\overset{\overset{OH}{|}}{C}}-Ph$$

Number of stereoisomers of the product

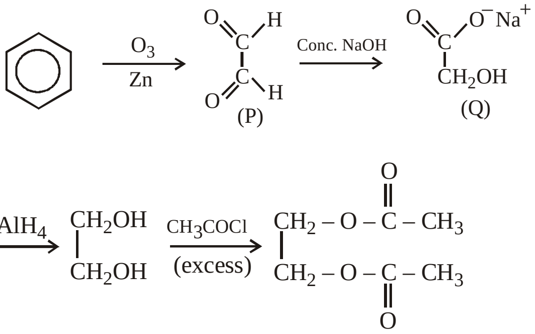
$$2^{n}-1=2^{2}-1=3$$

Three stereoisomers would be d, ℓ and meso.

(7) 4.



(8) 84.



Mol. weight (R) = 62, Mol. weight (S) = 146, Ans. 84

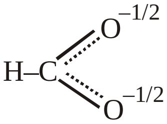
EXERCISE-4

(1) **(C).** $CH_3CH_2COOH\xrightarrow[\text{red P}]{Cl_2}Cl-CH_2-CH_2-COOH$

$$\xrightarrow[-HCl]{\text{Alc. KOH}}CH_2=CH-COOH$$

(2) **(C).** Acid without – COOH group.

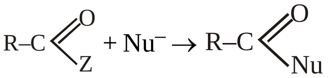
(3) **(A).**



(4) **(D).** $CH_2=CHCH_2OH$

(5) **(D).** The general formula $C_nH_{2n}O_2$ could be for open chain is carboxylic acid

(6) **(D).**



$+Z^-$ is fastest when Z is Cl.

(7) **(A).**

(8) **(D).** On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is $CH_3COOC_2H_5+NaCl$

(9) **(A).** Clemenson reduction

(10) **(D).** Butan-2-one

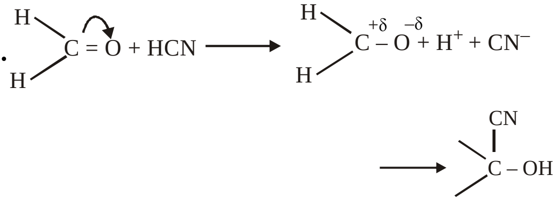
(11) **(C).** $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N$

(12) **(D).** b > c > d > a

(13) By Cannizzaro's reaction (without α-H containing carbonyl compounds give this reaction).

(14) **(D).** Chromic anhydride in glacial acetic acid

(15) **(B).**

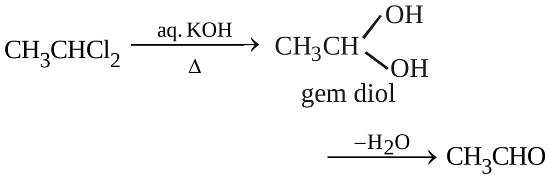


HCHO > CH_3COCH_3 > $PhCOCH_3$

(16) **(C).**

(17) **(C).** The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is benzoic acid.

(18) **(D).**

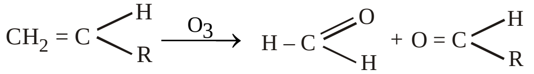


(19) **(D).** $CH_3COOH + C_2H_5OH \xrightarrow{Conc.\ H_2SO_4} CH_3COOC_2H_5 + H_2O$

Ethyl acetate (ester) has fruity smell.

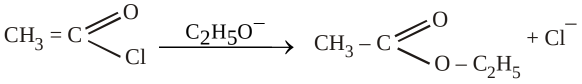
(20) **(C).** Cannizzaro reaction involves hydride transfer as the rate limiting step.

(21) **(B).**



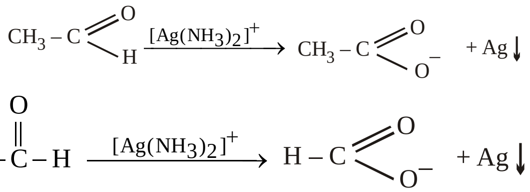
Presence of one vinyl group gives formaldehyde as one of the product in ozonolysis.

(22) **(D).**

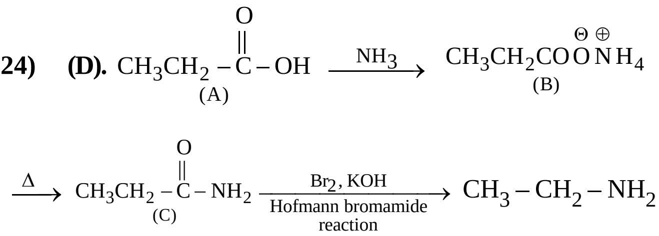


Ethylethanoate

(23) **(AC).**



(24) **(D).**



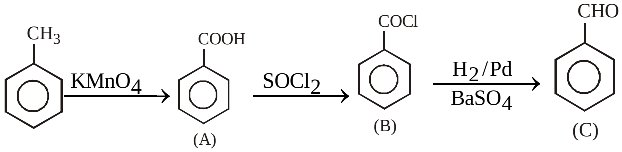
$$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2CO\overset{\ominus}{O}\overset{\oplus}{N}H_4}$$

$$\xrightarrow{\Delta} \underset{(C)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2,\ KOH} CH_3-CH_2-NH_2$$

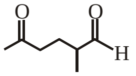
(25) **(A).** $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$

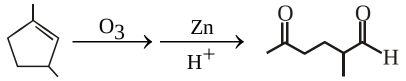
$\xrightarrow{PCl_3} CH_3CH_2Cl \xrightarrow{Alc.\ KOH} \underset{(Ethylene)}{H_2C=CH_2}$

(26) **(C).**



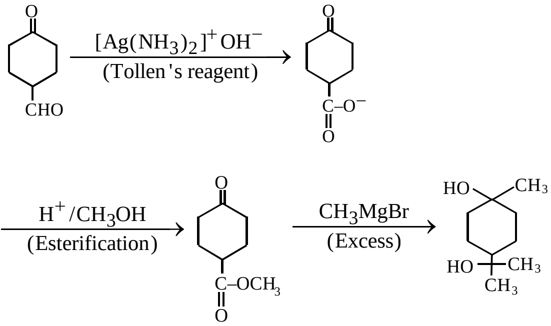
(27) **(A).** 5-keto-2-methylhexanal is





(28) **(C).** DIBAL–H reduces ester and carboxylic acid both into aldehyde at low temperature.

(29) **(B).**



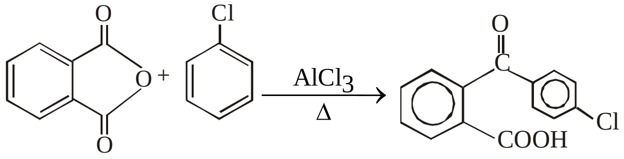
(30) **(A).** EWG increases acidic strength

$NO_2CH_2COOH > NCCH_2COOH$

$> FCH_2COOH > ClCH_2COOH$

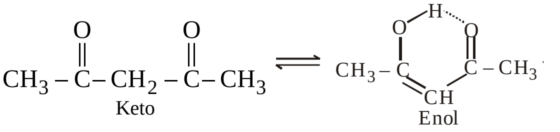
(31) **(A).** Aldehyde reacts at a faster rate than ketone during aldol and steric less hindered anion will be a better nucleophile so self aldol at $CH_3-\overset{O}{\overset{\|}{C}}-H$ will be the major product.

(32) **(C).**



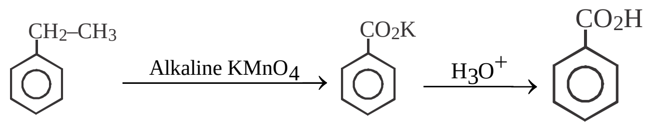
Fridel-craft acylation, –Cl group is an ortho & para directing.

(33) **(A).**

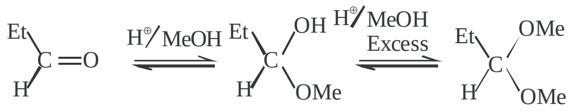


Due to intramolecular H-bonding and resonance stabilisation enol content is maximum.

(34) **(B).**



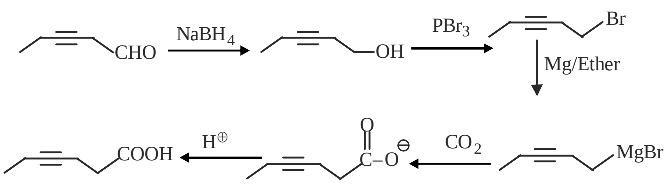
(35) **(D).**



Hemiacetal Acetal

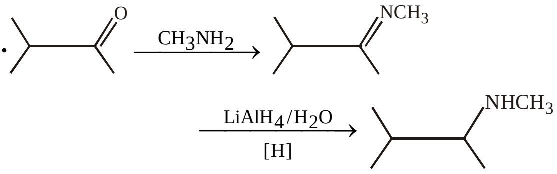
Acetone as substrate is less rective than propanal towards neucleophilic addition.

(36) **(A).**

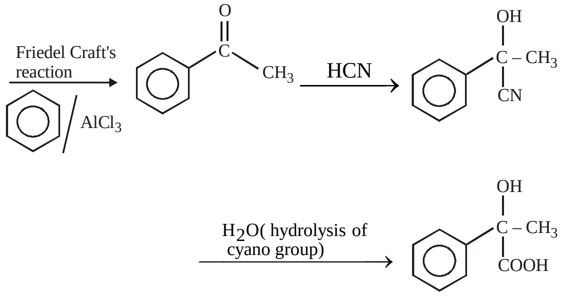


EXERCISE-5

(1) **(B).**

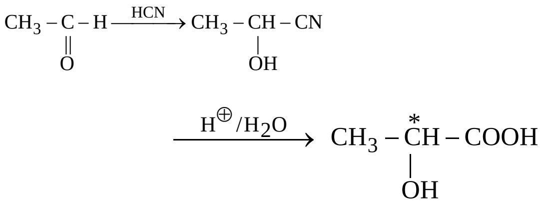


(2) **(D).** $CH_3COOH \xrightarrow{SOCl_2} CH_3-COCl$



(3) **(D).** Reactivity ∝ 1/steric-Hinderance

(4) **(A).**



$$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{HCN} CH_3-\underset{\underset{OH}{|}}{CH}-CN$$

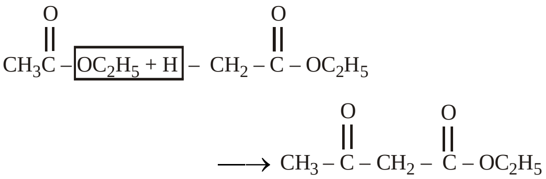
$$\xrightarrow{H^{\oplus}/H_2O} CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}H}-COOH$$

(Rac. mixture)

(5) **(D).** $CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl$

$$\xrightarrow{NH_3} CH_3CH_2CONH_2 \xrightarrow[Br_2]{KOH} CH_3CH_2CH_2NH_2$$

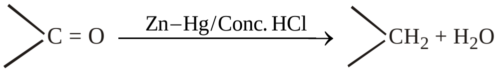
(6) **(A).**



$$CH_3\overset{\overset{O}{\|}}{C}-\boxed{OC_2H_5+H}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

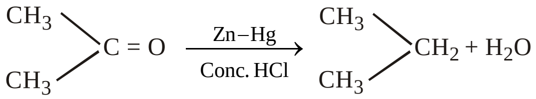
(ethyl acetoacetate)

(7) **(D).**



Clemmensen reduction

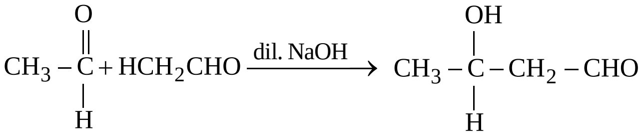
e.g.,



(8) **(A).** Aldehydes containing no α-hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation-reduction known as Cannizzaro's reaction

$$2C_6H_5CHO + NaOH \xrightarrow{50\%\ NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

(9) **(A).** Aldehyde and ketones having at least one α-hydrogen atom in presence of dilute alkali give β-hydroxy aldehyde or β-hyxroxy ketone.

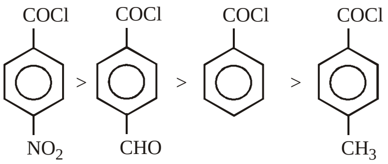


$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}+HCH_2CHO \xrightarrow{dil.\ NaOH} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CHO$$

Acetaldehyde Aldol

$$\xrightarrow[-H_2O]{\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH.CHO}$$

(10) **(C).** The degree of hydrolysis increases as the magnitude of positive charge on carbonyl group increases. Electron withdrawing group increases the positive charge and electron releasing group decreases the negative charge. Among these NO_2 and CHO are electron withdrawing group from which NO_2 has more – I effect than – CHO. On the other hand CH_3 is a electron releasing group therefore the order of reactivity towards hydrolysis is

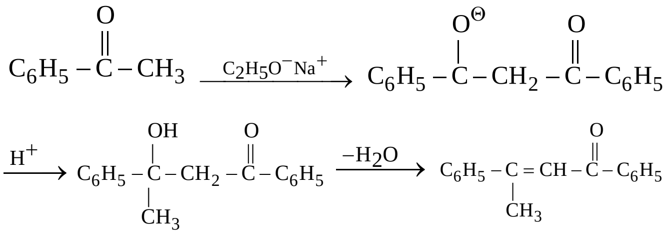


(11) **(C).** Electron withdrawing substituent increases the acidity by increasing the ionic character of – O – H by inductive effect.

Electronegativity decreases in the order : F > Cl > Br and hence – I effect also decreases in the same order, therefore the correct option is

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$$

(12) (B).



$$C_6H_5-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{C_2H_5O^-Na^+} C_6H_5-\overset{O^\ominus}{\overset{|}{C}}-CH_2-\overset{O}{\overset{||}{C}}-C_6H_5$$

$$\xrightarrow{H^+} C_6H_5-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{||}{C}}-C_6H_5 \xrightarrow{-H_2O} C_6H_5-\underset{CH_3}{C}=CH-\overset{O}{\overset{||}{C}}-C_6H_5$$

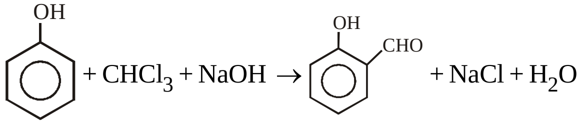
(13) (D). α-hydrogen of carbon of ketone is attached to electron withdrawing group (–I effect).

(14) (B). Weaker is basicity, better is the leaving group and more is rate of nucleophilic substitution.

(15) (C). Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces DDT (Dichlorodiphenyl trichloroethane).

(16) (C). α hydrogen is substituted by bromine.

(17) (B). (a) Reimer - Tiemann reaction,



(Here, a new C – C bond is formed.)

(b) Cannizaro reaction,

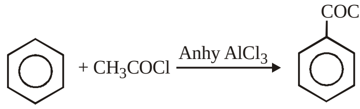
$$2HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOONa$$

(No new C – C bond is formed in this reaction.)

(c) Wrutz reaction : $2RX + \text{dry Na} \rightarrow R-R$

(one new C - C bond is formed.)

(d) Friedel - crafts acylation,



(New C - C bond is formed.)

Thus, among the given reactions, only cannizaro reaction does not involve the formation of a new C - C bond.

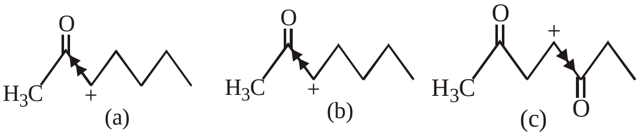
(18) (A). The reagent which can convert $-CONH_2$ group into $-NH_2$ group is used for this reaction.

Among the given reagents only $NaOH/Br_2$ converts $-CONH_3$ group to $-NH_2$ group, thus it is used for converting acetamide to methyl amine. This reaction is called Hoffmann bromamide reaction.

$$CH_3CONH_2 + NaOH + Br_2$$
$$\rightarrow \underset{\text{methyl amine}}{CH_2NH_2} + NaBr + Na_2CO_3 + H_2O$$

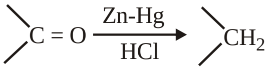
(19) (D). Lesser the electron density of acyl carbon atom, more will be the susceptibility of nucleophile to attack it. The Cl atom has strong –I effect because of the weak π-bond between the small sized C-atom and large sized Cl atom. Thus in CH_3COCl, acyl carbon has least electron density and hence, more susceptible for nucleophilic attack.

(20) (C). The ease of dehydration of the given compounds can be explained on the basis of the stability of the carbocation formed. In case of options (A), (B) and (D), a secondary carbocation is formed but the presence of an electron withdrawing > C=O group adjacent to the positively charged carbon, intensifies the charge and hence destabilies the species.



However, in case of option (C), a secondary carbocation is formed, but the electron withdrawing > C = O group is present away, as a farther result, the effect of this group is diminished and hence the carbocation is relatively more stable.

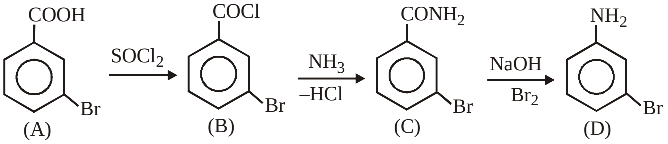
(21) (C).



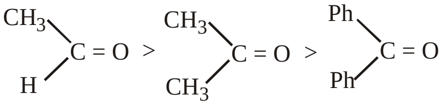
$$>C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2$$

Clemmensen reduction

(22) (D).



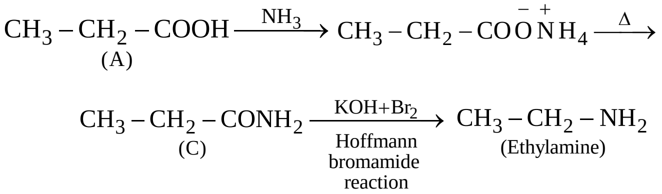
(23) (D). Correct reactivity order for nucleophilic addition reaction with PhMgBr



$$\begin{matrix}CH_3\\H\end{matrix}\!>C=O \;>\; \begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O \;>\; \begin{matrix}Ph\\Ph\end{matrix}\!>C=O$$

(due to steric crowding).

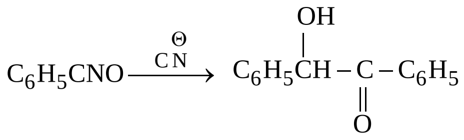
(24) (D).



$$\underset{(A)}{CH_3-CH_2-COOH} \xrightarrow{NH_3} CH_3-CH_2-CO\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta}$$

$$\underset{(C)}{CH_3-CH_2-CONH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{KOH+Br_2} \underset{\text{(Ethylamine)}}{CH_3-CH_2-NH_2}$$

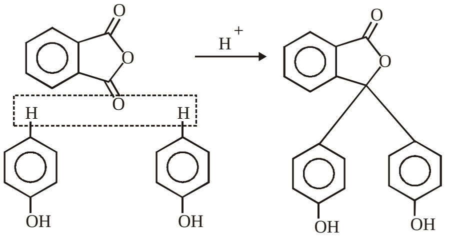
(25) (D). (a)



$$C_6H_5CNO \xrightarrow{\overset{\ominus}{C}N} C_6H_5\overset{OH}{\overset{|}{C}H}-\underset{O}{\underset{||}{C}}-C_6H_5$$

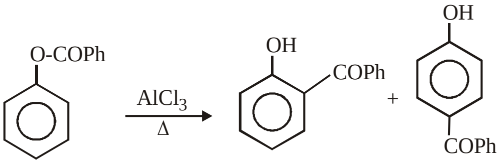
(Benzoin)

(b)



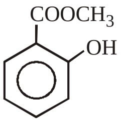
Phenolphthalein

(c)



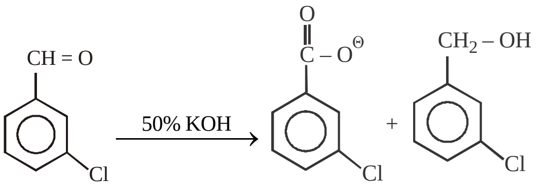
Fries rearrangement

(d)

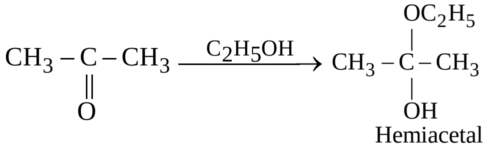


((Oil of wintergreen))

(26) **(C).** Cannizzaro reaction

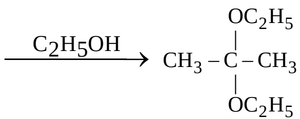


(27) **(D).**



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{C_2H_5OH} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}-CH_3$$

Hemiacetal

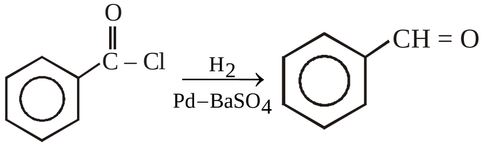


$$\xrightarrow{C_2H_5OH} CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}-CH_3$$

Acetal

(28) **(A).** $CF_3-COOH > CCl_3-COOH > HCOOH > CH_3COOH$ (K_a order)

(29) **(A).**



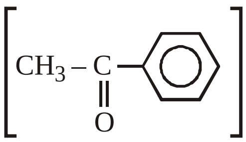
It is Rosenmund reaction.

(30) **(D).** $R-CH=O+H_2N-NH_2 \rightarrow R-CH=N-NH_2$

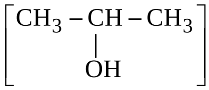
It is a Nucleophilic addition-elimination reaction.

(31) **(AD).** It is Iodoform reaction.

Acetophenone



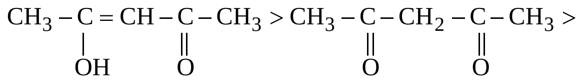
and 2-Hydroxypropane



$$\left[CH_3-\underset{\underset{OH}{|}}{CH}-CH_3\right]$$

both give a yellow precipitate of CHI_3 (iodoform) with iodine & alkali.

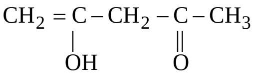
(32) **(C).** Stability order is



$$CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3 > CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 >$$

Intra molecular H-Bonding and conjugated diene and it has involved more acidic $-H\,[-CH_2-]$

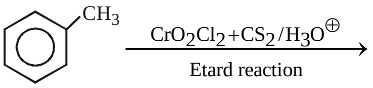
(No conjugated diene)

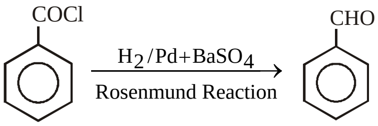


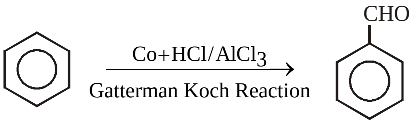
$$CH_2=\underset{\underset{OH}{|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Involvement of less acidic $-H$ in tautomerism

(33) **(A).** In presence of Zn – Hg and conc. HCl reduction is useful specially for aldehyde and ketone but carboxylic group remains uneffected.

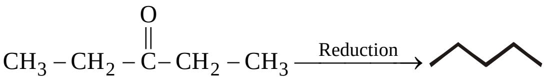






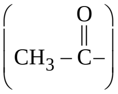
(34) **(D).** Electron withdrawing group i.e., – NO_2 favours nucleophilic attack.

(35) **(B).**



This ketone does not give tollens test.

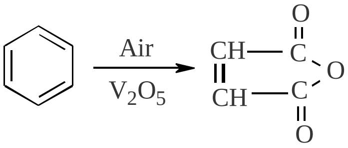
Also it does not give iodoform test because it does not have



$$\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$$

group.

(36) **(D).**

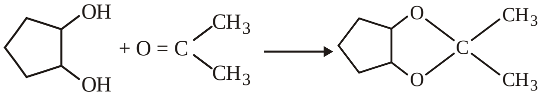


Maleic anhydride

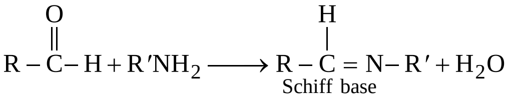
(37) **(D).** Reaction of carbonyl compounds with ammonia derivatives is an example of Nucleophilic addition elimination reaction.

(38) **(C).** EWG (electron withdrawing group) increases reactivity towards nucleophilic substitution reaction. $-NO_2$ is strong electron withdrawing group.

(39) **(A).** cis-cylopenta-1, 2-diol can form cyclic ketal whereas tran-cyclopenta-1, 2-diol can't form cyclic ketal.



(40) **(A).**



$$R-\overset{\overset{O}{\|}}{C}-H+R'NH_2 \longrightarrow \underset{\text{Schiff base}}{R-\overset{\overset{H}{|}}{C}=N-R'}+H_2O$$

(41) **(D).** It is known that basic need for the existence of Keto-enol tautomers is the presence of at least one hydrogen atom at adjacent sp^3 carbon of carbonyl carbon.

(42) **(C).**

(i) $CH_3-CH_2-CH_2-Br$

$\xrightarrow{\text{elimination}} CH_3-CH=CH_2$

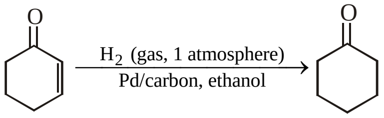
(ii)  $\xrightarrow{\text{elimination}} CH_3-CH=CH_2$

(iii) $CH_3-CH_2-CH_2-OH \xrightarrow{HBr}$

$CH_3-CH_2-CH_2-Br \xrightarrow{\text{elimination}} CH_3-CH=CH_2$

(iv) $CH_2=C=O \xrightarrow{HBr}$ No reaction.

(43) **(B).**



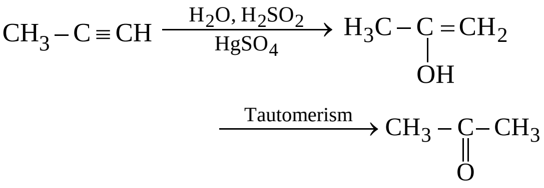
During hydrogenation of α,β unsaturated carbonyl compound by pd catalyst selective reduction is observed of double bond.

(44) **(B).** On the basis of –I effect, the correct acidic strength would be II > III > I

Acidic strength ∝ – I, – M effect

–I effect depends upon distance so II have stronger –I effect than III.

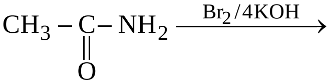
(45) **(C).**



$$CH_3-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\,H_2SO_2} H_3C-\underset{\underset{OH}{|}}{C}=CH_2$$

$$\xrightarrow{\text{Tautomerism}} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

(46) **(A).**

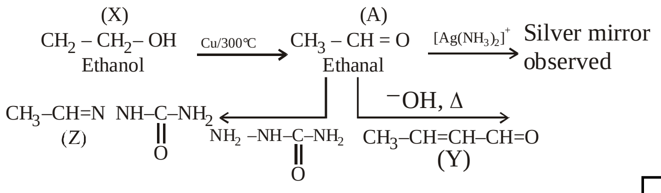


$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/4KOH}$$

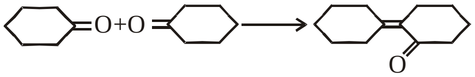
$$CH_3-NH_2+2KBr+K_2CO_3$$

This reaction is known as hoffmann hypobromamide reaction.

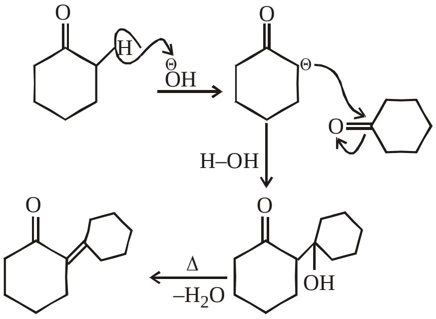
(47) **(B).**



(48) **(A).**

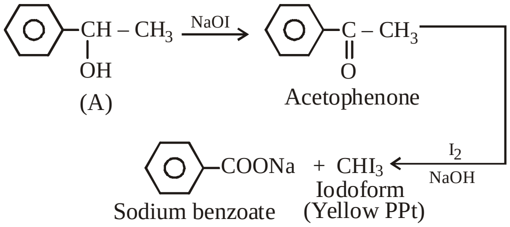


Mechanism :



(49) **(D).** Due to formation of intermolecular H-bonding in carboxylic acid, association occurs. Hence boiling point increases and become more than the boiling point of aldehydes, ketones and alcohols of comparable molecular masses.

(50) **(A).** Option (A) is secondary alcohol which on oxidation gives phenylmethyl ketone (Acetophenone). This on reaction with I_2 and NaOH form iodoform and sodium benzoate.



(51) **(B).**