Chapter 26

Aldehydes, Ketones and Carboxylic acids

(A) ALDEHYDES AND KETONES

Structure of carbonyl group

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.

The carbonyl group is polar in nature. The π–bond cloud is unsymmetrical because of the greater electronegativity of oxygen (3.5) than the carbon (2.5).

PREPARATION OF ALDEHYDES AND KETONES

I. For Both Aldehydes and Ketones

(i) By Oxidation of Alcohols

$$RCH_2OH\ (1°) \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} RCHO$$

$$R_2CHOH\ (2°) \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} RCOR$$

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.

Note : Collins reagent ($CrO_3 . 2C_5H_5N$) and pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$) are mild oxidising agents thereby preventing the further oxidation of aldehydes to carboxylic acids.

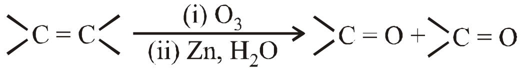
(ii) By Dehydrogenation of Alcohols

$$RCH_2OH\ (1°) \xrightarrow[573\text{ K}]{Cu} RCHO$$

$$R_2CHOH\ (2°) \xrightarrow[573\text{ K}]{Cu} R_2CO$$

(iii) From Hydrocarbons

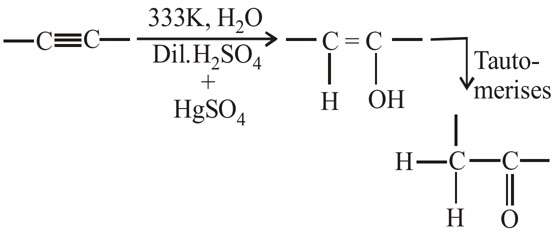
(a) By ozonolysis of alkenes



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

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

(b) By hydration of alkynes



$$-C\equiv C- \xrightarrow[\text{Dil.}H_2SO_4 + HgSO_4]{333K,\ H_2O} -\underset{H}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}- \xrightarrow{\text{Tautomerises}} H-\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{O}{\underset{\|}{C}}-$$

This is called Kucherov reaction.

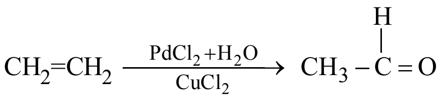
Note:

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

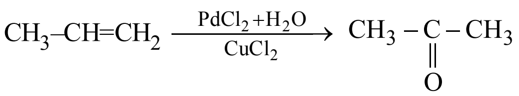
(ii) Only ethyne gives acetaldehyde while other alkynes give ketones.

(c) By Wacker's process

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



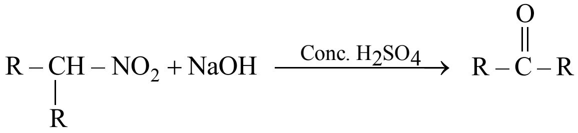
$$CH_2{=}CH_2 \xrightarrow[CuCl_2]{PdCl_2+H_2O} CH_3-\overset{H}{\overset{|}{C}}=O$$



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

(iv) Oxidation of Nitroalkane (NEF Reaction)

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

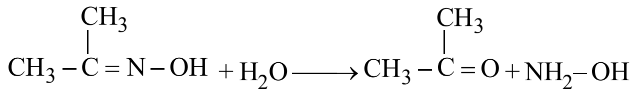


$$R-\underset{R}{\underset{|}{CH}}-NO_2 + NaOH \xrightarrow{\text{Conc. }H_2SO_4} R-\overset{O}{\overset{\|}{C}}-R$$

(v) By Hydrolysis of Oximes:

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

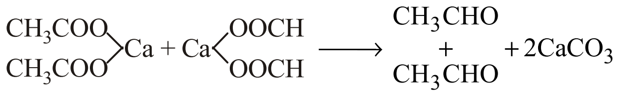
Acetaldoxime



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

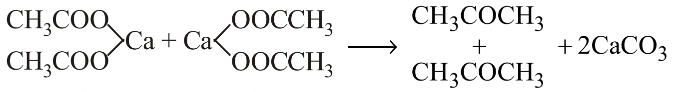
Acetone oxime

(vi) By Dry Distillation of Calcium Salts of Fatty Acids



$$(CH_3COO)_2Ca + Ca(OOCH)_2 \longrightarrow CH_3CHO + CH_3CHO + 2CaCO_3$$

Cal. acetate Cal. formate Acetaldehyde

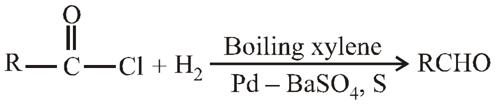


$$(CH_3COO)_2Ca + Ca(OOCCH_3)_2 \longrightarrow CH_3COCH_3 + CH_3COCH_3 + 2CaCO_3$$

Calcium acetate (2 moles) Acetone (2 moles)

II. For Aldehydes Only

(i) From Acyl/Acid Chloride



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{Pd}-BaSO_4,\ S]{\text{Boiling xylene}} RCHO$$

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

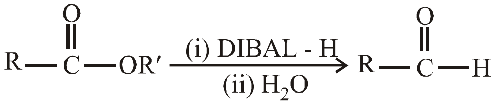
In the above reaction $BaSO_4$ acts as catalyst poison and decreases the catalytic efficiency of Pd, due to which further reduction of aldehyde to alcohol can't take place.

(ii) From Nitriles and Esters

$$R-C\equiv N + 2H \xrightarrow{SnCl_2/HCl} R-CH{=}NH.HCl$$

$$\xrightarrow{H_2O} RCHO + NH_4Cl$$

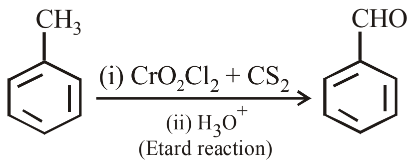
$$RCN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(iBu)_2 \text{ or DIBAL}-H} RCHO$$

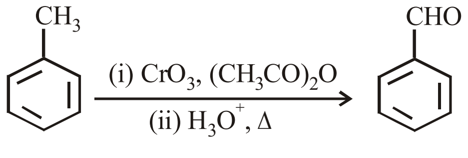


$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL - H}} R-\overset{O}{\overset{\|}{C}}-H$$

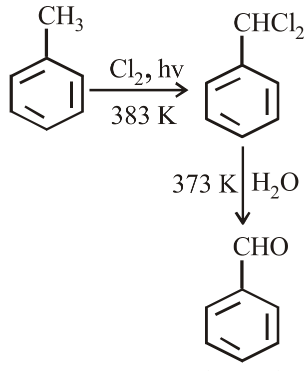
(iii) From Hydrocarbons

(a) By oxidation of methyl benezene





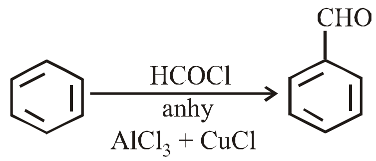
(b) By side-chain chlorination followed by hydrolysis



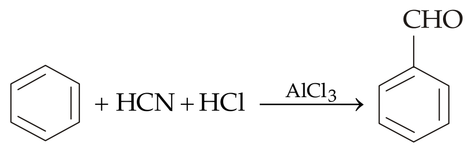
(c) By Gatterman-Koch reaction

$$CO + HCl \rightarrow HCOCl$$

Formyl chloride (unstable)

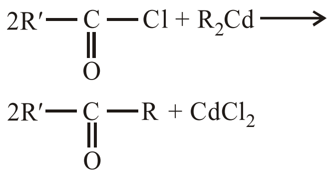


(d) By Gattermann reaction



III. For Ketones Only

(i) From Acyl Chloride



$$2R'-\underset{O}{\underset{\|}{C}}-Cl + R_2Cd \longrightarrow$$

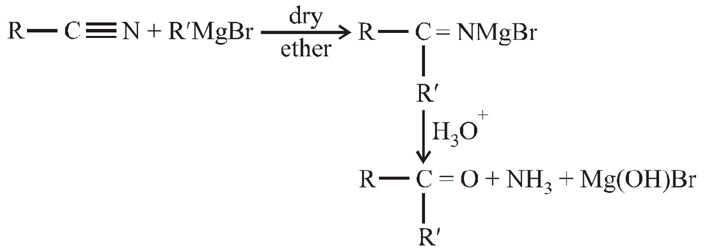
$$2R'-\underset{O}{\underset{\|}{C}}-R + CdCl_2$$

Dialkyl cadmium can be obtained by

$$2R-Mg-Cl + CdCl_2 \longrightarrow R-Cd-R + 2MgCl_2$$

This method is very important for synthesis of Ketones.

(ii) From Nitriles



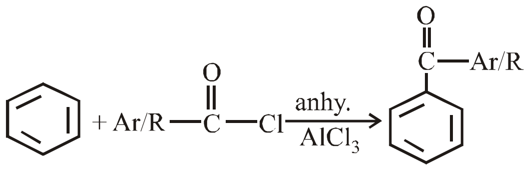
$$R-C\equiv N + R'MgBr \xrightarrow[\text{ether}]{\text{dry}} R-\underset{R'}{\underset{|}{C}}=NMgBr \xrightarrow{H_3O^+} R-\underset{R'}{\underset{|}{C}}=O + NH_3 + Mg(OH)Br$$

Note: If instead of alkyl or aryl nitriles, HCN is used aldehydes are formed.

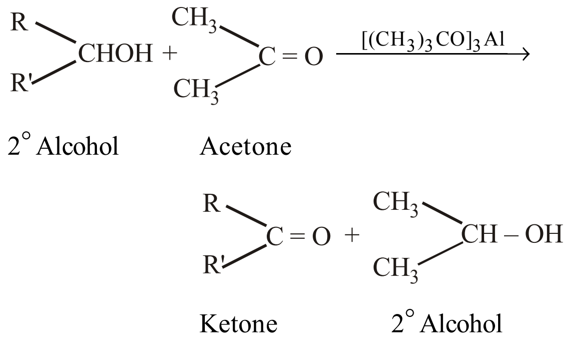
$$HCN + R-MgI \xrightarrow[\text{ether}]{\text{Dry}} [R-CH=NMgI]$$

$$\xrightarrow[-NH_3,]{H_3O^+} R-CHO + Mg(OH)I$$

(iii) By Friedal-Crafts Acylation Reaction



Note: Oppenauer oxidation:



PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

(i) 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.

(ii) Odour

Lower aldehydes have an unpleasant odour. Higher aldehydes and ketones have a pleasant odour.

(iii) Boiling and melting points:

Boiling point and melting point $\propto$ Molecular weight $\propto \dfrac{1}{\text{Branching}}$

Boiling point of aldehydes and ketones are higher than those of hydrocarbons and ethers. This is due to dipole-dipole interactions between the opposite ends of $>C=O$ dipoles.

Ketones have higher Boiling point than isomeric aldehydes. This is due to presence of two electrons donating alkyl groups around $>C=O$ group which makes them more polar.

Boiling point of alcohols and carboxylic acids are higher than aldehydes and ketones. This is due to intermolecular H-bonding in alcohols and acids which is much stronger than dipole-dipole interactions in aldehydes and ketones.

(iv) Solubility :

Lower aldehydes and ketones are soluble in water due to H-bonding between the polar carbonyl group and the water molecules. Solubility in H_2O decreases with increase in size of alkyl group. Due to larger hydrocarbon part, aromatic aldehydes and ketones are much less soluble than aliphatic analogues. All aldehydes and ketones are fairly soluble in organic solvents.

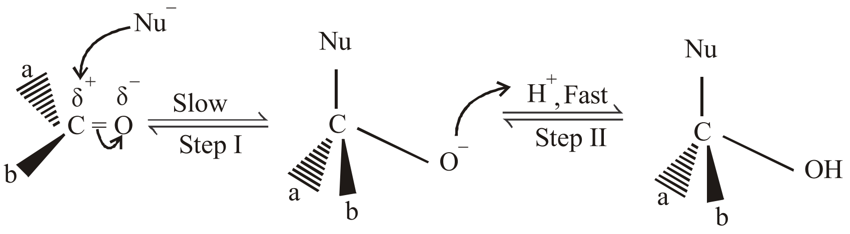
CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

The reaction of aldehydes and ketones can be divided into the following categories :

1. Nucleophilic addition reactions.
2. Reduction reactions.
3. Oxidation reactions
4. Reactions with alkalies.
5. Miscellaneous reactions.

1. Nucleophilic Addition Reactions

Mechanism of nucleophilic addition to carbonyl group.

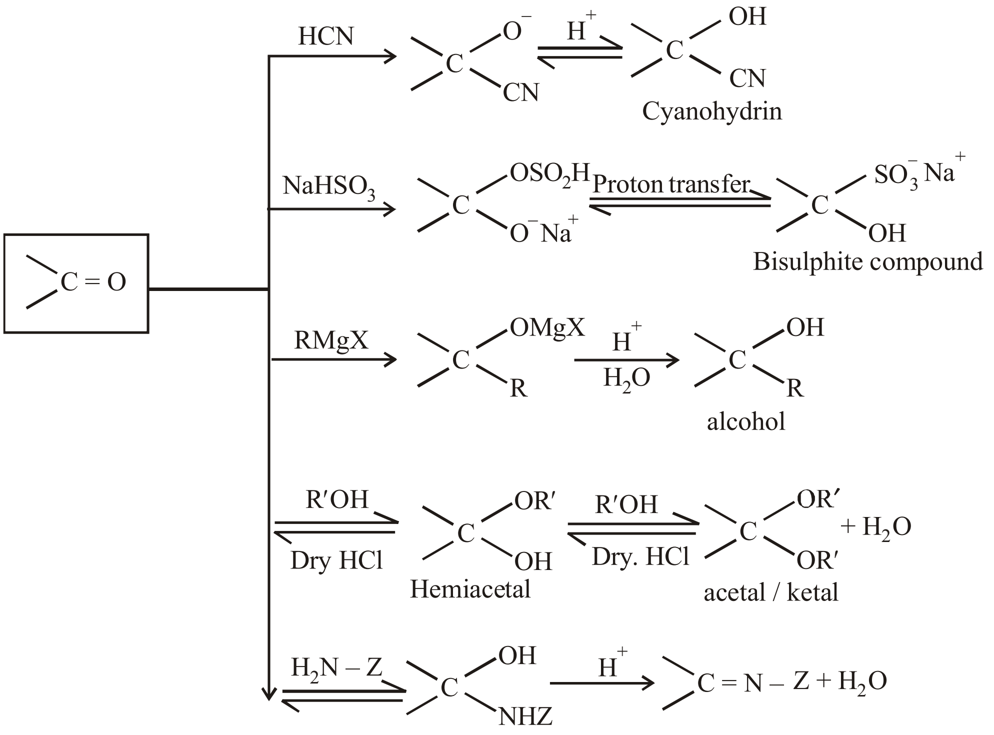


Aldehydes are more reactive than ketones due to:

(i) **Inductive effect:** Alkyl group has + I effect which decreases polarity of carbonyl group. Thus ketones containing two alkyl groups are more reactive in comparison to one alkyl group containing aldehydes.

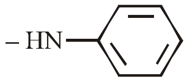
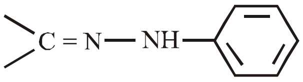
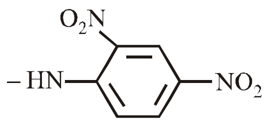
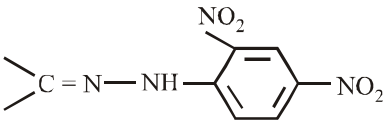
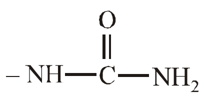
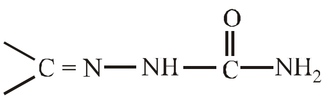
(ii) **Steric effects:** As the number and size of alkyl groups increases the attack of the nucleophile on carbonyl group C becomes more and more difficult due to steric hindrance.

The various nucleophilic addition reactions are:



(for Z → see table)

Some ammonia-substituted derivatives of aldehydes and ketones

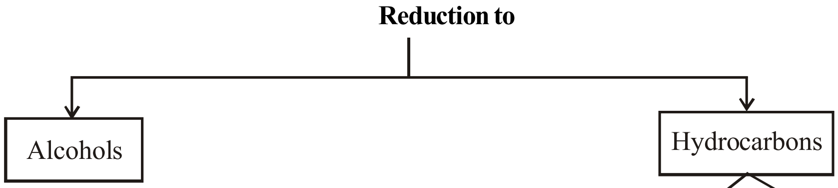
Z	Reagent Name	Carbonyl derivative	Product name
$-H$	Ammonia	$>C=NH$	Imine
$-R$	Amine	$>C=NR$	Substituted imine (Schiff's base)
$-OH$	Hydroxylamine	$>C-N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2, 4 - Dinitrophenyl-hydrazine		2, 4-Dinitrophenyl-hydrazone
 $-NH-\overset{O}{\overset{\Vert}{C}}-NH_2$	Semicarbazide	 $>C=N-NH-\overset{O}{\overset{\Vert}{C}}-NH_2$	Semicarbazone

Note: (i) Benzaldehyde forms $NaHSO_3$ adduct but acetophenone does not.

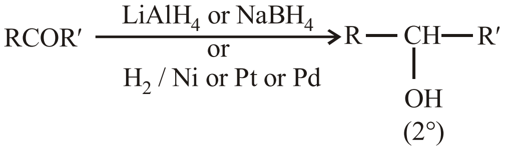
(ii) In addition of alcohols if dihydric alcohol is used a cyclic acetal or ketal is formed.

(iii) In addition of NH_3 derivatives resulting compounds formed are crystalline solids with sharp melting points. Thus these derivatives are used for identification and characterization of aldehydes and ketones.

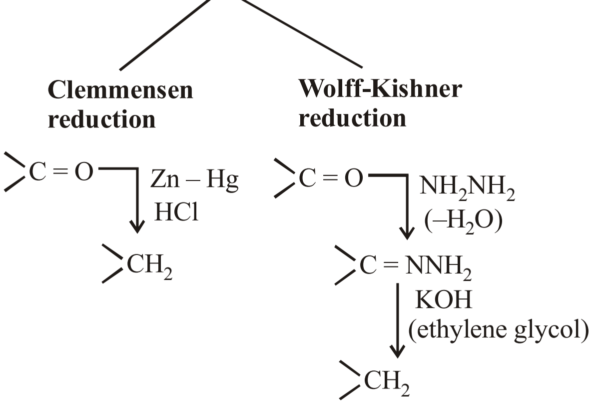
2. Reduction Reactions



$$RCHO \xrightarrow[\text{LiAlH}_4 \text{ or NaBH}_4]{H_2 / Pd \text{ or Ni or Pt} \text{ or}} RCH_2OH \ (1°)$$



$$RCOR' \xrightarrow[H_2 / \text{Ni or Pt or Pd}]{\text{LiAlH}_4 \text{ or NaBH}_4 \text{ or}} R-\underset{\underset{\text{OH}}{|}}{CH}-R' \ (2°)$$



Note: Aldehydes and ketones can be also reduced to corresponding hydrocarbons by heating with HI in presence of red P at 423K.

3. Oxidation Reactions

Oxidation of Aldehydes

$$R-CHO \xrightarrow{[O]} RCOOH$$

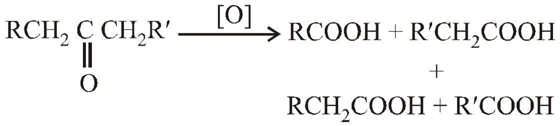
Aldehydes get easily oxidised by strong oxidising agents like HNO_3, $K_2Cr_2O_7$, $KMnO_4$ etc. as well as by weak oxidising agents like Fehling's and Tollen's reagents.

Oxidation of Ketones

Strong oxidising agent and elevated temperatures needed. In case of symmetrical ketones mixture of two acids is always obtained.

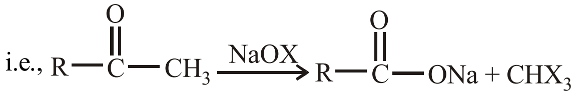
$$R-CH_2COCH_2-R \xrightarrow{[O]} RCH_2COOH + RCOOH$$

In case of unsymmetrical ketones (R ≠ R'), keto group stays with smaller alkyl group (Popoff's rule).



$$RCH_2\underset{\underset{O}{\|}}{C}CH_2R' \xrightarrow{[O]} RCOOH + R'CH_2COOH + RCH_2COOH + R'COOH$$

Note: Aldehydes and ketones having one methyl group linked to carbonyl C-atom, i.e., methyl ketones, show haloform reaction



i.e., $$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-ONa + CHX_3$$

$$R-COCH_3 \xrightarrow{NaOI} RCOO^-Na^+ + CHI_3$$

This is **Iodoform** test and is used for characterising compounds with CH_3CO group or $CH_3CH(OH)$ group.

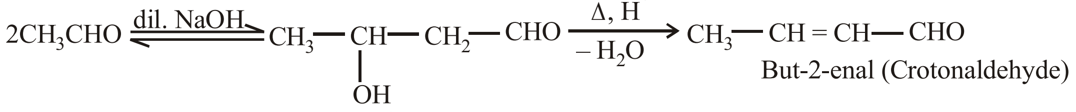
4. Reactions with Alkalies

Due to strong electron withdrawing nature (–I effect) of the carbonyl group and resonance stabilisation of the conjugate base, α-H-atoms of carbonyl compounds are acidic in nature. This acidic nature of α-H gives rise to a large number of reactions of carbonyl compounds.

(i) Aldol Condensation

Two molecules of aldehyde or ketone containing atleast one α-H atom condense in presence of a dilute alkali to form a β-hydroxyaldehyde or a β-hydroxyketone respectively.

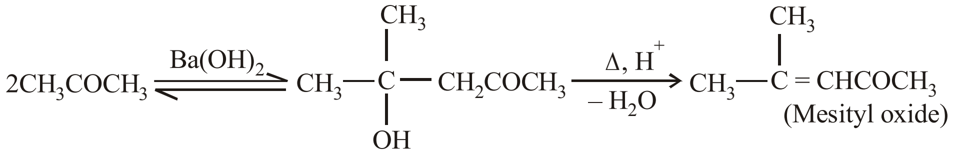
For example:



$$2CH_3CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta, H^+} CH_3-CH=CH-CHO$$

3-Hydroxybutanal (Aldol)

But-2-enal (Crotonaldehyde)

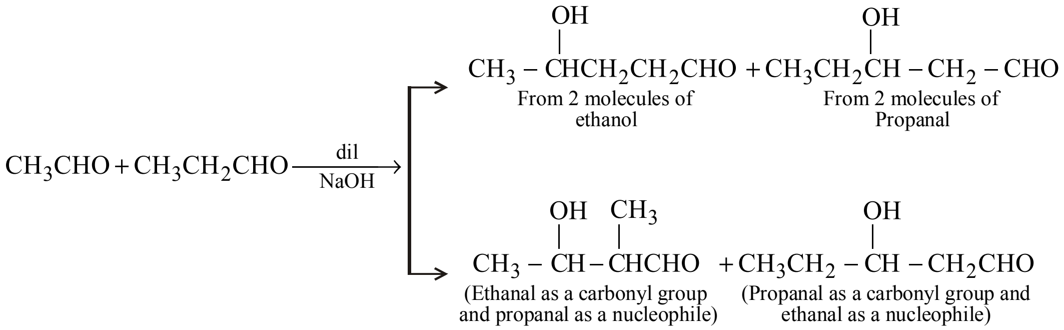


$$2CH_3COCH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta, H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=CHCOCH_3$$

(Mesityl oxide)

(ii) Cross-aldol condensation: An aldol condensation between two different aldehydes or two ketones or between one aldehyde and one ketone.

For example,



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[NaOH]{dil} CH_3-\overset{\overset{OH}{|}}{C}HCH_2CH_2CHO + CH_3CH_2\overset{\overset{OH}{|}}{C}H-CH_2-CHO$$

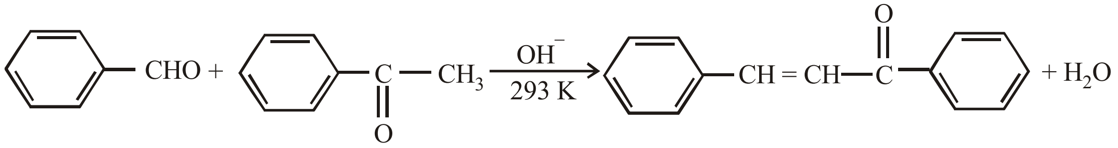
From 2 molecules of ethanol

From 2 molecules of Propanal

$$CH_3-\overset{\overset{OH}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}HCHO + CH_3CH_2-\overset{\overset{OH}{|}}{C}H-CH_2CHO$$

(Ethanal as a carbonyl group and propanal as a nucleophile)

(Propanal as a carbonyl group and ethanal as a nucleophile)



Note: Cross aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or a ketone is called Claisen-Schmidt condensation.

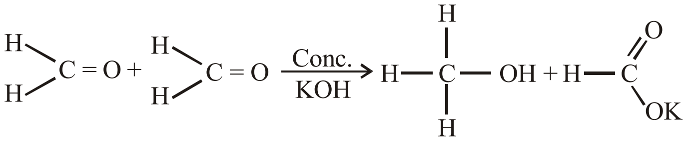
(iii) Cannizaro reaction: Those aldehydes, which do not contain α–hydrogen atoms give this reaction with conc. alkali like conc. NaOH or KOH. In this reaction two molecules of aldehyde react in such a way that one molecule gets oxidised and the other gets reduced. This type of reaction is called disproportionation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

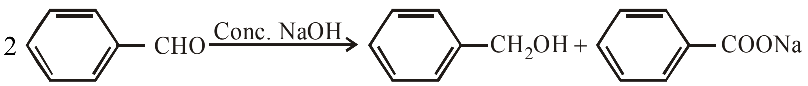
When two molecules in a reaction are same it is called simple Cannizzaro reaction. In case of different molecules, it is a mixed cross Cannizzaro reaction. In mixed cross Cannizzaro reaction

More reactive aldehyde ⟶ Gets oxidised

Less reactive aldehyde ⟶ Gets reduced

For example,





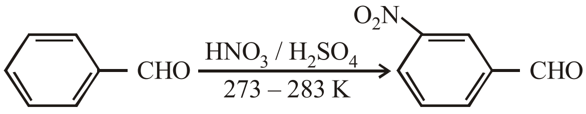
$$HCHO + C_6H_5CHO \xrightarrow{Conc.NaOH} HCOONa + C_6H_5CH_2OH$$

(Oxidation) (Reduction)

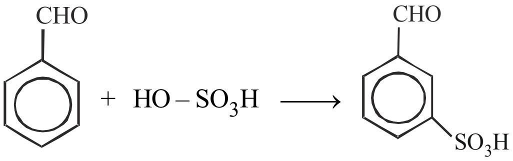
Miscellaneous Reactions

(i) Electrophilic substitution reactions: Carbonyl group is a deactivating and meta-directing group.

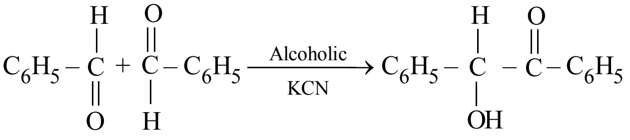
(a) Nitration :



(b) Sulphonation :



(ii) Benzoin condensation :

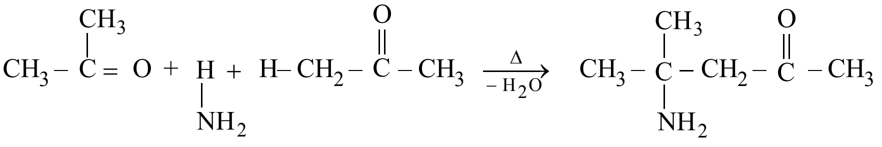


$$C_6H_5-\underset{\overset{\|}{O}}{\overset{\overset{H}{|}}{C}} + \underset{\overset{|}{H}}{\overset{\overset{O}{\|}}{C}}-C_6H_5 \xrightarrow[KCN]{Alcoholic} C_6H_5-\underset{\overset{|}{OH}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

Benzoin

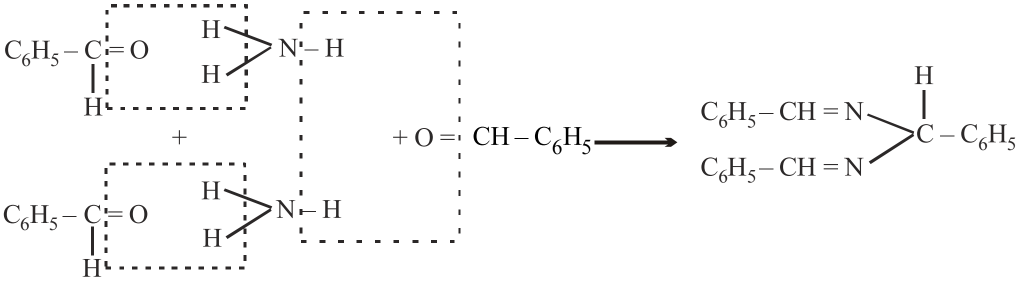
(iii) Cold dilute Schiff's reagent (colour less) + Aldehyde $\longrightarrow$ Pink coloured solution

(iv) With ammonia :



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

Diacetoneamine



Hydrobenzamide (amide without – $CONH_2$ group)

DISTINCTION BETWEEN ALDEHYDES AND KETONES

Test	Aldehydes	Ketones
1. With Tollen's reagent	give silver mirror $RCHO + 2\,[Ag(NH_3)_2]^+ + 3OH^-$ $\downarrow$ $RCOO^- + 2Ag + 2H_2O + 4NH_3$	No action
2. With Fehling's solution	give red ppt of Cu_2O (only aliphatic aldehydes)	No action
3. Reduction with $LiAlH_4$	1° alcohols are formed	2° alcohols are formed
4. Action with alcohols in presence of dry HCl gas	Form acetals easily	Do not form ketales easily
5. Action with ammonia	Give aldehyde-ammonia adducts	Form complex condensation products
6. With Schiff's reagent	Restore pink colour	No action

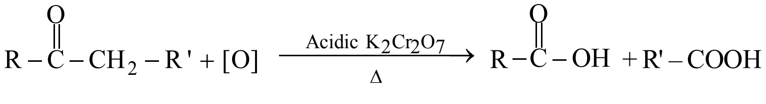
(B) CARBOXYLIC ACIDS

PREPARATION OF CARBOXYLIC ACIDS

(i) From 1° Alcohols, Aldehydes and Ketones.

$$RCH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\ alk.\ KMnO_4} RCOOH$$

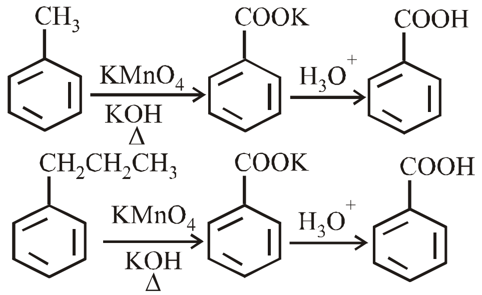
$$RCHO \xrightarrow{[O]} RCOOH$$



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

This gives poor yield of carboxylic acids.

(ii) From alkylbenzenes.



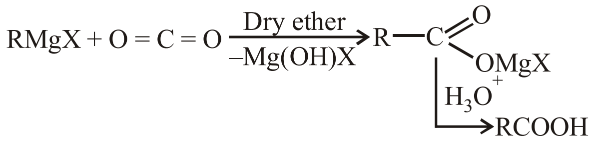
Note : Presence of electron withdrawing groups in benzene ring increases the reactivity of the benzylic hydrogens. Thus p-nitrotoluene is much more easily oxidised than toluene.

(iii) From Nitriles and Amides.

$$RCN \xrightarrow[H^+/OH^-]{H_2O} RCONH_2 \xrightarrow[H^+/OH^-]{H_2O} RCOOH$$

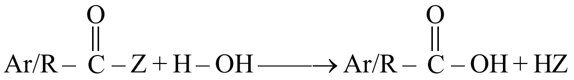
$$RCONH_2 \xrightarrow[\Delta]{H_3O^+} RCOOH + NH_3$$

(iv) From Grignard Reagent.



$$RMgX + O=C=O \xrightarrow[-Mg(OH)X]{\text{Dry ether}} R-C\overset{O}{\underset{OMgX}{}} \xrightarrow{H_3O^+} RCOOH$$

(v) From Hydrolysis of Acid Derivatives:



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

(a) $RCOOR' \overset{H_2O}{\rightleftharpoons} RCOOH + R'OH$

$RCOOR' \overset{NaOH}{\rightleftharpoons} RCOONa + R'OH \xrightarrow{H_3O^+} RCOOH$

(b) $RCOCl \xrightarrow{H_2O} RCOOH + HCl$

(c) $(RCO)_2O \xrightarrow{H_2O} 2\ RCOOH$

(d) $R-CONH_2 + HOH \xrightarrow{\text{dil.HCl}} RCOOH + NH_4Cl$

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

(i) 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 of the carbon chain which results in 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.

(ii) Boiling points: Boiling point ∝ Molecular weight

The boiling points of carboxylic acids are higher than hydrocarbons, aldehydes, ketones and even alcohols of comparable molecular masses.

This is due to extensive H-bonding resulting in association of carboxylic acid molecules. The H-bonds formed in carboxylic acids are even more stronger than alcohols. Carboxylic acids exist as cyclic dimer in vapour phase or in aprotic solvents.

(iii) Solubility: Simple aliphatic acids (upto 4 C-atoms) are soluble in H_2O due to H-bonding. Higher acids are insoluble in H_2O due to increased hydrophobic interaction of hydrocarbon part. Aromatic acids are also insoluble due to their large hydrocarbon part. Carboxylic acids are soluble in organic solvents like C_6H_6, ether, $CHCl_3$, etc.

CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

I. Reactionsd Due to Cleavage of O–H Bond:

Acid strength of acids

(i) $2RCOOH + 2Na \longrightarrow 2RCOO^-Na^+ + H_2$

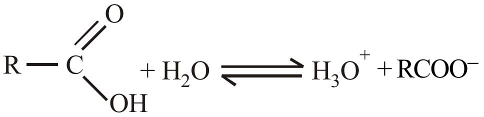
(ii) $RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$

(iii) $RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + CO_2$

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

(iv) $2RCOOH + Ca(OH)_2 \rightarrow (RCOO)_2Ca + 2H_2O$

In water, carboxylic acids dissociate as :



$$R-C\overset{O}{\underset{OH}{}} + H_2O \rightleftharpoons H_3O^+ + RCOO^-$$

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[H_2O][RCOOH]}$$

$$\Rightarrow K_a = K_{eq}[H_2O] = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

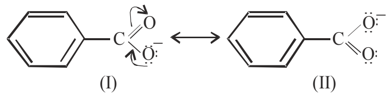
and $pk_a = -\log K_a$

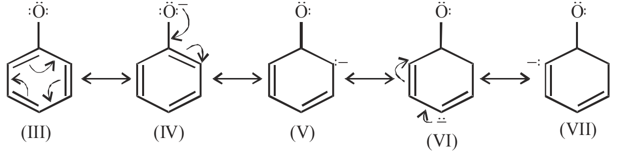
∴ smaller the pk_a, stronger the acid.

The acidity of carboxylic acids, phenols and alcohols follows the order:

Carboxylic acid > phenol > alcohol

Consider the resonating structures of carboxylate ion and phenoxide ion.





This is because the carboxylate ion is stabilised by two equivalent resonance structures with –ve charge at more electronegative O-atom. On the other hand, phenoxide ion has non-equivalent structures with –ve charge on less electronegative C-atom. Thus, contribution of resonating structures of phenoxide ion towards resonance is very small.

Therefore, carboxylate ion is more stable than phenoxide ion so carboxylic acids are more acidic than phenols.

EWG increase the acidity of acid by stabilising the carboxylate ion whereas EDG decrease the acidity by destabilising the ion.

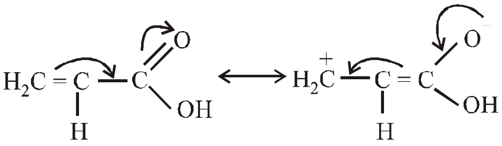
Note:

(i) More will be the electron withdrawing nature of substituent greater will be acidic strength.

(ii) More will be the number of electron withdrawing substituents greater will be acidic strength.

(iii) As the distance between electron withdrawing substituent and – COOH group increases acidic strength decreases.

(iv) Direct attachment of phenyl or vinyl groups increase the acidity of acid due to resonance:



In general, acidity increases as the electronegativity of the carbon atom directly attached to –COOH group increases or the hybridization of the carbon atom directly attached to –COOH changes from $sp^3 \rightarrow sp^2 \rightarrow sp$.

The order of acidity of various acids is as follows:

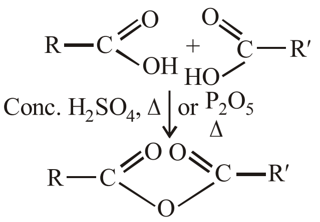
$$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NC-CH_2COOH > FCH_2COOH > ClCH_2COOH$$

$$> BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$$

Note: o–Substituted benzoic acids are usually stronger acids than benzoic acid regardless of the nature of the substituent.

II. Cleavage of C – OH Bond

(i) Anhydride Formation



Acid anhydrides can also be obtained by treating acid chlorides with carboxylic acids.

(ii) Esterification

$$RCOOH + R'OH \underset{\text{Conc. } H_2SO_4}{\overset{\text{Dry HCl or}}{\rightleftharpoons}} RCOOR' + H_2O$$

Note: As the number and size of the substituents around the –COOH or –OH group increases, the rate of esterification decreases.

(iii) Formation of Acid Chlorides.

Reaction with PCl_5, PCl_3 and $SOCl_2$

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

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

(iv) Reaction with NH_3

$$RCOOH + NH_3 \rightleftharpoons RCOO^-NH_4^+ \xrightarrow{\Delta(-H_2O)} RCONH_2$$

III. Reaction Involving — COOH Group

(i) Reduction:

(a) Reduction to alkanes:

$$RCOOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether or } B_2H_6/\text{ether}} RCH_2OH$$

$NaBH_4$ does not reduce the carboxyl group B_2H_6 does not reduce groups like ester, – NO_2, halo, etc.

(b) Reduction to alkanes:

$$R-COOH + 6HI \xrightarrow[473K]{\text{Red P}} R-CH_3 + 2H_2O + 3I_2$$

(ii) Decarboxylation

$$RCOONa \xrightarrow[\Delta]{NaOH + CaO \text{ (soda lime)}} R-H + Na_2CO_3$$

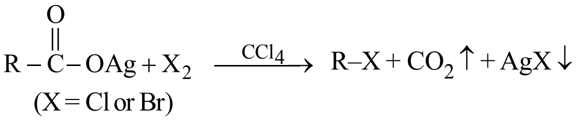
(iii) Kolbe's electrolytic synthesis :

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

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

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

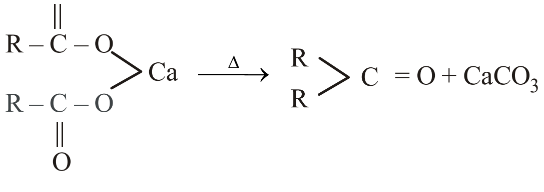
(iv) Hunsdiecker reaction :



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

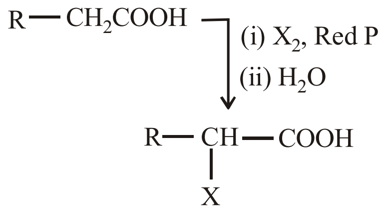
(X = Cl or Br)

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



IV. Substitution in Hydrocarbon Part

(i) Halogenation



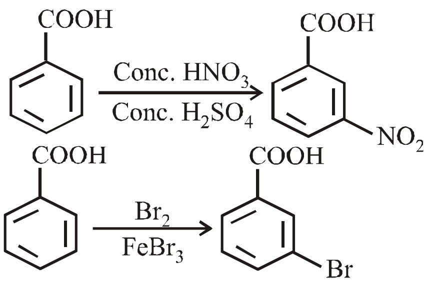
$$R-CH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{, Red P}} R-\underset{\substack{|\\X}}{CH}-COOH$$

α - Halocarboxylic acid (X = Cl, Br)

This is **Hell-Volhard-Zelinsky** (HVZ) reaction

Acids which do not have α–hydrogens do not show HVZ reaction

(ii) Ring Substitution :



Note: – COOH group is m-directing. Aromatic acids do not undergo Friedal Crafts reaction.

DISTINCTION BETWEEN PHENOL AND CARBOXYLIC ACID

Test	Carboxylic acid	Phenol
1. Sodium bicarbonate test	R – COOH with $NaHCO_3$, give brisk effervescence due to evolution of CO_2 gas	No reaction
2. Ferric chloride test	R – COOH give coloured ppt with neutral $FeCl_3$ sol Ex: $3CH_3COOH + FeCl_3 \longrightarrow \underset{\text{Buff coloured}}{(CH_3COO)_3Fe} + 3HCl$	C_6H_5OH give violet coloured ppt. with $FeCl_3$ solution $3C_6H_5OH + FeCl_3 \longrightarrow \underset{\substack{\text{ferric phenoxide}\\\text{(violet coloured)}}}{(C_6H_5O)_3Fe} + 3HCl$

CONCEPT MAP

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aldehydes and Ketones

Preparation of aldehydes and ketones

(a) $1^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Aldehyde}$

$2^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Ketone}$

(b) **Dehydrogenation of alcohols**

$1^\circ \text{ Alcohol} \xrightarrow{Cu,\ 573\ K} \text{Aldehyde}$

$2^\circ \text{ Alcohol} \xrightarrow{Cu,\ 573\ K} \text{Ketone}$

(c) **Ozonolysis of alkenes**

$CH_3CH - CHCH_3 + O_3 \xrightarrow[H_2O, Zn]{} 2CH_3CHO$

(d) **Hydration of alkynes**

$CH \equiv CH + H_2O \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4} CH_3 - CHO$

$CH_3C \equiv CH + H_2O \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4} CH_3 - \underset{\underset{O}{\|}}{C} - CH_3$

Preparation of aldehydes only

- **Rosenmund reduction**

  $\text{Acyl chloride} \xrightarrow{H_2\text{-Pd-BaSO}_4} \text{Aldehyde}$
- **Stephen reaction**

  $RCN + SnCl_2 + HCl \xrightarrow{H_3O^+} RCHO$
- **Gatterman-Koch reaction**

  $\text{Benzene} \xrightarrow[\text{Anhy. } AlCl_3/CuCl]{CO,\ HCl} \text{Benzaldehyde}$

Preparation of ketones only

- Friedel crafts acylation

  $C_6H_6 + Ar/R - \overset{\overset{O}{\|}}{C} - Cl \rightarrow C_6H_5COCl$
- $CH_3CH_2C \equiv N + C_6H_5MgBr$

  $\xrightarrow{\text{ether}} CH_3CH_2 - \overset{\overset{O}{\|}}{C} - C_6H_5$

Properties of aldehydes and ketones

- Aldehydes are more reactive than ketones in nucleophilic addition reactions. These reactions are following

  (a) $>C = O + :CN^- \rightleftharpoons >C<^{CN}_{OH}$

  (b) $>C = O + NaHSO_3 \rightleftharpoons >C<^{SO_2Na}_{OH}$

  (c) $>C = O \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) RMgX}}$

  $>\underset{R}{\underset{|}{C}}-OH + Mg<^{OH}_{X}$
- $\text{Aldehydes + alcohols} \xrightarrow{\text{dry HCl}} \text{Acetal}$
- $\text{Ketones + alcohols} \xrightarrow{\text{dry HCl}} \text{Ketal}$
- $>C = O + H_2N - Z \rightarrow >C = N - Z + H_2O$

  (Z = Alkyl, aryl, $-NH_2$, $-OH$, $-NH-C_6H_5$, $-NHCONH_2$ etc.)
- **Clemmensen reduction**

  $>C = O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$
- **Wolff – kishner reduction**

  $>C = O \xrightarrow[\text{(ii) KOH/ethylene glycol}]{\text{(i) } NH_2-NH_2} >CH_2 + N_2$
- Aldehydes gives positive test with Tollen's reagent and Fehling solution while ketones do not give such test
- **Aldol condensation**

  Condensation of aldehydes and ketones having atleast one $\alpha - H$ atom.
- **Cannizaro reaction**

  Aldehydes with no α- hydrogen undergoes, self oxidation and reduction.

Carboxylic acids

Preparation

- $RCH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alk. } KMnO_4} RCOOH$
- $RCN \xrightarrow[H_2O]{H^+/OH^-} R - \overset{\overset{O}{\|}}{C} - NH_2 \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH$
- $R-Mg-X + CO_2 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Dry ether}} RCOOH$
- $RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$

Properties

- Gives CO_2 with carbonates and $NaHCO_3$
- $2 \text{ Ethanoic acid} \xrightarrow[\text{or } P_2O_5, \Delta]{H^+, \Delta} \text{Ethanoic anhydride}$
- **Esterification**
- $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$
- $RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$
- $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$
- $RCOOH \xrightarrow[\Delta, H_2O]{NH_3} RCONH_2$
- $RCOOH \xrightarrow[\text{(ii) } H_3O^-]{\text{(i) } LiAlH_4} RCH_2OH$
- **Hell – Volhard Zelinsky reaction**

  $RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red;}} R\underset{\underset{X}{|}}{C}HCOOH$

EXERCISE - 1
Conceptual Questions

1. Benzaldehyde and alcohol KCN reacts to produce which of the following :
(a) ethyl benzoate (b) benzyl alcohol
(c) benzoin (d) benzyl benzoate

2. Reaction of phenylacetylene with dil. H_2SO_4 and $HgSO_4$ gives
(a) acetophenone (b) 2-phenylethanol
(c) phenylacetaldehyde (d) phenylacetic acid

3. A new C — C bond is formed in :
(a) Cannizzaro's reaction
(b) Reimer Tiemann reaction
(c) Friedel Crafts reaction
(d) both (b) and (c)

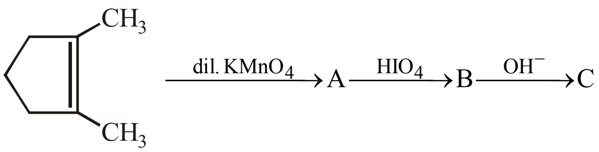
4. Two molecules of acetic acid on heating with phosphorous pentoxide produce :
(a) ethyl alcohol
(b) acetic anhydride
(c) acetyl pentaoxide
(d) pentaoxide of acetic acid

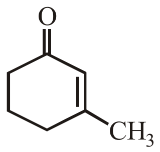
5. Which of the following gases does not form a ketone on treatment with dil H_2SO_4 and 1% $HgSO_4$?
(a) C_4H_6 (b) C_2H_2
(c) C_3H_4 (d) All of these

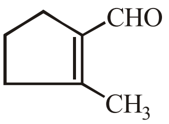
6. A compound X of formula C_3H_8O yields a ketone C_3H_6O on oxidation. To which of the following class of compounds would X belong?
(a) Aldehyde (b) Tertiary alcohol
(c) Secondary alcohol (d) Alkene

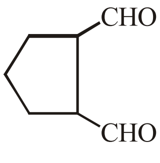
7. Clemmensen's reduction of ketones is carried out in :
(a) $LiAlH_4$ in H_2O (b) glycol and KOH
(c) Zn-Hg and HCl (d) H_2 and Pd catalyst

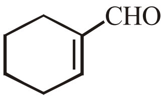
8. Suggest appropriate structures for the missing final compound. (The number of carbon atom remains the same throughout the reaction)



(a) 

(b) 

(c) 

(d) 

9. An unknown compound 'D' first oxidised to aldehyde and then acetic acid by a dilute solution of $K_2Cr_2O_7$ and H_2SO_4. The compound 'D' is :
(a) CH_3OH (b) C_2H_5OH
(c) CH_3CH_2COOH (d) CH_3CH_2CHO

10. Identify the product C in the series

$$CH_3CN \xrightarrow{Na/C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{Cu/573K} C$$

(a) CH_3COOH (b) CH_3CH_2NHOH
(c) CH_3CONH_2 (d) CH_3CHO

11. Benzaldehyde can be prepared by oxidation of toluene by
(a) Acidic $KMnO_4$ (b) $K_2Cr_2O_7 / H^+$
(c) CrO_2Cl_2 (d) All of these

12. Formalin is an aqueous solution of
(a) fluorescein (b) formic acid
(c) formaldehyde (d) furfuraldehyde

13. The reagent (s) which can be used to distinguish acetophenone from benzophenone is (are)
(a) 2,4- dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) benedict reagent
(d) $I_2$and Na_2CO_3.

14. The test used for the distinction of HCOOH and CH_3COOH is treatment with :
(a) sodium (b) sodium hydroxide
(c) Tollen's reagent (d) alcohol

15. Sodium formate on heating yields
(a) oxalic acid and H_2 (b) sodium oxalate and H_2
(c) CO_2 and NaOH (d) sodium oxalate.

16. $(CH_3)_2C = CHCOCH_3$ can be oxidized to $(CH_3)_2C = CHCOOH$ by
(a) Chromic acid (b) NaOI
(c) Cu at 300°C (d) $KMnO_4$.

17. Pinacolone is
(a) 2, 3-dimethyl-2 3-butanediol
(b) 3, 3-dimethyl-2 butanone
(c) 1-phenyl-2propanone
(d) 1,1-diphenyl-2-ethandiol.

18. Urotropine is obtained when ammonia reacts with
(a) HCHO (b) CH_3COCH_3
(c) CH_3CHO (d) C_6H_5OH

19. Benzaldehyde reacts with ethanoic KCN to give
(a) $C_6H_5CHOHCN$
(b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$
(d) $C_6H_5CHOHCHOHC_6H_5$

20. Aldehydes and ketones will not form crystalline derivatives with
(a) sodium bisulphite
(b) phenylhydrazine
(c) semicarbazide hydrochloride
(d) dihydrogen sodium phosphate.

21. When formaldehyde is polymerised in the presence of dilute H_2SO_4, the compound obtained is
(a) paraldehyde (b) paraformaldehyde
(c) metaldehyde (d) trioxy formaldehyde

22. $(CH_3)_3C–CHO$ does not undergo Aldol condensation due to
(a) three electron donating methyl groups
(b) cleavage taking place between —C— CHO bond
(c) absence of alpha hydrogen atom in the molecule
(d) bulky $(CH_3)_3$ C—group

23. In the reaction

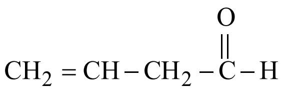
$CH_3CN + 2H \xrightarrow[Ether]{HCl} X \xrightarrow[H_2O]{Boiling} Y$; the term Y is :
(a) acetone (b) ethyl amine
(c) acetaldehyde (d) dimethyl amine

24. Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents?
(a) $LiAlH_4$ (b) Zn-Hg/HCl
(c) $NaBH_4$ (d) CH_3MgI

25. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?
(a) Acetamide (b) Acetic acid
(c) Ethyl acetate (d) Butan-2-one

26. Acetone reacts with bleaching powder to give
(a) CCl_4
(b) $CHCl_3$
(c) CCl_3-COCH_3
(d) none of these.

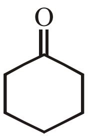
27. Appropriate reducing agent for the following conversion is–

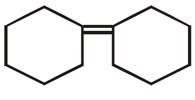
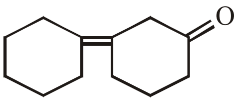
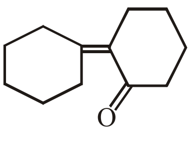
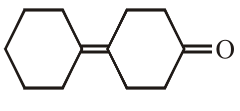


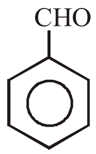
$CH_2=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

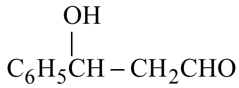
$\longrightarrow CH_3-CH_2-CH_2-CH_2OH$
(a) $LiAlH_4/H_2O$ (b) $NaBH_4/H_2O$
(c) $Na + C_2H_5OH$ (d) B_2H_6/H^+

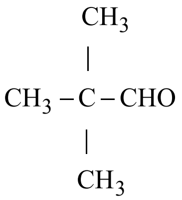
28. A compound called chloral whose formula is C_2Cl_3OH is a/an
(a) aldehyde (b) alcohol
(c) ketone (d) alkanoyl chloride

29. 2  $\xrightarrow[\Delta]{OH^-}$? Product is

(a) 
(b) 
(c) 
(d) 

30.  $+ CH_3CHO \xrightarrow{Dil.\ NaOH} \underset{(Major)}{A}$. (A) will be –

(a)  $C_6H_5\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2CHO$ (b) $C_6H_5CH=CH-CHO$
(c) $C_6H_5CH_2CH_2CHO$ (d) Both (b) & (c)

31.  $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CHO$ does not show aldol condensation because
(a) carbon is bounded by 3 heavy methyl group
(b) due to absence of α-hydrogen
(c) it is a neutral molecule
(d) due to hindrance created by methyl for carbanion.

32. Which of the following is best method for reducing 3-bromopropanal to 1-bromopropane –
(a) Wolf-Kishner reduction
(b) Clemmenson reduction
(c) Either (a) or (b)
(d) Stephen's reduction

33. Cannizzaro reaction occurs with
(a) CH_3-CH_2OH (b) C_6H_5CHO
(c) CH_3CHO (d) $CH_3-CO-CH_3$

34. In an alkaline medium, acetaldehyde undergoes:
(a) benzoin condensation (b) aldol condensation
(c) polymerisation (d) Cannizzaro reaction

35. Which of the following compound will show positive silver mirror test ?
(a) HCOOH (b) $CH_3(CHOH)_3CHO$
(c) $CH_3CO(CHOH)CH_3$ (d) Both (a) and (b)

36. Oxalic acid on heating with conc. H_2SO_4 produces
(a) $CO + CO_2$ (b) $CO_2 + H_2$
(c) $C + H_2O$ (d) $CO + H_2$

37. Aldehydes and ketones are generally reduced by :
(a) Clemmensen reduction (b) H_2S
(c) H_2/Ni (d) None of these

38. The product obtained by the reaction of an aldehyde and hydroxylamine is
(a) hydrazone (b) aldoxime
(c) primary amine (d) alcohol

39. In which reaction, $>C=O$ can be reduced to $>CH_2$?
(a) Wolf-Kishner reaction
(b) Reimer-Tiemann reaction
(c) Wurtz reaction
(d) None of these

40. In benzilic acid rearrangement,
(a) benzoin is converted into benzilic acid
(b) benzaldehyde is converted into benzoin
(c) benzil is converted into benzilic acid
(d) benzilic acid is converted into benzil

41. Which of the following does not show Cannizzaro reaction?
(a) CH_3CHO (b) $HCHO$
(c) C_6H_5CHO (d) $(CH_3)_3C.CHO$

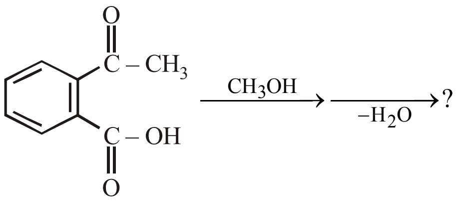
42. A compound does not react with 2, 4-dinitrophenylhydrazine, the compound is :
(a) Acetone (b) Acetaldehdye
(c) CH_3OH (d) $CH_3CH_2COCH_3$

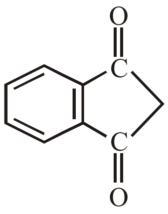
43. Which gives lactic acid on hydrolysis after reacting with HCN ?
(a) HCHO (b) CH_3CHO
(c) C_6H_5CHO (d) CH_3COCH_3

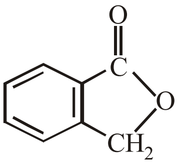
44. Ketones react with Mg-Hg over water to give :
(a) pinacolone (b) pinacols
(c) alcohols (d) none of these

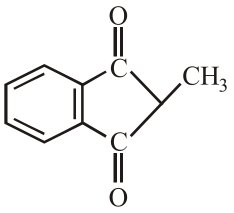
45. Which of the following functional groups cannot be reduced to alcohol using $NaBH_4$ in ethanolic solution ?
(a) $R-O-R$ (b) RCOCl
(c) $R-COOH$ (d) $R-CHO$

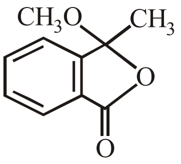
46. What is the final product of the following reaction ?



(a)


(b)


(c)


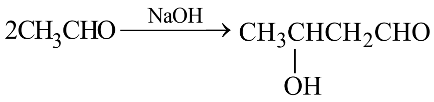
(d)


47. 2-pentanone and 3-pentanone can be distinguished by :
(a) Cannizaro's reaction
(b) Aldol condensation
(c) Iodoform reaction
(d) Clemmensen's reduction

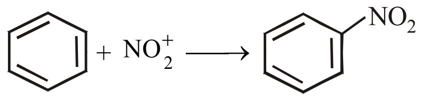
48. When dihydroxyacetone reacts with HIO_4, the product is/are :
(a) HCHO
(b) HCOOH
(c) HCHO and HCOOH
(d) HCHO and CO_2

49. Which of the following is disproportionation reaction?

(a) $2HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$

(b)


$2CH_3CHO \xrightarrow{NaOH} CH_3\underset{\underset{OH}{|}}{C}HCH_2CHO$

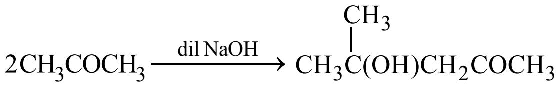
(c)


(d) Both (a) & (b)

50. Formaldehyde reacts with ammonia to give urotropine is
(a) $(CH_2)_6N_4$ (b) $(CH_2)_4N_3$
(c) $(CH_2)_6N_6$ (d) $(CH_2)_3N_3$

51. The property which distinguishes formic acid from acetic acid is
(a) only ammonium salt of formic acid on heating gives amide
(b) when heated with alcohol/H_2SO_4 only acetic acid forms ester
(c) only acetic acid forms salts with alkali
(d) only formic acid reduces Fehling's solution

52. Which of the following is an example of aldol condensation?

(a)


$2CH_3COCH_3 \xrightarrow{\text{dil NaOH}} CH_3\overset{\overset{CH_3}{|}}{C}(OH)CH_2COCH_3$

(b) $2HCHO \xrightarrow{\text{dil NaOH}} CH_3OH$

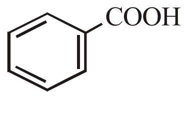
(c) $C_6H_5CHO + HCHO \xrightarrow{\text{dil NaOH}} C_6H_5CH_2OH$

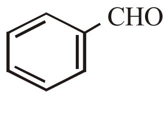
(d) None of the above

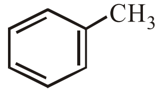
53. The reagent which does not give acid chloride on treating with a carboxylic acid is
(a) PCl_5 (b) Cl_2
(c) $SOCl_2$ (d) PCl_3

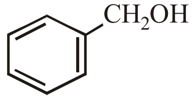
54. The reactant (X) in the reaction

$(X) \xrightarrow[(CH_3CO)_2O]{CH_3COONa}$ Cinnamic acid, is

(a)


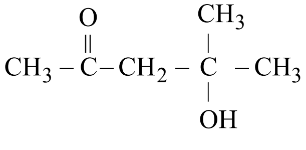
(b)


(c)


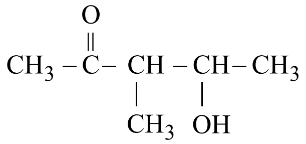
(d)


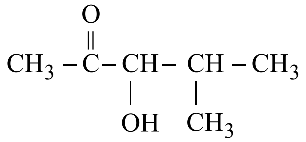
55. Main product obtained from the reaction of ammonia and formaldehyde is
(a) formic acid (b) methylamine
(c) methanol (d) urotropin

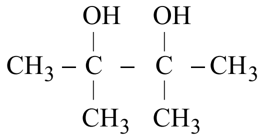
56. Which of the products is formed when acetone is reacted with barium hydroxide solution?

(a)


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

(b) 
$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$

(c) 
$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(d) 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

57. Hydride ion transfer takes place in
(a) Frankland method (b) Wurtz reaction
(c) Cannizzaro's reaction (d) Wolf-Kishner reduction

58. Ketone upon treatment with Grignard Reagent gives
(a) primary alcohol (b) secondary alcohol
(c) tertiary alcohol (d) aldehyde

59. Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?
(a) $CH_3CH=CH.CHO$ (b) $CH_3CH=CHCOCH_3$
(c) $(CH_3)_2C=CH.CHO$ (d) $(CH_3)_2C=CHCOCH_3$

60. What is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?
(a) Acetamide (b) Acetic acid
(c) Methyl cyanide (d) Acetic anhydride

61. Among acetic acid, phenol and *n*-hexanol, 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) acetic acid and phenol (d) phenol.

62. Formic acid is obtained when
(a) calcium acetate is heated with conc. H_2SO_4
(b) calcium formate is heated with calcium acetate
(c) glycerol is heated with oxalic acid at 373 K
(d) acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4.

63. Schotten-Baumann reaction is a reaction of phenols with
(a) benzoyl chloride and sodium hydroxide
(b) acetyl chloride and sodium hydroxide
(c) salicylic acid and conc. H_2SO_4
(d) acetyl chloride and conc H_2SO_4

64. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis ?
(a) A secondary alcohol
(b) A primary alcohol
(c) Phenol
(d) tert-Butyl alcohol

65. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is
(a) methyl acetate (b) ethyl acetate
(c) ethyl formate (d) ethyl benzoate

66. In the Friedel Craft's acylation reaction, the effective electrophile is
(a) $RCOCl^{\oplus}$ (b) $AlCl_3$
(c) RCOCl (d) $RCO^{\oplus}$

67. The compound which is not formed during the dry distillation of a mixture of calcium formate and calcium acetate is
(a) methanal (b) propanal
(c) propanone (d) ethanal

68. Which one of the following esters cannot undergo Claisen self-condensation?
(a) $CH_3-CH_2-CH_2-CH_2-COOC_2H_5$
(b) $C_6H_5COOC_2H_5$
(c) $C_6H_5CH_2COOC_2H_5$
(d) $C_6H_{11}CH_2COOC_2H_5$

69. The cyanohydrin of a compound on hydrolysis gives an optically active α-hydroxy acid. The compound is
(a) diethyl ketone (b) formaldehyde
(c) acetaldehyde (d) acetone

70. The product of following reaction is
$2CH_3MgBr + CH_2O \longrightarrow$
(a) CH_3OH (b) C_2H_5OH
(c) CH_4 (d) C_2H_6

71. $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} A \xrightarrow{\text{alc. KOH}} B$. What is *B*?
(a) CH_3CH_2COCl (b) CH_3CH_2CHO
(c) $CH_2=CHCOOH$ (d) $ClCH_2CH_2COOH$.

72. When dihydroxy acetone reacts with HIO_4, the product is/are
(a) HCHO
(b) HCOOH
(c) HCHO and HCOOH
(d) HCHO and CO_2

73. When $CH_2 = CH — COOH$ is reduced with $LiAlH_4$, the compound obtained will be
(a) $CH_2=CH—CH_2OH$ (b) $CH_3—CH_2—CH_2OH$
(c) $CH_3—CH_2—CHO$ (d) $CH_3—CH_2—COOH$

74. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is
(a) $CH_3COCl + C_2H_5OH + NaOH$
(b) $CH_3COONa + C_2H_5OH$
(c) $CH_3COOC_2H_5 + NaCl$
(d) $CH_3Cl + C_2H_5COONa$

75. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives
(a) 2-methyl-2-propanol (b) acetamide
(c) acetone (d) acetyl iodide

76. Acetic anhydride reacts with diethyl ether in the presence of anhydrous $AlCl_3$ to give :
(a) CH_3CH_2COOH (b) $CH_3CH_2COOC_2H_5$
(c) CH_3COOCH_3 (d) $CH_3COOC_2H_5$

77. An important reaction of acetone is auto condensation in presence of concentrated sulphuric acid to give the aromatic compound......
(a) Mesitylene (b) Mesityl oxide
(c) Trioxan (d) Phorone

78. The acid(s) which do not contain –COOH groups is/are :
(a) palmitic acid
(b) lactic acid
(c) ethanoic acid
(d) picric acid and *p*-toluene sulphonic acid

79. The best combination of reagents for carrying out the conversion $RCH_2CH_2OH \rightarrow RCH_2CH_2COOH$ is
(a) PBr_3, KCN, H_3O^+ (b) PBr_3, KCN, H_2/Pt
(c) KCN, H_3O^+ (d) PBr_3, H_3O^+

80. $CH_3COOH \xrightarrow{A} CH_3COCl$. What is A ?
(a) PCl_5 (b) Cl_2
(c) HCl (d) $COCl_2$

81. Ethyl acetate on reaction with Grignard's reagent, forms a/an
(a) alcohol (b) ketone
(c) ether (d) hydrocarbon

82. The compound not soluble in acetic acid is :
(a) $CaCO_3$ (b) CaO
(c) CaC_2O_4 (d) $Ca(OH)_2$

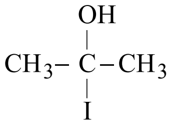
83. Among the following, the most acidic is :
(a) CH_3COOH (b) $ClCH_2COOH$
(c) $Cl_2CHCOOH$ (d) Cl_2CHCH_2COOH

84. The compound that neither forms semicarbazone for oxime is
(a) HCHO (b) CH_3COCH_2Cl
(c) CH_3CHO (d) $CH_3CONHCH_3$

85. Consider the following transformations :

$$CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{heat} B \xrightarrow[NaOH]{I_2} C$$

The molecular formula of C is

(a) 

$CH_3-\underset{I}{\overset{OH}{C}}-CH_3$

(b) $ICH_2—COCH_3$
(c) CHI_3 (d) CH_3I

86. In the following reaction

$$RCH_2COOH \xrightarrow{Br_2/P} X \xrightarrow{excess\ NH_3} Y$$

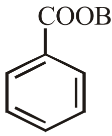
The major compounds X and Y are
(a) $RCHBrCONH_2$; $RCH(NH_2)COOH$
(b) $RCHBrCOOH$; $RCH(NH_2)COOH$
(c) RCH_2COBr ; RCH_2COONH_4
(d) $RCHBrCOOH$; RCH_2CONH_2

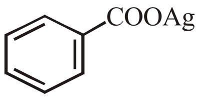
87. An organic compound C_3H_6O neither gives precipitate with semicarbazide nor reacts with sodium. It could be
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_2=CH—CH_2—OH$ (d) $CH_2=CH—O—CH_3$

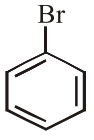
88. Which one of the following compounds will not react with CH_3MgBr?
(a) Ethyl acetate (b) Acetone
(c) Dimethyl ether (d) Ethanol

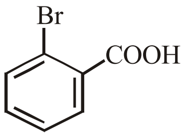
89. Some carboxylic acids and their IUPAC names are given below. Which of the following is not correctly matched?
(a) Formic acid — Methanoic acid
(b) Acetic acid — Ethanoic acid
(c) *n*-Butyric acid — Butanoic acid
(d) *Iso*-butyric acid — 2-methylbutanoic acid

90. Silver benzoate will react with bromine in CCl_4 to form :

(a) 

(b) 

(c) 

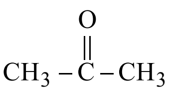
(d) 

91. Which of the following pairs can be distinguished by sodium hypoiodite?
(a) CH_3CHO and CH_3COCH_3
(b) CH_3CH_2CHO and CH_3COCH_3
(c) CH_3CH_2OH and $CH_3CH_2CHOHCH_3$
(d) CH_3OH and CH_3CH_2CHO

92. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
(a) Cope reduction
(b) Dow reduction
(c) Wolf-Kishner reduction
(d) Clemmensen reduction.

93. Which of the following represents the correct order of the acidity in the given compounds?
(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) $CH_3\ COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

94. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?
(a) C_6H_5CHO (b) $CH_3CH_2CH_2CHO$

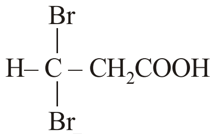
(c) 

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

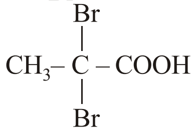
(d) $C_6H_5CH_2CHO$

95. The product formed in Aldol condensation is
(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

96. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:

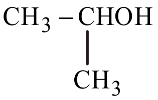
(a) 
$H-\overset{Br}{\underset{Br}{C}}-CH_2COOH$

(b) CH_2Br-CH_2-COBr

(c) 
$CH_3-\overset{Br}{\underset{Br}{C}}-COOH$

(d) $CH_2Br-CHBr-COOH$

97. Which of the following reactions will not result in the formation of carbon-carbon bonds?
(a) Reimer-Tieman reaction
(b) Cannizaro reaction
(c) Wurtz reaction
(d) Friedel-Crafts acylation

98. Following compounds are given:
(i) CH_3CH_2OH
(ii) CH_3COCH_3
(iii) 
$\underset{CH_3}{CH_3-CHOH}$
(iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?
(a) (i) and (ii)
(b) (i), (iii) and (iv)
(c) Only (ii)
(d) (i), (ii) and (iii)

99. Clemmensen reduction of a ketone is carried out in the presence of which of the following ?
(a) Glycol with KOH
(b) Zn-Hg with HCl
(c) $Li Al H_4$
(d) H_2 and Pt as catalyst

100. Match the compounds given in List-I with List-II and select the suitable option using the code given below :

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)	(B)	(C)	(D)
(a)	(iv)	(i)	(iii)	(ii)
(b)	(iv)	(ii)	(iii)	(i)
(c)	(ii)	(iii)	(iv)	(i)
(d)	(ii)	(i)	(iv)	(iii)

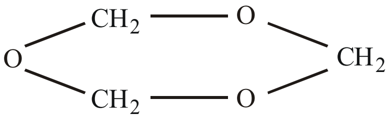
EXERCISE - 2

Applied Questions

1. The catalyst used in the Wacker process of oxidation of ethyne to ethanal is
(a) $PdCl_2$
(b) V_2O_5
(c) Nickel complexes
(d) $TiCl_4$ and $Al(CH_3)_3$

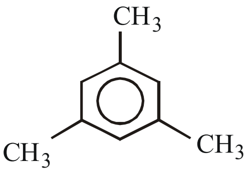
2. Which one of the following reagents enables the purification of benzaldehydes?
(a) HCN
(b) CH_3MgBr
(c) NH_2OH
(d) $NaHSO_3$

3. Which of the following is the correct decreasing order of acidic strength of
(i) Methanoic acid
(ii) Ethanoic acid
(iii) Propanoic acid
(iv) Butanoic acid
(a) (i) > (ii) > (iii) > (iv)
(b) (ii) > (iii) > (iv) > (i)
(c) (i) > (iv) > (iii) > (ii)
(d) (iv) > (i) > (iii) > (ii)

4. 

The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is
(a) Trioxane
(b) Formose
(c) Paraformaldehyde
(d) Metaldehyde

5. Which of the following gives reddish brown precipitate on heating with a solution of $CuSO_4$ and alkaline sodium potassium tartarate?
(a) Ethanol
(b) Ethanal
(c) Propanone
(d) Ethanoic acid

6. 

The above compound describes a condensation polymer which can be obtained in two ways : either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3\,C\equiv CH$) through a red hot tube. The polymer is
(a) Phorone
(b) Mesityl oxide
(c) Deacetonyl alcohol
(d) Mesitylene

7. In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation
(a) CH_3COCH_3
(b) CCl_3CH_2CHO
(c) $CH_3CH_2CH_2OH$
(d) CH_3CH_2CHO

8. Aldehydes that do not undergo aldol condensation are
1. propanal
2. trichloroethanal
3. methanal
4. ethanal
5. benzaldehyde

(a) 3 and 4 only
(b) 3 and 5 only
(c) 1, 2 and 3 only
(d) 2, 3 and 5 only

9. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively
(a) Soda-lime and copper
(b) Zn dust and NaOH
(c) Zn dust and soda-lime
(d) Soda-lime and zinc dust

10. An ester (A) with molecular fomula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The structure of (A) is
(a) $C_6H_5COOC_2H_5$
(b) $C_2H_5COOC_6H_5$
(c) $H_3COCH_2COC_6H_5$
(d) $p-H_3CO-C_6H_4-COCH_3$

11. Polarization of electrons in acrolein may be written as:

(a) $\overset{\delta-}{C}H_2 = CH - CH = \overset{\delta+}{O}$

(b) $\overset{\delta+}{C}H_2 = \overset{\delta-}{C}H - CH = O$

(c) $\overset{\delta+}{C}H_2 = CH - CH = \overset{\delta-}{O}$

(d) $\overset{\delta-}{C}H_2 = CH - \overset{\delta+}{C}H = O$

12. Which compound among the following gives positive iodoform test ?

1. Ethanol
2. Ethanal
3. 1-Butanol
4. 2-Butanol
5. Phenyl ethanol

(a) 1, 2 and 5 (b) 1, 3 and 4
(c) 1, 2 and 3 (d) 1, 2 and 4

13. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as

(a) an amine (b) an imine
(c) an enamine (d) a schiff's base

14. The increasing order of the rate of HCN addition to compound A – D is

(A) HCHO (B) CH_3COCH_3
(C) $PhCOCH_3$ (D) PhCOPh

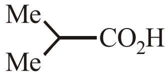
(a) D < C < B < A (b) C < D < B < A
(c) A < B < C < D (d) D < B < C < A

15. Reaction of butanone with methylmagnesium bromide followed by hydrolysis gives

(a) 2-methyl-2-butanol
(b) 2-butanol
(c) 3-methyl-2-butanol
(d) 2, 2-dimethyl-1-butanol

16. The correct order of increasing acid strength of the compounds

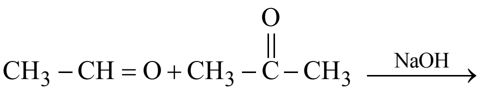
(A) CH_3CO_2H (B) $MeOCH_2CO_2H$
(C) CF_3CO_2H (D)



is

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

17. How many cross aldol products (without counting stereoisomers) are produced in the following reaction?



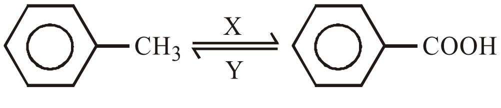
$$CH_3-CH=O+CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH}$$

(a) 5 (b) 2
(c) 3 (d) 1

18. Monocarboxylic acids are functional isomers of :

(a) Ethers (b) Amines
(c) Esters (d) Alcohols

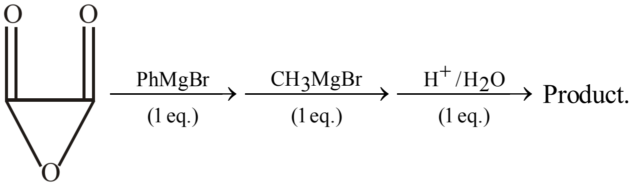
19.



In the above sequence of reaction X and Y are respectively

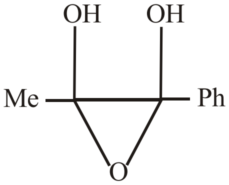
(a) H_2/Pt ; Br_2 (b) $KMnO_4$; H_2/Pt
(c) $KMnO_4$ (aq); HI/P (d) NH_2-NH_2/KOH, HI/P

20.

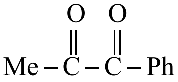


The product formed in the reaction is –

(a)

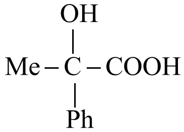


(b)



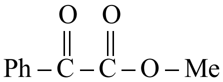
$Me-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-Ph$

(c)



$Me-\underset{\underset{Ph}{|}}{\overset{\overset{OH}{|}}{C}}-COOH$

(d)



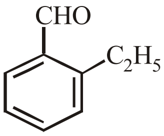
$Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-Me$

21. An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests. It

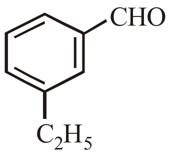
(i) forms 2, 4-DNP derivative
(ii) reduces Tollen's reagent
(iii) undergoes Cannizaro reaction and
(iv) on vigorous oxidation 1, 2-benzenedicarboxylic acid is obtained.

X is

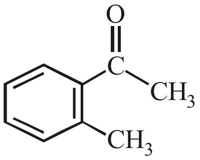
(a)



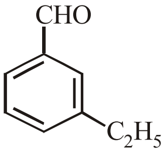
(b)



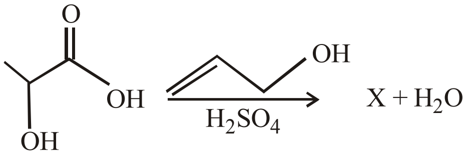
(c)



(d)

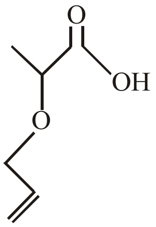


22.

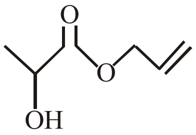


Product (X) of the reaction is–

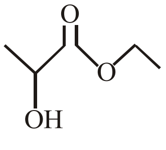
(a)



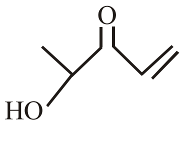
(b)



(c)



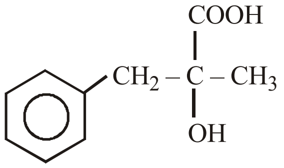
(d)

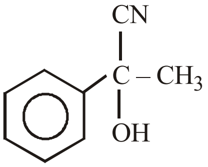


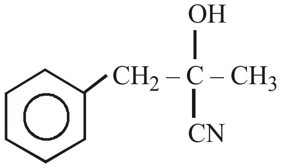
23. In a set of reactions acetic acid yielded a product D.

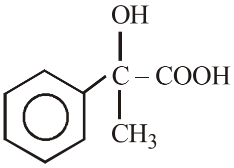
$$CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[AlCl_3]{Benzene} (B) \xrightarrow{HCN} (C) \xrightarrow{HOH} (D)$$

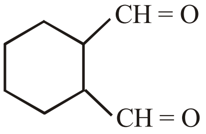
The structure of (D) would be –

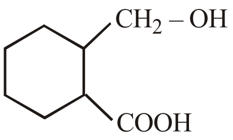
(a) 

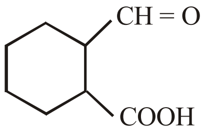
(b) 

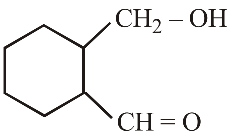
(c) 

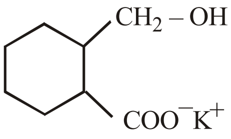
(d) 

24.  $\xrightarrow[(ii)\ H_2O/H^+]{(i)\ KOH/\Delta}$ [X]. What is [X]?

(a) 

(b) 

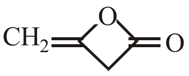
(c) 

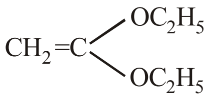
(d) 

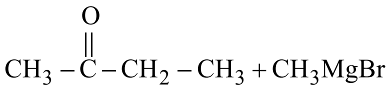
25. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B. Compound B is :

(a) CH_3COCH_2COOH

(b) CH_3COCH_3

(c) 

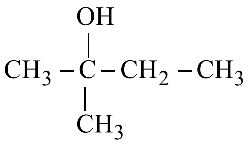
(d) 

26. 

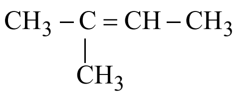
$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3+CH_3MgBr$$

$$\longrightarrow X \xrightarrow{H_3O^+} Y \xrightarrow[170°C]{H_2SO_4} Z.$$

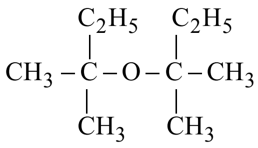
What is Z ?

(a) 

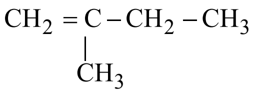
$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_3$$

(b) 

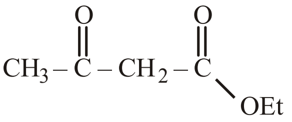
$$CH_3-\underset{CH_3}{C}=CH-CH_3$$

(c) 

$$CH_3-\underset{CH_3}{\overset{C_2H_5}{C}}-O-\underset{CH_3}{\overset{C_2H_5}{C}}-CH_3$$

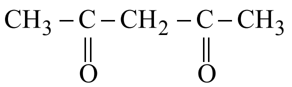
(d) 

$$CH_2=\underset{CH_3}{C}-CH_2-CH_3$$

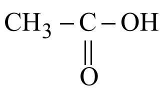
27. 

$$\xrightarrow{Na\ (1\ mole)} \xrightarrow{CH_3-\underset{O}{\underset{||}{C}}-Cl} \xrightarrow[dil.\ H^{\oplus}]{dil.\ KOH}$$

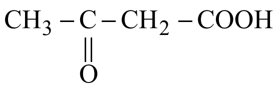
The final product is –

(a) 

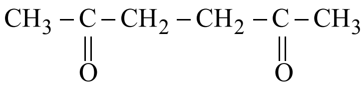
$$CH_3-\underset{O}{\underset{||}{C}}-CH_2-\underset{O}{\underset{||}{C}}-CH_3$$

(b) 

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

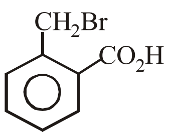
(c) 

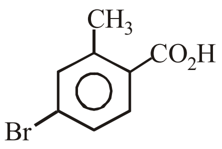
$$CH_3-\underset{O}{\underset{||}{C}}-CH_2-COOH$$

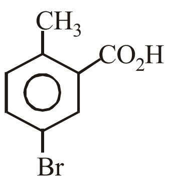
(d) 

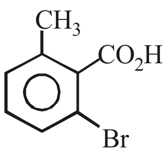
$$CH_3-\underset{O}{\underset{||}{C}}-CH_2-CH_2-\underset{O}{\underset{||}{C}}-CH_3$$

28. *o*-Toluic acid on reaction with Br_2 + Fe gives

(a) 

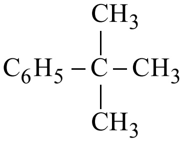
(b) 

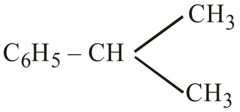
(c) 

(d) 

29. Which of the following compound will not give benzoic acid on oxidation with $KMnO_4/\overset{\ominus}{OH}/\Delta$ –

(a) $C_6H_5-CH_3$

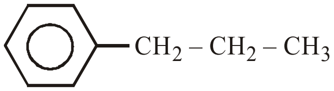
(b) 
$C_6H_5-C(CH_3)_2-CH_3$

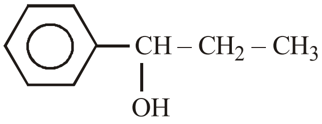
(c) 

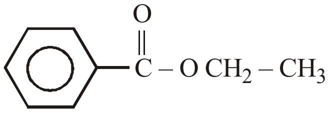
(d) $C_6H_5-CH_2-COOH$

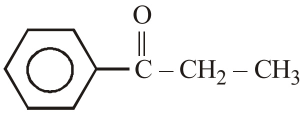
30. The final product (III) obtained in the reaction sequence –

$$CH_3-CH_2-COOH \xrightarrow{PCl_3} I \xrightarrow{C_6H_6/AlCl_3} II \xrightarrow[\text{base/heat}]{NH_2-NH_2} III$$

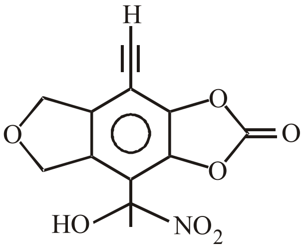
(a) 

(b) 

(c) 

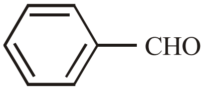
(d) 

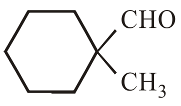
31. Calculate number of molecules of Grignard reagent consumed by 1 molecule of following compound.



(a) 5
(b) 2
(c) 3
(d) 1

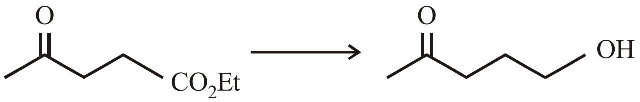
32. Cannizaro's reaction is not given by :

(a) 

(b) 

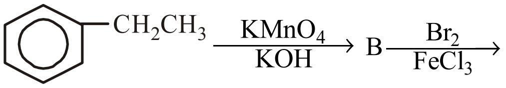
(c) CH_3CHO
(d) HCHO

33. Which of the following reagent(s) used for the conversion?



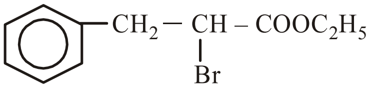
(a) glycol/$LiAlH_4/H_3O^+$
(b) glycol/NaH/H_3O^+
(c) $LiAlH_4$
(d) $NaBH_4$

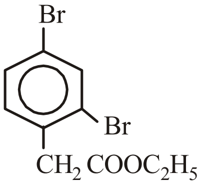
34. In a set of reactions, ethylbenzene yield a product D.

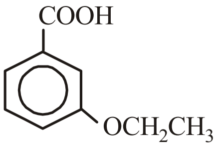


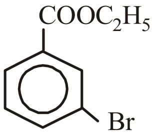
$$C \xrightarrow[H^+]{C_2H_5OH} D$$

Identify D :

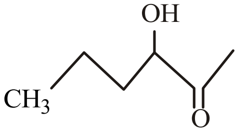
(a) 

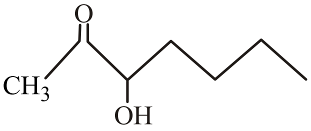
(b) 

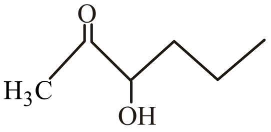
(c) 

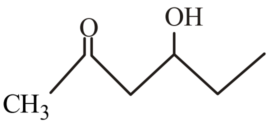
(d) 

35. Which one of the following compounds will be most readily dehydrated?

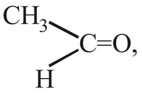
(a) 

(b) 

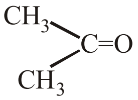
(c) 

(d) 

36. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds

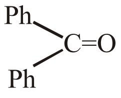


I



II

and

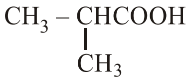


III

(a) III > II > I
(b) II > I > III
(c) I > III > II
(d) I > II > III

37. 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:

(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$

(d) CH_3CH_2COOH

38. In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{:\overset{\ominus}{O}H} PhCH_2OH + PhC\ddot{O}_2^{\ominus}$$

the slowest step is :

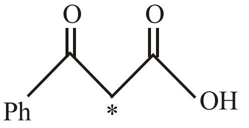
(a) the transfer of hydride to the carbonyl group

(b) the abstraction of proton from the carboxylic group

(c) the deprotonation of Ph CH_2OH

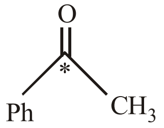
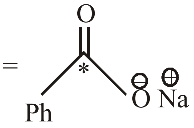
(d) the attack of : $\overset{\ominus}{O}H$ at the carboxyl group

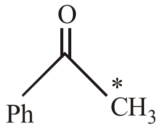
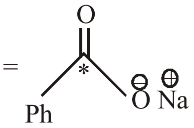
39. In the following reaction sequence, the correct structures of E, F and G are

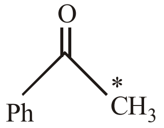
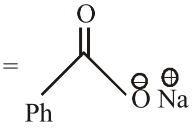


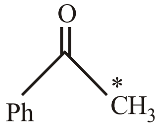
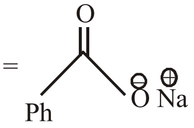
$$\xrightarrow{\text{Heat}}[E]\xrightarrow[\text{NaOH}]{I_2}[F]+[G]$$

[* implies ^{13}C labelled carbon)

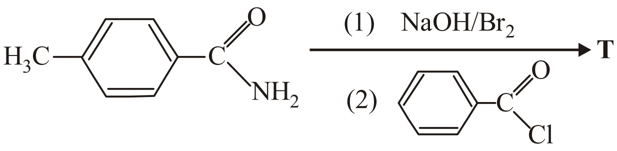
(a) E=  F =  $G = CHI_3$

(b) E=  F =  $G = CHI_3$

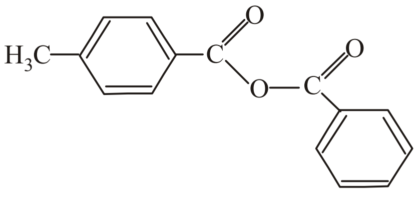
(c) E=  F =  $G = \overset{*}{C}HI_3$

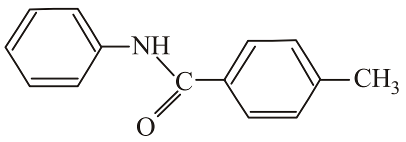
(d) E=  F =  $G \overset{*}{=} CH_3I$

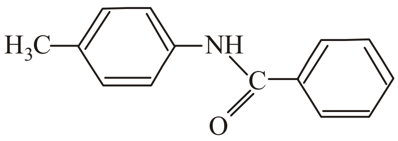
40. In the reaction

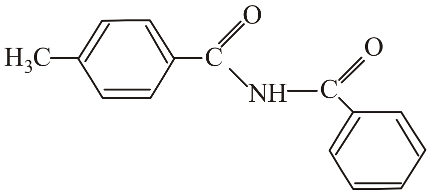


the structure of the product **T** is :

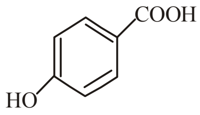
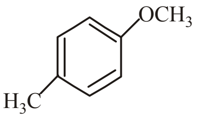
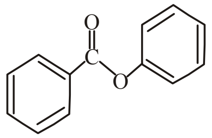
(a) 

(b) 

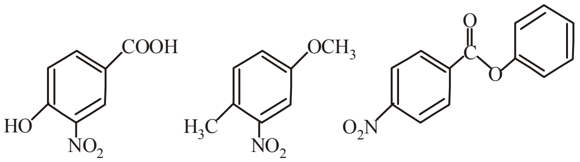
(c) 

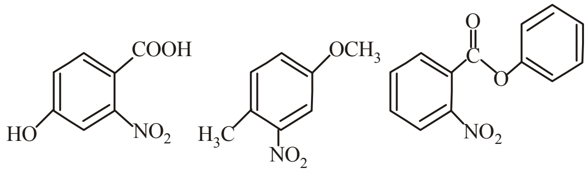
(d) 

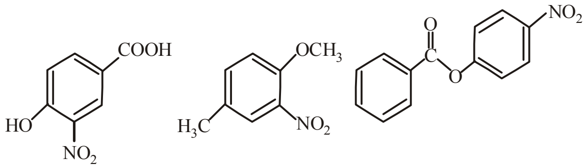
41. The compounds P, Q and S

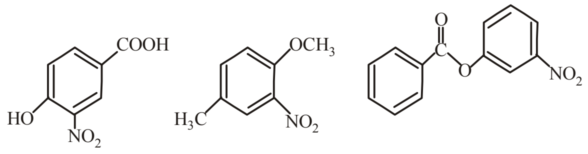
 P
 Q
 S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is :

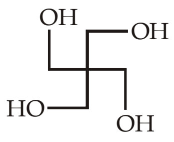
(a) 

(b) 

(c) 

(d) 

42. The number of aldol reaction(s) that occurs in the given transformation is :

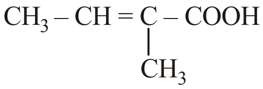
$$CH_3CHO + 4HCHO \xrightarrow{\text{conc. aq. NaOH}}$$ 

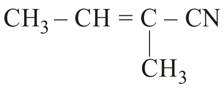
(a) 1 (b) 2

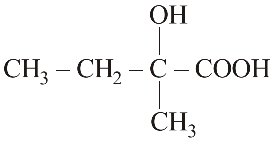
(c) 3 (d) 4

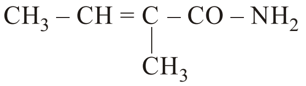
43. The major product **H** of the given reaction sequence is

$$CH_3—CH_2—CO—CH_3 \xrightarrow{CN^{\ominus}} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

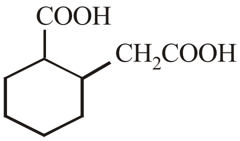
(a) 
$CH_3-CH=C(CH_3)-COOH$

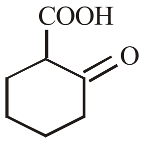
(b) 
$CH_3-CH=C(CH_3)-CN$

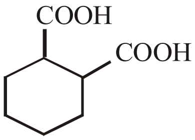
(c) 
$CH_3-CH_2-C(OH)(CH_3)-COOH$

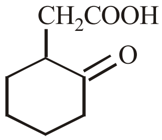
(d) 
$CH_3-CH=C(CH_3)-CO-NH_2$

44. The compound that undergoes decarboxylation most readily under mild condition is

(a) 

(b) 

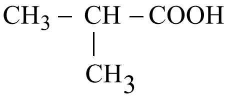
(c) 

(d) 

45. 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 :

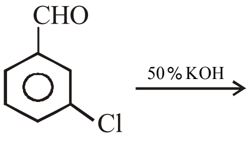
(a) CH_3COOH

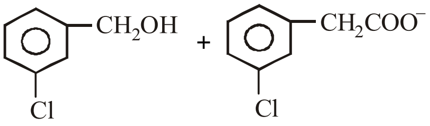
(b) $CH_3CH_2CH_2COOH$

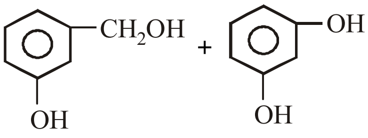
(c) 
$CH_3-CH(CH_3)-COOH$

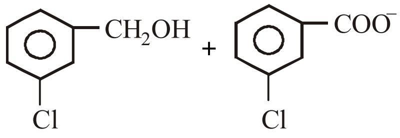
(d) CH_3CH_2COOH

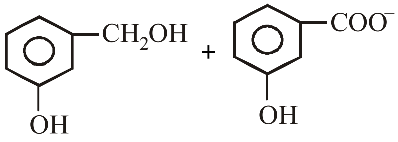
46. Predict the product in the given reaction.



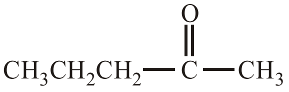
(a) 

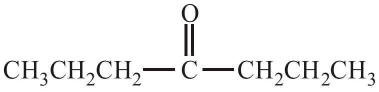
(b) 

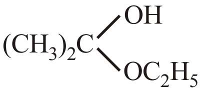
(c) 

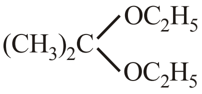
(d) 

47. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is :

(a) 
$CH_3CH_2CH_2—C(=O)—CH_3$

(b) 
$CH_3CH_2CH_2—C(=O)—CH_2CH_2CH_3$

(c) 
$(CH_3)_2C(OH)(OC_2H_5)$

(d) 
$(CH_3)_2C(OC_2H_5)(OC_2H_5)$

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1

(b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

48. **Statement-1 :** Acetic acid does not undergo haloform reaction.

Statement-2 : Acetic acid has no alpha hydrogens.

49. **Statement-1 :** Benzaldehyde is more reactive than ethanol towards nucleophilic attack.

Statement-2 : The overall effect of –I and + R effect of phenyl group decreases the electron density on the carbon atom of > C = O group in benzaldehyde.

50. **Statement-1 :** Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.

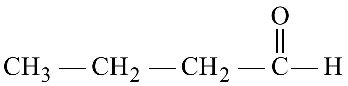
Statement-2 : Aldehydes and ketones can be distinguished by Tollen's reagent.

EXERCISE - 3

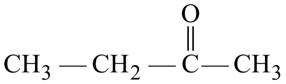
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

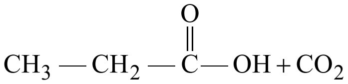
1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but - 1-yne under these conditions?

(a) 

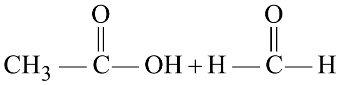
$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

(b) 

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

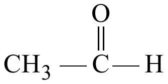
(c) 

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH+CO_2$

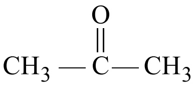
(d) 

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

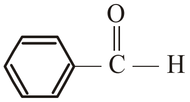
2. Which of the following compounds is most reactive towards nucleophilic addition reactions?

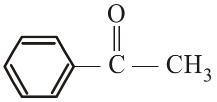
(a) 

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

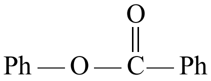
(b) 

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

(c) 

(d) 

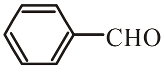
3. The correct order of increasing acidic strength is ....
(a) phenol < ethanol < chloroacetic acid < acetic acid
(b) ethanol < phenol < chloroacetic acid < acetic acid
(c) ethanol < phenol < acetic acid < chloroacetic acid
(d) chloroacetic acid < acetic acid < phenol < ethanol

4. Compound  $Ph-O-\overset{O}{\overset{\|}{C}}-Ph$ can be prepared by the reactions of ....
(a) phenol and benzoic acid in the presence of NaOH
(b) phenol and benzoyl chloride in the presence of pyridine
(c) phenol and benzoyl chloride in the presence of $ZnCl_2$
(d) phenol and benzaldehyde in the presence of palladium

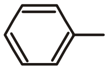
5. The reagent which does not react with both, acetone and benzaldehyde?
(a) Sodium hydrogen sulphite
(b) Phenyl hydrazine
(c) Fehling's solution
(d) Grignard reagent

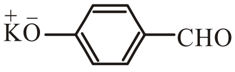
6. Cannizzaro's reaction is not given by ....

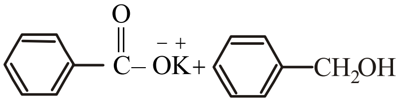
(a) 

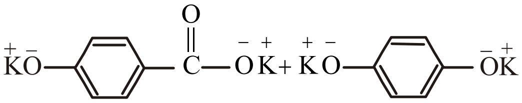
(b) 

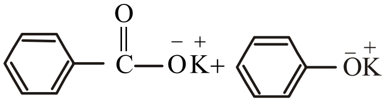
(c) HCHO
(d) CH_3CHO

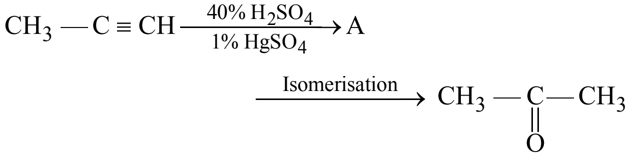
7. Which product is formed when the compound  CHO is treated with concentrated aqueous KOH solution?

(a) 

(b) 

(c) 

(d) 

8. 

$$CH_3-C\equiv CH\xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4}A\xrightarrow{\text{Isomerisation}}CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

structure of 'A' and type of isomerism in the above reaction are respectively
(a) Prop-1-en-2-ol, metamerism
(b) Prop-1-en-1-ol, tautomerism
(c) Prop-2-en-2-ol, geometrical isomerism
(d) Prop -1-en-2-ol, tautomerism

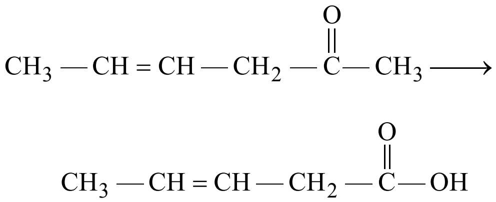
9. Compounds A and C in following reaction are ....

$$CH_3CHO\xrightarrow[(ii)H_2O]{(i)\ CH_3MgBr}(A)\xrightarrow{H_2SO_4,\Delta}(B)$$

$$\xrightarrow{\text{Hydroboration oxidation}}(C)$$

(a) identical
(b) positional isomers
(c) functional isomers
(d) optical isomers

10. Which is the most suitable reagent for the following conversion?



$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\longrightarrow$$

$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

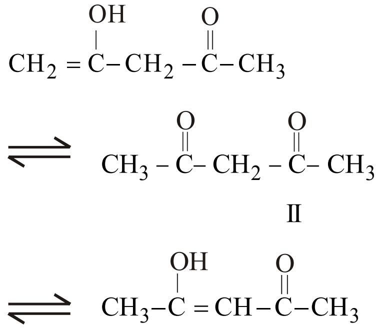
(a) Tollen's reagent
(b) Benzoyl peroxide
(c) I_2 and NaOH solution
(d) Sn and NaOH solution

11. 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 (a) and (b)
(d) None of these

12. In Clemmensen reduction, carbonyl compounds is treated with ....
(a) zinc amalgam + HCl
(b) sodium amalgam + HCl
(c) zinc amalgan + nitric acid
(d) sodium amalgam + HNO_3

NEET/AIPMT (2013-2017) Questions

13. The order of stability of the following tautomeric compounds is :



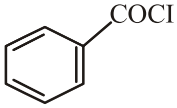
$$CH_2=\overset{\overset{OH}{|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

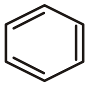
II

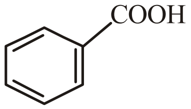
[2013]

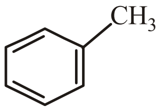
(a) III > II > I
(b) II > I > III
(c) II > III > I
(d) I > II > III

14. Reaction by which Benzaldehyde cannot be prepared : **[2013]**

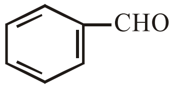
(a)  + H_2 in presence of Pd - $BaSO_4$

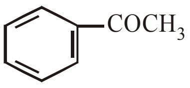
(b)  + CO + HCl in presence of anhydrous $AlCl_3$

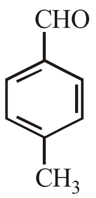
(c)  + Zn/Hg and conc. HCl

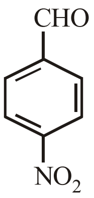
(d)  + CrO_2Cl_2 in CS_2 followed by H_3O^+

15. Which one is most reactive towards Nucleophilic addition reaction? **[2014]**

(a) 

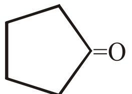
(b) 

(c) 

(d) 

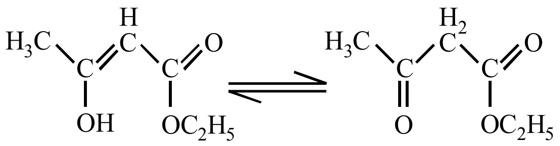
16. An organic compound 'X' having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the Iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be :- **[2015]**

(a) 2-pentanone
(b) 3-pentanone
(c) n-amyl alcohol
(d) pentanal

17. Treatment of cyclopentanone  with methyl lithium gives which of the following species? **[2015]**

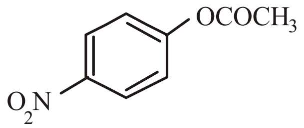
(a) Cyclopentanonyl cation
(b) Cyclopentanonyl radical
(c) Cyclopentanonyl biradical
(d) Cyclopentanonyl anion

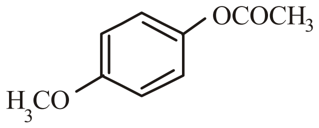
18. The enolic form of ethyl acetoacetate as below has: **[2015]**

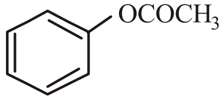


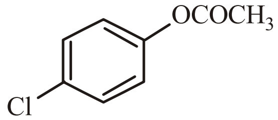
(a) 16 sigma bonds and 1 pi - bond
(b) 9 sigma bonds and 2 pi - bonds
(c) 9 sigma bonds and 1 pi - bond
(d) 18 sigma bonds and 2 pi - bonds

19. Which one of the following esters gets hydrolysed most easily under alkaline conditions? **[2015 RS]**

(a) 

(b) 

(c) 

(d) 

20. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is : **[2015 RS]**

(a) a Grignard reagent
(b) hydrazine in presence of feebly acidic solution
(c) hydrocyanic acid
(d) sodium hydrogen sulphite

21. The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is : ***[2016]***

(a) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.

(b) a carbonyl compound with a hydrgen 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.

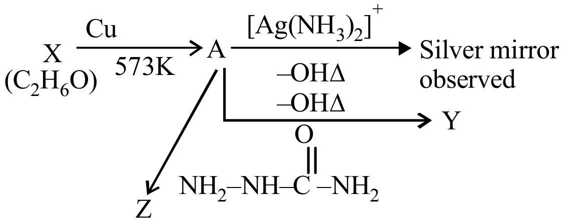
(d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

22. The product formed by the reaction of an aldehyde with a primary amine is ***[2016]***

(a) Schiff base (b) Ketone

(c) Carboxylic acid (d) Aromatic acid

23. Consider the reactions :- ***[2017]***



Identify A, X, Y and Z

(a) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.

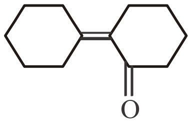
(b) A - Ethanal, X-Ethanol, Y - But - 2-enal, Z-Semicarbazone

(c) A-Ethanol, X-Acetaldehyde, Y - Butanone, Z-Hydrazone

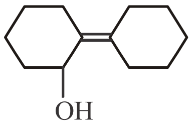
(d) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine.

24. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating ? ***[2017]***

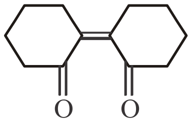
(a)



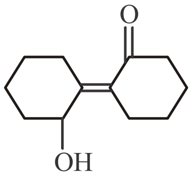
(b)



(c)



(d)

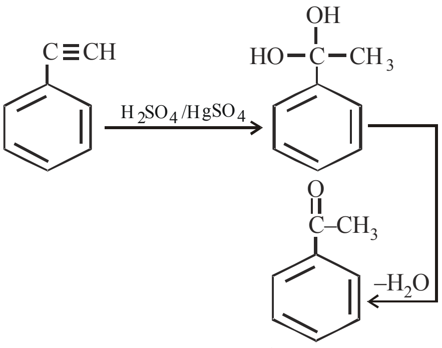


Hints & Solutions

EXERCISE - 1

1. (c) Benzaldehyde and alcoholic KCN react to form Benzoin. This is known as Bezoin condensation.

2. (a)



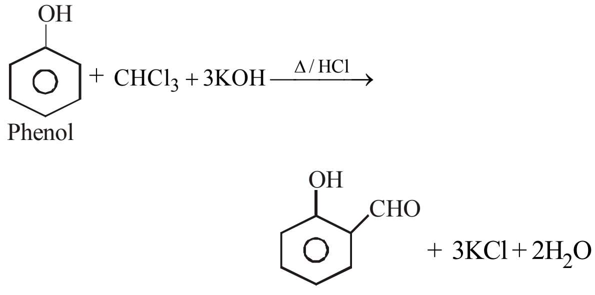
Acetophenone

3. (d) (a) Cannizzaro reaction

$$2HCHO \xrightarrow{NaOH} CH_3OH + HCOO^-$$

No new C—C bond is formed

(b) Reimer - Tiemann reaction :

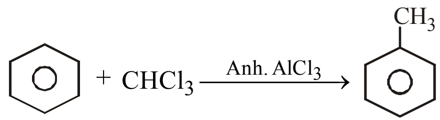


Phenol

Salicylaldehyde

New C—C bond is formed

(c) Fridel-Craft reaction :



Benzene

Toluene

New C—C bond is formed

(d) Clemmensen reduction

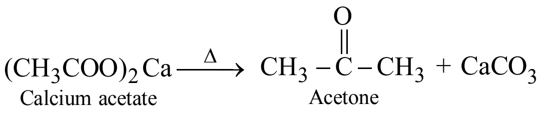
$$>C = O \xrightarrow[HCl]{Zn/Hg} > CH_2$$

4. (b) Acetic Anhydride is produced due to dehydration of two molecules of acetic acid by P_2O_5

$$CH_3CO\boxed{OH \quad H}COOCH_3 \longrightarrow$$

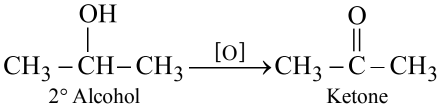
$$(CH_3CH)_2O + H_2O$$

5. (b)



$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + CaCO_3$$

6. (c) $\underset{(x)}{C_3H_8O} \xrightarrow{[O]} C_3H_6O$ (Ketone)

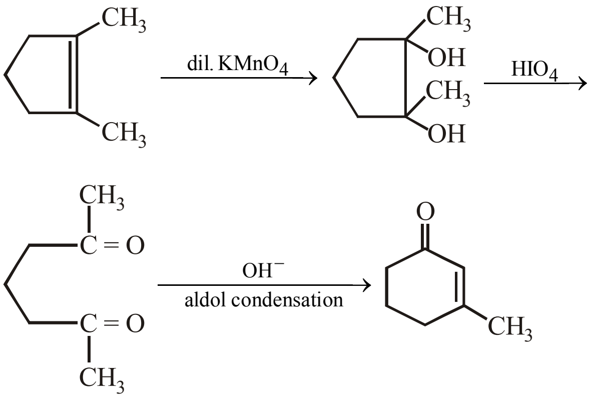


$$\underset{2^\circ\text{ Alcohol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow{[O]} \underset{\text{Ketone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

Ketones are oxidation products of 2° alcohols.

7. (c) Clemensen's Reduction of ketones is carried out in Zn–Hg and HCl.

8. (a)



9. (b) The compound is C_2H_5OH.

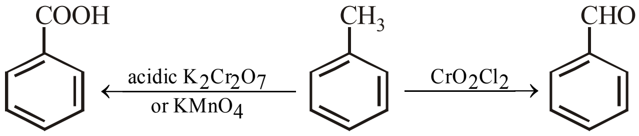
$$C_2H_5OH \xrightarrow{[O]} CH_3CHO$$

$$\xrightarrow{[O]} CH_3COOH$$

10. (d) $CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{[A]}{CH_3CH_2NH_2} \xrightarrow{HNO_2}$

$$\underset{[B]}{CH_3CH_2OH} \xrightarrow{Cu/573K} \underset{[C]}{CH_3CHO}$$

11. (c)



(Etard reaction)

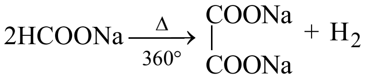
Acidic $KMnO_4$ and $K_2Cr_2O_7$ oxidise toluene to benzoic acid but CrO_2Cl_2 oxidises it to Benzaldehyde.

12. (c) Formalin is an aqueous solution (40%) of formaldehyde.

13. (d) I_2 and Na_2CO_3 react with acetophenone ($C_6H_5COCH_3$) to give yellow ppt. of CHI_3 but benzophenone ($C_6H_5COC_6H_5$) does not and hence can be used to distinguish between them.

14. (c) The test used for the distinction of HCOOH and CH_3COOH is treatment with Tollen's reagent because formic acid can reduce Tollen's reagent but acetic acid can not.

15. (b)



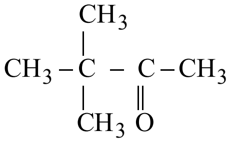
$$2HCOONa \xrightarrow[360^\circ]{\Delta} \begin{array}{l} COONa \\ | \\ COONa \end{array} + H_2$$

16. (b) Chromic acid and $KMnO_4$ will cleave the molecule at the site of double bond while Cu at 300°C cannot oxidise $COCH_3 \longrightarrow COOH$. The only reagent suitable for this conversion is NaOI or NaOH + I_2 (iodoform test):

$$(CH_3)_2C = CHCOCH_3 \xrightarrow{NaOI}$$

$$(CH_3)_2C = CHCOOH + CHI_3.$$

17. (b) Pinacolone is 3,3-dimethyl-2 butanone.

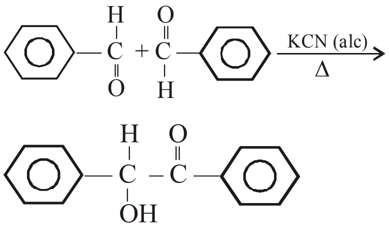


$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{O}{\underset{||}{C}}-CH_3$$

18. (a) Formaldehyde reacts with ammonia to form hexamethylene tetramine which is also known as urotropine. It is used as urinary tract antiseptic

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

19. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin



Benzoin

20. (d) Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence does not react with aldehydes and ketones.

21. (d) The compound formed is trioxy formaldehyde.

22. (c) Aldol condensation is given by the compounds which contain α hydrogen atom. As the given compound does not contain α hydrogen atom. Hence it does not undergo aldol condensation.

23. (c) Acetaldehyde is formed

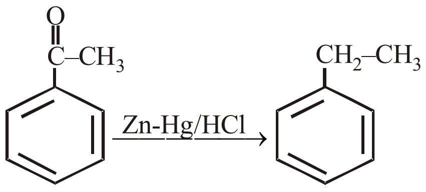
$$CH_3CN + 2H \xrightarrow[Ether]{HCl} CH_3CH = NH.HCl$$

$$\xrightarrow[H_2O]{Boiling} CH_3CHO + NH_4Cl$$

$$2CH_3COCH_3 + 3I_2 \xrightarrow{NaOH} 2CHI_3$$

$$+ 2CH_3COONa$$

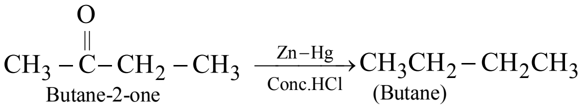
24. (b)



Phenyl methyl ketone — Ethyl benzene

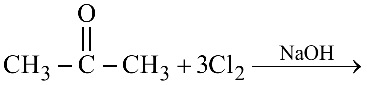
This reaction is known as Clemmensen's reduction.

25. (d) It is Clemmensen's reduction



$$\underset{\text{Butane-2-one}}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3} \xrightarrow[Conc.HCl]{Zn-Hg} \underset{\text{(Butane)}}{CH_3CH_2-CH_2CH_3}$$

26. (b)



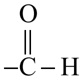
$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + 3Cl_2 \xrightarrow{NaOH}$$

$$CCl_3COCH_3 + 3HCl$$

$$CCl_3COCH_3 + NaOH \longrightarrow$$

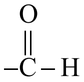
$$CHCl_3 + CH_3COONa$$

27. (d) $LiAlH_4/H_2O$ will reduce only



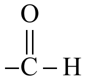
$$-\overset{O}{\overset{||}{C}}-H$$

$NaBH_4/H_2O$ will reduce only



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

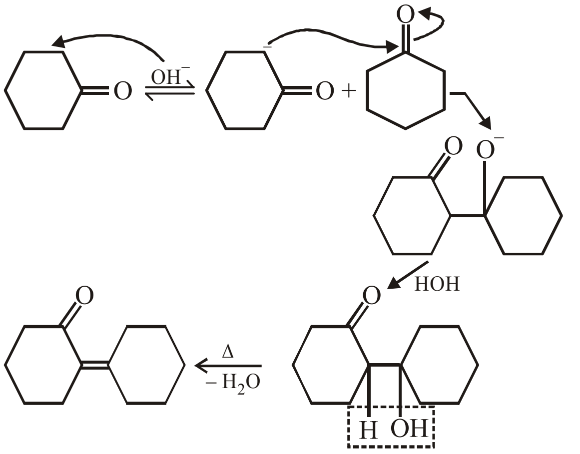
Na + C_2H_5OH will reduce only



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

28. (a) Chloral is CCl_3CHO so, it is an aldehyde.

29. (c) In the presence of base, cyclohexanone show aldol condensation.



30. (b) Aldol formed in aromatic aldehydes itself loses water molecule without heating because double bond formed is more stable due to conjugation with benzene ring. $C_6H_5CH{=}CHCHO$ is commonly known as cinnamaldehyde.

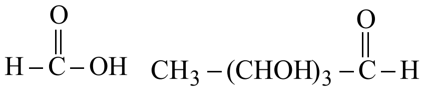
31. (b) $(CH_3)_3C - CHO$ does not show aldol condensation because it does not contain α-hydrogen atom.

32. (b) In Wolf-Kishner reduction $NH_2NH_2/\overline{OH}$ is used. Br^- can be replaced by OH^-.

33. (b) Cannizzaro reaction is given by aldehydes and ketones which do not have α-hydrogen atom. Benzaldehyde (C_6H_5CHO) does not have α-H atom and hence gives Cannizzaro reaction.

34. (b) Acetaldehyde has $\alpha - H$ atoms. In alkaline medium it will undergo aldol condensation to produce aldol (β-hydroxyaldehyde).

35. (d) Compounds having – CHO group reduce Tollen's reagent to silver mirror. It is called silver mirror test.



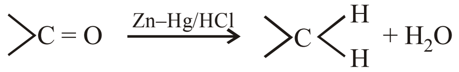
$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \qquad \mathrm{CH_3-(CHOH)_3-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

(a) (b)

Both (a) and (b) have $\mathrm{-\overset{\overset{\displaystyle O}{\|}}{C}-H}$ group so both of them give positive silver mirror test.

36. (a) $\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + H_2SO_{4(conc.)} \rightarrow CO + CO_2 + H_2O$

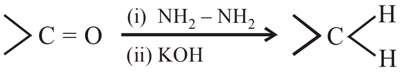
37. (a) Aldehydes and ketones are reduced to alkanes by Clemmensen reduction.



$$>C=O \xrightarrow{Zn-Hg/HCl} >C<^{H}_{H} + H_2O$$

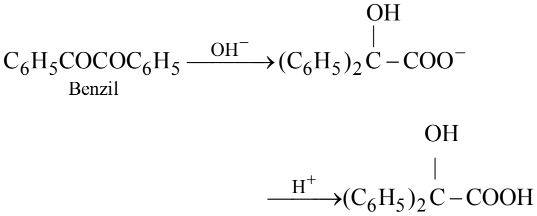
38. (b)

39. (a) Wolf- Kishner reduction



$$>C=O \xrightarrow[\text{(ii) KOH}]{\text{(i) } NH_2-NH_2} >C<^{H}_{H}$$

40. (c)



$$\underset{\text{Benzil}}{C_6H_5COCOC_6H_5} \xrightarrow{OH^-} (C_6H_5)_2\overset{\overset{\displaystyle OH}{|}}{C}-COO^-$$

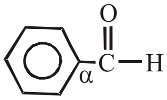
$$\xrightarrow{H^+} (C_6H_5)_2\overset{\overset{\displaystyle OH}{|}}{C}-COOH$$

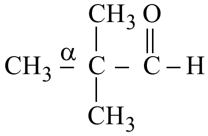
Benzilic acid.

41. (a) Aldehydes having α -hydrogen atom do not show Cannizzaro reaction.

$\overset{\alpha}{CH_3}CHO$ HCHO

(a) (b)





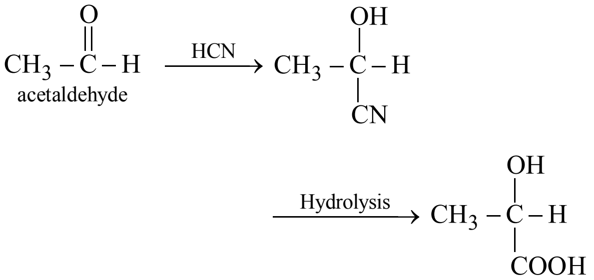
$$CH_3\overset{\alpha}{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(c) (d)

Thus only CH_3CHO has α -hydrogen atom and hence it will not show Cannizzaro reaction.

42. (c) Only aldehydes and ketones react with 2, 4-dinitrophenylhydrazine.

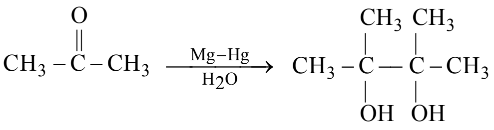
43. (b)



$$\underset{\text{acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} \xrightarrow{HCN} CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

$$\xrightarrow{\text{Hydrolysis}} \underset{\text{Lactic acid}}{CH_3-\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H}$$

44. (b) Example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[H_2O]{Mg-Hg} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

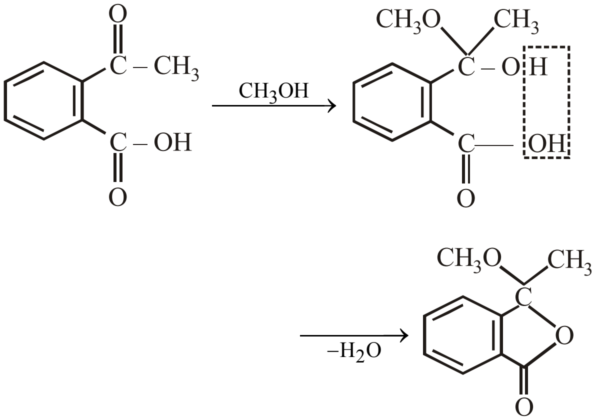
Pinacol

(Pinacols have adjacent hydroxyl groups)

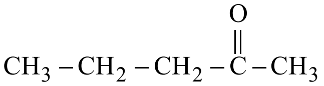
45. (a) Compounds having $\mathrm{-\overset{\overset{\displaystyle O}{\|}}{C}-}$ moiety in their structure are reduced to alcohols using $NaBH_4$ in ethanolic solution.

Thus $\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$, $\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$ and $\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}$ are reduced while, R – O – R (ethers) are inert and can't be reduced by $NaBH_4$.

46. (d)

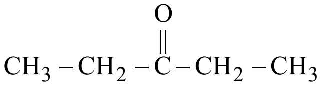


47. (c) Iodoform test is given by compounds which have CH_3CO group.



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

2-pentanone

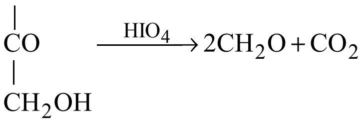


$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

3-pentanone

∵ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.

48. (d)



$$\begin{array}{l}CH_2OH\\ |\\ CO\\ |\\ CH_2OH\end{array} \xrightarrow{HIO_4} 2CH_2O + CO_2$$

49. (a) In this reaction, one molecule is oxidised and other is reduced simultaneously.

50. (a) $6HCHO + 4NH_3 \longrightarrow \underset{\substack{\text{urotropine}\\ \left(\text{hexamethylene tetramine}\right)}}{(CH_2)_6N_4} + 6H_2O$

51. (d) We can distinguish between formic acid and acetic acid by their action on Fehling's solution. Formic acid gives a red ppt of cuprous oxide but acetic acid does not give red ppt.

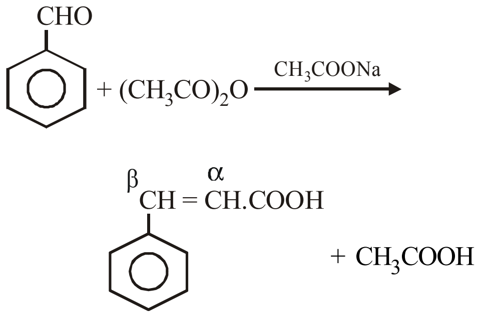
52. (a) Aldol condensation involves an aldehyde or ketone having an α–hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH).

Only CH_3COCH_3 will give aldol condensation (Both HCHO and C_6H_5CHO lack α-hydrogen).

53. (b) Cl_2 does not give acid chloride on treating it with a carboxylic acid.

While PCl_3, PCl_5 and $SOCl_2$ gives nucleophilic substitution reaction with carboxylic acid (Cl^- replaces OH^- group of – COOH)

54. (b) Benzaldehyde forms cinnamic acid as follows.

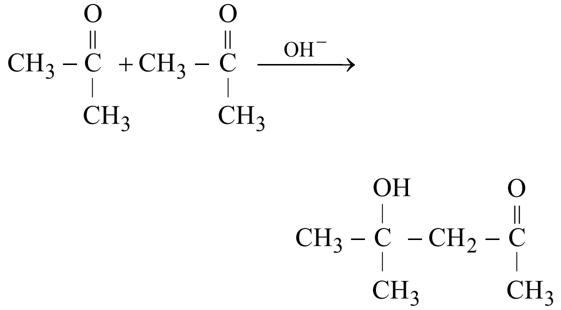


Cinnamic acid

55. (d) Formaldehyde on reaction with ammonia forms a crystalline compound, hexamethylene tetramine.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\substack{\text{Urotropine}\\\text{(hexamethylene}\\\text{tetramine)}}}{(CH_2)_6N_4} + 6H_2O$$

56. (a) Completing the given reaction.

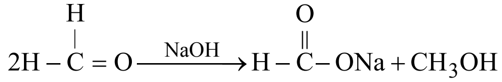


$$CH_3-\underset{CH_3}{\overset{O}{\overset{\|}{C}}} + CH_3-\underset{CH_3}{\overset{O}{\overset{\|}{C}}} \xrightarrow{OH^-} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\underset{CH_3}{\overset{O}{\overset{\|}{C}}}$$

Diacetonyl alcohol

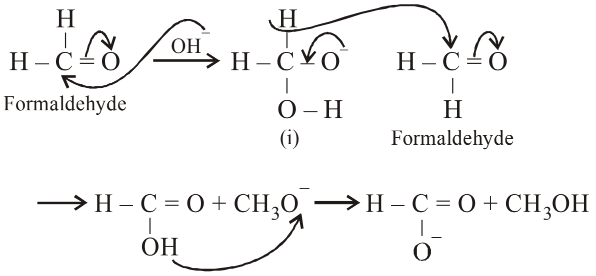
[**Note:** Carbonyl compounds having α – H atom undergoes **aldol condensation** in presence of dilute base {e.g., NaOH, $Ba(OH)_2$ etc.} to form a class of compounds known as **aldol**].

57. (c) In the Cannizzaro reaction, two moles of carbonyl compounds having no α-hydrogen atom when treated with strong alkali undergo, redox or disproportionation reaction.

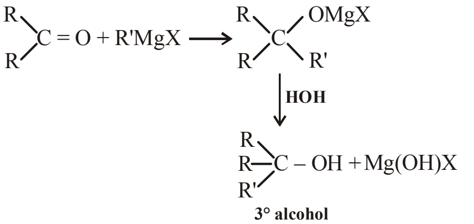


$$2H-\overset{H}{\overset{|}{C}}=O \xrightarrow{NaOH} H-\overset{O}{\overset{\|}{C}}-ONa+CH_3OH$$

Mechanism : First of all base OH^- acts as a nucleophile and attack other one of carbonyl compound to generate a hydroxy alkoxide ion which acts as a hydride ion donor to the other molecule of carbonyl compounds. In the final step there is a exchange of proton from acid to alkoxide ion to get stable product.

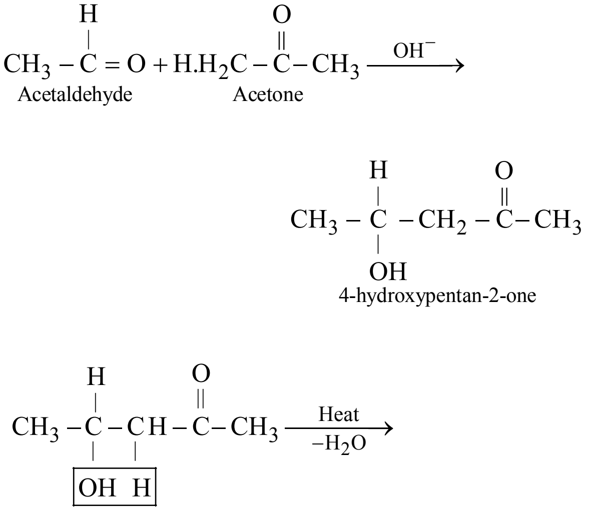


58. (c)



3° alcohol

59. (b) When aldehyde condensed with ketone, α-hydrogen of the ketone involved in condensation.



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O} + \underset{\text{Acetone}}{H.H_2C-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{OH^-} \underset{\text{4-hydroxypentan-2-one}}{CH_3-\underset{OH}{\overset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

$$CH_3-\underset{\boxed{OH}}{\overset{H}{C}}-\underset{\boxed{H}}{CH}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-H_2O]{Heat}$$

$$CH_3CH = CHCOCH_3$$

60. (a) When acetonitrile is hydrolysed partially with cold concentrated HCl it forms acetamide.

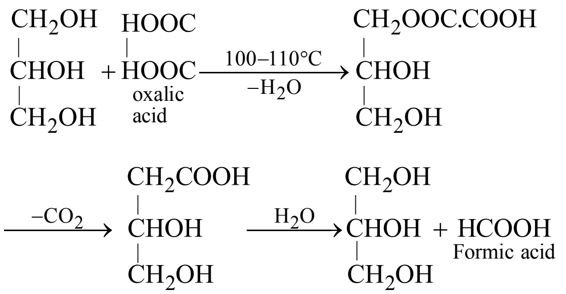
$$\underset{\text{Acetonitrile}}{CH_3-C\equiv N} \xrightarrow{HCl} \underset{\text{Acetamide}}{CH_3CONH_2}$$

On further hydrolysis acetamide may give either CH_3COOH (acetic acid) or its salt.

61. (a) among acetic acid, phenol and n-hexanol only CH_3COOH reacts with $NaHCO_3$ to evolve CO_2 gas.

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

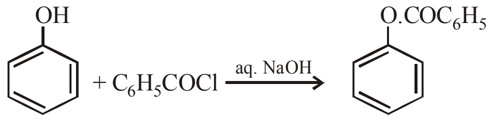
62. (c) When glycerol is heated with oxalic acid following reaction occurs.



$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{l}HOOC\\ |\\ HOOC\\ \text{oxalic}\\ \text{acid}\end{array} \xrightarrow[-H_2O]{100-110°C} \begin{array}{l}CH_2OOC.COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

$$\xrightarrow{-CO_2} \begin{array}{l}CH_2COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \xrightarrow{H_2O} \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \underset{\text{Formic acid}}{HCOOH}$$

63. (a)



phenyl benzoate

The function of NaOH is

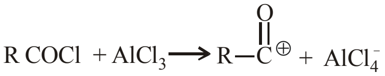
(i) To convert phenol to more stronger nucleophile PhO^-

(ii) To neutralize the acid formed

64. (a) Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols.

65. (d) Methyl acetate and ethyl acetate on hydrolysis give CH_3COOH which is a liquid. Similarly ethyl formate on hydrolysis will give formic acid which is also a liquid. Only ethyl benzoate on hydrolysis will give benzoic acid which is a solid.

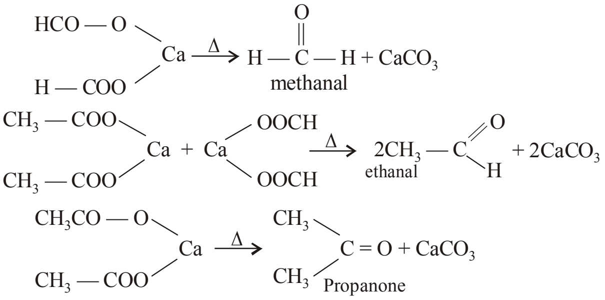
66. (d)



$$R\,COCl + AlCl_3 \longrightarrow R-\overset{\overset{O}{||}}{C}{}^{\oplus} + AlCl_4^-$$

Electrophile

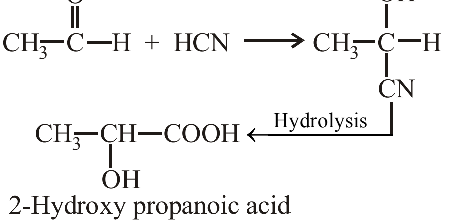
67. (b) Propanal is not formed during the dry distillation of a mixture of calcium formate and calcium acetate. While methanal, propanone and ethanal are formed as follows:



68. (b) The ester having α hydrogen atom show Claisen condensation reaction.

We know that ethyl benzoate $(C_6H_5COOC_2H_5)$ does not contain α-hydrogen. Therefore $C_6H_5COOC_2H_5$ does not undergo Claisen self condensation.

69. (c)



2-Hydroxy propanoic acid

(As it has a chiral C-atom thus it is optically active)

70. (b) $2CH_3MgBr + HCHO \longrightarrow CH_3CH_2OH + Mg(OH)Br$

71. (c) $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} CH_3CHClCOOH$

$\xrightarrow[-HCl]{\text{alc.KOH}} \underset{\text{Acrylic acid}}{CH_2 = CHCOOH}$

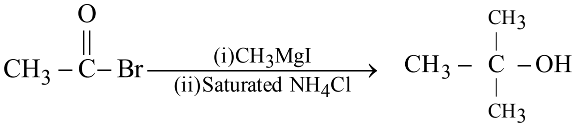
72. (d)

73. (a) $LiAlH_4$ can reduce COOH group and not the double bond.

$CH_2 = CH - COOH \xrightarrow{LiAlH_4} CH_2 = CH - CH_2OH$

74. (c) There is no reaction hence the resultant mixture contains $CH_3COOC_2H_5 + NaCl$.

75. (a)

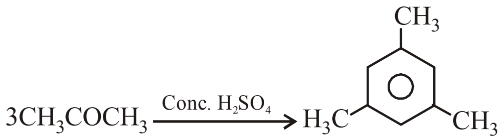


$$CH_3-\overset{\overset{O}{||}}{C}-Br \xrightarrow[\text{(ii)Saturated }NH_4Cl]{\text{(i)}CH_3MgI} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

2–methyl–2–propanol

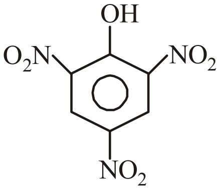
76. (d) $\underset{\text{acetic anhydride}}{(CH_3CO)_2O} + \underset{\text{diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow{AlCl_3} 2CH_3COOC_2H_5$

77. (a) When distilled with conc. H_2SO_4, three molecules of acetone condense to form mesitylene, i.e. 1, 3, 5-trimethylbenzene.

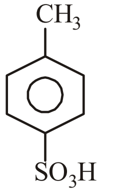


Mesitylene

78. (d)



picric acid



p-toluene sulphonic acid

Other three acids contain – COOH group.

Palmitic acid	$CH_3(CH_2)_{14}COOH$
Lactic acid	$CH_3CH(OH)COOH$
Ethanoic acid	CH_3COOH

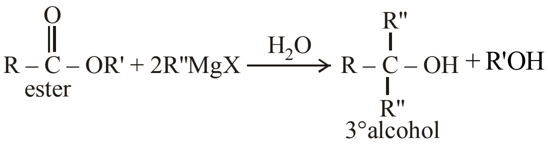
79. (a) $RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br \xrightarrow{KCN}$

$RCH_2CH_2CN \xrightarrow{H_3O^+} RCH_2CH_2COOH + NH_3$

80. (a) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl + HCl$

∴ A is PCl_5. It can also be $SOCl_2$.

81. (a)



$$\underset{\text{ester}}{R-\overset{\overset{O}{||}}{C}-OR'} + 2R''MgX \xrightarrow{H_2O} \underset{\text{3°alcohol}}{R-\underset{\underset{R''}{|}}{\overset{\overset{R''}{|}}{C}}-OH} + R'OH$$

82. (c) CaC_2O_4 is the only compound of Ca which is not soluble in acetic acid. This property of Ca is used in inorganic salt analysis.

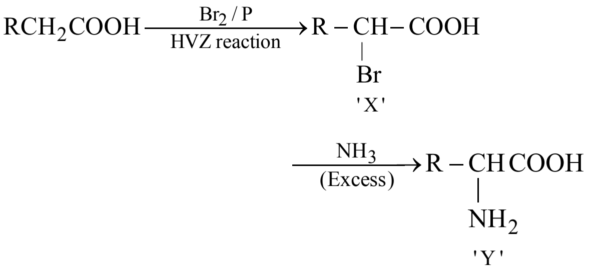
83. (c) $Cl_2CHCOOH$ is most acidic because it has two chlorine at α-position.

84. (d)

85. (c) $CH_3COOH + CaCO_3 \rightarrow (CH_3COO)_2Ca$

$$\xrightarrow{\text{Heat}} \begin{matrix}CH_3\\CH_3\end{matrix}\!>CO \xrightarrow{I_2+NaOH} CHI_3$$

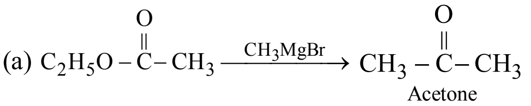
86. (b)



$$RCH_2COOH \xrightarrow[\text{HVZ reaction}]{Br_2/P} \underset{\substack{|\\ Br\\ 'X'}}{R-CH-COOH} \xrightarrow[(\text{Excess})]{NH_3} \underset{\substack{|\\ NH_2\\ 'Y'}}{R-CHCOOH}$$

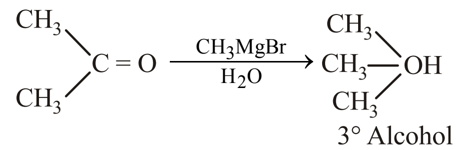
87. (d) Ethers neither react with sodium nor with semicarbazide.

88. (c) (a)



$$C_2H_5O-\overset{\substack{O\\ ||}}{C}-CH_3 \xrightarrow{CH_3MgBr} \underset{\text{Acetone}}{CH_3-\overset{\substack{O\\ ||}}{C}-CH_3}$$

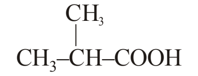
(b)



(c) $CH_3OCH_3 \xrightarrow{CH_3MgBr}$ No reaction

(d) $C_2H_5OH \xrightarrow{CH_3MgBr} \underset{\text{methane}}{CH_4}$

89. (d)

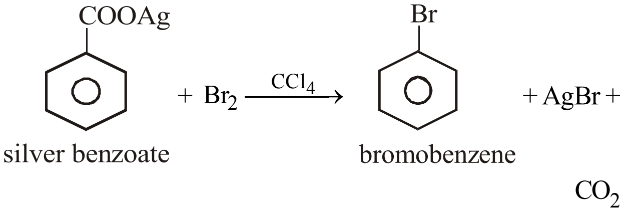


$$CH_3-\overset{\substack{CH_3\\ |}}{C}H-COOH$$

General : Iso-butyric acid

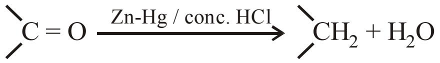
IUPAC: 2-methylpropanoic acid.

90. (c) This is Hunsdiecker's reaction.



91. (b) Oxidation of acetal aldehydes and methyl ketones with sodium hypoiodite gives this test. So, here in option (b) ketone is having (CH_3CO—) group and the other is having (CH_3CH_2CO—) group which do not give hypoiodite test. So thus they can be distinguished.

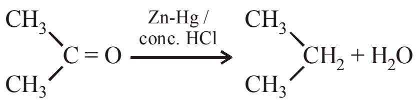
92. (d)



$$>C=O \xrightarrow{\text{Zn-Hg / conc. HCl}} >CH_2 + H_2O$$

Clemmensen reduction

e.g.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg /}} \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH_2 + H_2O$$

93. (c) Electron withdrawing substituent (like halogen, —NO_2, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

Electronegativity decreases in order

$$F > Cl > Br$$

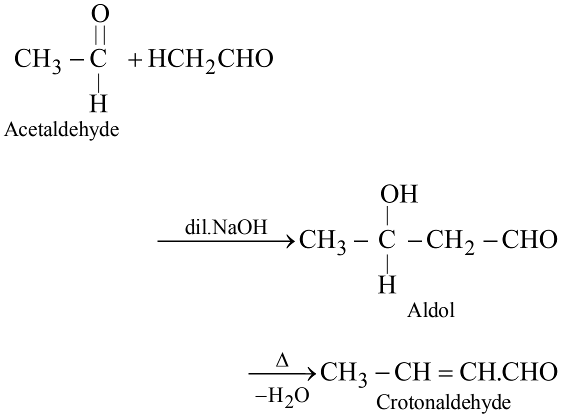
and hence –I effect also decreases in the same order, therefore the correct option is

$$[FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH]$$

94. (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.

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

95. (a) Aldehydes and ketones having at least one α-hydrogen atom in presence of dilute alkali give β-hydroxy aldehyde or β-hydroxy ketone

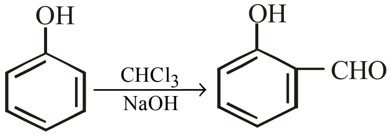


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\substack{O\\ ||}}{\underset{\substack{|\\ H}}{C}}} + HCH_2CHO \xrightarrow{\text{dil.NaOH}} \underset{\text{Aldol}}{CH_3-\overset{\substack{OH\\ |}}{\underset{\substack{|\\ H}}{C}}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH.CHO}$$

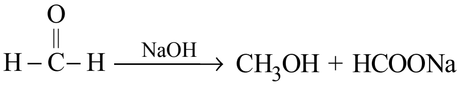
96. (c) This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing α – H on treatment with X_2 /P give di-halo substituted acid.

$$CH_3-CH_2COOH \xrightarrow{Br_2/P} CH_3-CBr_2-COOH$$

97. (b) (a)



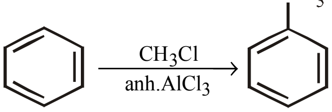
(b)



$$H-\overset{\substack{O\\ ||}}{C}-H \xrightarrow{NaOH} CH_3OH + HCOONa$$

(c) $2CH_3Cl \xrightarrow[\text{dry ether}]{Na} CH_3-CH_3$

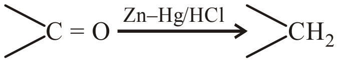
(d)



Note that new C–C bond is formed in a, c and d.

98. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

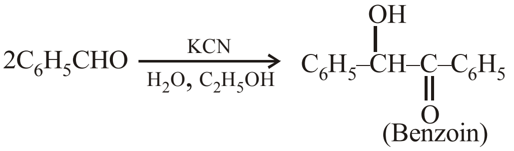
99. (b) Clemmensen reduction is



$$>C=O \xrightarrow{\text{Zn–Hg/HCl}} >CH_2$$

100. (d)

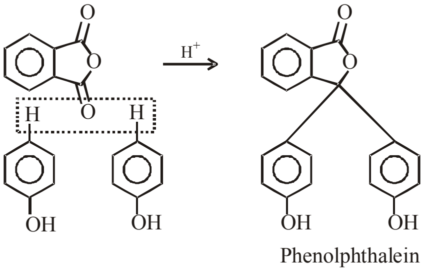
(a)



$$2C_6H_5CHO \xrightarrow[H_2O,\ C_2H_5OH]{KCN} C_6H_5-\overset{OH}{\overset{|}{C}H}-\underset{O}{\underset{\|}{C}}-C_6H_5$$

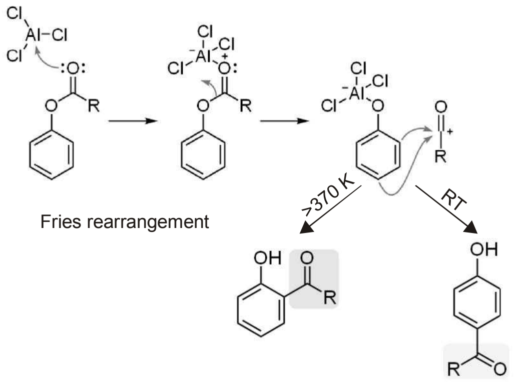
(Benzoin)

(b)



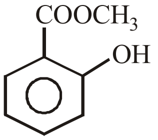
Phenolphthalein

(c)



Fries rearrangement

(d)



(Oil of wintergreen)

EXERCISE - 2

1. (a) Ethyne get converted to aldehydes and ketones when treated with an acidified aqueous solution of palladium chloride ($PdCl_2$) and cupric chloride ($CuCl_2$) in presence of air or oxygen. This method is known as Wacker's process.

$$\underset{\text{Ethyne}}{CH\equiv CH} + PdCl_2 + H_2O \xrightarrow[\text{air or } O_2]{CuCl_2} \underset{\text{ethanal}}{CH_3CHO} + Pd + 2HCl$$

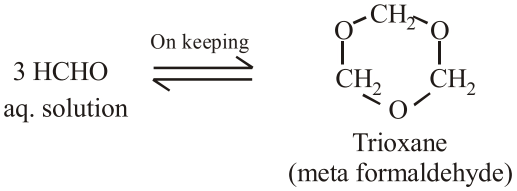
2. (d) Carbonyl compound form crystalline addition product with $NaHSO_3$ which on treatment with dilute acid or alkali regenerates the carbonyl compound.

3. (a) An electron releasing substituent (+I) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid. Hence acid character decreases as the + I-effect of the alkyl group increases as

$CH_3^- < CH_3CH_2^- < CH_3CH_2CH_2^- < CH_3CH_2CH_2CH_2^-$

Hence the order becomes : (i) > (ii) > (iii) > (iv)

4. (a)



$$\underset{\text{aq. solution}}{3\,HCHO} \overset{\text{On keeping}}{\rightleftharpoons} \text{Trioxane}$$

Trioxane
(meta formaldehyde)

5. (b) Only aldehydes give reddish brown ppt. with Fehling's solution.

6. (d) Acetone or Propyne form mesitylene (1,3,5-trimethyl benzene) on distillation with conc. H_2SO_4.

7. (a) Ketones on oxidation give carboxylic acids with lesser number of carbon atoms, i.e.,

$$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$

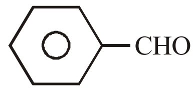
8. (d) Structures of given aldehydes

CH_3CH_2CHO
propanal

Cl_3CCHO
trichloroethanal

$HCHO$
methanal

CH_3CHO
ethanal



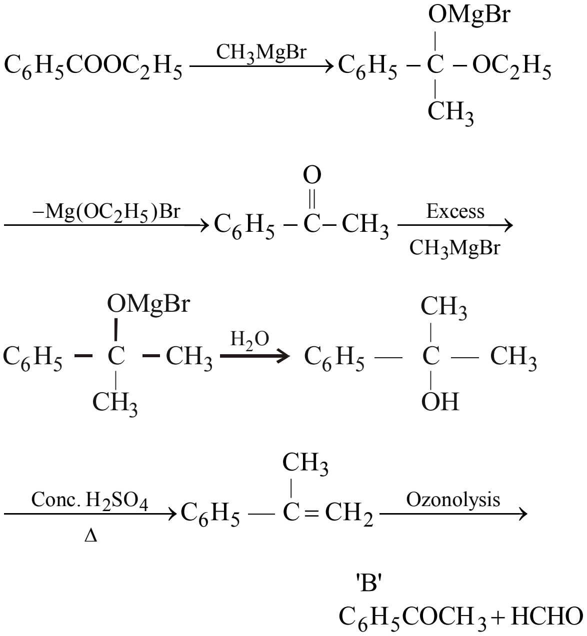
benzaldehyde

Trichloroethanal, methanal and benzaldehyde do not undergo aldol condensation. Aldol condensation is not given by aldehydes and ketones which do not contain α-hydrogen atom(s).

9. (d) $C_6H_5COOH \xrightarrow{\text{Soda-lime (X)}} C_6H_6 + Na_2CO_3 + H_2O$

$C_6H_5OH \xrightarrow{\text{Zn dust (Y)}} C_6H_6 + ZnO$

10. (a)



$$C_6H_5COOC_2H_5 \xrightarrow{CH_3MgBr} C_6H_5-\overset{OMgBr}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OC_2H_5$$

$$\xrightarrow{-Mg(OC_2H_5)Br} C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[CH_3MgBr]{\text{Excess}}$$

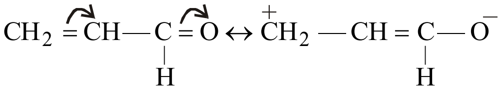
$$C_6H_5-\overset{OMgBr}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow{H_2O} C_6H_5-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$$

$$\xrightarrow[\Delta]{\text{Conc. } H_2SO_4} C_6H_5-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{\text{Ozonolysis}}$$

$$\underset{\text{'B'}}{C_6H_5COCH_3} + HCHO$$

$$C_6H_5COCH_3 \xrightarrow{3I_2+4\,NaOH} CHI_3$$

11. (c) In $CH_2 = CH — CHO$ due to — M effect of — CHO group polarization of electron takes place as follows



$$CH_2 = CH—\underset{|\atop H}{C} = O \leftrightarrow \overset{+}{C}H_2 — CH = \underset{|\atop H}{C} — \overset{-}{O}$$

Hence partial polarization is represented as

$$\overset{\delta+}{C}H_2 = CH — CH = \overset{\delta-}{O}$$

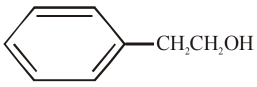
12. (d) Structures of given compounds

CH_3CH_2OH
Ethanol

CH_3CHO
Ethanal

$CH_3CH_2CH_2CH_2OH$
Butanol

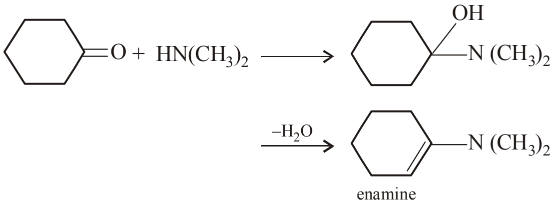
$CH_3CH_2CH(OH)CH_3$
2-Butanol



Phenyl ethanol

Compounds containing $CH_3-\overset{O}{\overset{||}{C}}-$ or $CH_3-CHOH-$ group give positive iodoform test.

13. (c)

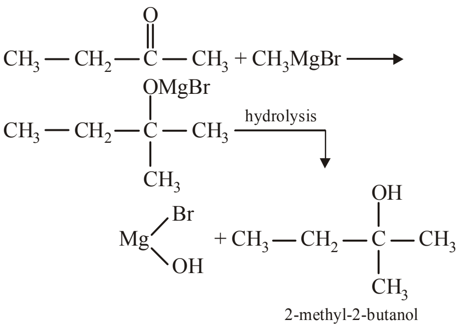


14. (a) Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is
Aldehydes (smaller to higher) Ketones (smaller to higher), Then

$$HCHO > CH_3COCH_3 > Ph.COCH_3 > PhCOPh$$

The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.

15. (a)



$$CH_3—CH_2—\overset{O}{\overset{||}{C}}—CH_3 + CH_3MgBr \longrightarrow CH_3—CH_2—\overset{OMgBr}{\overset{|}{\underset{|\atop CH_3}{C}}}—CH_3 \xrightarrow{\text{hydrolysis}} Mg\begin{matrix}Br\\OH\end{matrix} + CH_3—CH_2—\overset{OH}{\overset{|}{\underset{|\atop CH_3}{C}}}—CH_3$$

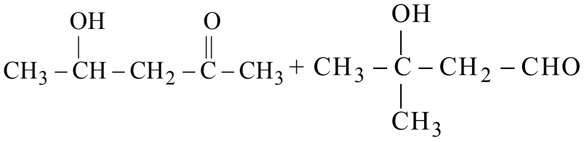
2-methyl-2-butanol

16. (a) The correct order of increasing acid strength

$$CF_3.COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$$

Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

17. (b)



$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{||}{C}}-CH_3 + CH_3-\overset{OH}{\overset{|}{\underset{|\atop CH_3}{C}}}-CH_2-CHO$$

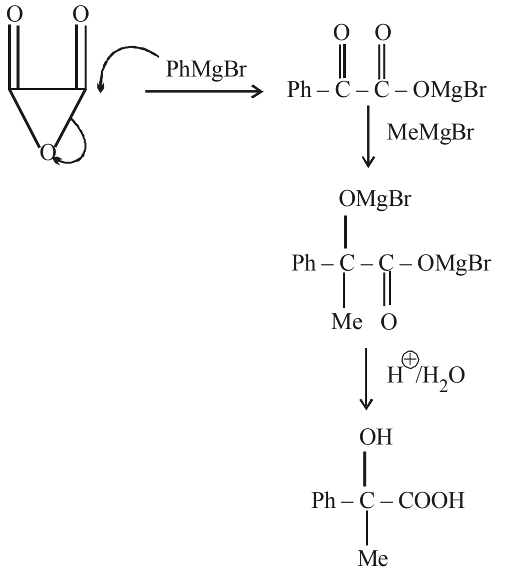
Two products are formed.

18. (c) Mono-carboxylic acids are functional isomers of esters.

e.g., CH_3COOH (Acetic acid) $HCOOCH_3$ (Methyl formate)

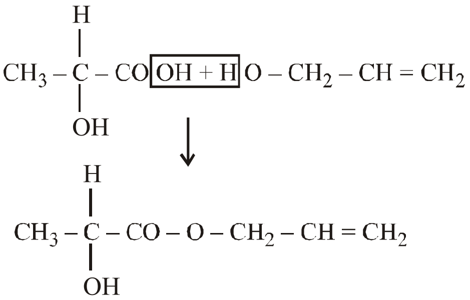
19. (c) $KMnO_4$ converts $-CH_3$ group of toluene into $-COOH$ while HI reduces $-COOH$ group into $-CH_3$ group.

20. (c)



21. (a)

22. (b)

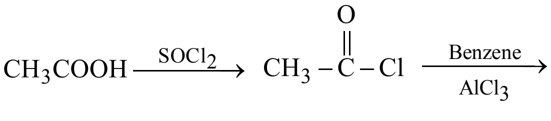


$$CH_3-\overset{H}{\overset{|}{\underset{|\atop OH}{C}}}-CO\boxed{OH + H}O-CH_2-CH=CH_2$$

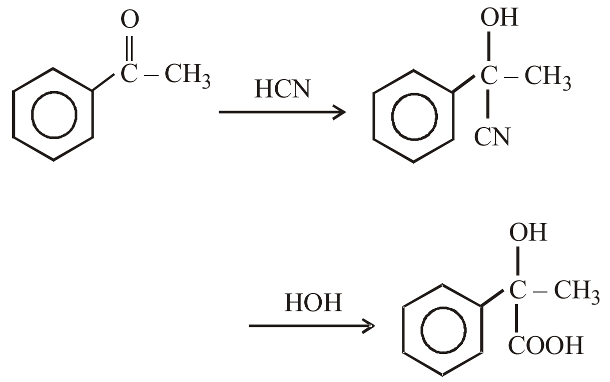
$$\downarrow$$

$$CH_3-\overset{H}{\overset{|}{\underset{|\atop OH}{C}}}-CO-O-CH_2-CH=CH_2$$

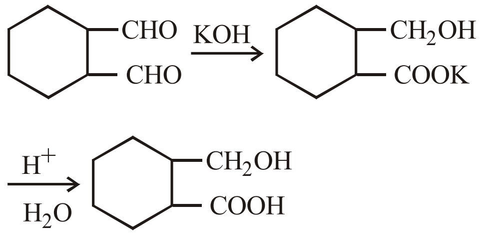
23. (d)



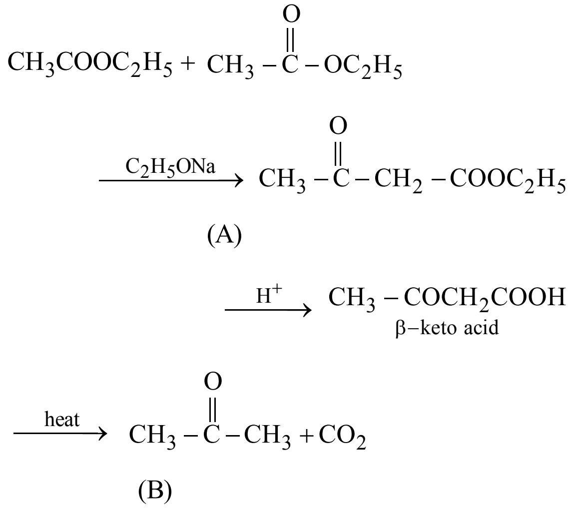
$$CH_3COOH \xrightarrow{SOCl_2} CH_3-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[AlCl_3]{\text{Benzene}}$$



24. (a) It is an example of intramolecular cannizaro reaction.



25. (b)



$$CH_3COOC_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

$$\xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5$$

(A)

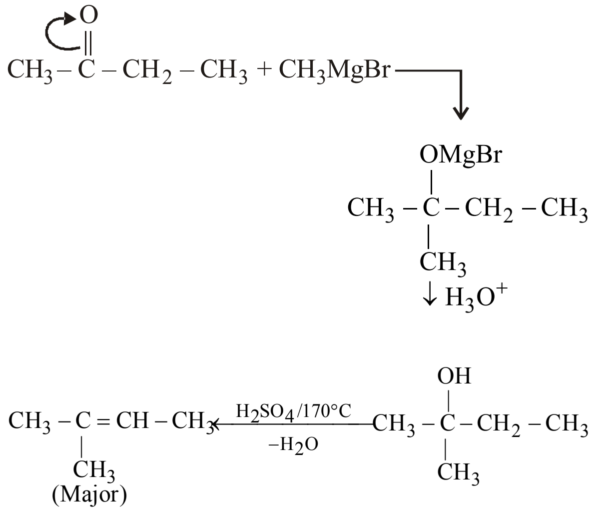
$$\xrightarrow{H^+} \underset{\beta-\text{keto acid}}{CH_3-COCH_2COOH}$$

$$\xrightarrow{\text{heat}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3+CO_2$$

(B)

β-Keto acids, on heating, undergo decarboxylation.

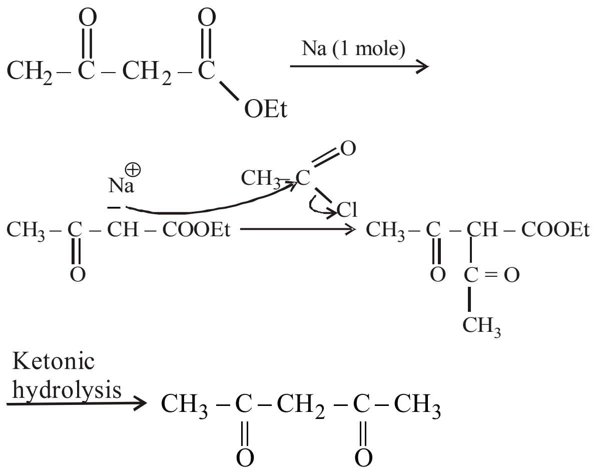
26. (b)



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + CH_3MgBr \longrightarrow CH_3-\overset{OMgBr}{\underset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{H_3O^+} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

$$\underset{\text{(Major)}}{CH_3-\underset{CH_3}{C}=CH-CH_3} \xleftarrow[-H_2O]{H_2SO_4/170°C} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

27. (a)

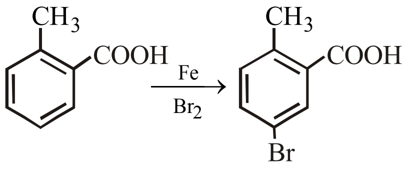


$$CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{Na\ (1\ mole)}$$

$$CH_3-\underset{O}{\underset{\|}{C}}-\overset{\ominus\ \overset{\oplus}{Na}}{CH}-COOEt \xrightarrow{CH_3-COCl} CH_3-\underset{O}{\underset{\|}{C}}-\underset{\underset{CH_3}{C=O}}{CH}-COOEt$$

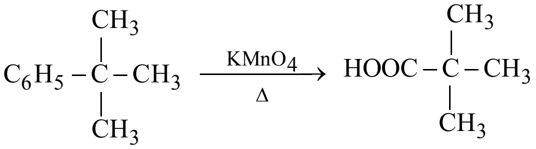
$$\xrightarrow{\text{Ketonic hydrolysis}} CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

28. (c) In *o* - toluic acid, $-CH_3$ group is *ortho-para* directing



and –COOH group is *meta*-directing. So, the resulting product will be (c) in which Br is attached at *para to* $-CH_3$ and *meta* to –COOH group.

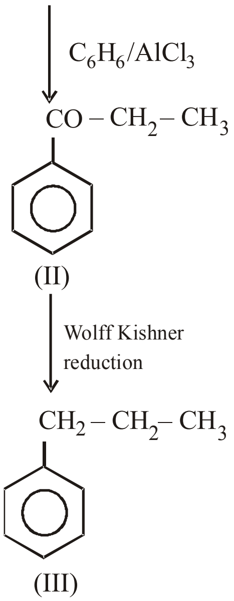
29. (b) Generally benzene ring is very resistant to oxidation thus side chain is always oxidised to – COOH group. But if the side chain is tert-alkyl group, oxidation is difficult, but on vigrous oxidation benzene ring is oxidised.



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{KMnO_4} HOOC-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

30. (a) $CH_3-CH_2-COOH \xrightarrow{PCl_3} CH_3-CH_2-CO-Cl$

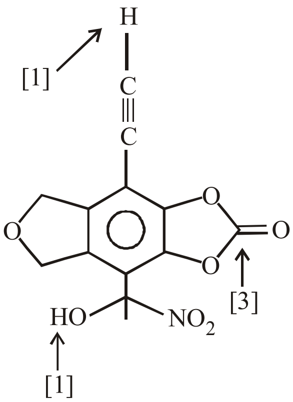
(I)



(II)

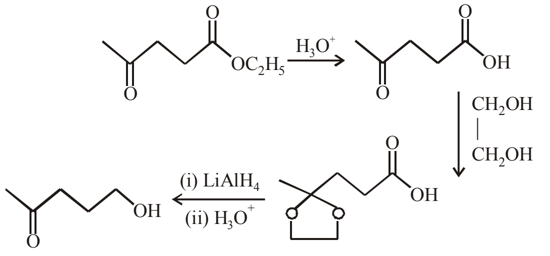
(III)

31. (a)

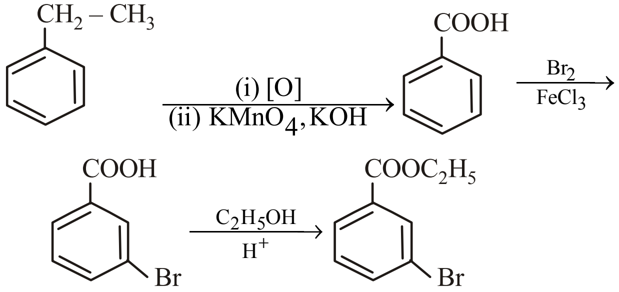


32. (c) Only those aldehydes which do not have α-H atom undergo Cannizaro's reaction. Hence CH_3CHO will not undergo Cannizaro's reaction as it has 3 α H atoms.

33. (a)

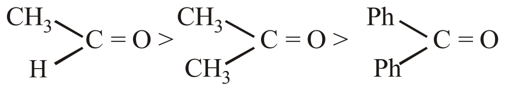


34. (d)



35. (d) The intermediate is carbocation which is destabilised by C = O group in the first three cases. In (d), α–hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C = O group.

36. (d) The reactivity of the carbonyl group toward the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carbonyl carbon atom in the transition state (steric factor). Both these factors predict the following order



$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O > \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O > \begin{matrix}Ph\\Ph\end{matrix}\!\!>C=O$$

(due to steric crowding).

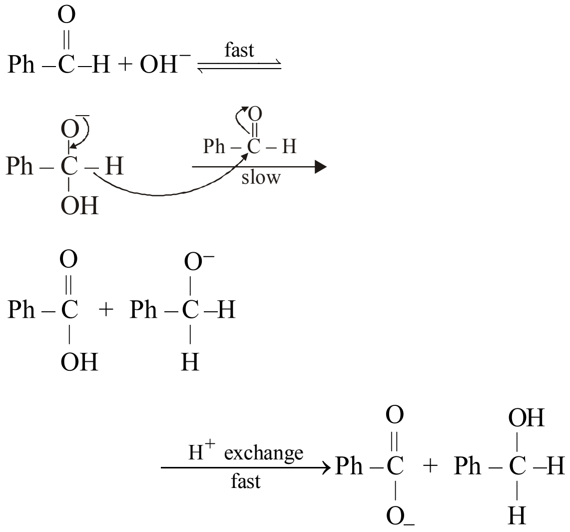
37. (d) Since, C when heated with Br_2 in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows.

$$\underset{(A)}{CH_3-CH_2-COOH}\xrightarrow{NH_3}$$

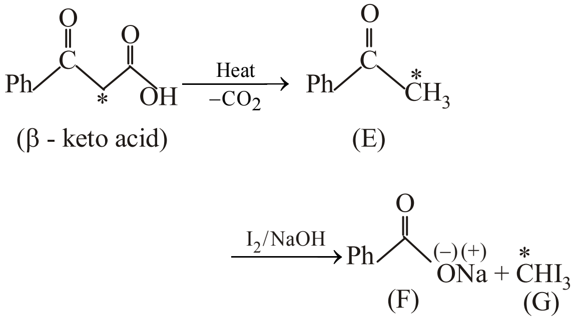
$$\underset{(B)}{CH_3-CH_2-CO\overset{-}{O}\overset{+}{N}H_4}\xrightarrow{\Delta}$$

$$CH_3-CH_2-CONH_2\xrightarrow[\text{Hoffmann bromamide reaction}]{KOH+Br_2}\underset{\text{(Ethylamine)}}{CH_3-CH_2-NH_2}$$

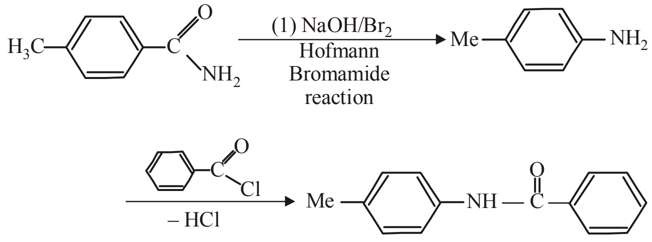
38. (a)



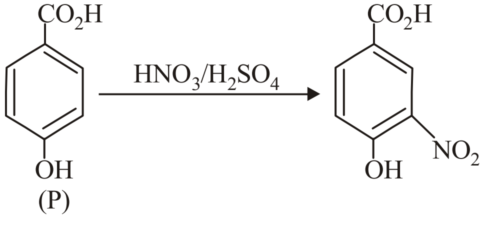
39. (c)



40. (c)

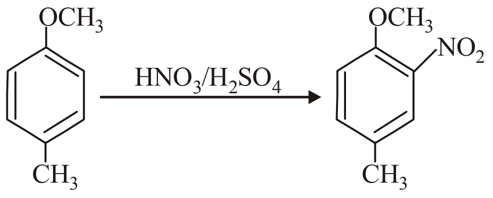


41. (c)



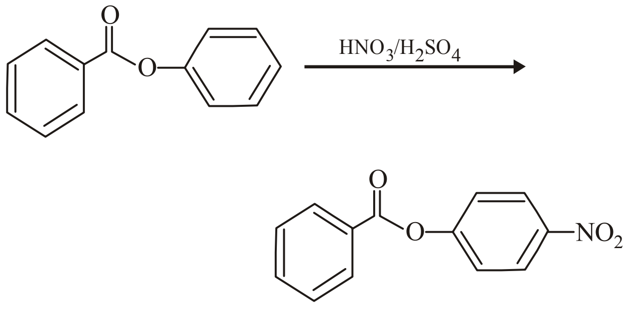
(P)

(OH group is activing)



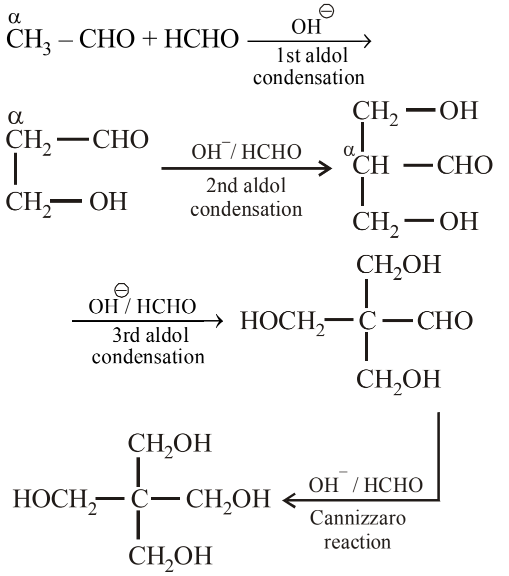
(Q)

(OCH_3 group is more activating)



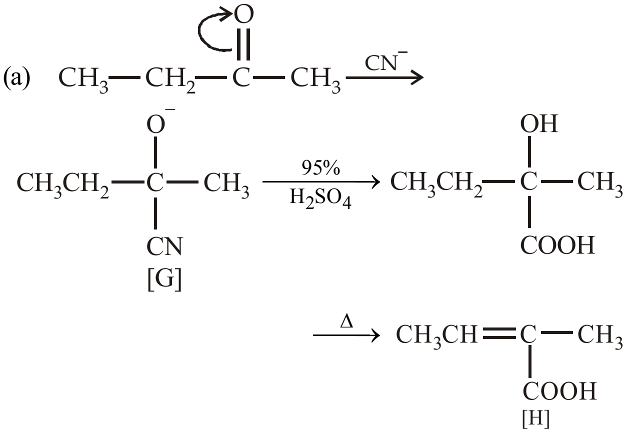
(Benzene ring having –O– is activated)

42. (c)



$$\overset{\alpha}{CH_3}-CHO + HCHO \xrightarrow[\text{1st aldol condensation}]{OH^{\ominus}} \overset{\alpha}{CH_2}(CHO)-CH_2-OH \xrightarrow[\text{2nd aldol condensation}]{OH^-/HCHO} \overset{\alpha}{CH}(CH_2-OH)_2-CHO \xrightarrow[\text{3rd aldol condensation}]{OH^{\ominus}/HCHO} HOCH_2-C(CH_2OH)_2-CHO \xrightarrow[\text{Cannizzaro reaction}]{OH^-/HCHO} HOCH_2-C(CH_2OH)_2-CH_2OH$$

43. (a)

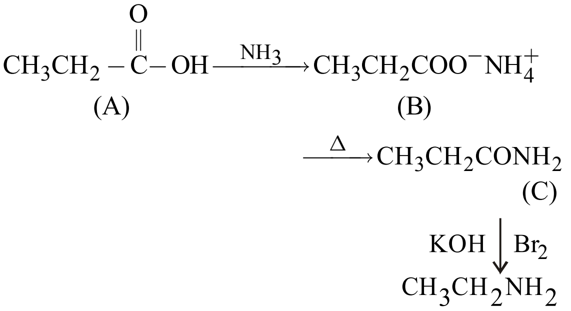


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CN^-} \underset{[G]}{CH_3CH_2-C(O^-)(CN)-CH_3} \xrightarrow[H_2SO_4]{95\%} CH_3CH_2-C(OH)(COOH)-CH_3 \xrightarrow{\Delta} \underset{[H]}{CH_3CH{=}C(COOH)-CH_3}$$

44. (b) β-Ketoacids undergo decarboxylation easily.

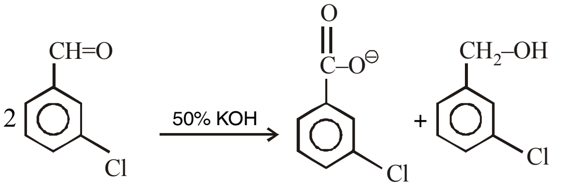
45. (d) $A \xrightarrow[(I)]{NH_3} B \xrightarrow[II]{\Delta} C \xrightarrow[KOH,(III)]{Br_2} CH_3CH_2NH_2$

Reaction (III) is a Hofmann bromamide reaction. Now formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$(C) which can be obtained from the compound $CH_3CH_2COO^-NH_4^+$ (B).
Thus (A) should be CH_3CH_2COOH

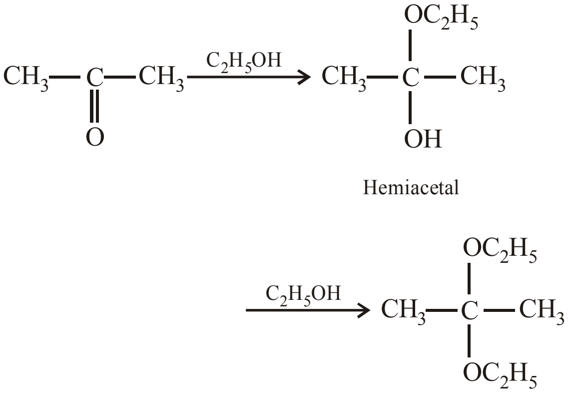


$$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO^-NH_4^+} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2CONH_2} \xrightarrow{KOH\ |\ Br_2} CH_3CH_2NH_2$$

46. (c) Cannizzaro reaction - when an aldehyde containing no α – H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.



47. (d) Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.



Hemiacetal

Acetal

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{C_2H_5OH} CH_3-C(OC_2H_5)(OH)-CH_3 \xrightarrow{C_2H_5OH} CH_3-C(OC_2H_5)_2-CH_3$$

48. (c)

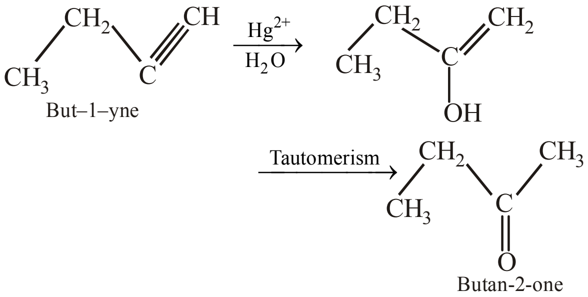
49. (d) Benzaldehyde is less reactive than ethanol towards nucleophilic attack. The combined effect of –*I* and +*R* effect of phenyl group is electron donating which increases the electron density on the carbon atom of the > C = O in benzaldehyde.

50. (b) It is true that lower aldehyde and ketones are soluble in water but as the molecular mass increases their solubility decreases. On adding Tollen's reagent to a solution of Carbonyl compound if silver mirror is obtained than it is aldehyde. Therefore Tollen's reagent is used for the identification of aldehydes and ketones. Here, Statement-1 and Statement-2 both are true but the Statement-2 is not the correct explanation of Statement-1.

EXERCISE - 3

Exemplar Questions

1. (b) But-1-yne on reaction with water in presence of Hg^{2+} ions as a catalyst produces butan-2-one.



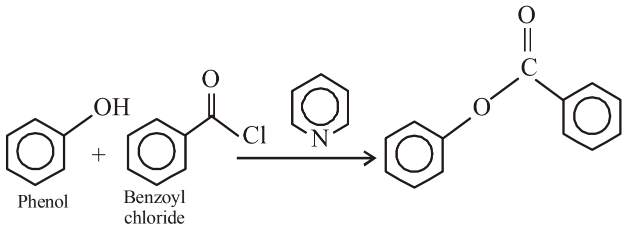
2. (a) The carbonyl group in ketones being influenced by two alkyl group is less reactive than in aldehydes where the carbonyl group is under the influence of one alkyl group only. As the number of alkyl group increases both the +I effect and the steric hinderance get increases preventing the attack of nucleophile.

   Now among benzaldehyde and acetaldehyde former is less electrophilic than carbon atom of carbonyl group present in ethanal. The polarity of carbonyl group is reduced in benzaldehyde due to resonance hence it is less reactive than ethanal.

3. (c) Due to the electron withdrawing characteristic of –Cl, chloroacetic acid is more acidic than acetic acid further, in phenol phenoxide ion obtained on ionisation of phenol is stabilised due to resonance where as no such stabilisation occurs in case of ethanol. Hence phenol is stronger acid than ethanol. Thus acidic strength increases in the order.

   ethanol < phenol < acetic acid < chloro acetic acid

4. (b) Compound Ph — COO — Ph can be prepared by the reaction of phenol & benzoyl chloride

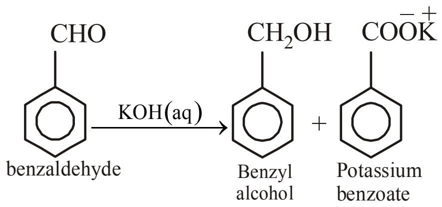


This an example of **Schotten-Baumann reaction.**

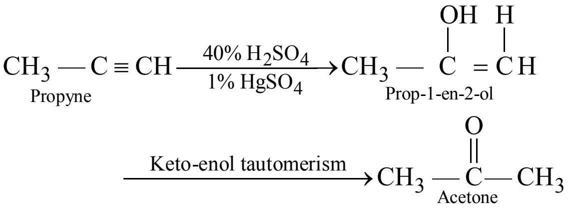
5. (c) Acetone and benzaldehyde both do not react with Fehling's solution.

6. (d) Cannizzaro reaction is given by those aldehydes which have absence of α-hydrogen atom. So, CH_3CHO will not give Cannizzaro reaction.

7. (b) Benzaldehyde having no α-hydrogen on reaction with aqueous KOH solution undergo Cannizzaro reaction and produces benzyl alcohol and potassium benzoate.



8. (d) Chemical reaction can be shown as



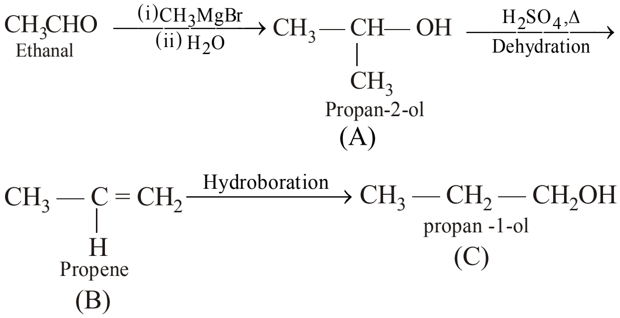
$$CH_3-C\equiv CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} CH_3-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}H$$

Propyne Prop-1-en-2-ol

$$\xrightarrow{\text{Keto-enol tautomerism}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetone

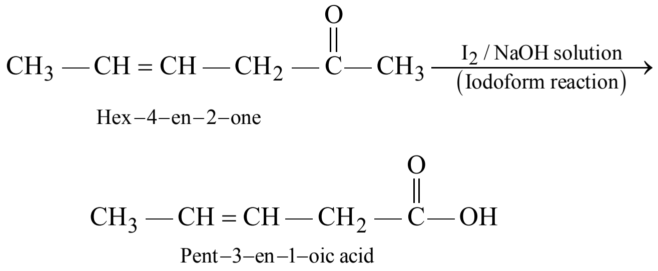
9. (b) Chemical reaction can be shown as



$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[(ii)\ H_2O]{(i) CH_3MgBr} \underset{\substack{\text{Propan-2-ol}\\(A)}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-OH} \xrightarrow[\text{Dehydration}]{H_2SO_4,\Delta}$$

$$\underset{\substack{\text{Propene}\\(B)}}{CH_3-\underset{H}{\underset{|}{C}}=CH_2} \xrightarrow{\text{Hydroboration}} \underset{\substack{\text{propan -1-ol}\\(C)}}{CH_3-CH_2-CH_2OH}$$

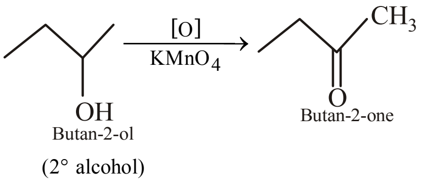
10. (c)



$$\underset{\text{Hex–4–en–2–one}}{CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[(\text{Iodoform reaction})]{I_2 / NaOH\ \text{solution}}$$

$$\underset{\text{Pent–3–en–1–oic acid}}{CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH}$$

11. (b) 2° alcohols on oxidation with alkaline $KMnO_4$ solution produce ketones.



12. (a) Clemmensen reduction is used to convert carbonyl group as follows

$$>C=O \xrightarrow{Zn(Hg)+HCl} >CH_2$$

Zinc amalgam and HCl act as reagent in this reaction.

NEET/AIPMT (2013-2017) Questions

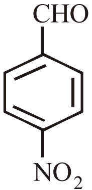
13. (a) Enolic form predominates in compounds containing two carbonyl groups separated by a – CH_2 group. This is due to following two factors.
    (i) Presence of conjugation which increases stability.
    (ii) Formation of intramolecular hydrogen bond between enolic hydroxyl group and second

carbonyl group which leads to stablisation of the molecule. Hence the correct answer is III > II > I.

14. (c) Zn/Hg and conc. HCl reduce carboxyl group to methylene group (Clemmensen reduction).

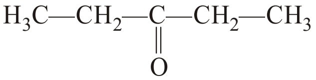
15. (d) Any substituent in the carbonyl compound that increases the positive charge on the carbonyl carbon will increase reactivity towards nucleophilic addition.

$-NO_2$ shows –M effect hence



is most reactive towards nucleophilic addition reaction.

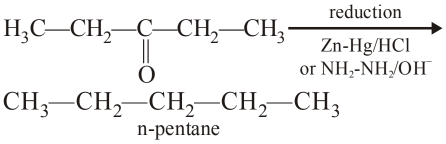
16. (b)



$$H_3C-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

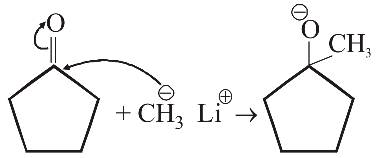
does not give iodoform test due to absence of

$(CH_3-\overset{\overset{O}{\|}}{C}-)$ group. It also does, not give Tollen's test. On reduction it gives n-pentane



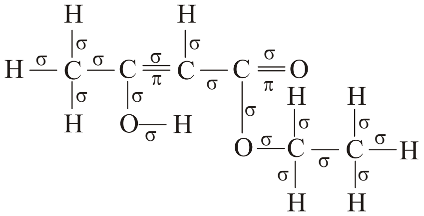
$$H_3C-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[\text{Zn-Hg/HCl or } NH_2\text{-}NH_2/OH^-]{\text{reduction}} \underset{\text{n-pentane}}{CH_3-CH_2-CH_2-CH_2-CH_3}$$

17. (d)

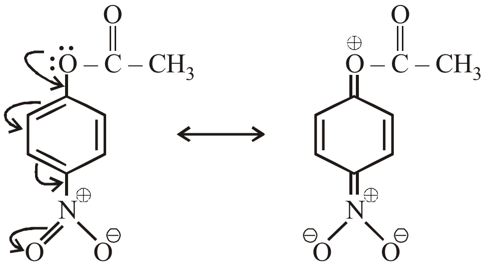


Cylopentanoyl anion

18. (d) Enolic form of ethyl acetoacetate has 18 sigma and 2 pi-bonds as shown below:

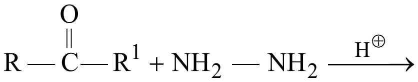


19. (a) Among the substituent attached to the benzene ring, $-NO_2$ group is the most electron withdrawing, thus withdraws electron density from carbonyl carbon thus facilitate the attack of $OH^{\ominus}$ ion.

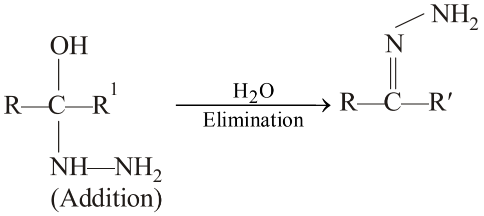


(–R effect of $-NO_2$ group)

20. (b)

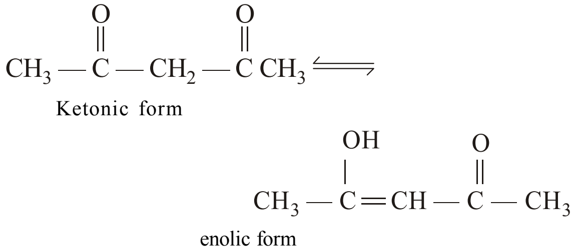


$$R-\overset{\overset{O}{\|}}{C}-R^1+NH_2-NH_2\xrightarrow{H^{\oplus}}$$

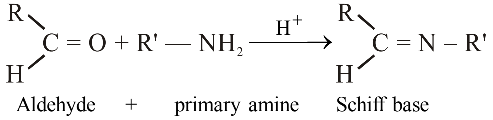


While in all other case no elimination take place.

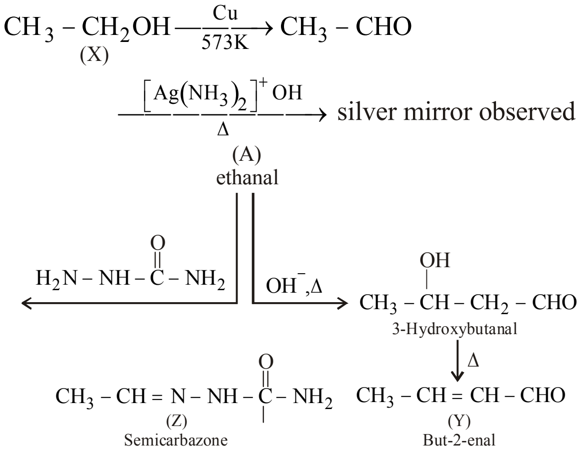
21. (d) Keto-enol tautomerism is possible only in those aldehydes and ketones which have at least one α-hydrogen atom, which can convert the ketonic group to the enolic group. e.g.



22. (a) Schiff base is formed when 1° amine reacts with aldehydes.



23. (b) Since 'A' gives positive silver mirror test therefore, it must be an aldehyde of α-Hydroxyketone. Also, reaction with OH^- i.e., aldol condensation (by assuming alkali to be dilute) indicates that A is aldehyde as aldol reaction of ketones is reversible and carried out in special apparatus. It indicates that A is an aldehyde



24. (a)