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NEET SYLLABUS

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only); identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. **Phenols** : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols. **Ethers** : Nomenclature, methods of preparation, physical and chemical properties uses. Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties and reactivity of alpha hydrogen in aldehydes, Carboxylic acid : Nomenclature, acidic nature, methods of preparation, physical and chemical properties;

OBJECTIVES

After studying this unit, we will be able to :

- Name alcohols, phenols and ethers according to the IUPAC system of nomenclature;
- Discuss the reactions involved in the preparation of alcohols from
(i) alkenes (ii) aldehydes, ketones and carboxylic acids;
- Discuss the reactions involved in the preparation of phenols from
(i) haloarenes (ii) benzene sulphonic acids
(iii) diazonium salts and (iv) cumene;
- Discuss the reactions for preparation of ethers from
(i) alcohols and
(ii) alkyl halides and sodium alkoxides/aryloxides;
- Correlate physical properties of alcohols, phenols and ethers with their structures;
- Discuss chemical reactions of the three classes of compounds on the basis of their functional groups.
- Write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- Write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- Describe the important methods of preparation and reactions of these classes of compounds;
- Correlate physical properties and chemical reactions of aldehydes, ketones and carboxylic acids, with their structures;
- Explain the mechanism of a few selected reactions of aldehydes and ketones;
- Understand various factors affecting the acidity of carboxylic acids and their reactions;
- Describe the uses of aldehydes, ketones and carboxylic acids.

"If you fail, never give up because FAIL means "first attempt in Learning"

– End is not the end, in fact END means "Efforts never dies"

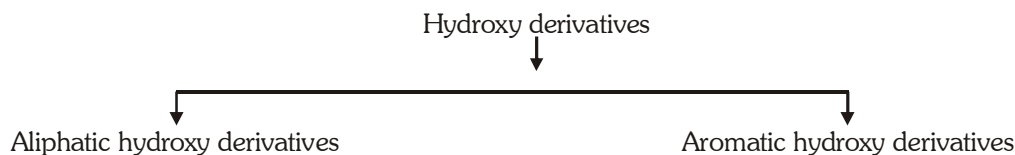
– If you get No as an answer, remember NO means "Next Opportunity"

So Let's be positive. "Dr. A.P.J. Abdul Kalam of feel LIFE"

A.P.J. Abdul Kalam

OXYGEN CONTAINING COMPOUND

1.0 HYDROXY DERIVATIVES



1.1 Aliphatic Hydroxy Derivatives

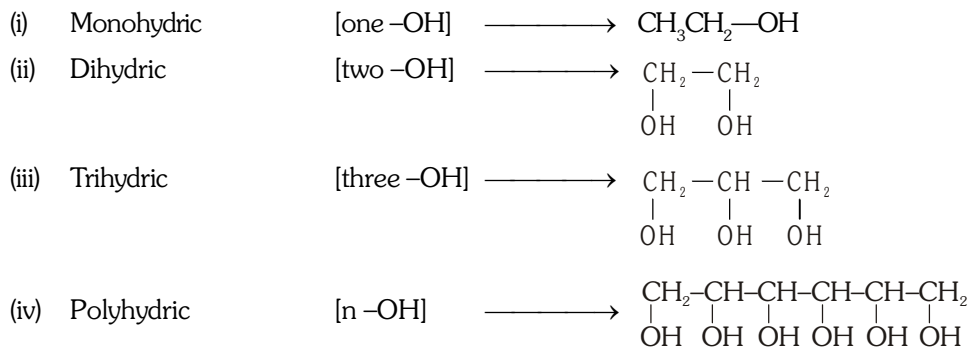
Hydroxy derivatives in which —OH is directly attached to sp^3 'C' (Alcoholic compounds).

1.2 Aromatic Hydroxy Derivatives

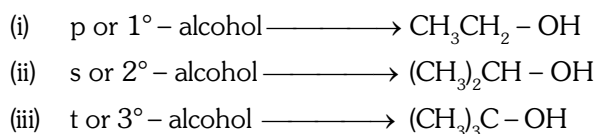
Hydroxy derivatives in which —OH is directly attached to sp^2 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :



(b) Classification according to nature of carbon :



2.0 MONOHYDRIC ALCOHOL

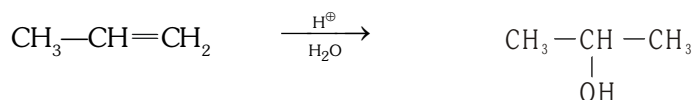
2.1 General Methods of Preparation

(i) From alkanes (By oxidation):

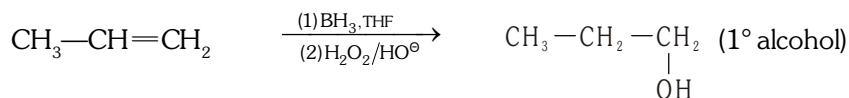


(ii) From alkenes :

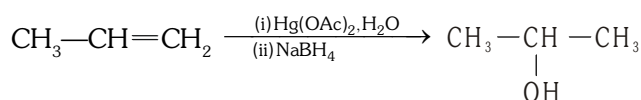
(a) By hydration :



(b) By hydroboration oxidation :



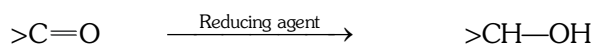
(c) By oxymercuration demercuration :



(iii) From alkyl halides (By hydrolysis) :

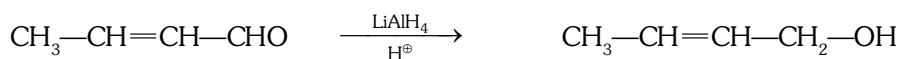
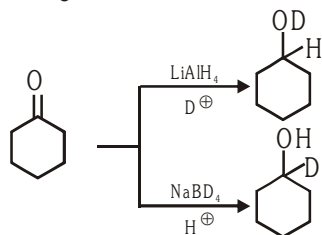
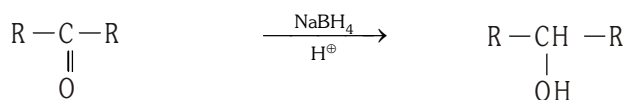
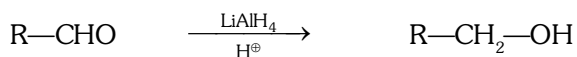
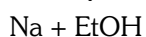
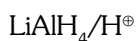


(iv) From carbonyl compounds (By reduction) :



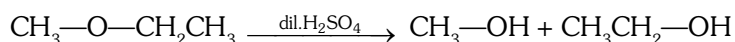
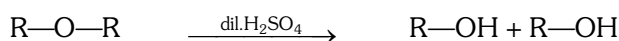
GOLDEN KEY POINTS

Reducing agents may be,

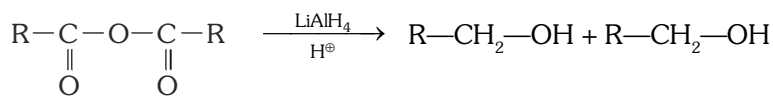
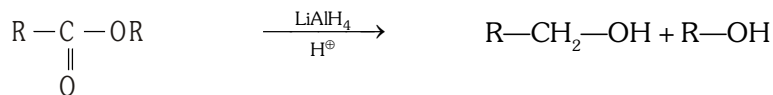
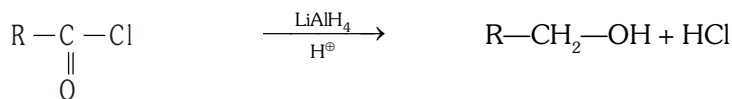
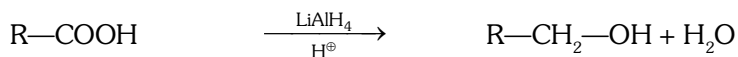


Crotonaldehyde

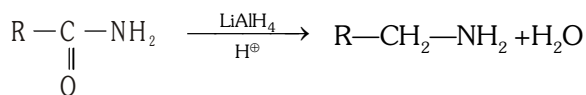
(v) From ethers :



(vi) From acid and derivatives (By reduction) :

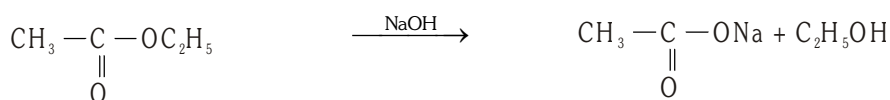
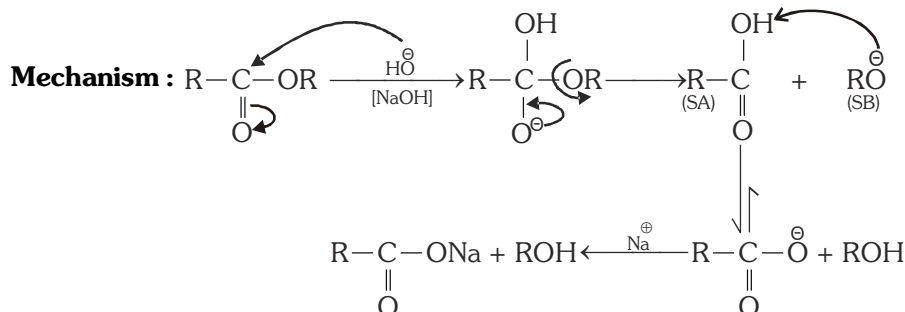
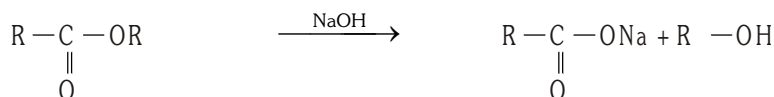


Note : Amide on reduction gives amine not alcohol.

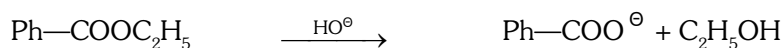


(vii) From esters (By hydrolysis) :

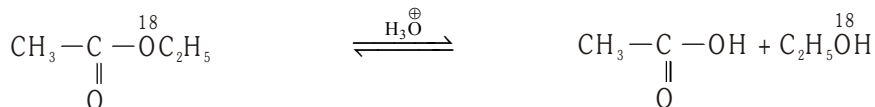
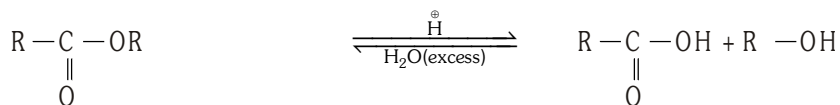
(a) By alkaline hydrolysis :



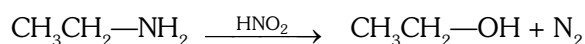
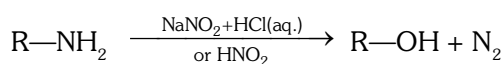
Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification



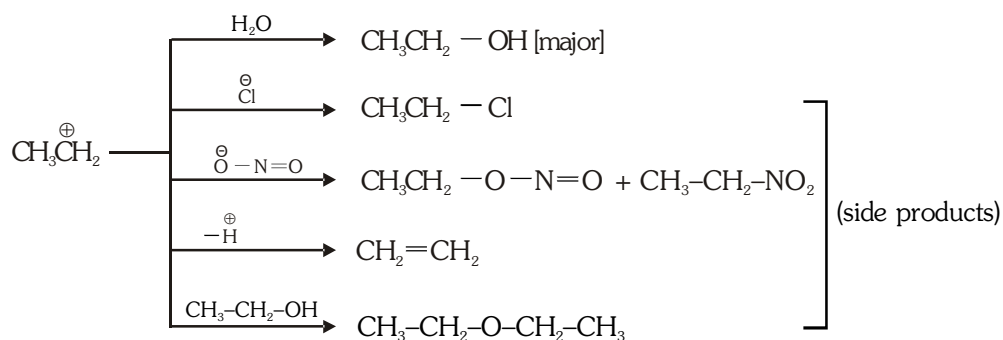
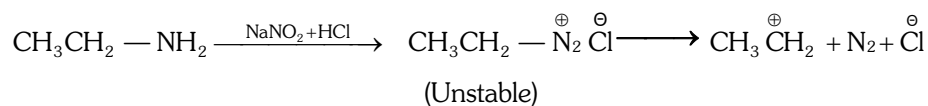
(b) By acidic hydrolysis :



(viii) From p-amines :



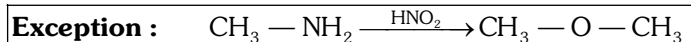
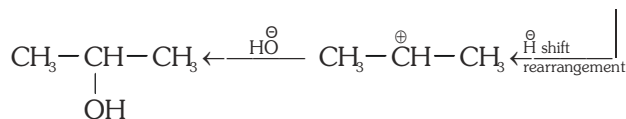
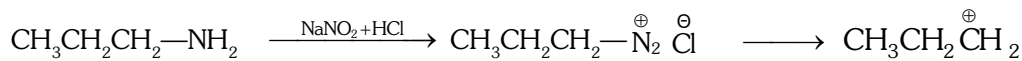
Mechanism :



Intermediate is carbocation so rearrangement may be possible.

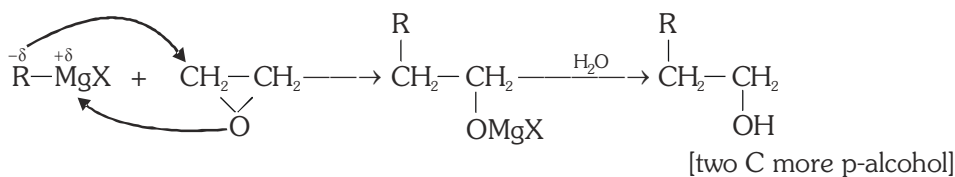
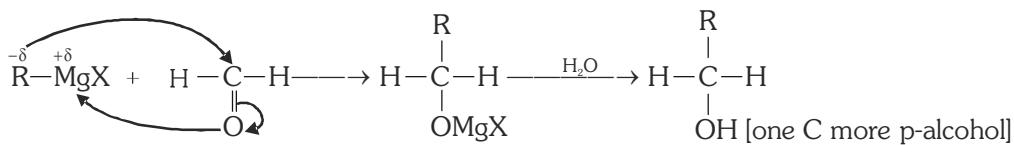
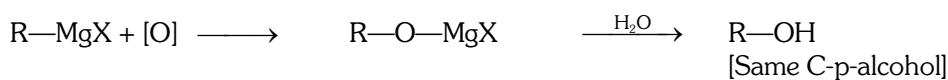
Illustrations

Illustration 1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{—NH}_2 \xrightarrow{\text{NaNO}_2+\text{HCl}} ?$
Solution. **Mechanism :**

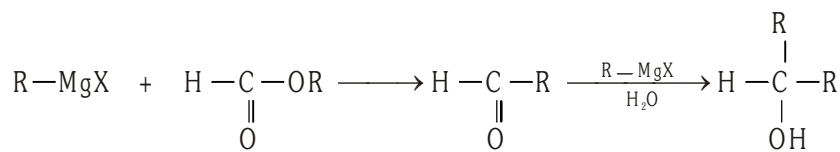
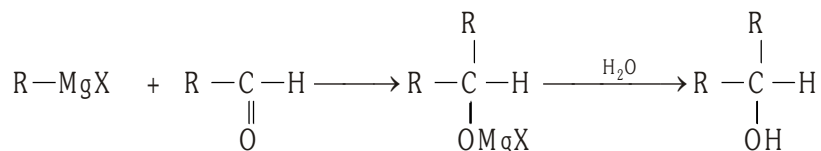


(ix) From Grignard reagent :

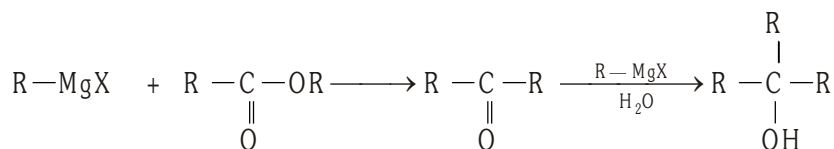
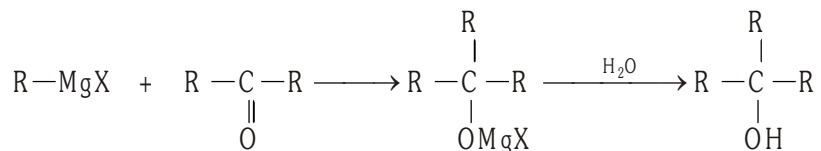
(a) p-alcohol :



(b) s-alcohol :



(c) t-alcohol :

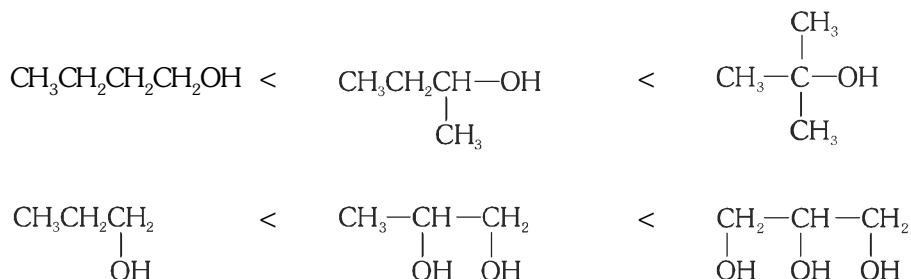


Physical properties :

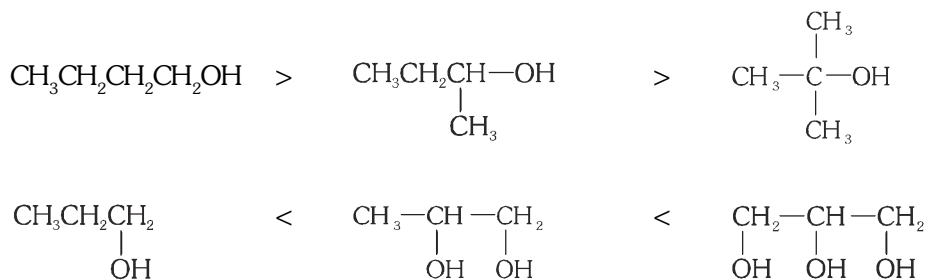
- (i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.
- (ii) Density of monohydric alcohol is less than H_2O .
- (iii) Density $\propto$ mol. wt. (for monohydric alcohol).

Z:\NODE02\B0A1-B0\TARGET\CHEM\ENG\MODULE-6\02 OXYGEN CONTAINING COMPOUND\01-THEORY.P65

Order of solubility :



(v) **Boiling points :** $BP \propto \frac{\text{molecular weight}}{\text{No. of side chains}}$



Illustrations

Solution. H-bonding in alcohol.

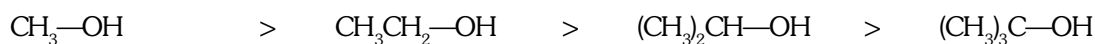
Solution. Dimer formation in carboxylic acid.



Monohydric alcohol shows following reactions

- 25

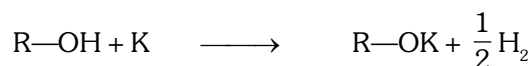
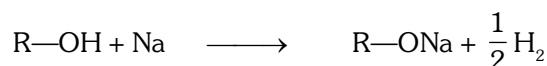
(A) Reaction involving cleavage of $\text{O}-\text{H}$: Reactivity order (Acidic nature) is



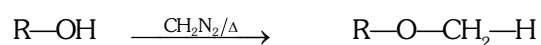
(i) Acidic nature :



Alcohols are less acidic than H_2O and neutral for litmus paper and give H_2 with active metals (Na, K)

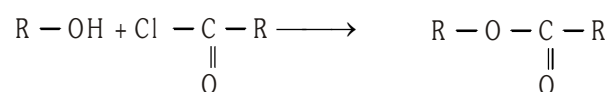


(ii) Alkylation:

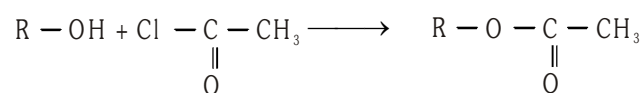


(Williamson synthesis)

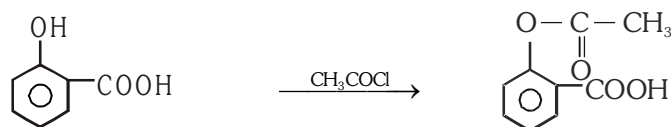
(iii) Acylation :



(Acylation)



(Acetylation)



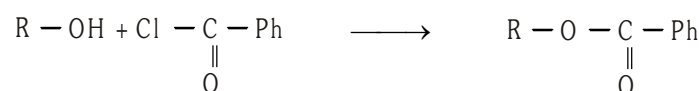
Salicylic acid

Acetoxy benzoic acid

Acetyl salicylic acid

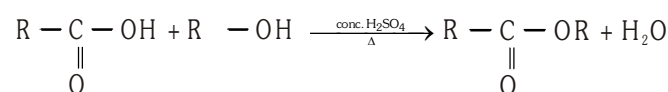
Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation : (Schotten Baumann's Reaction) :



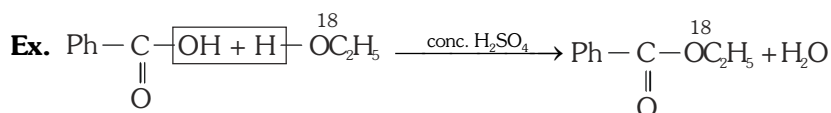
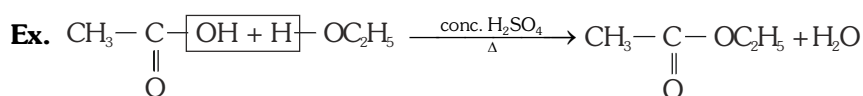
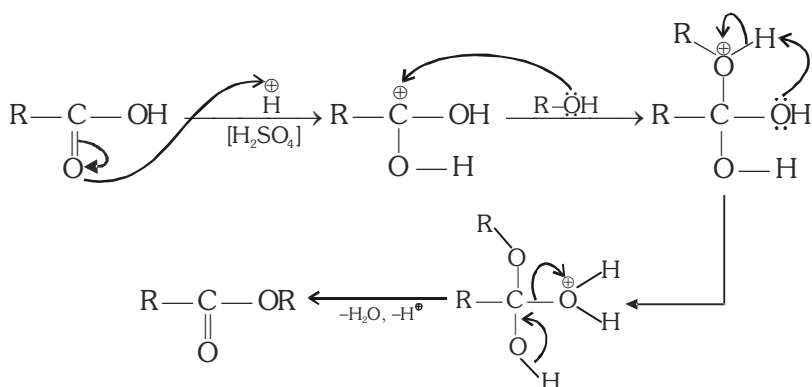
(Benzoylation)

(v) Esterification :

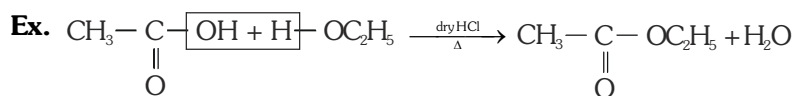


Conc. H_2SO_4 is used as catalyst and dehydrating agent.

Mechanism :

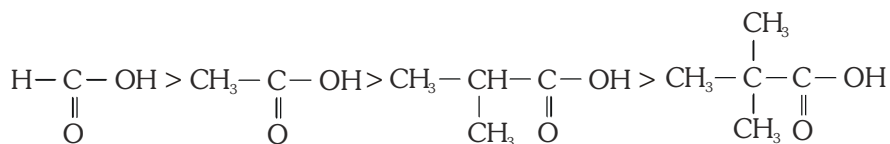


Dry HCl can also be used as dehydrating agent.

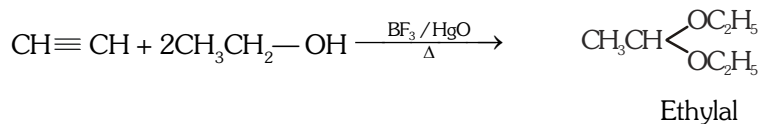
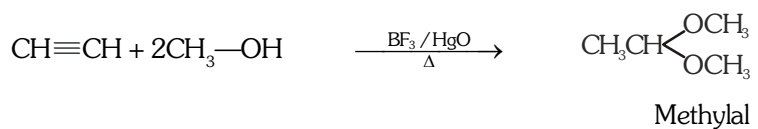


GOLDEN KEY POINTS

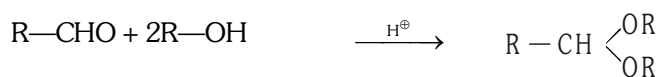
- Reactivity for esterification $\propto \frac{1}{\text{Steric hindrance}}$.
- Reactivity of $\text{R}-\text{OH}$ [If acid is same] : $\text{CH}_3-\text{OH} > 1^\circ > 2^\circ > 3^\circ$ alcohol
- Reactivity of RCOOH [If alcohol is same] :



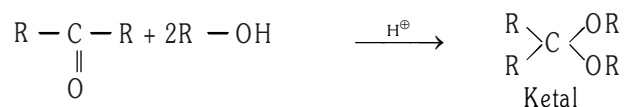
(vi) Reaction with $\text{CH}\equiv\text{CH}$:



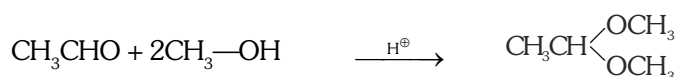
(vii) Reaction with carbonyl compounds :



Acetal

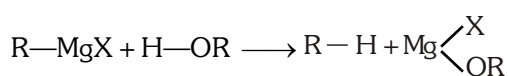


Ketal

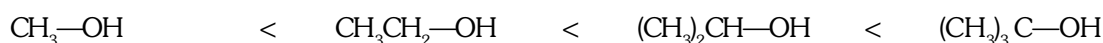


Methylal

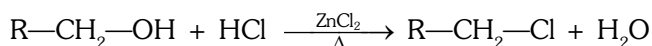
(viii) Reaction with Grignard reagent :



(B) Reaction involving cleavage of $C-\dot{O}H$: Reactivity order or basic nature is

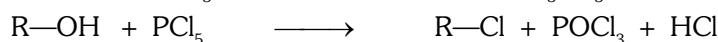
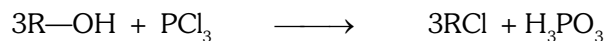


(i) Reaction with halogen acid :

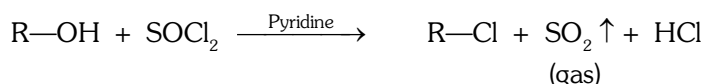


Reactivity order of the acids is $HI > HBr > HCl$

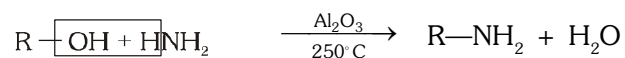
(ii) Reaction with phosphorous halides :



(iii) Reaction with thionyl chloride ($SOCl_2$) :



(iv) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

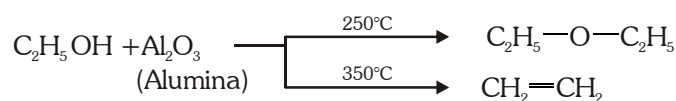
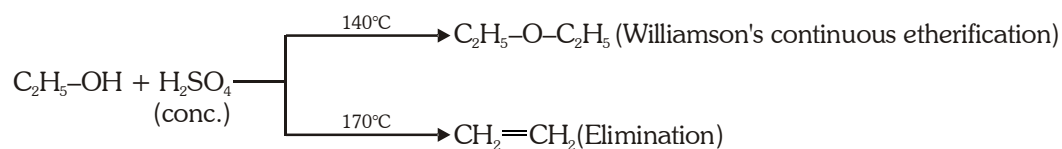


(C) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O

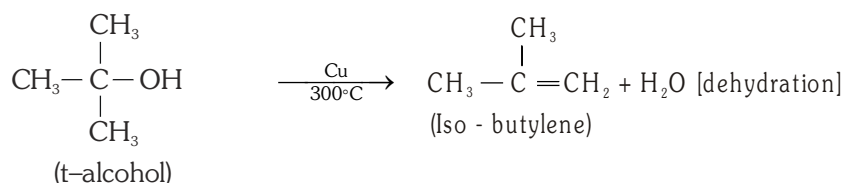
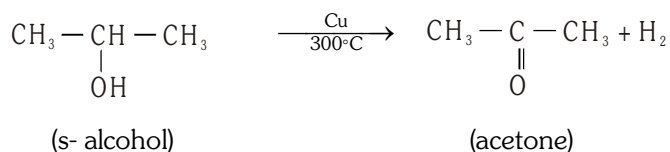
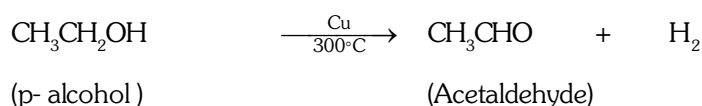
(a) Intermolecularly removal of H_2O [formation of ether]

(b) Intramolecularly removal of H_2O [formation of alkene]

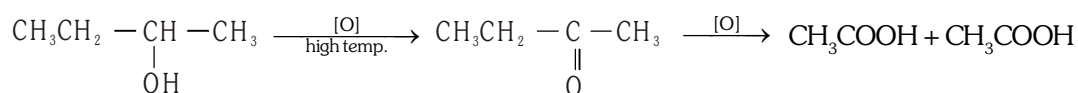
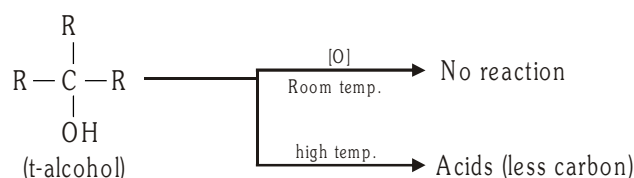
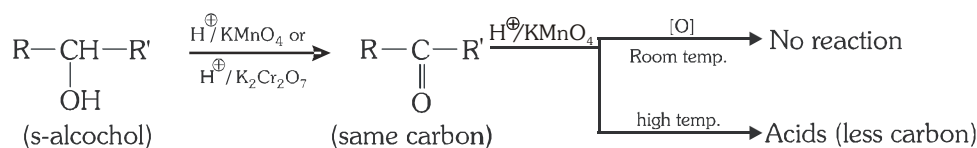
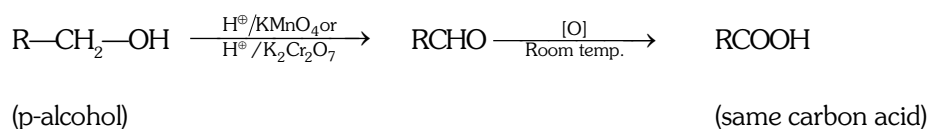


Ease of dehydration follows the order : **$3^\circ ROH > 2^\circ ROH > 1^\circ ROH$**

(ii) Catalytic Dehydrogenation :



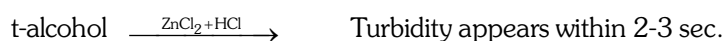
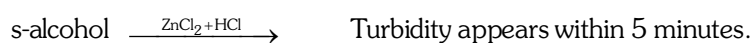
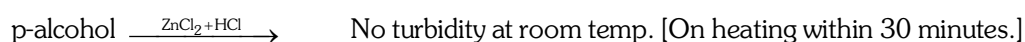
(iii) Oxidation :

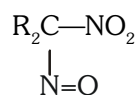
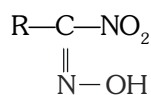
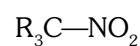
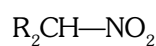
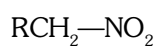
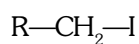
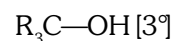
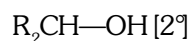
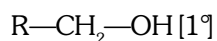


Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1°, 2° and 3° alcohols :

(a) **Lucas test :** A mixture of HCl(conc.) and anhydrous ZnCl₂ is called Lucas reagent.



(b) Victor - Meyer test :p-alcohol $\longrightarrow$ Red colours-alcohol $\longrightarrow$ Blue colourt-alcohol $\longrightarrow$ No colour

No reaction

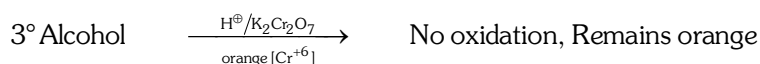
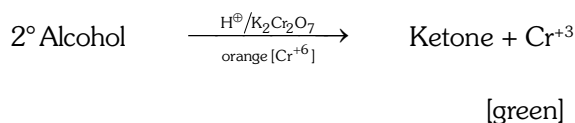
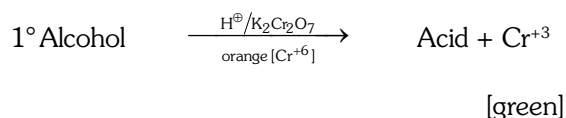
Nitrolic acid (blue)

Pseudonitrol (blue)

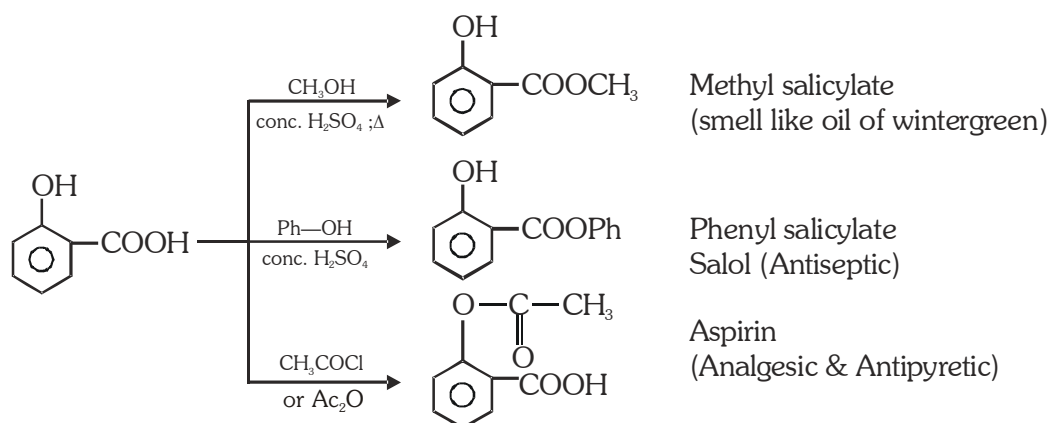
Colourless



Sodium nitroate (Red) No reaction (Remains blue)

(C) Dichromate test :**(v) Distinction between CH_3-OH and C_2H_5OH**

	CH_3OH	CH_3CH_2OH
B.P.	65°C	78°C
$I_2 + NaOH$	No ppt	Yellow ppt of CHI_3
$Cu/300^\circ C$	Smell of formalin [$HCHO$]	No smell
Salicylic acid	Smell like oil of wintergreen	No smell



BEGINNER'S BOX-1

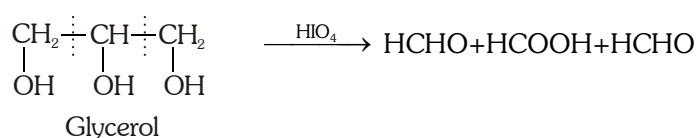
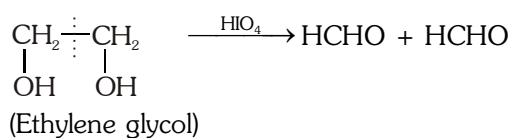
- Which of the following reactions of alkanols does not involve C-O bond breaking
 (1) $\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2$ (2) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{PBr}_3$
 (3) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH}$ (4) $\text{ROH} + \text{HX}$
- Which of the following alkanols is most soluble in water
 (1) 1-Butanol (2) 2-Butanol (3) Isobutyl alcohol (4) t-Butyl alcohol
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_3} \text{A} \xrightarrow{\text{Alc.KOH}} \text{B} \xrightarrow{\text{H}_3\text{O}^+} \text{C}$
 Find product 'C' is
 (1) $\text{CH}_3\text{CH}=\text{CH}_2$ (2) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (3) $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$ (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

Important facts about alcohols

- Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]
- Absolute alcohol : Ethyl alcohol - 99.5%-100%
- Power alcohol : Rectified spirit + C_6H_6 + Petrol for generation of power
- Methylated spirit : Methanol + Pyridine + mineral naptha + rectified spirit.
- 70% CH_3OH is known as wood spirit.
- 90% $\text{C}_2\text{H}_5\text{OH}$ is known as Raw spirit.
- $\text{C}_2\text{H}_5\text{OH}$ is technically called WASH.
- Rectified spirit contains 95.5% alcohol and 4.5% H_2O .

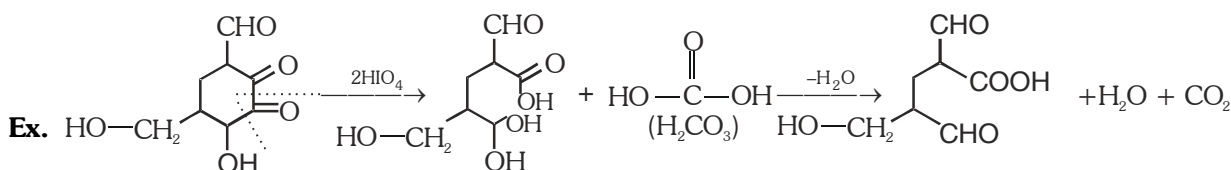
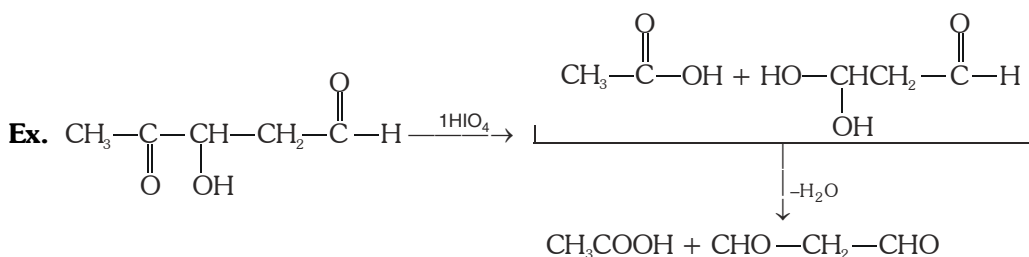
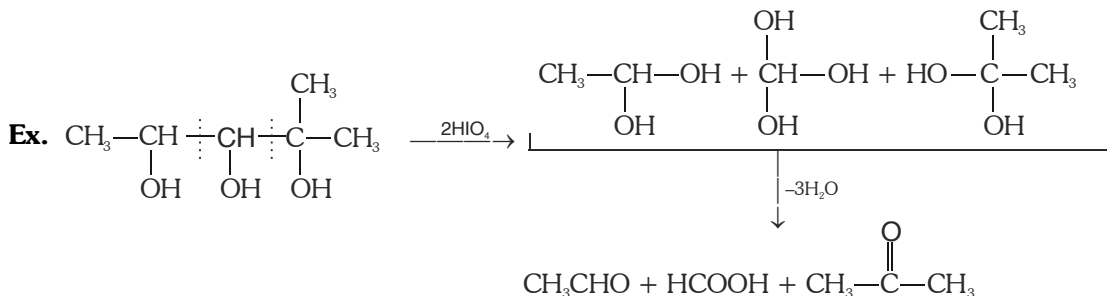
GOLDEN KEY POINTS

Oxidation by HIO_4 [per iodic acid] or $(\text{CH}_3\text{COO})_4\text{Pb}$ [lead tetraacetate] :



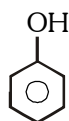
Condition for oxidation by HIO_4 or $(\text{CH}_3\text{COO})_4\text{Pb}$

- (i) At least 2 $-\text{OH}$ or 2 $>\text{C}=\text{O}$ or 1 $-\text{OH}$ and 1 $>\text{C}=\text{O}$ should be at vicinal carbons.
- (ii) One HIO_4 breaks one $\text{C}-\text{C}$ bond and adds one $-\text{OH}$ to each carbon.

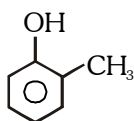


4.0 AROMATIC HYDROXY DERIVATIVES

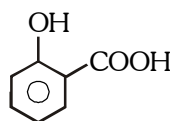
Phenolic compounds : Compounds in which $-\text{OH}$ group is directly attached to sp^2c [Benzene ring]



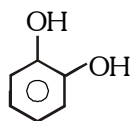
Phenol



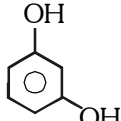
o-Cresol



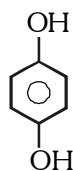
Salicylic acid



Catechol



Resorcinol



Quinol

All phenolic compounds give colour with neutral FeCl_3 .

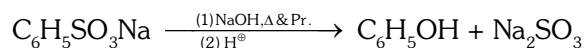


PHENOL (C₆H₅OH)

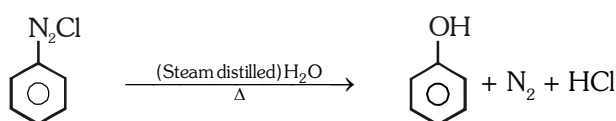
Phenol is also known as carboic acid. In phenol —OH group is attached with sp² hybridised carbon.

4.1 General Methods of Preparation

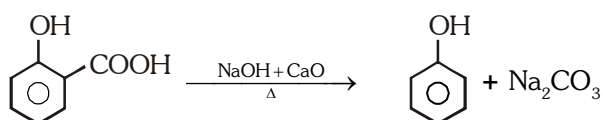
(1) From benzene sulphonic acid : When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.



(2) From benzene diazonium chloride : When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.

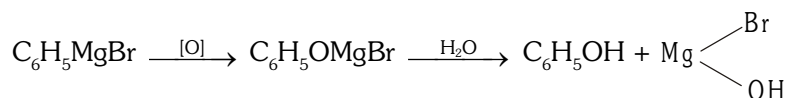


(3) By distilling a phenolic acid with sodalime (decarboxylation):

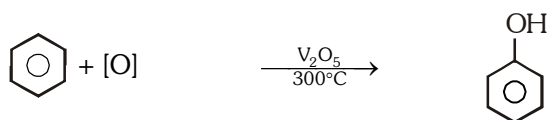


Salicylic acid

(4) From Grignard reagent : The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.



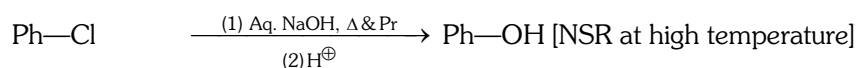
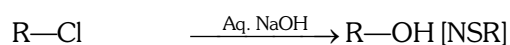
(5) From benzene :



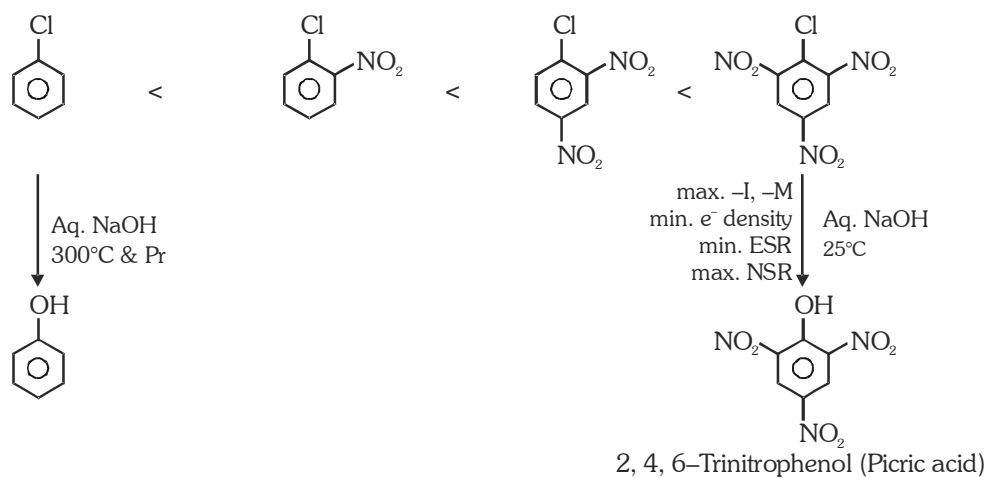
(6) From chloro benzene :



Stable by resonance



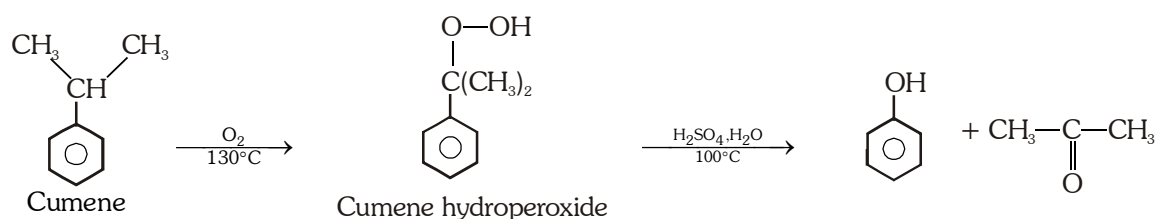
Order for NSR :



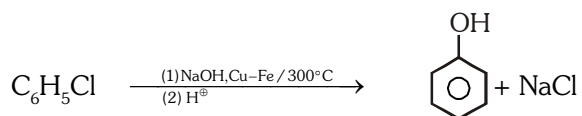
(7) Industrial preparation of phenol: Phenol can be prepared commercially by :

- (a) Cumene
- (b) Dow's process

(a) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.

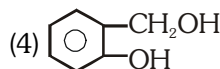
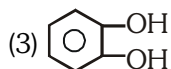
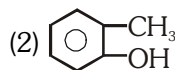
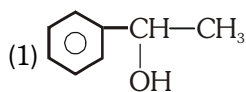


(b) Dow process : This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.



BEGINNER'S BOX-2

1. Which of the following compounds does not show phenolic properties :-



2. The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-

(1) 2

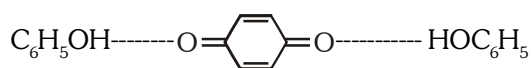
(2) 3

(3) 4

(4) 5

4.2 Physical Properties

- (i) Phenol is a colourless, crystalline solid.
- (ii) It attains pink colour on exposure to air and light. (slow oxidation)



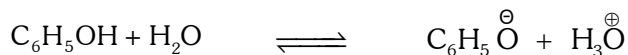
Phenoquinone (pink colour)

- (iii) It is poisonous in nature but acts as antiseptic and disinfectant.
- (iv) Phenol is slightly soluble in water, readily soluble in organic solvents.
- (v) Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- (vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides.

4.3 Chemical Properties

(A) Reactions due to -OH group :

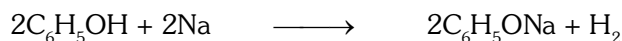
- (i) **Acidic Nature** : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-\text{NO}_2$, $-\text{Cl}$) increase the acidity of phenol while electron releasing groups ($-\text{CH}_3$ etc.) decrease the acidity of phenol.



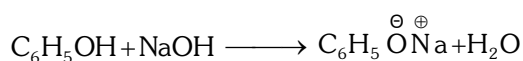
Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

GOLDEN KEY POINTS

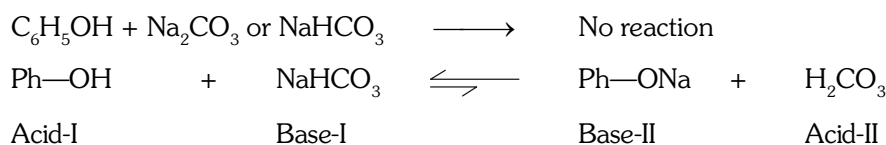
- The acidic nature of phenol is observed as the following:
 - (i) Phenol changes blue litmus to red.
 - (ii) Highly electro positive metals react with phenol.



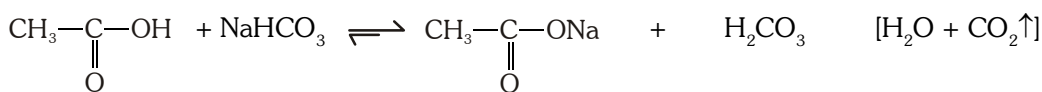
(iii) Phenol reacts with strong alkalies to form phenoxides.



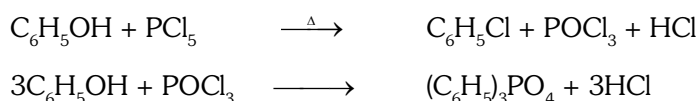
(iv) However phenol does not decompose Na_2CO_3 or NaHCO_3 because phenol is weaker acid than carbonic acid.



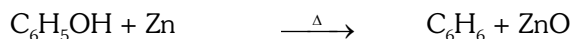
Note : Acetic acid reacts with NaHCO_3 and gives effervescence of CO_2 .



(ii) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. POCl_3 formed as biproduct reacts with phenol to form triphenyl phosphate.

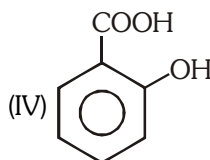
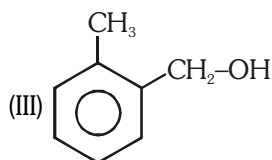
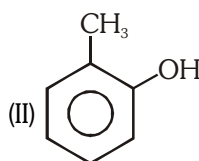
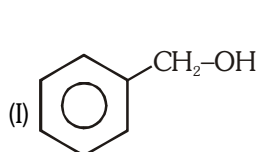


(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.



Illustrations

Illustration 4. In which of the following compound deoxygenation is possible when heated with Zn



(1) I, II, III

(2) I, III, IV

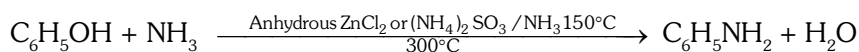
(3) II, IV

(4) II, III

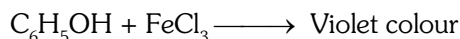
Solution

Ans.(3) Observed in phenolic compound.

(iv) Reaction with NH_3 (Bucherer reaction): Phenol reacts with NH_3 in presence of anhydrous ZnCl_2 to form aniline.

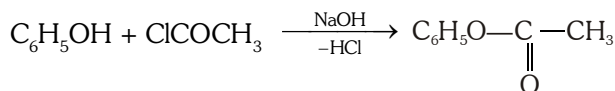


- (v) **Reaction with FeCl_3 :** Phenol gives violet colouration with FeCl_3 solution (neutral) due to formation of a complex.

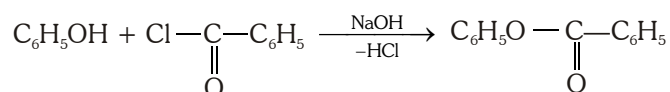


This reaction is used to differentiate phenol from alcohols.

- (vi) **Acetylation :** Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

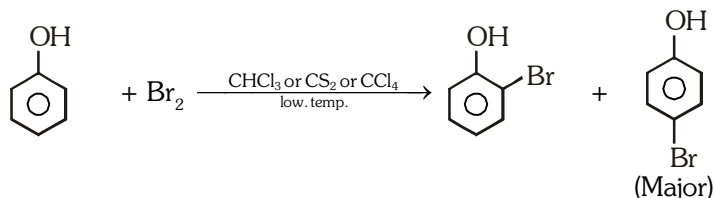


- (vii) **Benzoylation (Schotten-Baumann reaction)**

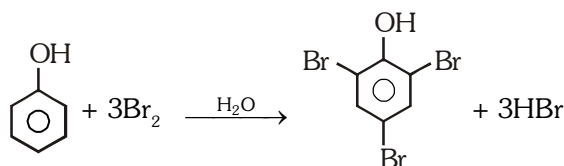


- (B) **Reaction of Benzene Ring :** The $-\text{OH}$ group is ortho and para directing. It activates the benzene nucleus.

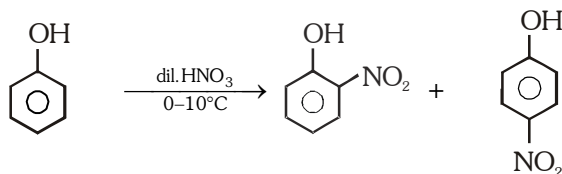
- (i) **Halogenation :** Phenol reacts with bromine in CCl_4 to form mixture of o- and p-bromo phenol.



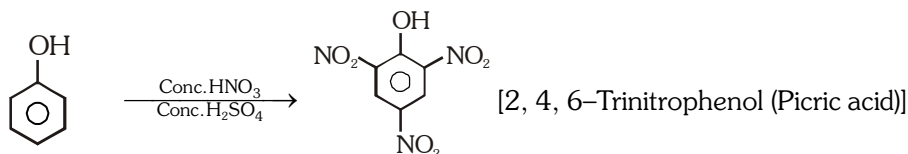
Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)



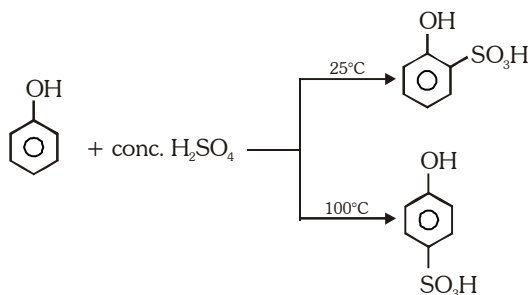
- (ii) **Nitration :** Phenol reacts with dil. HNO_3 at $0^\circ\text{--}10^\circ\text{C}$ to form o- and p- nitro phenols.



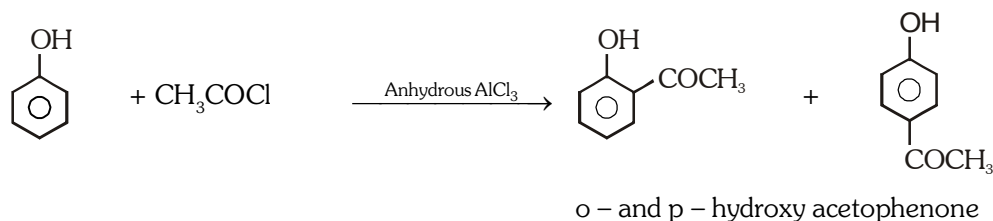
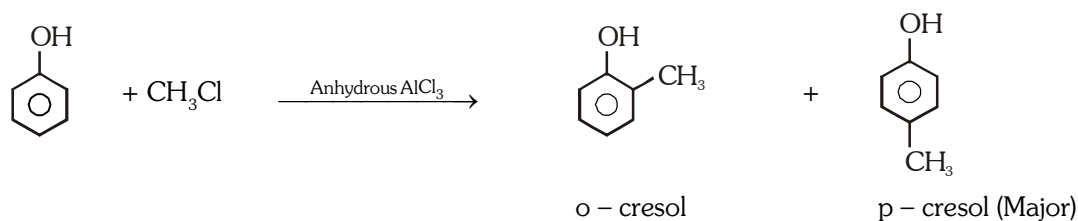
When phenol is treated with nitrating mixture it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Bezoquinone



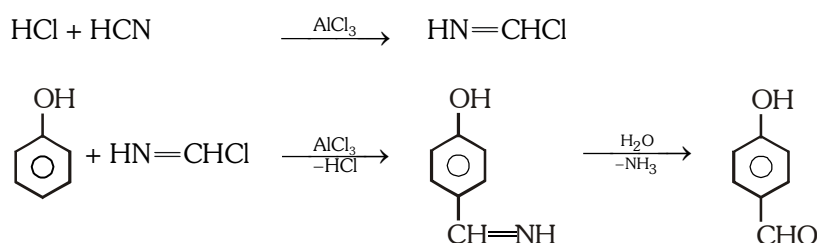
- (iii) **Sulphonation:** Phenol reacts with fuming H_2SO_4 to form o- and p-hydroxy benzene sulphonic acid at different temperatures.



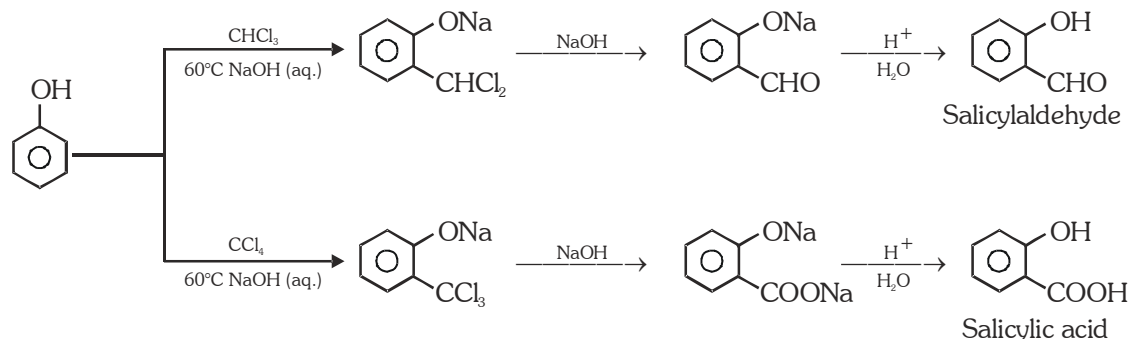
(iv) Friedel - Craft 's reaction:



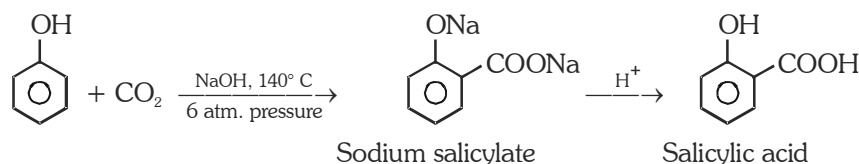
(v) Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous AlCl_3 it yields mainly p- hydroxy benzaldehyde (formylation)



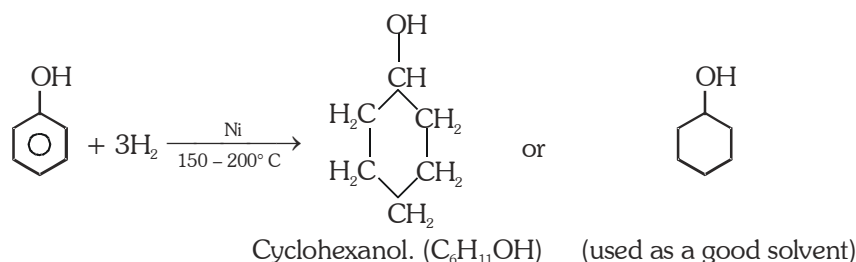
(vi) Reimer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



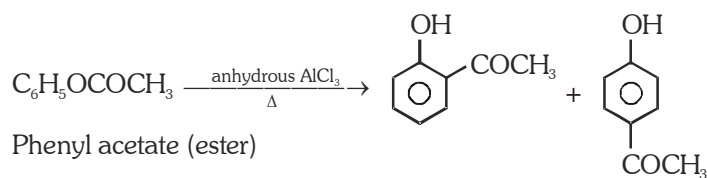
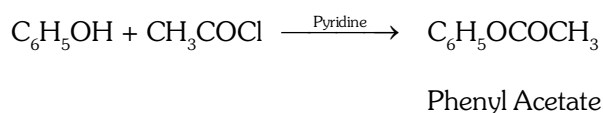
(vii) Kolbe's Schmidt reaction : It involves the reaction of $\text{C}_6\text{H}_5\text{OH}$ with CO_2 and NaOH at 140°C followed by acidification to form salicylic acid.



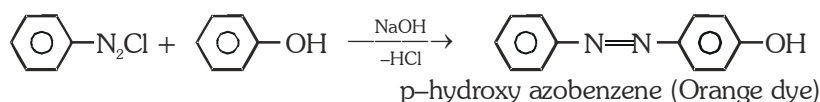
(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at $150\text{-}200^\circ\text{C}$ forms cyclohexanol.



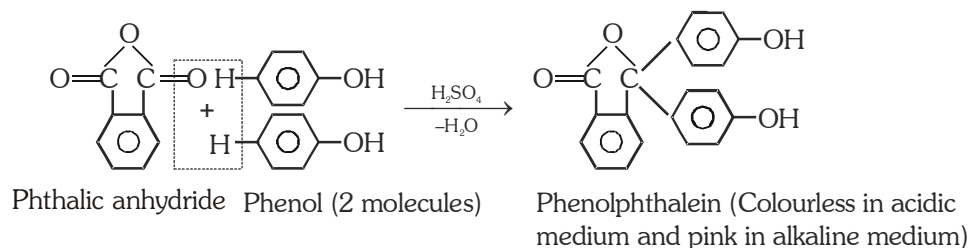
(ix) Fries rearrangement reaction:



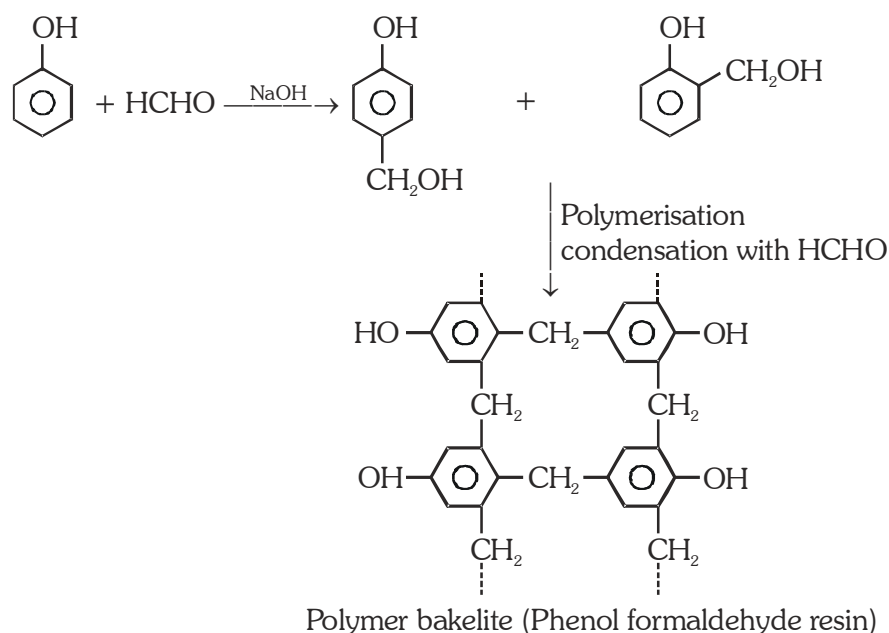
(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.



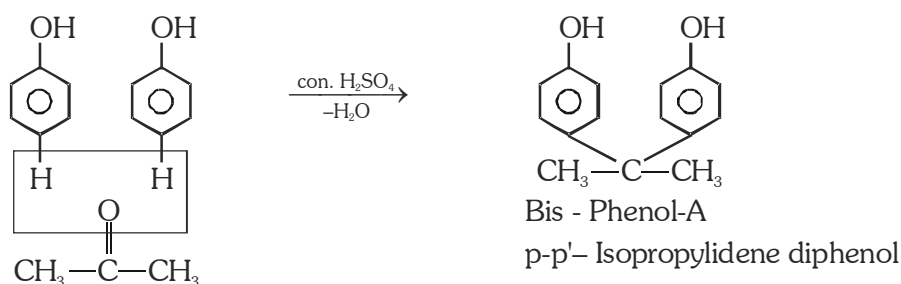
Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.



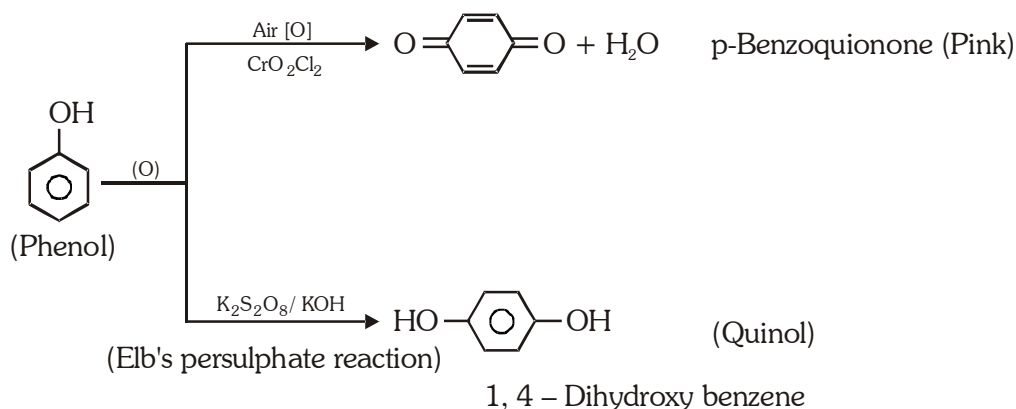
(xi) Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (resin).



(xii) Reaction with acetone: (Condensation with acetone)



(xiii) Oxidation:



BEGINNER'S BOX-3

- Reimer-Tiemann formylation reaction involves addition of :-
 - (1) Chloroform on phenoxide ion
 - (2) Trichloromethyl carbanion on phenoxide ion
 - (3) Dichlorocarbene on phenoxide ion
 - (4) Hydroxide ion on phenol
- Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-
 - (1)
 - (2)
 - (3)
 - (4)
- Phenol $\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{NaNO}_2}$ Green colour $\xrightarrow{\text{H}_2\text{O}}$ red colour $\xrightarrow{\text{NaOH}}$ Blue colour

This reaction is associated with the name of :-

- (1) Gattermann
- (2) Hofmann
- (3) Liebermann
- (4) Reimer-Tiemann

Test of Phenol :

- (1) Phenol turns blue litmus to red.
- (2) Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- (3) Phenol gives Liebermann's nitroso test.
- (4) Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.
- (5) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

Differences between phenol and alcohol (C₂H₅OH) :

- (1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- (2) Phenol gives violet colour with FeCl₃ while aliphatic alcohol does not give.
- (3) Phenol gives triphenyl phosphate with PCl₅ while aliphatic alcohol does not.
- (4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

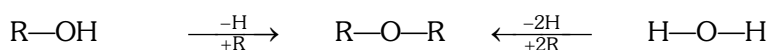
- (1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)
- (2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.
- (3) In manufacture of drugs like aspirin, salol, phenacetin etc.
- (4) As preservative for ink.

5.0 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is C_nH_{2n+2}O.

CH₃—O—CH₂CH₃ (Methoxy ethane) or Ethyl methyl ether

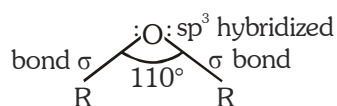
Ether is monoalkyl derivative of R—OH and dialkyl derivative of H₂O



Classification : They may be classified as :

- (a) Simple or symmetrical ether. e.g. R—O—R
- (b) Mixed or unsymmetrical ether e.g. R—O—R'

Structure :

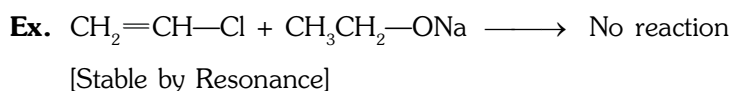
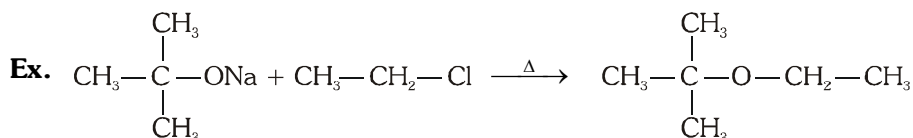
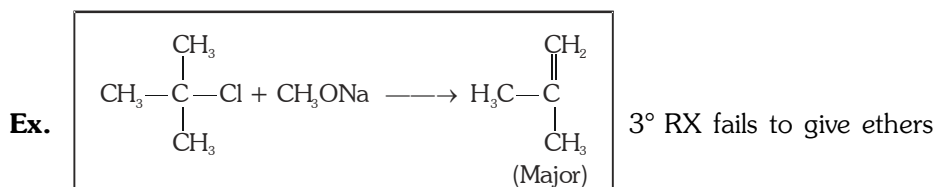
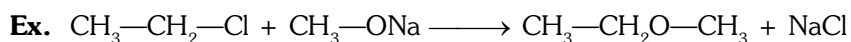
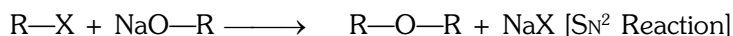


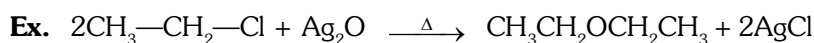
The molecule of ether is bent due to presence of lone pair. The bond angle is 110°. It is greater than that of water (105°) due to the repulsion between bulkier alkyl groups. Due to bent structure, it possesses dipole moment and hence are polar molecules.

5.1 General Methods of Preparation

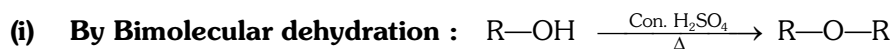
(a) From alkyl halides :

(i) By Williamson's synthesis :

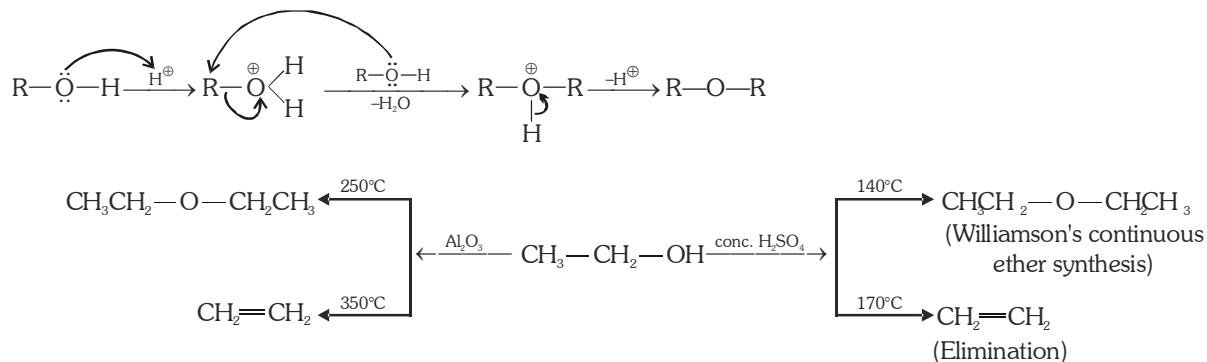




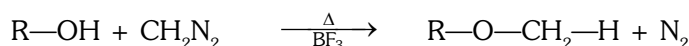
(b) From R-OH:



Mechanism :



(ii) **Reaction with CH₂N₂** (diazomethane) :



5.2 Physical Properties

- (i) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher ethers are volatile liquids.
- (ii) Ether are less polar.
- (iii) Ethers are less soluble in H_2O .
- (iv) Ethers have less BP than corresponding alcohol.

Illustrations

Illustration 5. Ethers are less soluble in H_2O . Why ?

Solution. Due to less polarity, it forms weaker H-Bonding with H_2O .

Illustration 6. Ethers have less BP than corresponding alcohol. Why ?

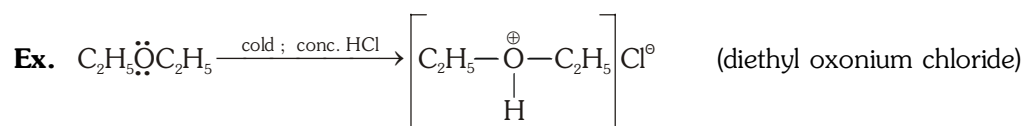
Solution. No H-Bonding in ether molecules.

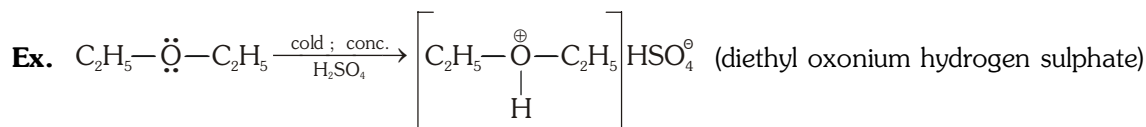
5.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

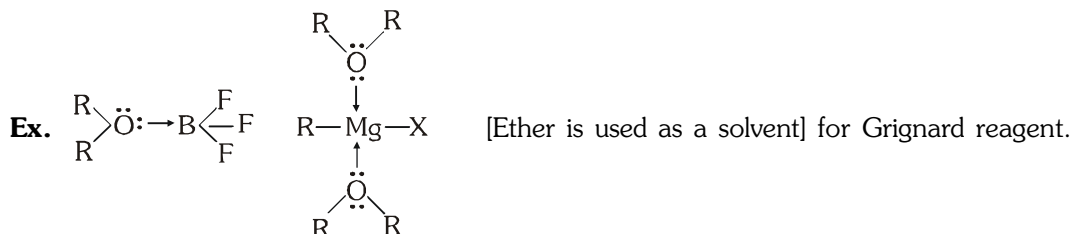
(1) Basic nature : Due to presence of $\ell.p$ on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

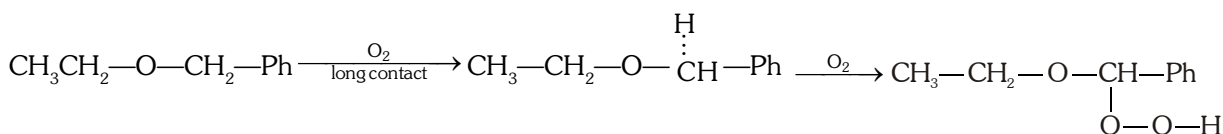
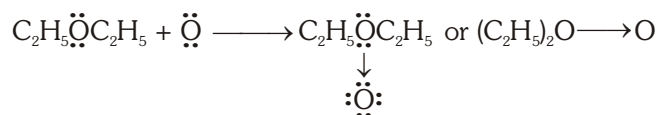
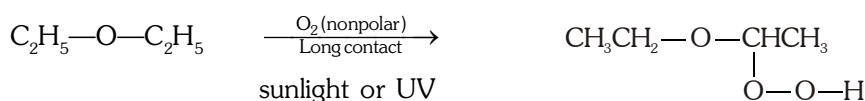




Ethers form dative bond with Lewis acids like BF_3 , AlCl_3 , RMgX etc.



(2) Formation of peroxides : Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.



Peroxides are unstable and explosives.

GOLDEN KEY POINTS

Test for peroxides

Ether (peroxide) $\xrightarrow{\text{FeSO}_4/\text{KCNs}}$ Red colour

Ether (Peroxides) + $\text{Fe}^{+2} \longrightarrow \text{Fe}^{+3} \xrightarrow{\text{CNS}^-} \text{Fe}(\text{CNS})_3$
(Red)

(3) Reaction with PCl_5 : $\text{ROR} + \text{PCl}_5 \xrightarrow{\text{heat}} 2\text{RCl} + \text{POCl}_3$

(4) Reduction : $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow[\text{heat}]{\text{Red P} + \text{HI}} 2\text{CH}_3\text{CH}_3$

(5) Reaction with HX : $\text{R}-\text{O}-\text{R}' + \text{HI} \longrightarrow \text{R}-\text{OH} + \text{R}'-\text{I}$

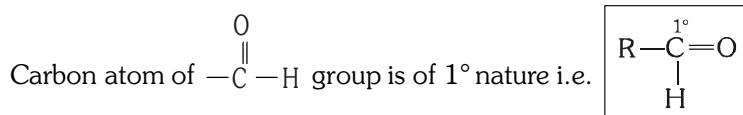
Uses of ether :

- (i) General anaesthetic agent.
- (ii) Solvent for oil, fats, resins, Grignard reagent.
- (iii) For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.
- (iv) In perfumery.
- (v) Di-isopropyl ether $\longrightarrow$ In petrol as an antiknock comp.
- (vi) Mixture of alcohol and ether is used as a substitute of petrol. Trade name "**Natalite**"

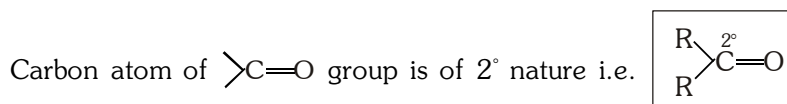
6.0 CARBONYL COMPOUNDS

Organic Compounds having $>\text{C}=\text{O}$ group are called carbonyl compounds and $>\text{C}=\text{O}$ group is known as carbonyl group. Its general formula is $\text{C}_n\text{H}_{2n}\text{O}$ ($n = 1, 2, 3, \dots$) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—H}$ (also known as formyl group). It is a monovalent group



(b) Ketones : The carbonyl group ($>\text{C}=\text{O}$) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

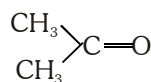


Ketones are further classified as :

(i) **Simple or Symmetrical ketones :** Having two similar alkyl groups. $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array} \text{=O}$

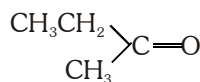
(ii) **Mixed or unsymmetrical ketones :** Having two different alkyl groups. $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}' \end{array} \text{=O}$

Ex. (Ketones) : Symmetrical

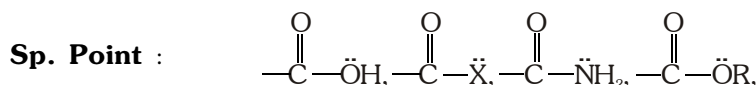


(Acetone or Dimethyl ketone)
Propanone

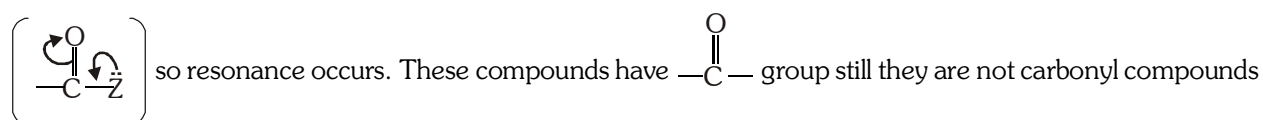
Unsymmetrical



(Ethyl methyl ketone)
Butanone

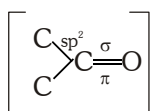


In all the compounds given above, lone pair of electrons and double bond are in conjugate system.



because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In $>\text{C}=\text{O}$ compounds C-atom is sp^2 hybridised which forms two σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>\text{C}=\text{O}$ group



The C—C—O / H—C—O bond angle is of 120°

Due to electro-negativity difference in C & O atoms, the $>\text{C}=\text{O}$ group is polar.

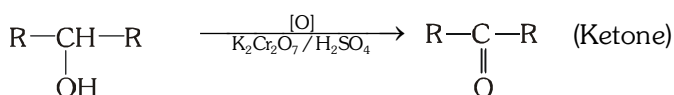
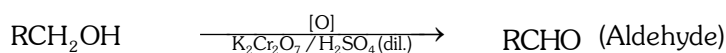
$\text{>C}^{\delta+}=\text{O}^{\delta-}$ Hence aldehydes and Ketones possess considerable dipole moment.

6.1 General Methods of Preparation

(A) For both Aldehydes and Ketones

(1) By Oxidation of Alcohols :

(a) **By $\text{K}_2\text{Cr}_2\text{O}_7$ / H_2SO_4** : Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones.

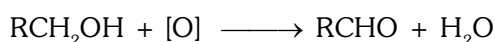


Aldehydes are quite susceptible to further oxidation to acids -



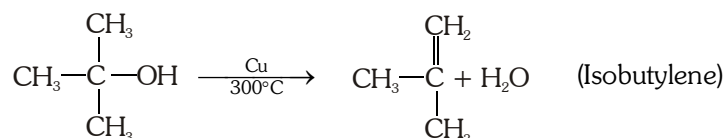
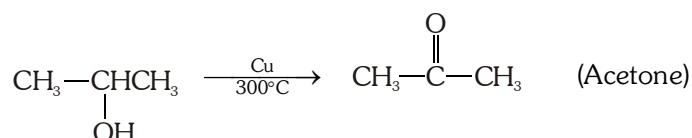
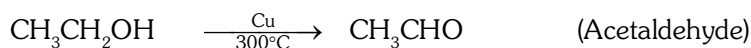
Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) **Mild Oxidising Agent** : 1° alcohols will get oxidised with CrO_3 / Pyridine, (**collin's reagent**) or P.C.C (Pyridinium chloro chromate $\text{CrO}_3 + \text{C}_5\text{H}_5\text{N} + \text{HCl}$) to aldehyde and 2° alcohols to ketone.

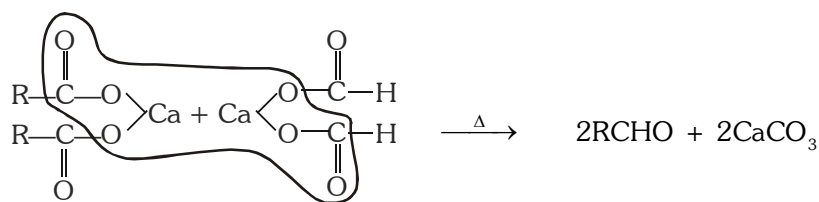


By this reaction, **good yield of aldehyde** is possible.

(2) Dehydrogenation of alcohols :



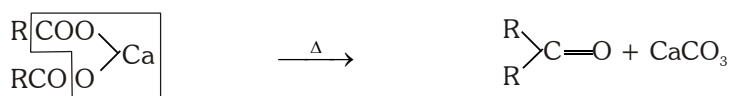
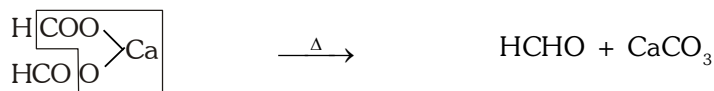
(3) By dry distillation of Ca-salts of carboxylic acid :



Calcium alkanoate

Calcium formate

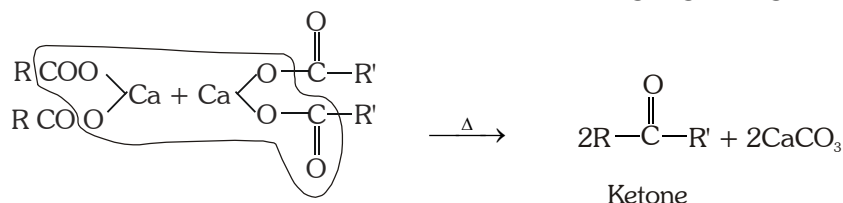
($\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$ and HCHO are also formed)



Calcium-alkanoate

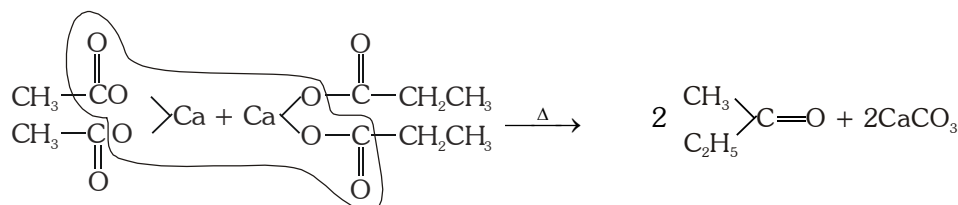
Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone



Ketone

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

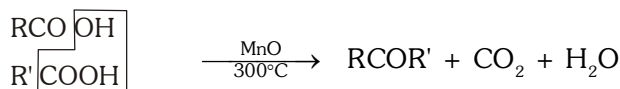
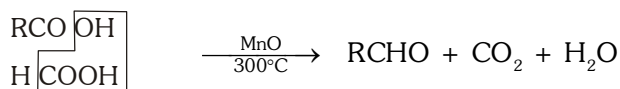
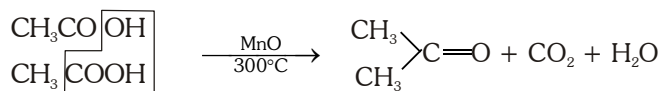
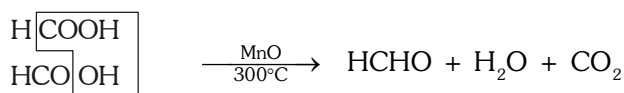


Calcium Acetate

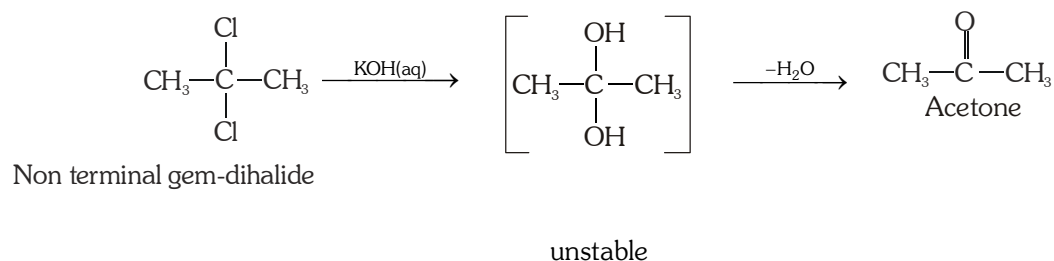
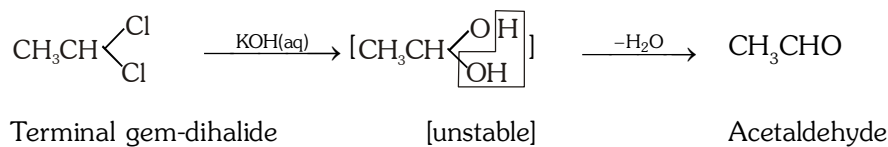
Calcium propionate

Ethyl methyl ketone

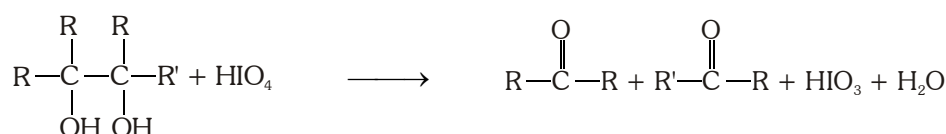
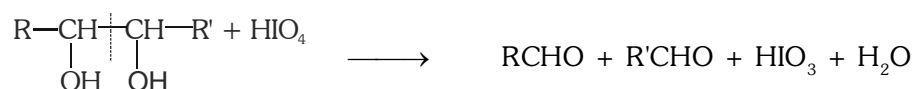
(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over $\text{MnO}/300^\circ\text{C}$ give carbonyl compounds



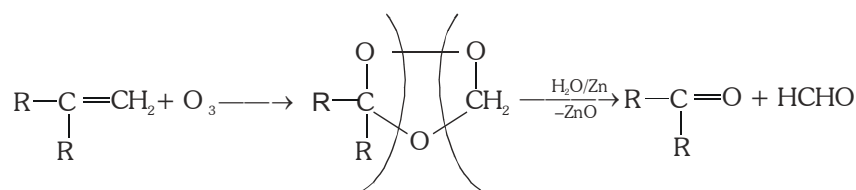
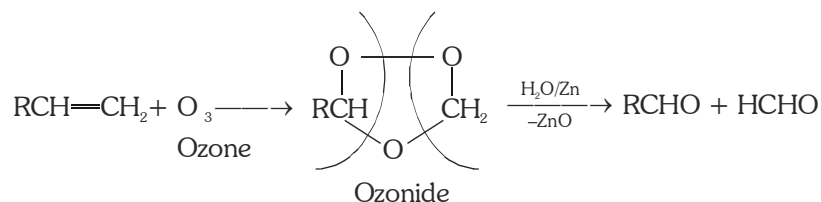
- (5) By Hydrolysis of gem dihalides :** Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.



- (6) By Oxidation of diols :** With periodic acid (HIO_4) or lead tetra acetate $(\text{CH}_3\text{COO})_4\text{Pb}$ vicinal diols get oxidised to form carbonyl compounds

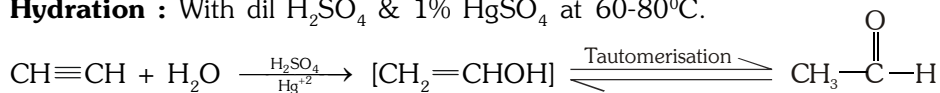


- (7) By Ozonolysis of alkenes :** This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H_2O_2 formed during hydrolysis.

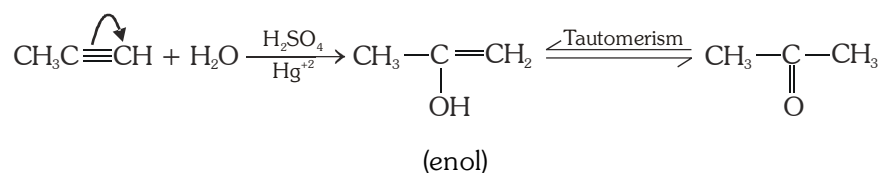


- (8) From Alkyne :**

(a) Hydration : With dil H_2SO_4 & 1% HgSO_4 at $60-80^\circ\text{C}$.

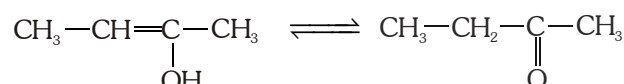
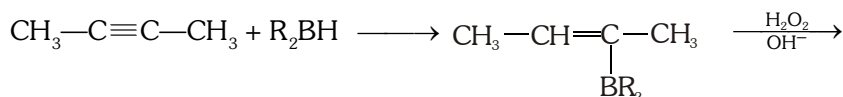
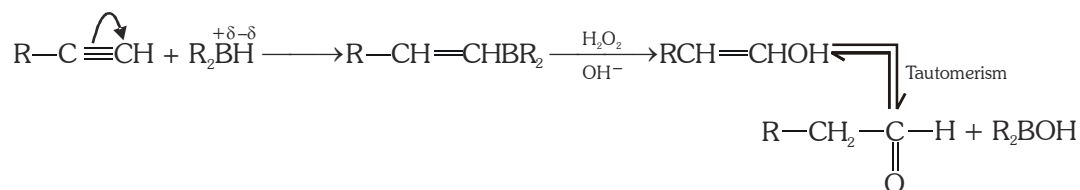


Other alkynes mainly give ketone :



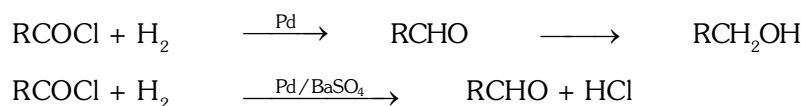
(b) Hydroboration : Reaction with B_2H_6 or R_2BH give alkenyl dialkyl borane.

1-alkyne gives $\longrightarrow$ aldehyde
other alkynes $\longrightarrow$ ketone

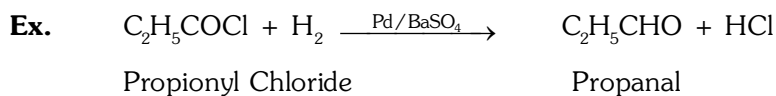


(B) For Aldehydes only

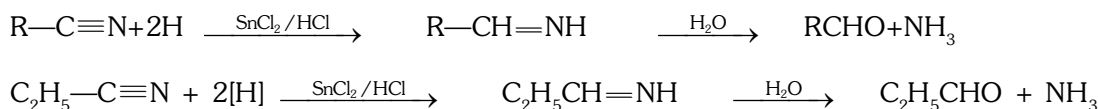
(1) Rosenmund's reduction :



$BaSO_4$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

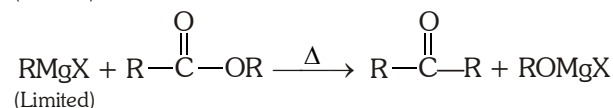
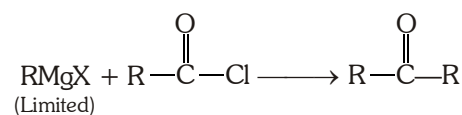
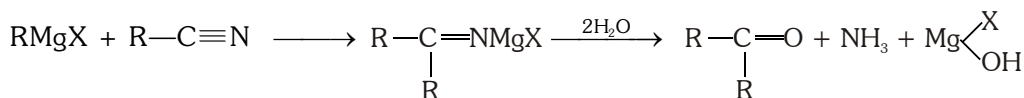


(2) Stephen's reduction :



(C) For Ketones only

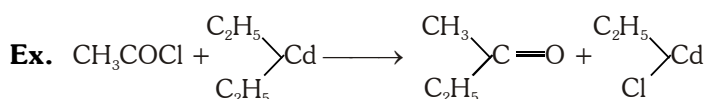
(1) From Grignard's reagent :



(2) From dialkyl Cadmium : $R'CdR'$ (dialkyl Cadmium) is an organometallic compound.



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



6.2 Physical Properties

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

Solubility : C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $\overset{\delta+}{>C}=\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.



H-bonding

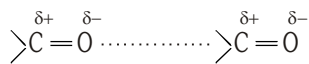
$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

Boiling point :

$$\text{Boiling point} \propto \text{Molecular weight}$$

Boiling point order is - **Alcohol > Ketone > Aldehydes > Alkane** (of comparable molecular mass)

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



Density : Density of carbonyl compounds is lower than water.

BEGINNER'S BOX-4

- Acids do not give the characteristic reactions of $C=O$ group because of :-
(1) Dimerisation (2) Resonance (3) Cyclic structures (4) Attached alkyl radical
- The vapour density of a compound is 45. Its molecular formula will be -
(1) C_2H_5O (2) $C_3H_6O_2$ (3) $C_4H_{10}O$ (4) $C_5H_{14}O$
- 23 gm of sodium of reaction with methyl alcohol gives :
(1) Half mole of H_2 (2) One mole of H_2 (3) One mole of O_2 (4) none

6.3 Chemical Properties

Carbonyl compounds undergo following reactions :

6.3.1 Nucleophilic addition reactions (Already discussed in Reaction Mechanism Part-2)

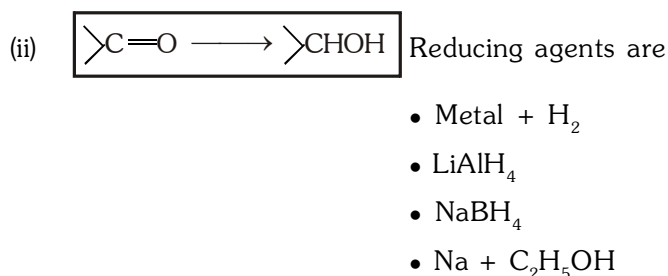
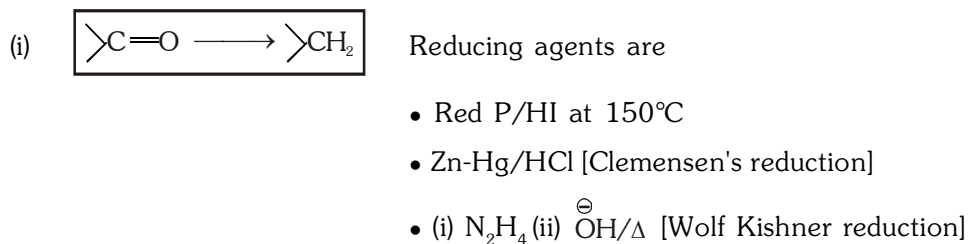
6.3.2 Other reactions

6.3.3 Reactions of only aldehyde

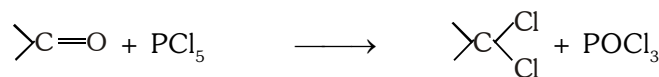
6.3.4 Reactions of only ketones

6.3.2 Other reactions

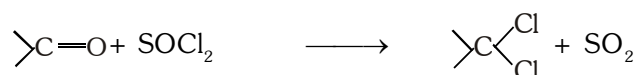
(a) **Reduction** : The nature of product depends upon the reducing agent used.



(b) **Reaction with PCl_5 & SOCl_2 :**

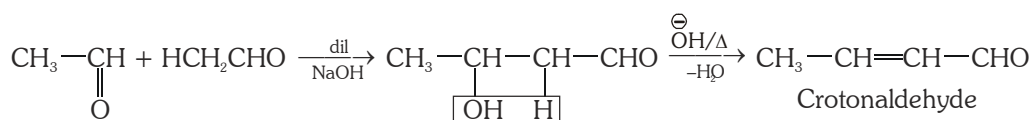


Phosphorus penta chloride



Thionyl chloride

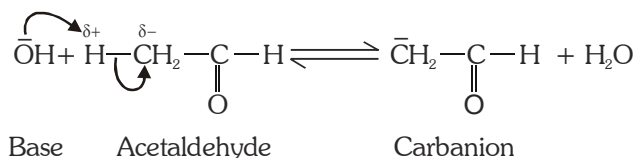
(c) **Aldol Condensation** : Carbonyl compounds which contain α -H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β -unsaturated carbonyl compound.



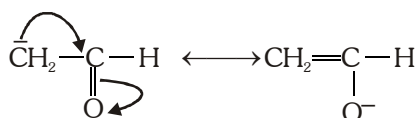
Mechanism of aldol condensation : It takes place in the following two stages :

- Formation of Carbanion
- Combination of carbanion with other carbonyl molecule.

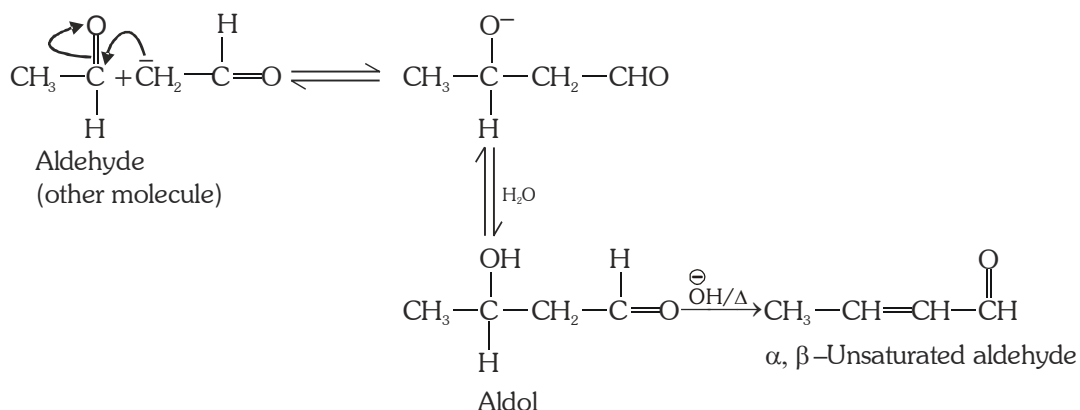
(i) **Formation of Carbanion** : α -H atom of $>\text{C}=\text{O}$ group are quite acidic which can be removed easily as proton, by a base



Carbanion thus formed is stable because of resonance -

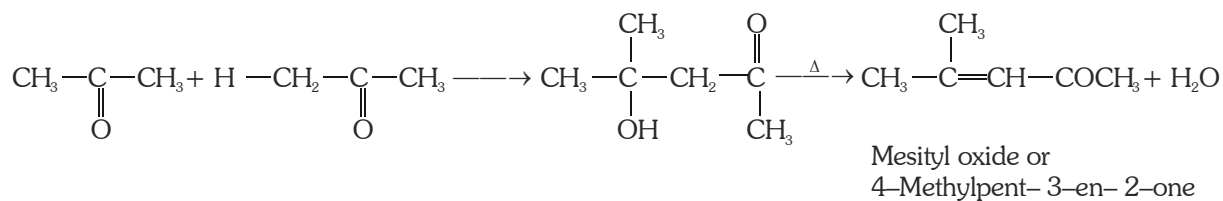


(ii) Combination of carbanion with other carbonyl molecule :

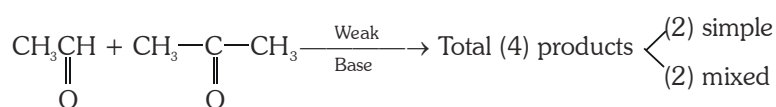


Identical carbonyl compounds $\longrightarrow$ Simple or self aldol condensation.
 Different carbonyl compounds $\longrightarrow$ Mixed or crossed aldol condensation.

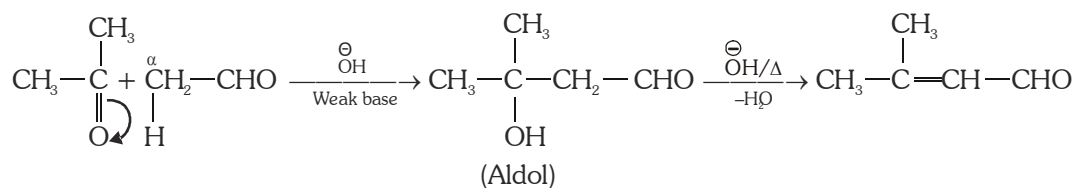
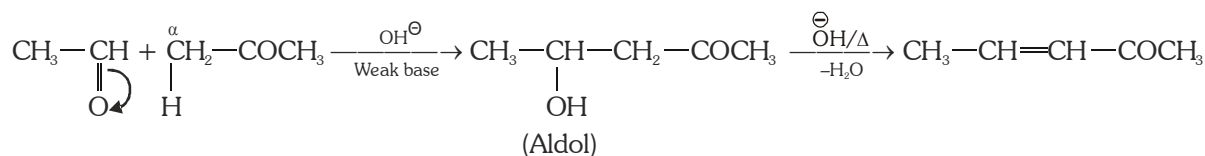
Simple or Self condensation :



Mixed or Crossed aldol Condensation :



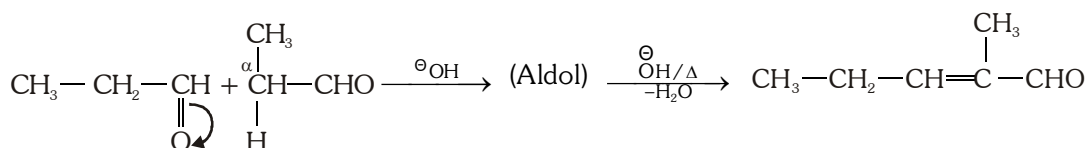
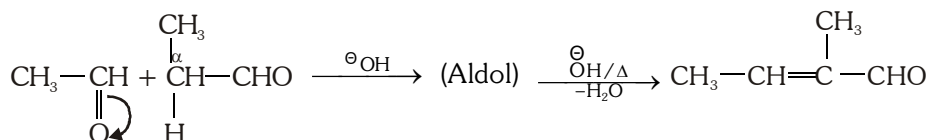
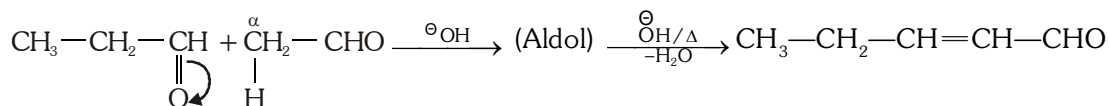
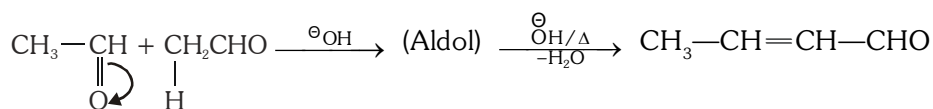
Mixed aldol condensation products of the above reaction are :



Illustrations

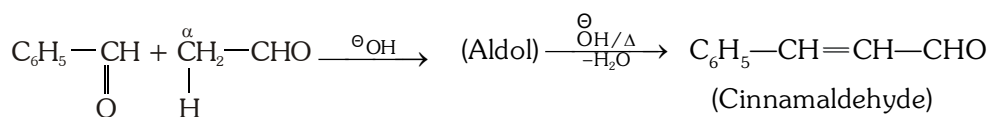
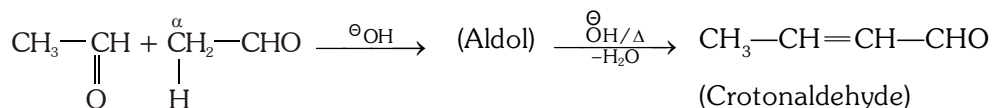
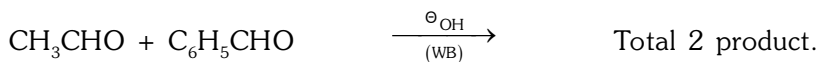
Illustration 7. $\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow[\text{(WB)}]{^\ominus\text{OH}}$ Total 4 products. Write structure of products ?

Solution.

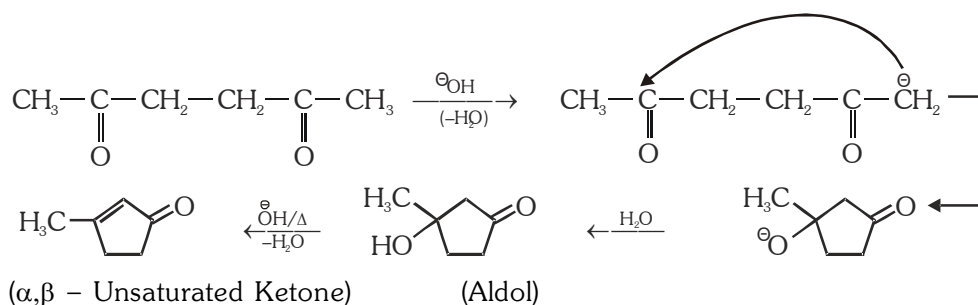


GOLDEN KEY POINTS

- If in crossed aldol condensation reaction, only one carbonyl compound have α -H then total two products are formed.



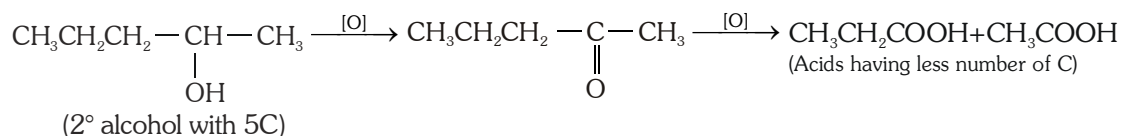
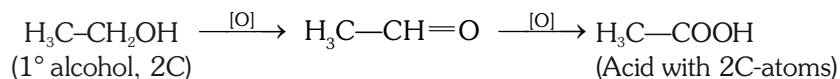
- Intramolecular** aldol condensation :



Here one more product having 3 membered ring is also possible, but 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

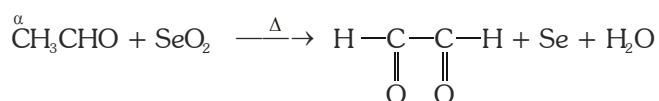
(d) Oxidation reactions :

- (i) By $K_2Cr_2O_7/H_2SO_4$:** On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using $KMnO_4/H^+$, it gets oxidised to give acids with less number of C-atom.

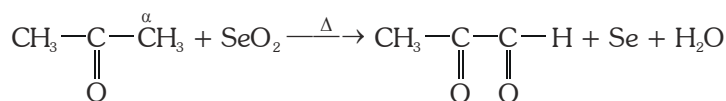


- (ii) SeO_2 (Selenium dioxide) :** Ketones or aldehydes on oxidation with SeO_2 give dicarbonyl compounds. This reaction is possible only in compounds containing $\alpha-CH_2-$ unit.

HCHO doesn't show this reaction.



Glyoxal

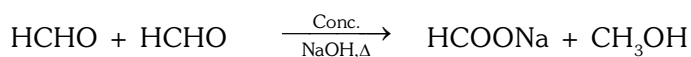


Methyl glyoxal (Pyruvaldehyde)

6.3.3 Reactions of only aldehydes :

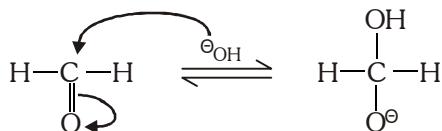
- (a) Cannizzaro's reaction :** Those aldehydes which do not contain α - H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol

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

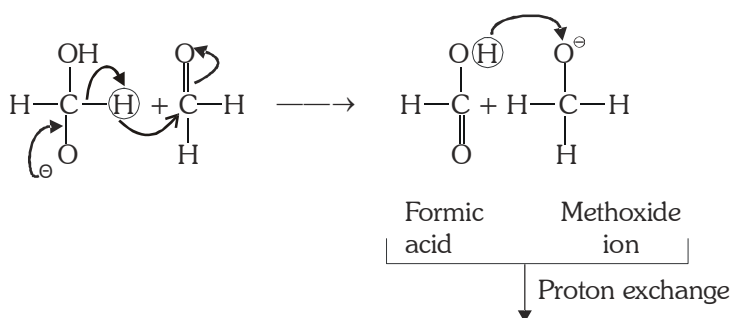


Mechanism involved in cannizzaro's reaction :

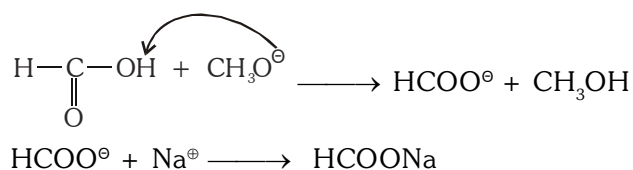
- (a) Rapid reversible addition of $\bar{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion $\text{H}^{\ominus}$ to second molecule of HCHO

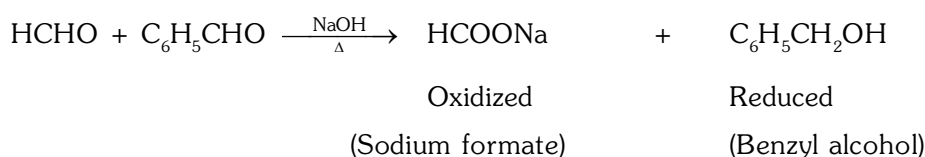


(c) Proton exchange

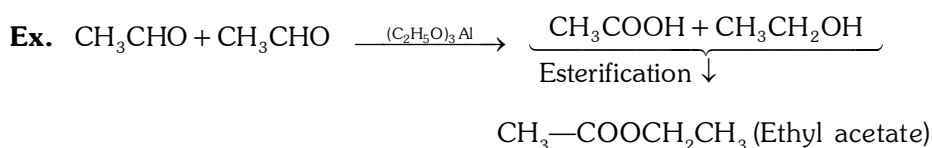
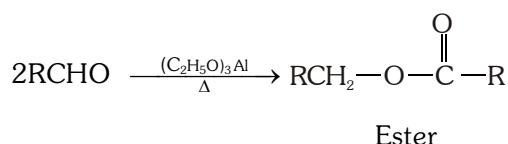


When molecules are same	————→ Simple cannizaro reaction (disproportionation reaction)
Two different molecules	————→ Mixed cannizaro reaction (Redox reaction)

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

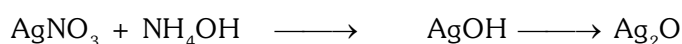
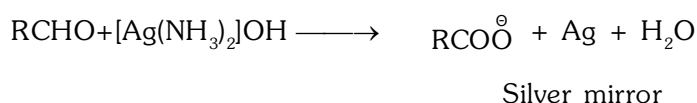
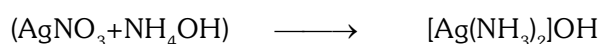


(b) Tischenko reaction : It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_2Al$, to form ester.



(c) Reducing character :Aldehydes are easily oxidised so they are strong reducing agents.

(i) Tollen's reagent : It oxidises aldehydes. Tollen's reagent is ammoniacal silver nitrate solution

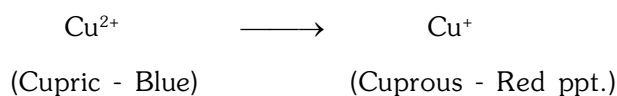
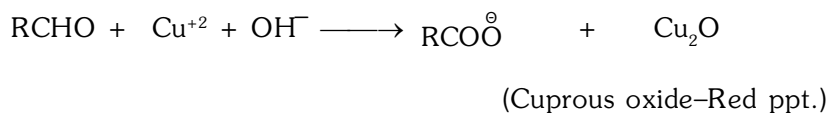


(ii) Fehling's solution : It is a mixture of aqueous CuSO_4 , NaOH and sodium potassium tartarate.

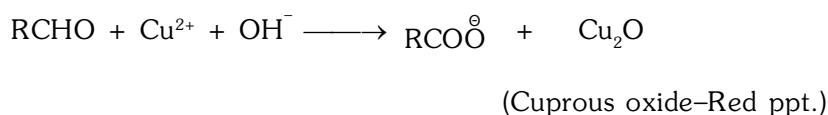
Fehling solution A– (aq.) solution of CuSO_4

Fehling solution B– Roschelle salt (Sodium potassium tartarate + NaOH)

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



(iii) Benedict's solution : It is a mixture of CuSO_4 + sodium citrate + NaOH . It provides Cu^{+2} . It is reduced by aldehyde to give red ppt of cuprous oxide.

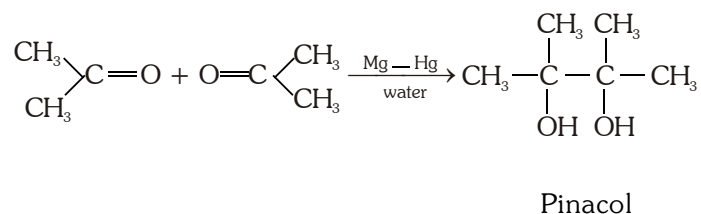


(iv) Schiff's reagent : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

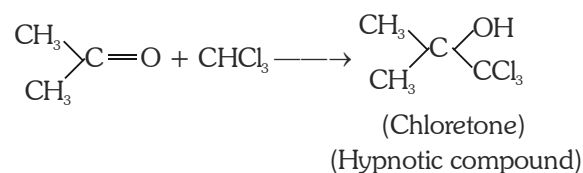
Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

6.3.4 Reaction of Only Ketones

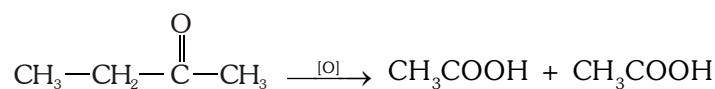
(1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



(2) Reaction with chloroform :

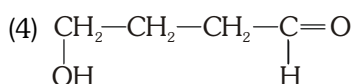
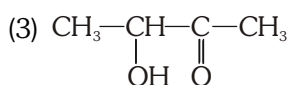
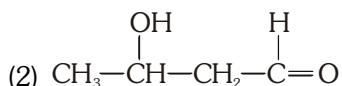
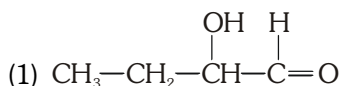


(3) Oxidation reaction : According to popoff's rule $\text{>C}=\text{O}$ group stays with smaller alkyl group.



BEGINNER'S BOX-5

1. The compounds capable in reaction with Tollen's reagent is (are):
 (1) Formaldehyde (2) Formic acid (3) Acetaldehyde (4) All the above
2. Acetaldehyde reacts with NaOH to form :-



3. Fehling's solution is a :-
 (1) Solution of magenta dye bleached by SO_2
 (2) Ammonical solution of AgNO_3
 (3) Mixture of a solution of CuSO_4 and a solution of caustic soda and sodium potassium tartarate
 (4) Alcoholic solution of 2,4-dinitrophenylhydrazine

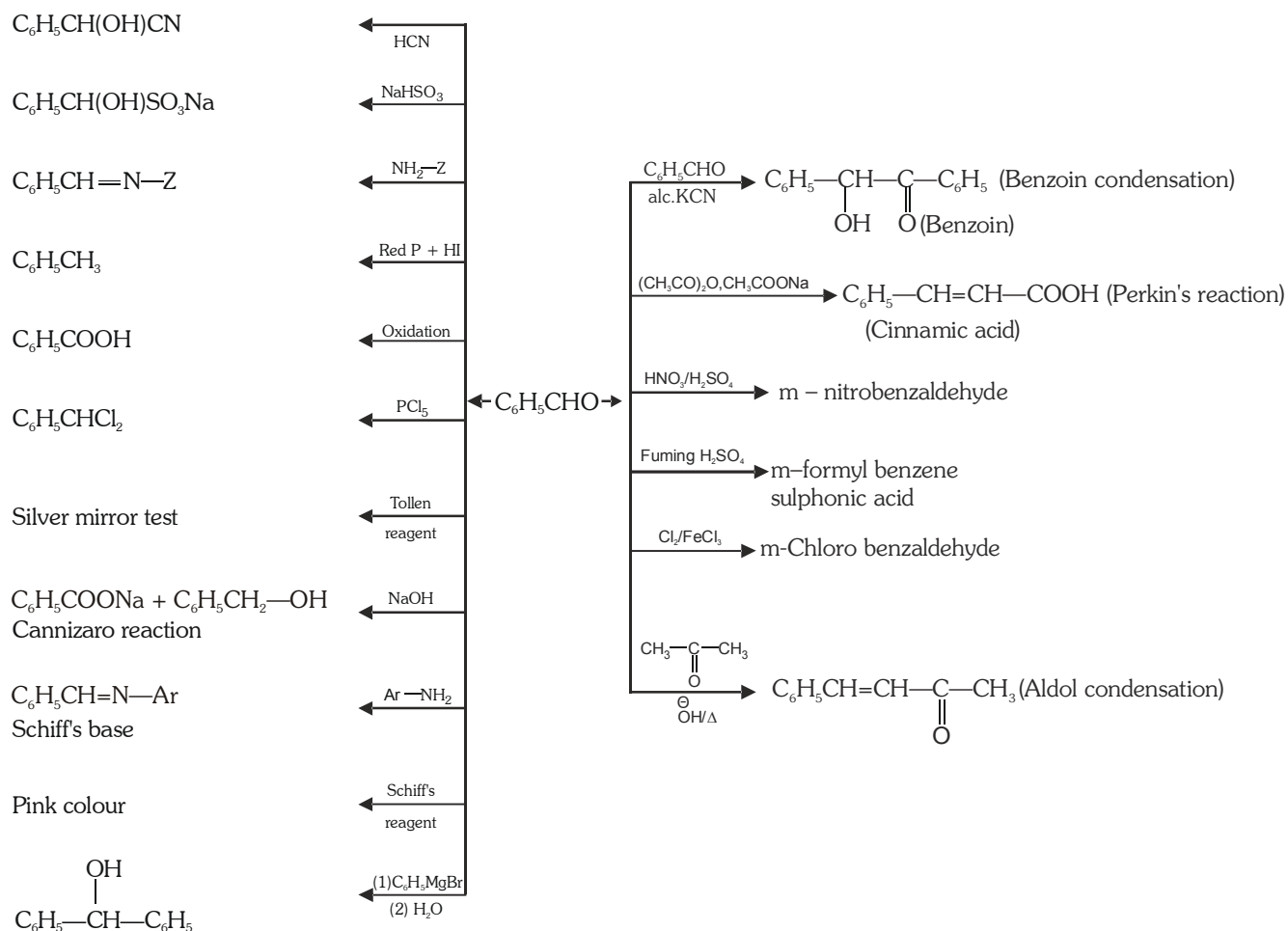
7.0 BENZALDEHYDE ($\text{C}_6\text{H}_5\text{CHO}$) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.1 General Methods of Preparation

C_6H_6	$\text{CO/HCl} + \text{ZnCl}_2$	(Gattermann-koch aldehyde synthesis)
$\text{C}_6\text{H}_5\text{CH}_3$	(1) CrO_2Cl_2 (2) H_2O	(Etard reaction)
$\text{C}_6\text{H}_5\text{COCl}$	Pd/BaSO_4	(Rosenmund reaction)
$\text{C}_6\text{H}_5\text{CN}$	(i) SnCl_2/HCl (ii) H_2O	(Stephen's reaction)
$(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$	$(\text{HCOO})_2\text{Ca}/\Delta$	
$\text{C}_6\text{H}_5\text{CHCl}_2$	aq. KOH	
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	$[\text{O}]$ (controlled oxidation)	
$\text{C}_6\text{H}_5\text{MgBr}$	HCOOC_2H_5	
C_6H_6	(1) $\text{HCN/HCl} + \text{ZnCl}_2$ (2) H_2O	(Gattermann aldehyde synthesis)

$\rightarrow \text{C}_6\text{H}_5\text{CHO}$

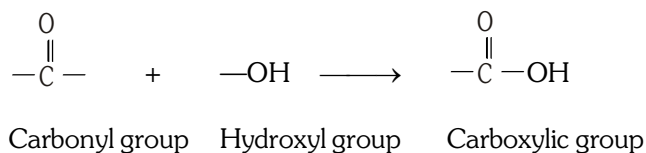
7.2 Chemical Properties



8.0 CARBOXYLIC ACID

Organic compounds having $-COOH$ group are called Carboxylic acids. This functional group is composed of

Carbonyl ($\text{—}\overset{\overset{O}{\parallel}}{C}\text{—}$) and hydroxyl (—OH) group.



The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification :

Monocarboxylic acid (RCOOH) : Having one carboxylic group, also called monobasic acid.

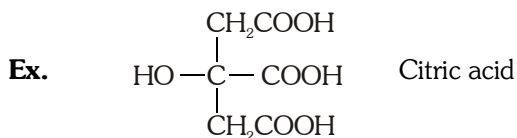
General formula - $C_nH_{2n}O_2$ ($n = 1, 2, 3, \dots$). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.



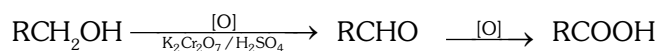
Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.



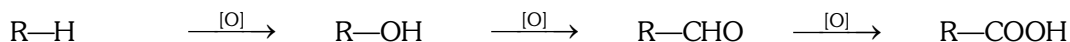
Structure : The carbon atom of $-\text{COOH}$ group is sp^2 hybridised, this C-atom is in centre and thus bond angle around C-atom is 120° .

8.1 General Methods of Preparation

8.1.1 By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .



Acids are third oxidation products of alkane.



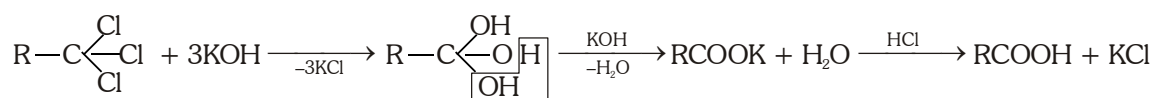
GOLDEN KEY POINTS

- Aldehyde on oxidation give acids having same no. of C-atoms.
- Ketones on oxidation give acids having less no. of C-atoms.
- Oxidation of Ketones occurs on prolonged treatment with strong oxidising agent.

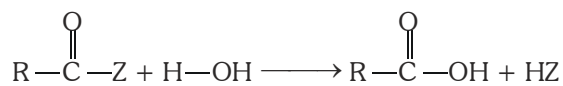
8.1.2 By hydrolysis of alkane nitriles or cyanides : Complete hydrolysis takes place in acidic medium (dil. HCl). In alkaline medium there is partial hydrolysis.



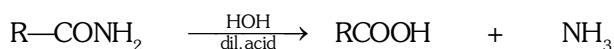
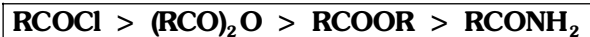
8.1.3 By alkaline hydrolysis of 1, 1, 1-trihaloalkane :



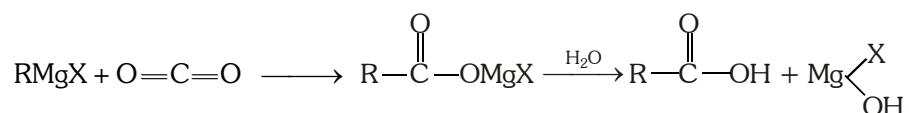
8.1.4 By hydrolysis of acid derivatives :



Reactivity order of acid derivatives :



8.1.5 From Grignard's reagent :



Carbon dioxide

Solid CO_2 (dry ice) is used

8.2 Physical Properties

Carboxylic acids from C_1-C_4 are completely soluble in water.

$$\text{Solubility} \propto \frac{1}{\text{molecular weight}}$$

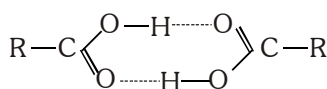
Solubility is due to intermolecular H - bonding with water molecules.

Boiling point : $B. P. \& M. P. \propto \text{Molecular weight,}$

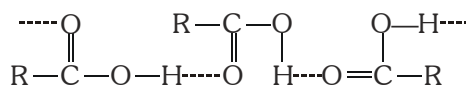
Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur
in the form of dimers.



But in liquid state it exists in polymer form.

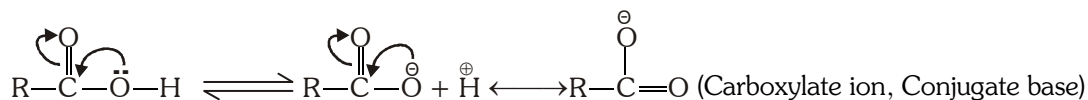


Melting point : Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms. The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.

8.3 Chemical Properties

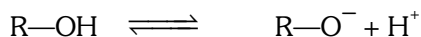
8.3.1 Reaction due to - H atom of - COOH group

(a) Acidic character :



Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.



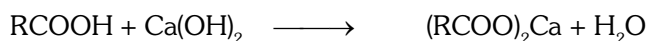
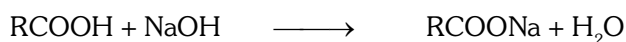
alkoxide ion

(a) Carboxylic acids turn blue litmus to red.

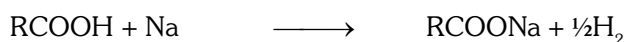
(b) Addition of carboxylic acid to NaHCO_3 in water gives out effervescence of CO_2 .



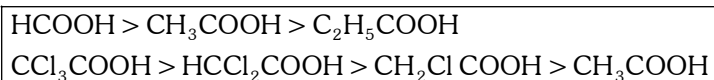
(c) Form salts with alkalis.



(d) Action of metals.

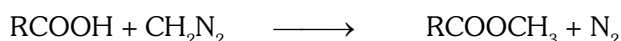


The acidic character order is :



Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH_2N_2 : Methyl ester can be prepared by this method.



Methyl ester

8.3.2 Reaction due to - OH group

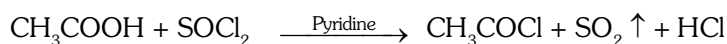
(a) Esterification :



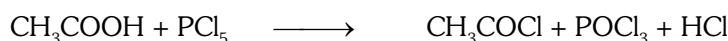
(b) Reaction with NH_3 :



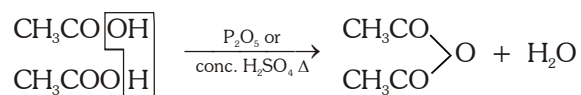
(c) Reaction with thionyl chloride :



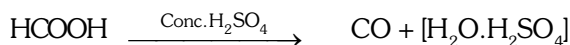
(d) Reaction with PCl_5 :



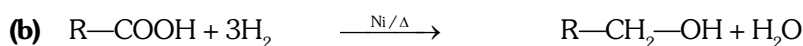
(e) Reaction with P₂O₅ (dehydrating agent) :



HCOOH is dehydrated by Conc. H₂SO₄

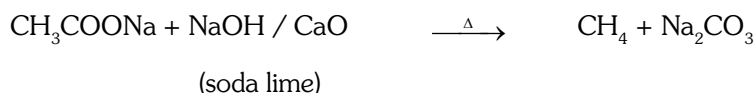


8.3.3 Reaction due to $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ group of COOH :

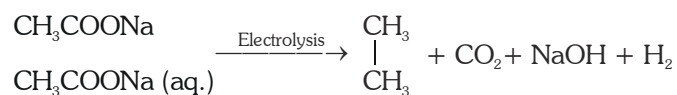


8.3.4 Reaction due to —COOH group :

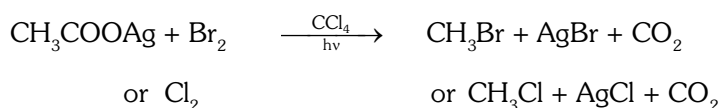
(a) Decarboxylation :



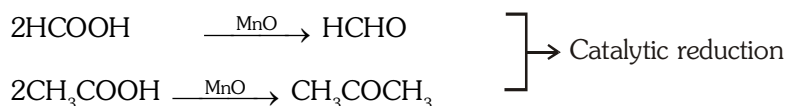
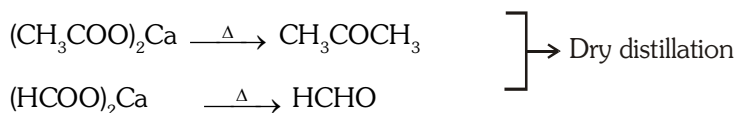
(b) Kolbe's electrolysis :



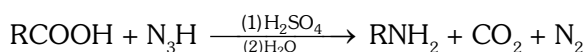
(c) Hunsdiecker reaction :



(d) Formation of carbonyl compounds :



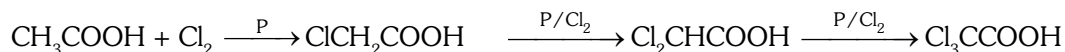
(e) Schmidt reaction : The amine formed has one C - atom less than the reactant acid.



Hydrazoic acid

8.3.5 Reaction due to alkyl (R) group :

(a) **Halogenation [HVZ reaction] : Hell volhard Zelinsky reaction] :** In this reaction α - H atoms are replaced by halogen atoms.



GOLDEN KEY POINTS

Test for HCOOH and CH₃COOH

Test	HCOOH	CH ₃ COOH
1. Reducing character		
Reducing agents -		
Tollen reagent	Silver mirror	×
Fehling solution	Cu ₂ O red ppt.	×
K ₂ Cr ₂ O ₇	Cr ⁺³ (green)	×
2. Decarboxylation.	Na ₂ CO ₃ + H ₂	CH ₄

Uses of Formic Acid :

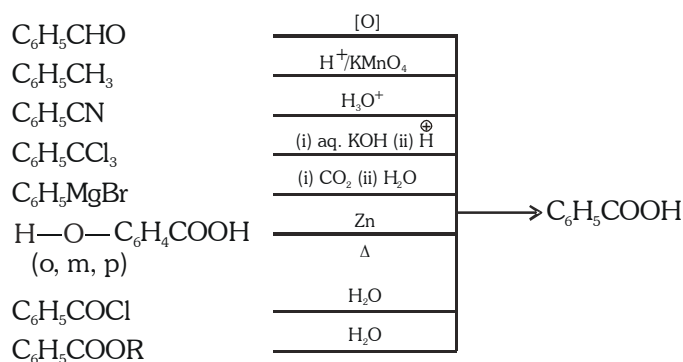
- (i) As an antiseptic
- (ii) For preservation of fruits.
- (iii) For leather tanning.
- (iv) In dying wool and cotton fabrics.

Uses of Acetic Acid :

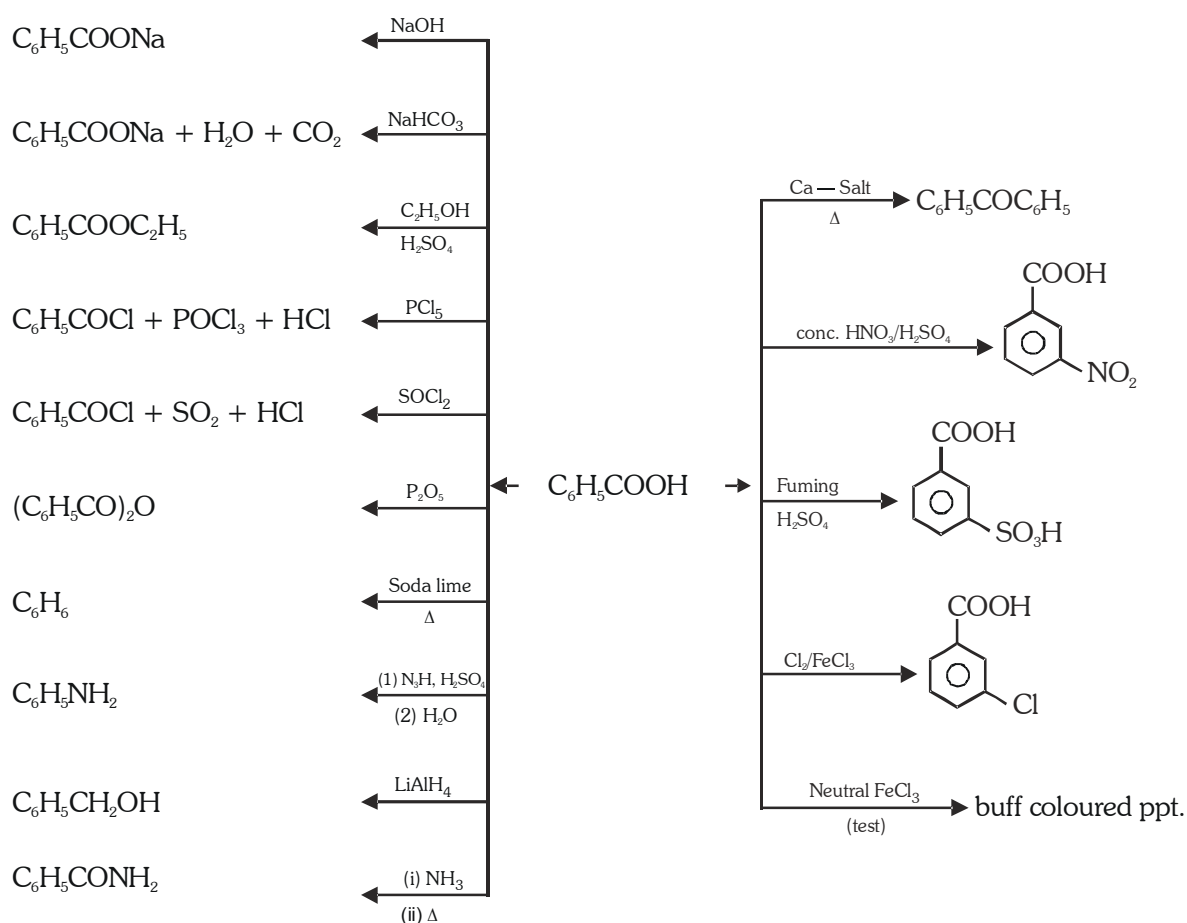
- (i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.
- (ii) For manufacture of rubber from latex and casein from milk CH₃COOH is used as coagulant.
- (iii) As a solvent and laboratory reagent.

9.0 BENZOIC ACID (C₆H₅COOH)

9.1 General Method of Preparation :

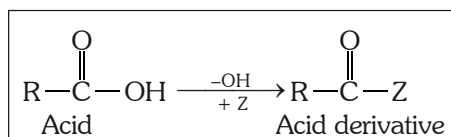


9.2 Chemical properties



10.0 ACID DERIVATIVES

Replacement of $-OH$ group from a carboxylic group ($-COOH$) by a nucleophile like Cl^- , CH_3COO^- , $C_2H_5O^-$, NH_2^- , forms acid derivatives.

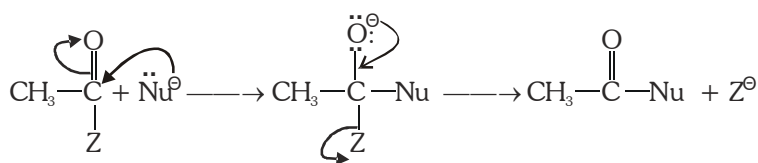


$R-\overset{O}{\parallel}C-$ is Acyl group and Z is nucleophile $Cl^\ominus$, $CH_3COO^\ominus$, $C_2H_5O^\ominus$, $NH_2^\ominus$

Ex. $CH_3-\overset{O}{\parallel}C-$ Acetyl group

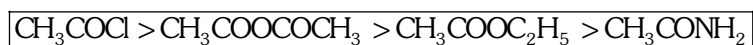
Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



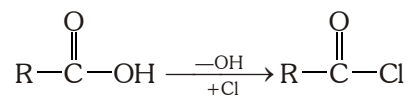
In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivity order :



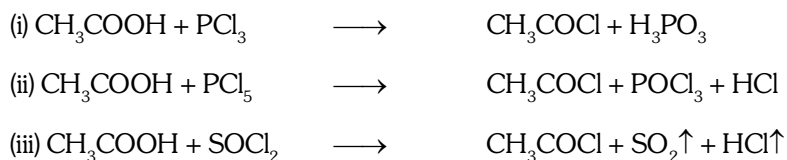
10.1 Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

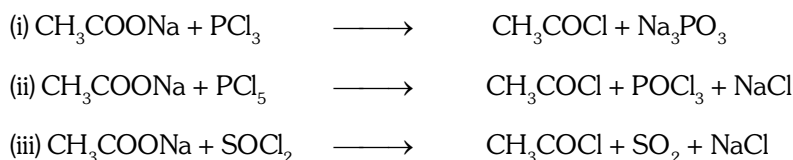


10.1.1 General Method of Preparation :

(a) By heating CH_3COOH with PCl_3 , PCl_5 & SOCl_2 :



(b) By heating the salt of acids with PCl_3 , PCl_5 or SOCl_2 :



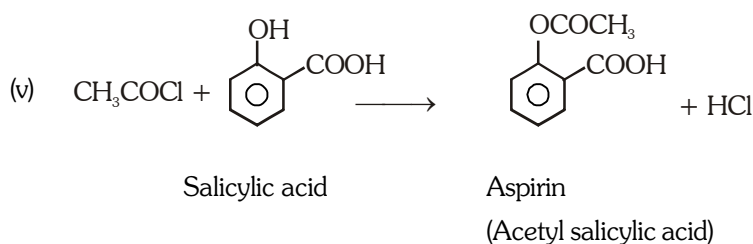
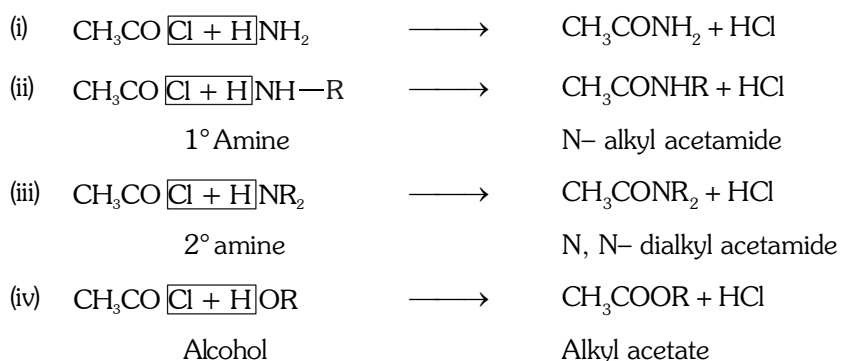
10.1.2 Physical properties :

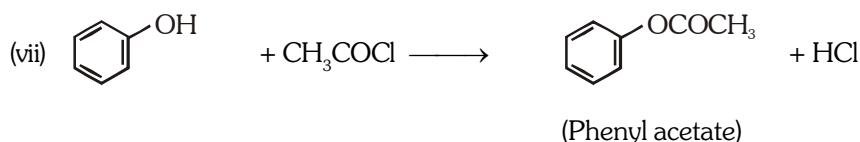
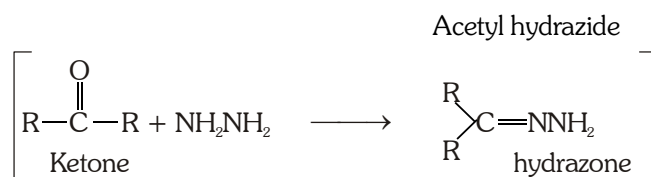
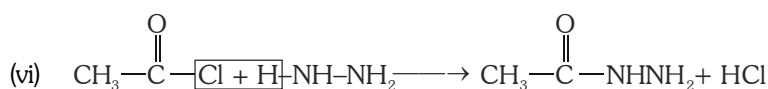
- (i) Pungent smelling liquid.
- (ii) Boiling point 52°C .
- (iii) Soluble in organic solvent, slowly soluble in water.
- (iv) It produces fumes in moist air due to the formation of HCl.

10.1.3 Chemical properties :

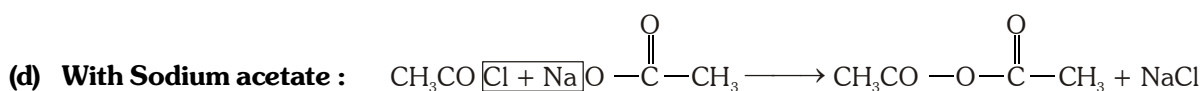
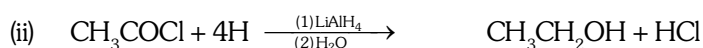
(a) Hydrolysis : $\text{CH}_3\text{CO}[\text{Cl} + \text{H}]\text{OH} \longrightarrow \text{CH}_3\text{COOH} + \text{HCl}$

(b) Reaction with active H - containing compounds (Acetylation) :

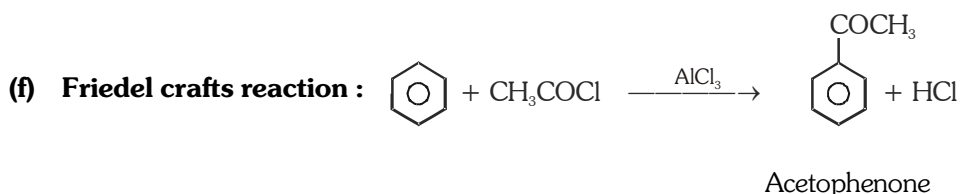
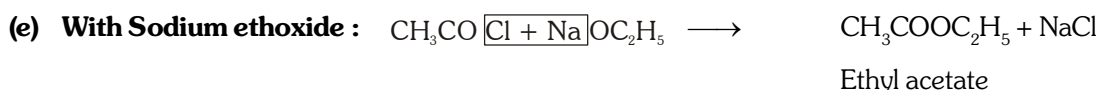




(c) Reduction :



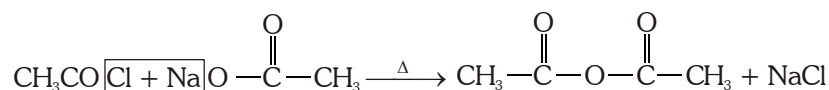
Acetic anhydride



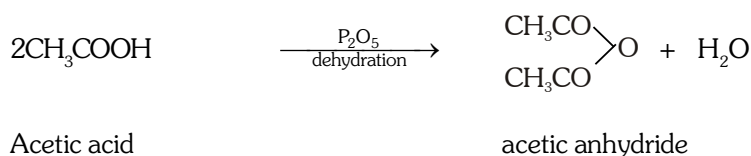
10.2 Acetic Anhydride (Ethanoic Anhydride)

10.2.1 General Method of Preparation :

(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method] :



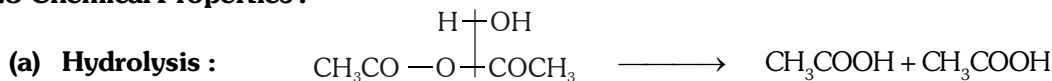
(b) By Dehydration of acetic acid :



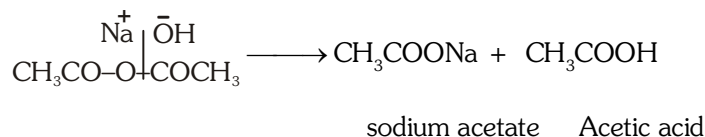
10.2.2 Physical Properties :

- (i) It is pungent smelling liquid.
- (ii) Sparingly soluble in water, soluble in ether & alcohol.
- (iii) Boiling point 139°C.

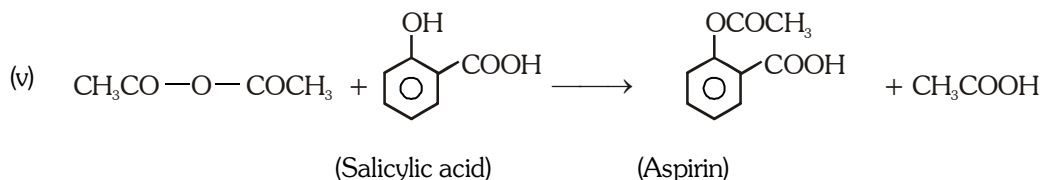
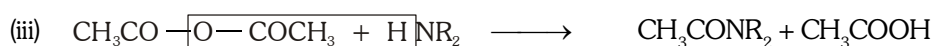
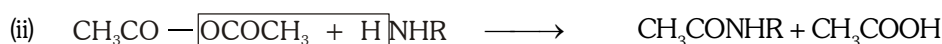
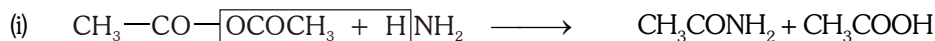
10.2.3 Chemical Properties :



Hydrolysis order : **Alkaline > Acidic > neutral**



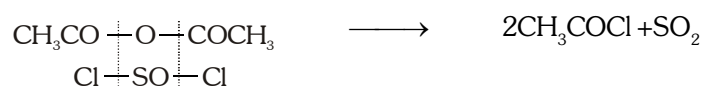
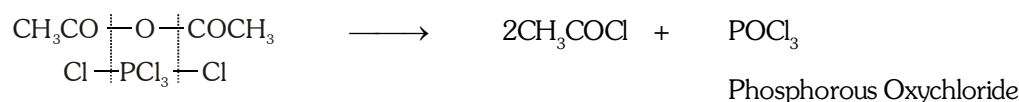
(b) **Reaction with active H - containing compounds (Acetylation) :**



(c) **Reduction :** With LiAlH_4 in ether gives ethyl alcohol



(d) **Reaction with PCl_5 & SOCl_2 :**



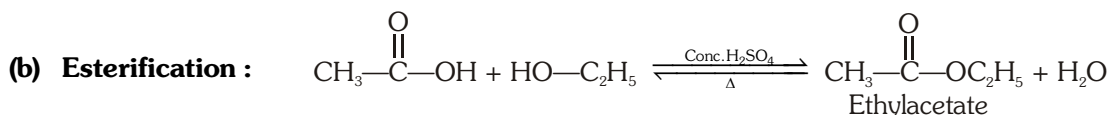
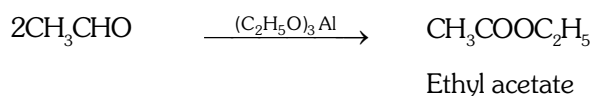
10.2.4 Uses

- As an acetylating agent
- In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.
- For detection and estimation of hydroxyl and amino group.

10.3 Ethyl acetate

10.3.1 General Method of Preparation :

(a) **Tischenko reaction :** By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)



BEGINNER'S BOX-6

1. Alkanoic acids can be prepared by hydrolysis of:-

(1) Trihaloalkanes	(2) 1,1,1-trihaloalkanes
(3) Grignard reagents	(4) Ketones
2. Acids have much higher boiling points than isomeric esters because :-
 - (1) Acids form dimers by H-Bonding
 - (2) Acids are volatile in steam
 - (3) Esters are non-volatile
 - (4) Acids can ionise to give protons in aqueous solution
3. Which of the following compounds can form intermolecular H-bonds :-

(1) Ethyl acetate	(2) Methyl formate
(3) Acetamide	(4) Acetic anhydride
4. Reaction of ethyl acetate with sodium ethoxide gives acetoacetic ester. This reaction is known with the name of :-

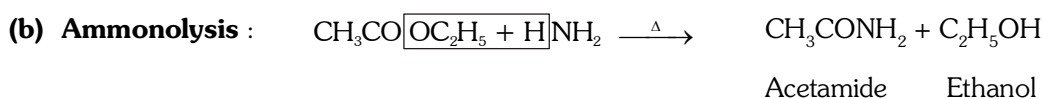
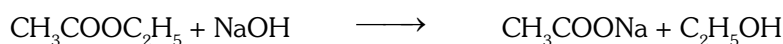
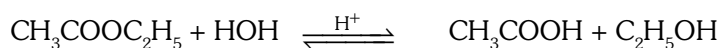
(1) Claisen	(2) Clemmensen
(3) Cannizaro	(4) Etard

10.3.2 Physical Properties

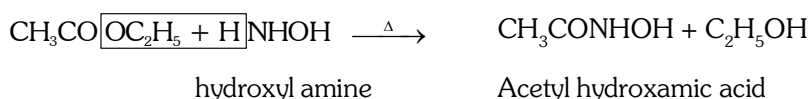
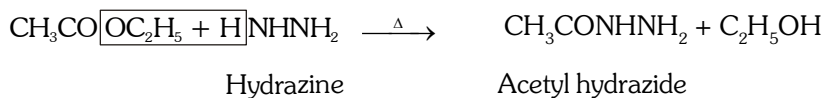
- (i) Fruity smell liquid.
- (ii) Boiling point 77° C.
- (iii) Slightly soluble in water, soluble in organic solvent.

10.3.3 Chemical Properties :

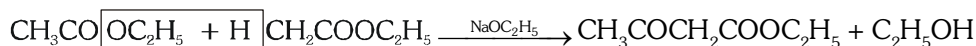
(a) Hydrolysis : In acidic medium reaction is reversible and in alkaline medium reaction is irreversible.



(c) Reaction with NH_2NH_2 & NH_2OH :



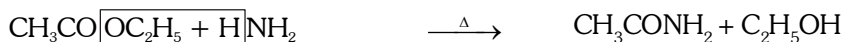
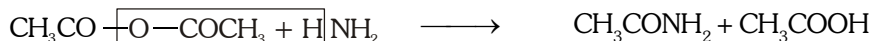
(e) Claisen condensation :



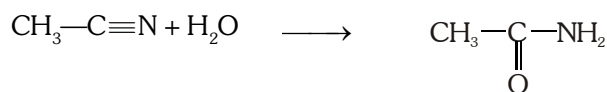
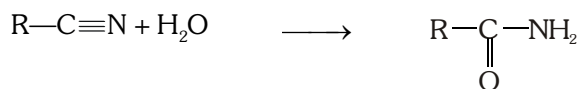
10.4 Acetamide

10.4.1 General Method of Preparation :

(a) Ammonolysis of acid derivatives :

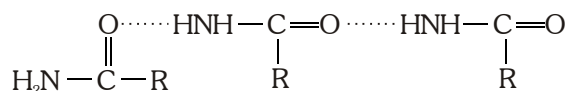


(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.



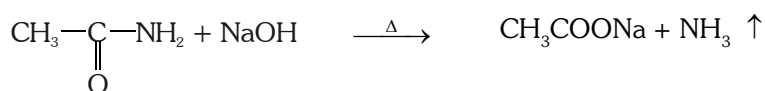
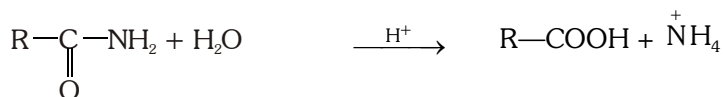
10.4.2 Physical Properties :

- (i) Acetamide is white crystalline solid.
- (ii) Pure acetamide is odourless.
- (iii) Impure acetamide - Smell like mouse.
- (iv) Lower amides are soluble in water, due to H-bonding.
- (v) Their higher M. P. and B. P. are due to intermolecular H-bonding.

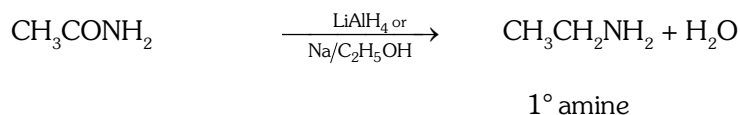


10.4.3 Chemical Properties :

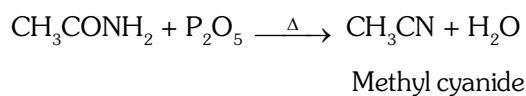
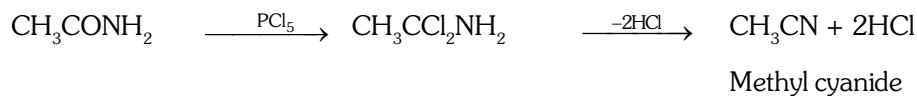
(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.



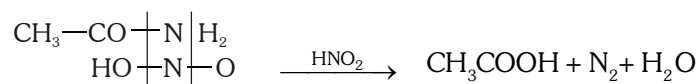
(b) Reduction to primary amines : Amine contains same number of carbon atoms.



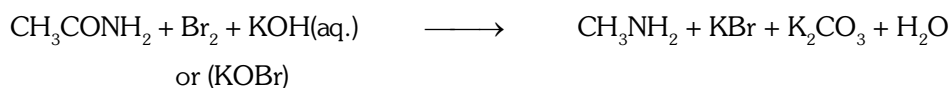
(c) Dehydration with PCl_5 , SOCl_2 or P_2O_5 :



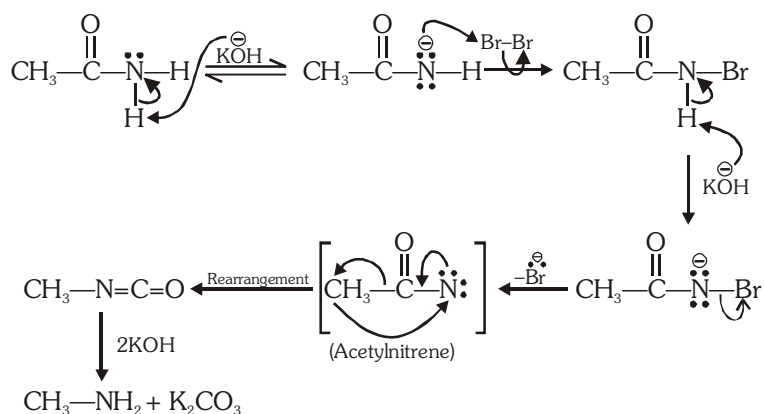
(d) Reaction with nitrous acid :



(e) Hoffmann's bromamide degradation reaction : Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C-atom less than the amides.



Mechanism :



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	3	4	2							

BEGINNER'S BOX-2	Que.	1	2								
	Ans.	1	2								

BEGINNER'S BOX-3	Que.	1	2	3							
	Ans.	3	2	3							

BEGINNER'S BOX-4	Que.	1	2	3							
	Ans.	2	4	1							

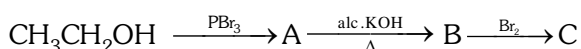
BEGINNER'S BOX-5	Que.	1	2	3							
	Ans.	4	2	3							

BEGINNER'S BOX-6	Que.	1	2	3	4						
	Ans.	2	1	3	1						

Build Up Your Understanding

ALCOHOL

1. The compound A, B and C in the reaction sequence



are given by the set

- (1) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHBr_2 .
- (2) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{CHBr}$
- (3) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2=\text{CH}_2$, $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$
- (4) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_3\text{CH}_2\text{OH}$, $\text{BrCH}_2-\text{CH}_2\text{Br}$

2. Primary amines can be converted into alkanols by reaction with

- (1) Aqueous HCl (2) Tilden's reagent
(3) NaNO_2 and dil. HCl (4) Hypochlorous acid

3. Which of the following alcohols gives a red colour in Victor Meyer test

- (1) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--OH}$ (2) $\begin{array}{c} \text{CH}_3\text{--CH--OH} \\ | \\ \text{CH}_3 \end{array}$
- (3) $(\text{CH}_3)_3\text{C--OH}$ (4) $\begin{array}{c} \text{CH}_3\text{--CH--CH}_2\text{--CH}_3 \\ | \\ \text{OH} \end{array}$

4. Methanol on heating with salicylic acid and a few drops of conc. H_2SO_4 gives the smell of

- (1) Bitter almonds (2) Oil of wintergreen
(3) Rotten eggs (4) Mustard oil

5. Which of the following does not turn orange colour of chromic acid to green

- (1) 1° alcohol (2) 2° alcohol
(3) 3° alcohol (4) Allyl alcohol

6. p, s and t-alcohols can be distinguished by :-

- (1) Reimer-Tiemann reaction
- (2) Tollen's reagent
- (3) Lucas test
- (4) Lassaigne's test

7. Consider the following reaction :

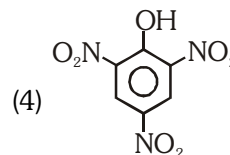
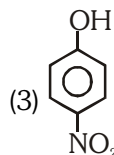
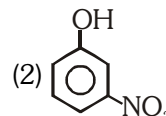
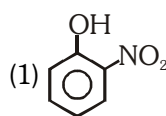


Among the following, which one cannot be formed as a product under any conditions ?

- (1) $\text{C}_2\text{H}_5\text{OSO}_3\text{H}$
- (2) $\text{H}_2\text{C}=\text{CH}_2$
- (3) $\text{HC}\equiv\text{CH}$
- (4) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$

PHENOL

8. Nitration of phenol with conc. nitric acid gives :-

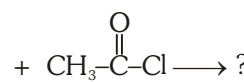
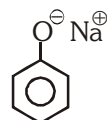


9. Deoxygenation of phenol can be achieved by distillation with :-

- (1) Raney nickel
- (2) Lithium aluminium hydride
- (3) Sodium borohydride
- (4) Zinc dust

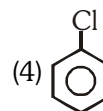
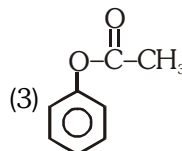
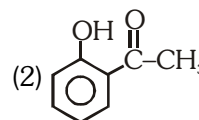
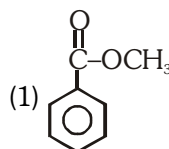
10. Which of the following compounds shows intramolecular hydrogen bonding :-

- (1) p-Nitrophenol (2) Ethanol
(3) o-Nitrophenol (4) Methanamine

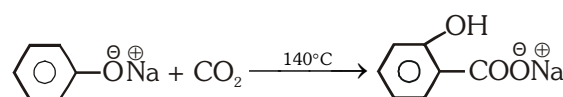


11.

Sodium phenate



12. The reaction



is called :-

- (1) Schotten Bauman reaction
- (2) Kolbe Schmidt reaction
- (3) Reimer–Tiemann reaction
- (4) Lederer–Manasse reaction

13. Phenol can be distinguished from ethanol by reactions with the following except :-

- (1) Iodine and alkali (2) Ferric chloride
(3) Acetyl chloride (4) Bromine water

14. Phenol on treatment with methyl chloride in the presence of anhydrous AlCl_3 gives chiefly :-

- (1) o-cresol (2) m-cresol
(3) anisole (4) p-cresol

15. Phenol on heating with NaNO_2 and a few drops of conc. H_2SO_4 mainly gives :-

- (1) p-nitrophenol (2) p-nitrosophenol
(3) o-nitrophenol (4) m-nitrosophenol

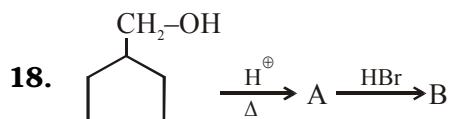
16. Phenol and benzoic acid are distinguished by :-

- (1) Lucas reagent (2) Victor Meyer test
(3) Caustic soda (4) Sodium bicarbonate

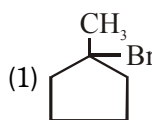
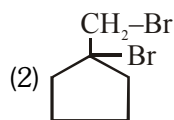
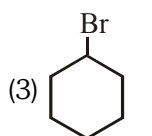
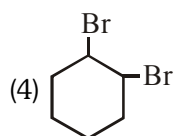
17. Phenol can be distinguished from ethanol by the reaction with

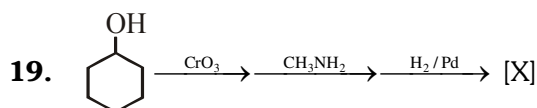
- (1) Na (2) Br_2/Water
(3) Neutral AlCl_3 (4) 1 and 2 Both

ETHER

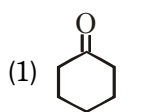
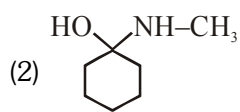
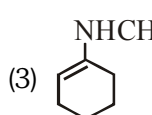
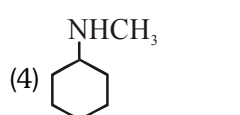


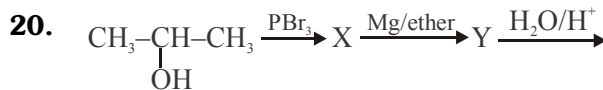
What is the structure of B :-

- (1)  (2) 
(3)  (4) 

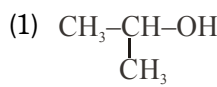
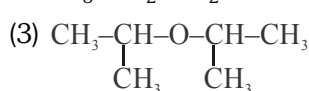


Product [X] of given reaction is :-

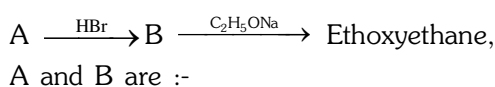
- (1)  (2) 
(3)  (4) 



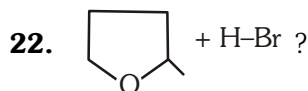
The final product is :-

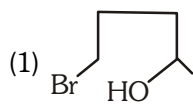
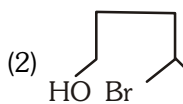
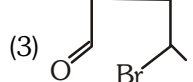
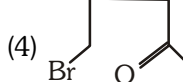
- (1) 
(2) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
(3) 
(4) $\text{CH}_3-\text{CH}_2-\text{CH}_3$

21. In the reaction sequence



- (1) C_2H_6 , $\text{C}_2\text{H}_5\text{Br}$
(2) CH_4 , CH_3Br
(3) $\text{CH}_2=\text{CH}_2$, $\text{C}_2\text{H}_5\text{Br}$
(4) $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{CHBr}$



- (1)  (2) 
(3)  (4) 

23. $\text{CH}_3-\text{CH}_2-\text{OH} + \text{Ph}-\text{CH}_2-\text{OH} \xrightarrow[140^\circ\text{C}]{\text{H}^+}$ of which is not obtained?

- (1) $\text{CH}_3-\text{CH}_2-\text{OCH}_2-\text{CH}_3$
(2) $\text{Ph}-\text{CH}_2-\text{OCH}_2-\text{Ph}$
(3) $\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
(4) $\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_3$

24. Oxonium ion of ether has the structure :-

- (1) $\text{C}_2\text{H}_5-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\overset{\oplus}{\text{O}}-\text{H}$
(2) $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{O}}-\text{CH}_2-\text{CH}_3$
(3) $(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{O}$
(4) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\overset{\oplus}{\text{O}}-\text{H}$

25. What will happen when diethyl ether treated with hot and conc. HI :-

- (1) Ethyl alcohol (2) Ethyl iodide
(3) Methyl iodide (4) Methanol

26. Which of the following does not react with aq. NaOH :-

- (1) Phenol (2) Benzoic acid
(3) CH_3COOH (4) $\text{CH}_3\text{-O-C}_6\text{H}_5$

CARBONYL COMPOUNDS

27. Acetaldehyde on warming with Fehling's solution gives a red precipitate of :-

- (1) Elemental copper
(2) Cuprous oxide
(3) Cupric oxide
(4) Mixture of all of the above

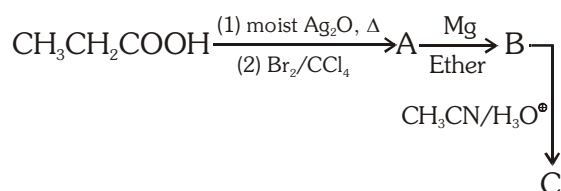
28. Acetone does not form :-

- (1) A phenylhydrazone with phenylhydrazine
(2) A sodium bisulphite adduct with sodium bisulphite
(3) A silver mirror with Tollen's reagent
(4) An oxime with hydroxylamine

29. CH_3CHO and CH_3COCH_3 can not be distinguished by :-

- (1) Fehling solution (2) Grignard reagent
(3) Schiff's reagent (4) Tollen's reagent

30. In the reaction

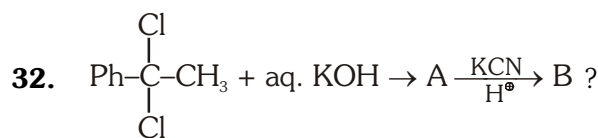


The product C is -

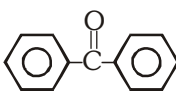
- (1) $\text{CH}_3\text{CH}_2\text{-CH(OH)-CH}_3$
(2) $\text{CH}_3\text{CH}_2\text{-CN}$
(3) $\text{CH}_3\text{CH}_2\text{-C(=O)-CH}_3$
(4) $\text{CH}_3\text{-CH}_2\text{-CH(COOH)-CH}_3$

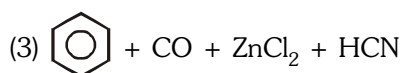
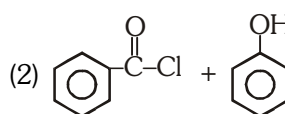
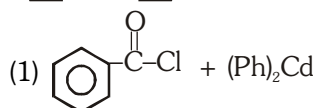
31. Acetone is obtained by the hydrolysis of the addition product of methyl magnesium iodide and :-

- (1) HCHO (2) CH_3CHO
(3) CH_3COCH_3 (4) $\text{CH}_3\text{-C}\equiv\text{N}$



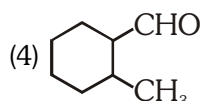
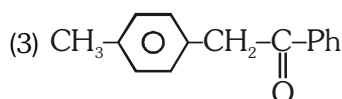
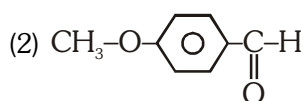
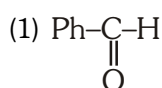
- (1) 50% d + 50% l (2) 80% d + 20% l
(3) Meso compound (4) optically active

33.  can be obtained by :-



(4) None of the above

34. Which does not react with NaHSO_3 .



35. Ketones can be prepared by :-

- (1) Rosenmund reduction
(2) Etard reaction
(3) Cannizzaro reaction
(4) Friedel-Craft reaction

36. Carbonyl compounds are best purified by :-

- (1) Steam distillation
(2) Hydrolysis of sodium bisulphite adducts
(3) Fractional crystallisation
(4) Sublimation

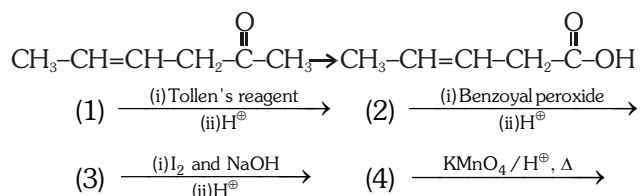
37. Carbonyl compounds readily undergo :-

- (1) Nucleophilic substitutions
(2) Electrophilic addition reactions
(3) Nucleophilic addition reactions
(4) Free radical substitution reactions

38. $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ and $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ are readily distinguished by their reaction with :-
 (1) Iodine and alkali
 (2) 2,4-dinitrophenylhydrazine
 (3) Tollen's reagent
 (4) All the above

39. Formaldehyde and acetaldehyde are readily distinguished by reaction with :-
 (1) A solution of 2,4-dinitrophenylhydrazine
 (2) Fehling's solution
 (3) Tollen's reagent
 (4) Iodine and alkali

40. Which is the most suitable reagent for the following conversion



41. Formaldehyde reacts with conc. alkali to form :-
 (1) A resinous mass
 (2) Formic acid
 (3) A mixture of methanol and sodium formate
 (4) Methanol

42. Which of the following compounds does not give aldol condensation :-
 (1) CH_3CHO (2) $\text{CH}_3\text{CH}_2\text{CHO}$
 (3) HCHO (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

43. Cannizzaro reaction is given by :-
 (1) Aldehydes containing α -hydrogen atoms
 (2) Aldehydes as well as ketones containing α -hydrogen atoms
 (3) Aldehydes not containing α -hydrogen atoms
 (4) Aldehydes containing β -hydrogen atoms

44. Benzaldehyde reacts with formaldehyde in the presence of alkali to form :-

- (1) CH_3-OH and $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{Na}^+$
 (2) $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$ and $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{Na}^+$
 (3) $\text{C}_6\text{H}_5-\text{COOH}$ and $\text{CH}_3\text{CH}_2-\text{OH}$
 (4) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$

45. Which of the following can be converted to $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$:-

- (1) Acetone (2) Acetaldehyde
 (3) Propanaldehyde (4) Formaldehyde

46. The product of reaction with primary amine and aldehyde is -

- (1) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ (2) $\text{R}-\text{ONO}$
 (3) $\text{R}'-\text{CH}=\text{N}-\text{R}$ (4) $\text{R}-\text{NO}_2$

47. Brady's reagent is

- (1) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (2) $\text{KMnO}_4/\text{NaIO}_4$
 (3) $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)-\text{NH.NH}_2$
 (4) $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)-\text{F}$

48. A compound with molecular formula $\text{C}_3\text{H}_6\text{O}$, not gives silver mirror with Tollen's reagent but forms oxime with hydroxyl amine. Compound will be -

- (1) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$
 (2) $\text{CH}_3\text{CH}_2\text{CHO}$
 (3) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$
 (4) CH_3COCH_3

49. Aldehyde and ketone are distinguished by reagent

- (1) Fehling solution (2) H_2SO_4
 (3) NaHSO_3 (4) NH_3

50. Carbonyl group is converted into methylene group by -

- (1) Acidic reduction
 (2) Raney Ni
 (3) Basic hydrolysis
 (4) Normal Hydrogenation

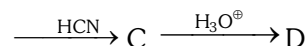
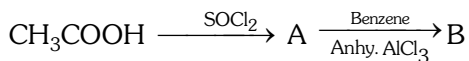
51. When acetaldol is treated with excess of acid then unsaturated product will be :-

- (1) Alcohol (2) Aldehyde
 (3) Acid (4) Alkyl halide

52. The reagent used for the separation of acetaldehyde from acetophenone is -

- (1) NaHSO_3 (2) $\text{C}_6\text{H}_5\text{NHNH}_2$
 (3) NH_2OH (4) $\text{NaOH} + \text{I}_2$

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



The structure of D would be –

- (1)
- (2)
- (3)
- (4)

ACID DERIVATIVE

62. The compounds A and B in the reaction sequence



are given by the set :-

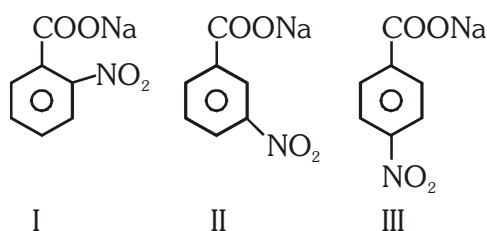
- (1) $\text{CH}_3\text{CO}-\text{O}-\text{COCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (2) $\text{CH}_3\text{CO}-\text{O}-\text{COCH}_3$, $\text{C}_6\text{H}_5\text{OCOCH}_3$
 (3) CH_3COCH_3 , $\text{C}_6\text{H}_5\text{OCOCH}_3$
 (4) $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$,
 $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_5$

63. $\text{CH}_3-\text{CH}_2-\text{COOH} \xrightarrow{\text{P}/\text{Cl}_2} \text{A} \xrightarrow[\text{KOH}]{\text{Alc.}} \text{B}$

structure of B is :-

- (1) $\text{CH}_2=\text{CH}-\text{COOH}$
 (2) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{COOH}$
 (3) $\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{COOH}$
 (4) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{Cl}$

64. Correct reactivity order of decarboxylation is



- (1) I > II > III (2) I > III > II
 (3) III > II > I (4) III > I > II

65. Which is most reactive towards hydrolysis.

- (1)
- (2)
- (3)
- (4)

66. Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

- (1) Victor-Mayer test
 (2) Neutral FeCl_3
 (3) Aqueous NaOH
 (4) Tollen's reagent

67. Acyl chlorides undergo :-

- (1) Nucleophilic addition reactions
 (2) Nucleophilic substitution reactions
 (3) Electrophilic substitution reactions
 (4) Electrophilic addition reactions

68. The reaction of ethanol on acetic anhydride is an example of :-

- (1) Nucleophilic addition
 (2) Nucleophilic substitution
 (3) Electrophilic addition
 (4) Free radical substitution

69. The reduction of acetamide gives :-

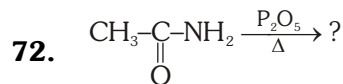
- (1) $\text{CH}_3\text{CH}_2\text{NH}_2$
- (2) $(\text{CH}_3)_2\text{CHNH}_2$
- (3) $(\text{CH}_3)_3\text{CNH}_2$
- (4) $(\text{CH}_3\text{CH}_2)_2\text{NH}$

70. Which is used in preparation of aldehyde by rosenmund reduction

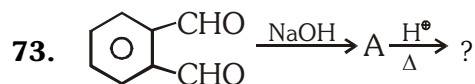
- (1) Ester
- (2) Acid
- (3) Acid halide
- (4) Alcohol

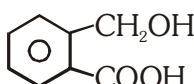
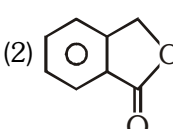
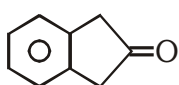
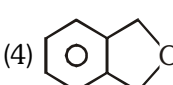
71. Which is maximum reactive :-

- (1) CH_3CONH_2
- (2) $\text{CH}_3\text{COOCH}_3$
- (3) CH_3COCl
- (4) $\text{CH}_3\text{COOC}_2\text{H}_5$



- (1) CH_3COOH
- (2) CH_3CN
- (3) CH_3CH_3
- (4) CH_3CHO



- (1) 
- (2) 
- (3) 
- (4) 

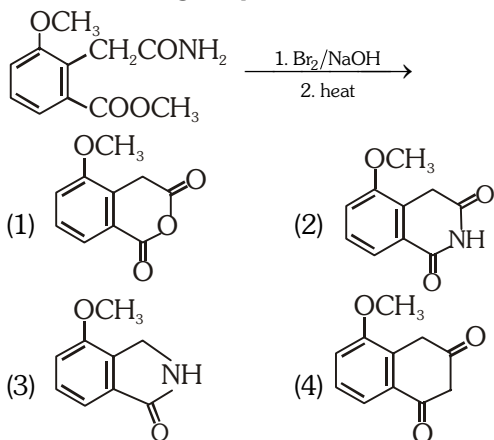
EXERCISE-I (Conceptual Questions)

ANSWER KEY

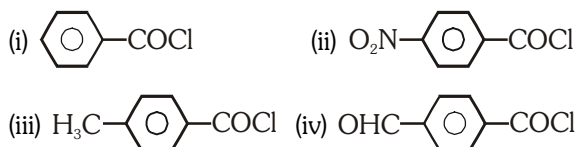
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	1	2	3	3	3	4	4	3	3	2	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	4	4	3	1	4	2	2	4	2	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	1	1	3	4	2	3	3	4	3	3	3	3	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	3	4	1	1	2	1	4	2	2	2	2	1	2	4
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73		
Ans.	1	2	1	1	2	2	2	2	1	3	3	2	2		

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIIMS 2006**

1. The following sequence of reactions gives

**AIPMT 2007**

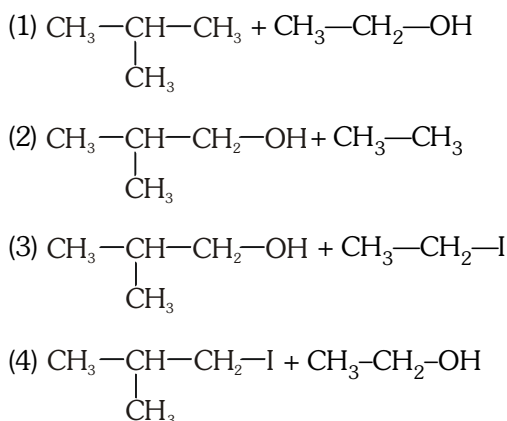
2. Consider the following compounds:



The correct order of reactivity towards hydrolysis is:-

- (1) (i) > (ii) > (iii) > (iv) (2) (iv) > (ii) > (i) > (iii)
 (3) (ii) > (iv) > (i) > (iii) (4) (ii) > (iv) > (iii) > (i)
3. Which one of the following on treatment with 50% aq. NaOH yields the corresponding alcohol and acid
- (1) C_6H_5CHO (2) $CH_3CH_2CH_2CHO$
 (3) CH_3COCH_3 (4) CH_3CHO

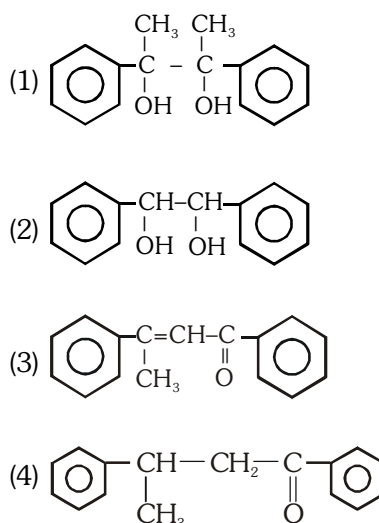
4. In the reaction : $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \longrightarrow \dots\dots\dots$
 which of following compounds will be formed :



5. The product formed in aldol reaction is :-
 (1) a β -hydroxy aldehyde or ketone
 (2) an α -hydroxy aldehyde or ketone
 (3) an α, β -unsaturated ester
 (4) a β -hydroxy acid

AIPMT 2008

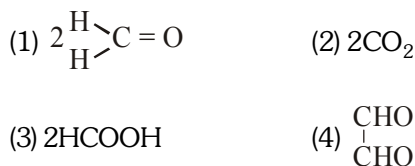
6. Acetophenone when reacted with a base, C_2H_5ONa , yields a stable compound which has the structure :-



7. A strong base can abstract an α -hydrogen from
 (1) Ketone (2) Alkane
 (3) Alkene (4) Amine

AIPMT 2009

8. $H_2COH.CH_2OH$ on heating with periodic acid gives :-

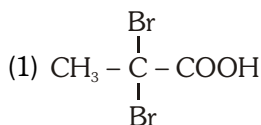


9. Consider the following reaction,
 ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{alc. KOH}$ Y
 (i) H_2SO_4 room temperature
 (ii) H_2O $\longrightarrow$ Z ;

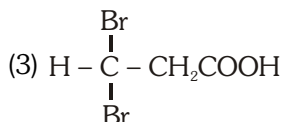
the product Z is :-

- (1) CH_3CH_2OH
 (2) $CH_2=CH_2$
 (3) $CH_3CH_2-O-CH_2-CH_3$
 (4) $CH_3-CH_2-O-SO_3H$

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

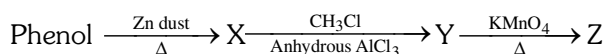


- (2) $\text{CH}_2\text{Br} - \text{CHBr} - \text{COOH}$



- (4) $\text{CH}_2\text{Br} - \text{CH}_2 - \text{COBr}$

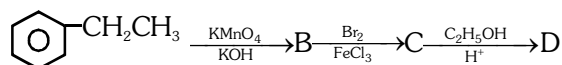
- 11.** Consider the following reaction :



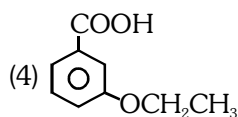
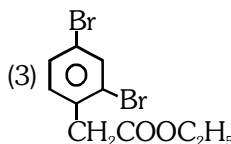
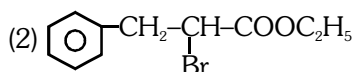
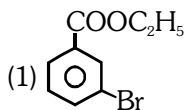
the product Z is :-

- (1) Benzene (2) Toluene
(3) Benzaldehyde (4) Benzoic acid

- 12.** In a set of reactions, ethyl benzene yielded a product D



'D' would be :-



AIPMT 2010

- 13.** Which of the following reactions will not result in the formation of carbon-carbon bonds?

- (1) Friedel-Crafts acylation
- (2) Reimer-Tieman reaction
- (3) Cannizzaro reaction
- (4) Wurtz reaction

- 14.** When glycerol is treated with excess of HI, it produces :-

- (1) allyl iodide
- (2) propene
- (3) glyceryl triiodide
- (4) 2-iodopropane

- 15.** Match the compounds given in List-I with their characteristic reactions given in List-II. Select the correct option.

List-I

Compounds

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 (b) $\text{CH}_3\text{C}\equiv\text{CH}$
 (c) $\text{CH}_3\text{CH}_2\text{COOCH}_3$
 (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

List-II

Reactions

- (i) Alkaline hydrolysis
- (ii) With KOH (alcohol) and CHCl_3 produces bad smell
- (iii) Gives white ppt. with ammonical AgNO_3
- (iv) With Lucas reagent cloudiness appears after 5 minutes

Options :

- | | (a) | (b) | (c) | (d) |
|-----|-------|-------|-------|-------|
| (1) | (iii) | (ii) | (i) | (iv) |
| (2) | (ii) | (iii) | (i) | (iv) |
| (3) | (iv) | (ii) | (iii) | (i) |
| (4) | (ii) | (i) | (iv) | (iii) |

AIIMS 2010

- 16.** The suitable reagent to convert $\text{CH}_3\text{-CH=CH-CHO}$ into $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$ is :-

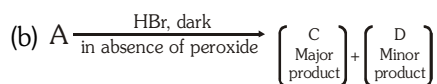
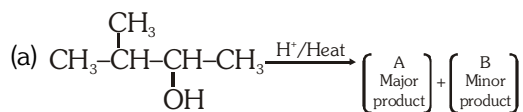
- (1) NaBH_4
- (2) LiAlH_4
- (3) Zn-Hg/HCl
- (4) H_2/Pd

17. $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{COOCH}_3 \xrightarrow{\text{NaBH}_4} :-$

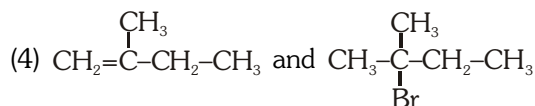
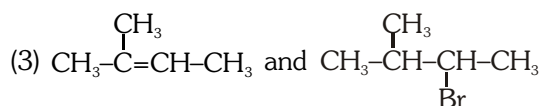
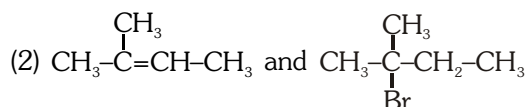
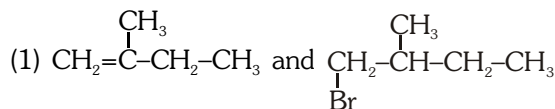
- (1) $\text{CH}_3\text{--}\underset{\text{OH}}{\text{CH}}\text{--CH}_2\text{COOCH}_3$
- (2) $\text{CH}_3\text{--}\underset{\text{OH}}{\text{CH}}\text{--CH}_2\text{--CH}_2\text{--OH}$
- (3) $\text{CH}_3\text{--}\underset{\text{O}}{\underset{\parallel}{\text{C}}}\text{--CH}_2\text{CH}_2\text{--OH}$
- (4) $\text{CH}_3\text{--}\underset{\text{OH}}{\text{CH}}\text{--CH}_2\text{COOH}$

AIPMT Pre. 2011

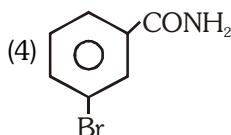
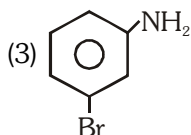
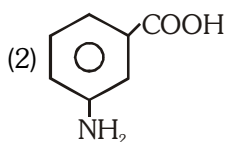
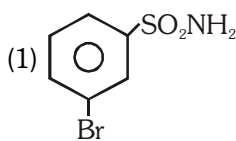
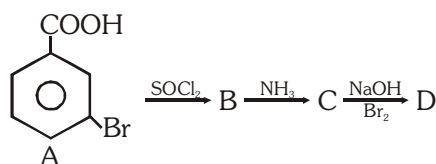
18. In the following reactions,



the major products (A) and (C) are respectively :-



19. In a set of reactions m-bromobenzoic acid gave a product D. Identify the product D



20. Clemmensen reduction of a ketone is carried out in the presence of which of the following ?

- (1) Glycol with KOH
- (2) Zn-Hg with HCl
- (3) LiAlH_4
- (4) H_2 and Pt as catalyst

AIPMT Mains 2011

21. 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 :-

- (1) $\text{CH}_3\text{CH}_2\text{COOH}$
- (2) CH_3COOH
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
- (4) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}\text{COOH}$

22. 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)
(1) (ii)	(i)	(iv)	(iii)
(2) (iv)	(i)	(iii)	(ii)
(3) (iv)	(ii)	(iii)	(i)
(4) (ii)	(iii)	(iv)	(i)

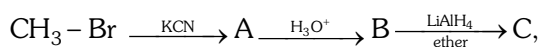
AIIMS 2011

23. Decarboxylation occurs with maximum rate in:

- (1) CH_3COOH
- (2) $\text{C}_6\text{H}_5-\text{COOH}$
- (3) $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
- (4) $\text{CH}_3\text{COCH}_2\text{COOH}$

AIPMT Pre. 2012

24. In the following sequence of reactions

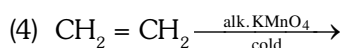
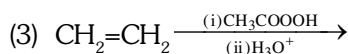
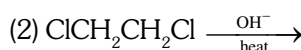
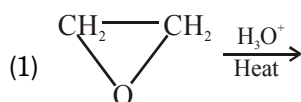
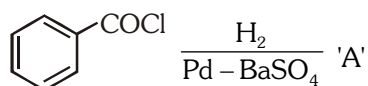


the end product (C) is:

- (1) Acetaldehyde
- (2) Ethyl alcohol
- (3) Acetone
- (4) Methane

O=Cc1ccccc1Cl

$\xrightarrow{50\% \text{ KOH}}$



33. Which of the following will not be soluble in sodium hydrogen carbonate?

- (1) 2, 4, 6-trinitrophenol
- (2) Benzoic acid
- (3) o-Nitrophenol
- (4) Benzenesulphonic acid

AIIMS 2014

34. Which of the following reagents cannot be used to prepare acetophenone :-

- (1) $C_6H_5COCl + (CH_3)_2Cd$
- (2) $C_6H_5COCl + CH_3MgBr$
- (3) $C_6H_5CN + C_2H_5MgBr$
- (4) $C_6H_6 + (CH_3CO)_2O/AlCl_3$

AIPMT 2015

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

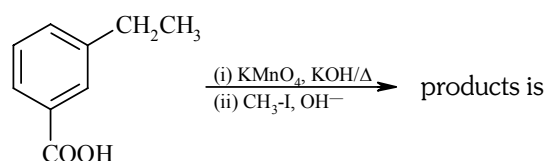
- (1) 2-pentanone
- (2) 3-pentanone
- (3) n-amyl alcohol
- (4) pentanal

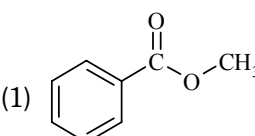
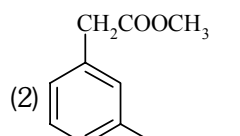
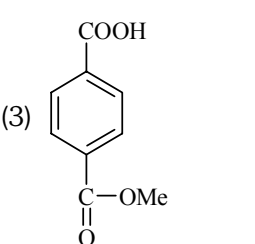
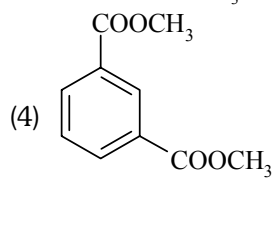
RE-AIPMT 2015

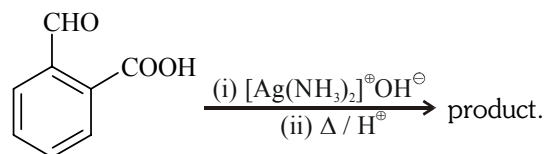
36. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group ?

- (1) $-CHCl_2$
- (2) $-CHO$
- (3) $-CH_2Cl$
- (4) $-COOH$

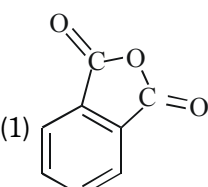
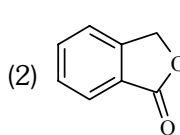
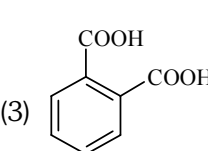
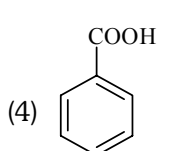
AIIMS 2015

37.  products is

- (1) 
- (2) 
- (3) 
- (4) 

38.  product.

Product of above reaction is

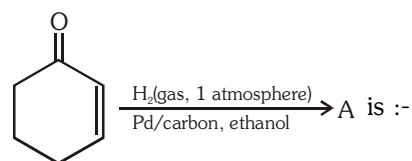
- (1) 
- (2) 
- (3) 
- (4) 

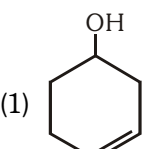
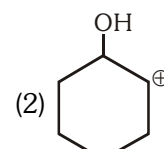
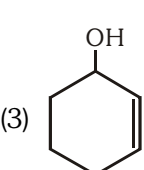
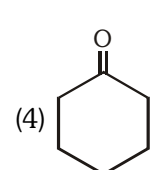
39. Correct order of boiling point is

- (i) $CH_3(CH_2)_3OH$
- (ii) $C_2H_5-O-C_2H_5$
- (iii) $CH_3-(CH_2)_3CH_3$
- (iv) $CH_3-(CH_2)_3-Cl$
- (1) i > iv > ii > iii
- (2) iii > ii > iv > i
- (3) i > ii > iii > iv
- (4) iv > iii > ii > i

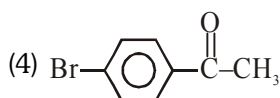
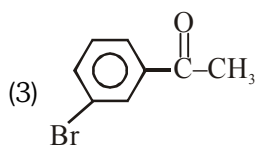
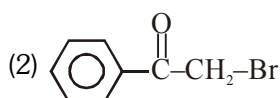
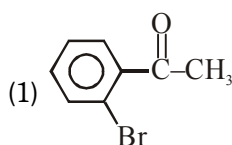
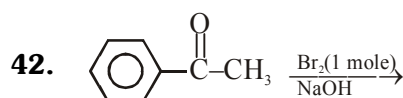
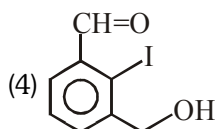
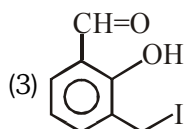
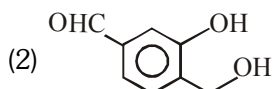
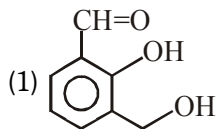
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40. The **correct** structure of the product A formed in the reaction

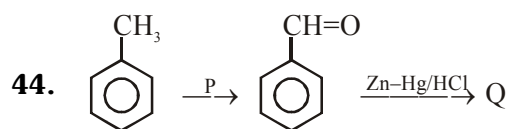
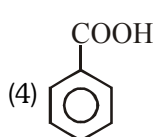
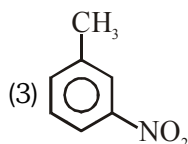
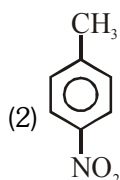
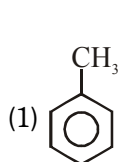
 A is :-

- (1) 
- (2) 
- (3) 
- (4) 

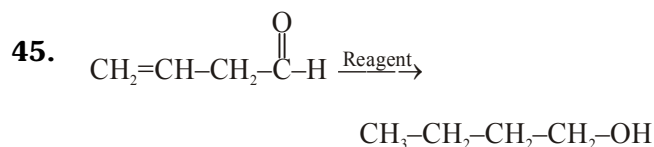
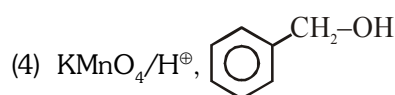
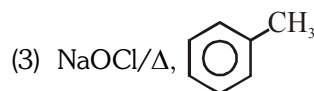
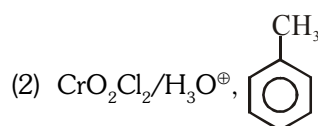
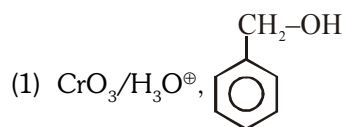
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43. The best starting substrate to prepare 2-Bromobenzoic acid.

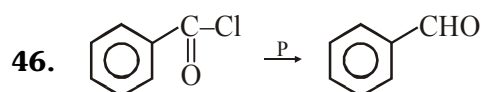


P & Q respectively are :-



Appropriate reagent for above conversion will be:-

- (1) Metal + H_2 (2) LiAlH_4
 (3) NaBH_4 (4) All



P will be :-

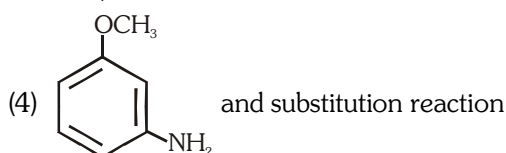
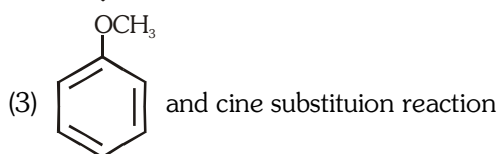
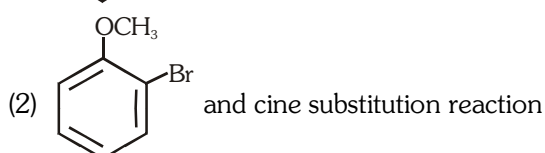
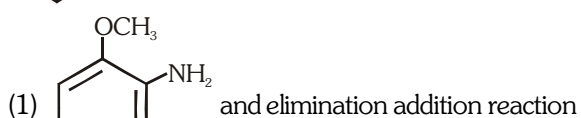
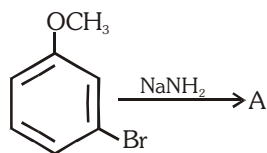
- (1) $\text{Pd}/\text{BaSO}_4 + \text{H}_2$ (2) LiAlH_4
 (3) NaBH_4 (4) $\text{Pd} + \text{H}_2$

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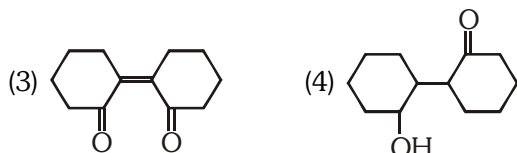
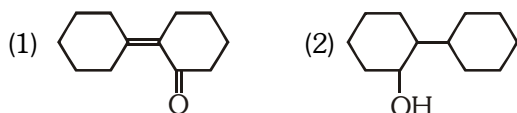
47. The heating of phenyl-methyl ethers with HI produces

- (1) iodobenzene
 (2) phenol
 (3) benzene
 (4) ethyl chlorides

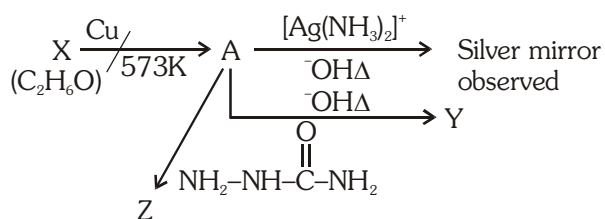
48. Identify A and predict the type of reaction



49. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating ?



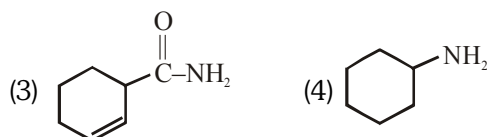
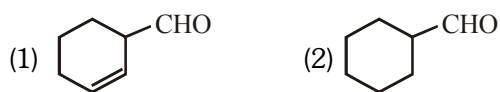
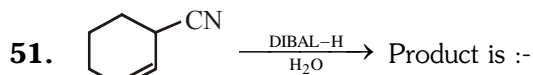
50. Consider the reactions :-



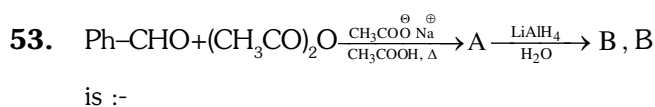
Identify A, X, Y and Z

- (1) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.
- (2) A-Ethanal, X-Ethanol, Y-But-2-enal, Z-Semicarbazone
- (3) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone
- (4) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine

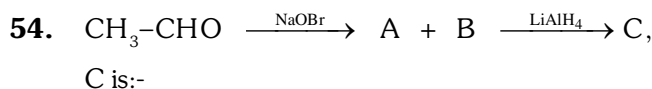
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52. Which of the following is the better reactant for the production of m-cresol.



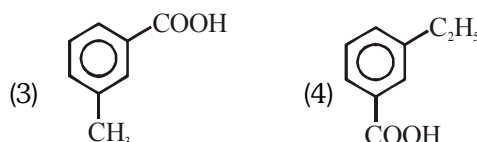
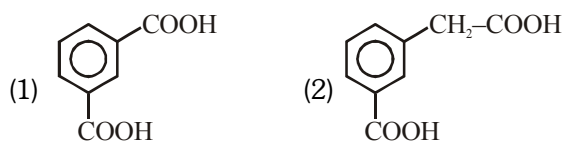
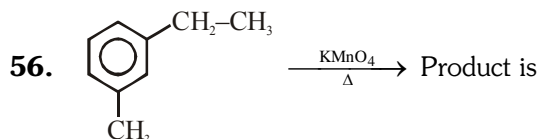
- (1) $\text{Ph-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
- (2) $\text{Ph-CH=CH-CH}_2\text{-OH}$
- (3) $\text{Ph-CH}_2\text{-CH}_2\text{-COOH}$
- (4) Ph-CH=CH-CHO



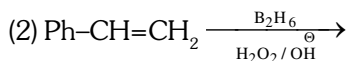
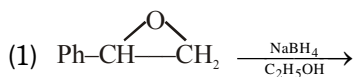
- (1) $\text{CH}_3\text{-OH}$ (2) CH_3CHO
- (3) HCHO (4) HCOOH

55. Reagent can not be used to convert alcohol into alkyl halide

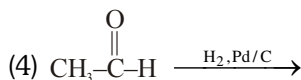
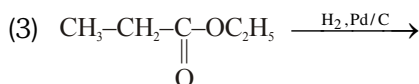
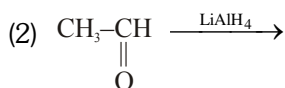
- (1) Red P/ Br_2 (2) KI / acetone
- (3) SOCl_2 (4) HCl/ZnCl_2



57. $\text{Ph-CH=CH}_2 \xrightarrow{\text{Reagent}} \text{Ph-CH}_2\text{-CH}_2\text{-OH}$
Which reagent is suitable for given conversion.



58. Which of the following cannot form ethanol ?



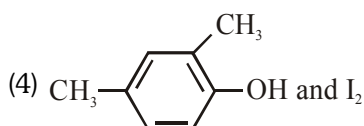
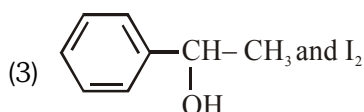
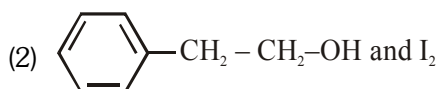
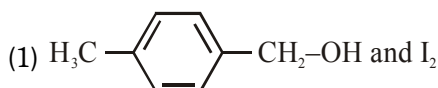
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59. Carboxylic acid have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

- (1) formation of intramolecular H-bonding
- (2) formation of carboxylate ion
- (3) more extensive association of carboxylic acid via van der Waals force of attraction
- (4) formation of intermolecular H-bonding.

60. Compound A, $\text{C}_8\text{H}_{10}\text{O}$, is found to react with NaOI (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell.

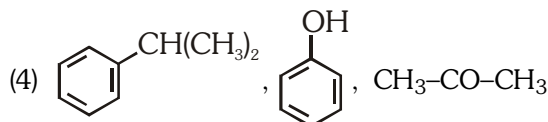
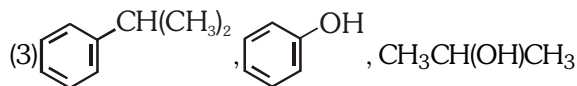
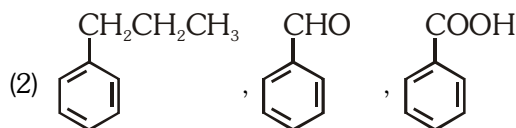
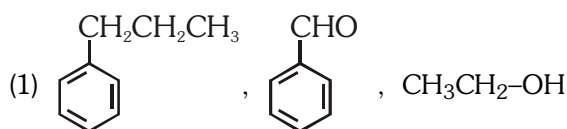
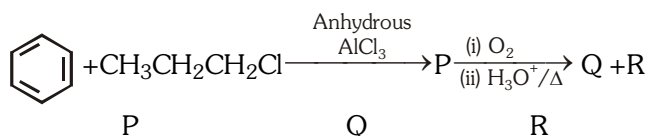
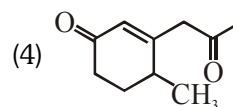
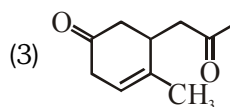
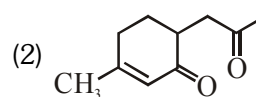
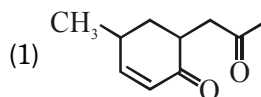
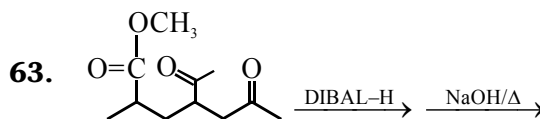
A and Y are respectively

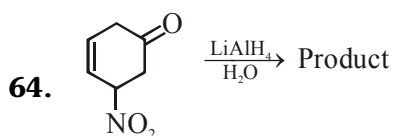


61. The compound A on treatment with Na gives B, and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order

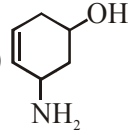
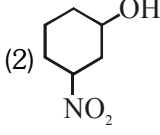
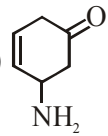
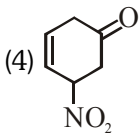
- (1) $\text{C}_2\text{H}_5\text{OH}$, C_2H_6 , $\text{C}_2\text{H}_5\text{Cl}$
- (2) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{ONa}$
- (3) $\text{C}_2\text{H}_5\text{Cl}$, C_2H_6 , $\text{C}_2\text{H}_5\text{OH}$
- (4) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_2\text{H}_5\text{Cl}$

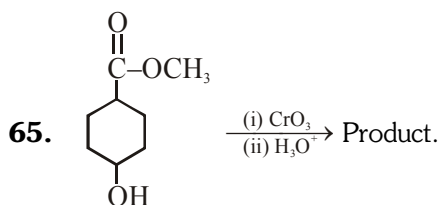
62. Identify the major products P, Q and R in the following sequence of reaction :

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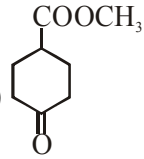
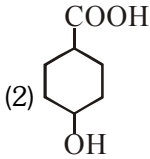
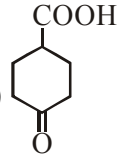
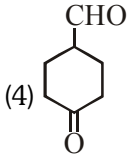


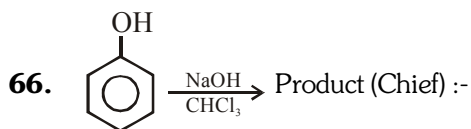
Product of the above reaction is

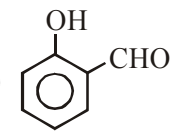
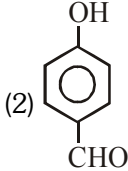
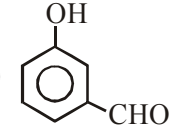
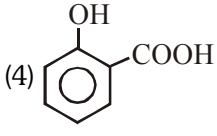
- (1)  (2) 
 (3)  (4) 

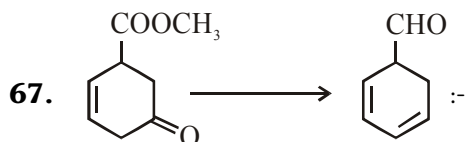


Product of reaction is :-

- (1)  (2) 
 (3)  (4) 

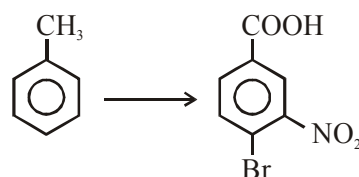


- (1)  (2) 
 (3)  (4) 

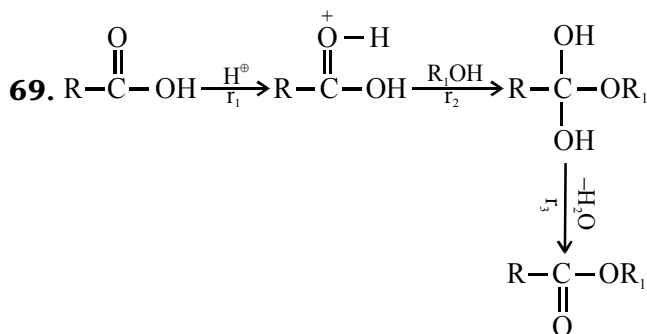


- (1) NaBH_4 , DIBAL-H, $\text{H}_3\text{O}^+/\Delta$
 (2) DIBAL-H, $\text{H}_3\text{O}^+/\Delta$, NaBH_4
 (3) B_2H_6 , NaBH_4 , $\text{H}_3\text{O}^+/\Delta$
 (4) $\text{H}_3\text{O}^+/\Delta$, DIBAL-H, NaBH_4

68. Correct sequence of reagents to get the given product-

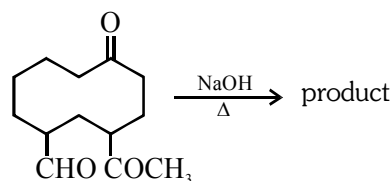


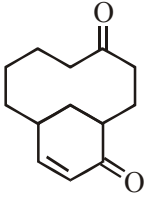
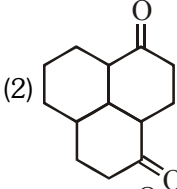
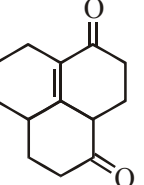
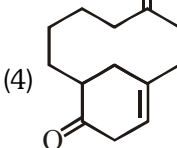
- (1) Br_2/Fe , $\text{HNO}_3/\text{H}_2\text{SO}_4$, KMnO_4/H^+
 (2) KMnO_4/H^+ , $\text{Br}_2/\text{FeBr}_3$, $\text{HNO}_3/\text{H}_2\text{SO}_4$
 (3) KMnO_4/H^+ , $\text{HNO}_3/\text{H}_2\text{SO}_4$, $\text{Br}_2/\text{FeBr}_3$
 (4) $\text{Br}_2/\text{FeBr}_3$, KMnO_4/H^+ , $\text{HNO}_3/\text{H}_2\text{SO}_4$

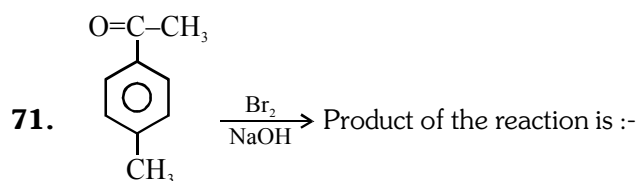


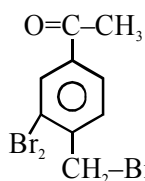
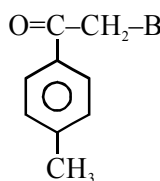
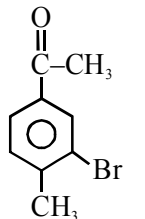
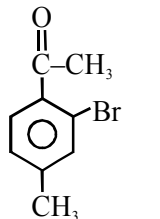
- (1) Fast, Slow, Fast (2) Slow, Fast, Fast
 (3) Fast, Fast, Slow (4) Slow, Fast, Slow

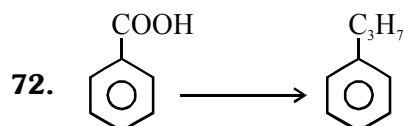
70. For the reaction :-



- (1)  (2) 
 (3)  (4) 

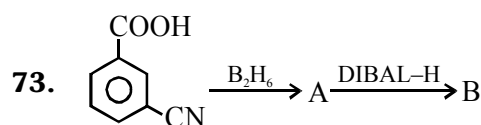


- (1)  (2) 
- (3)  (4) 

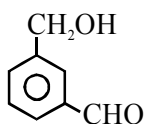
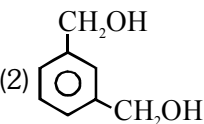
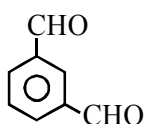
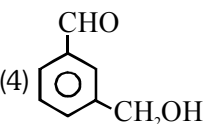


Select the correct sequence of reagents to carry out the above conversion :-

- (1) $\text{SOCl}_2, \text{Cd}(\text{C}_2\text{H}_5)_2, \text{NH}_2\text{-NH}_2/\text{OH}^\ominus$
 (2) $\text{SOCl}_2, \text{C}_2\text{H}_5\text{MgBr}, \text{Zn-Hg/HCl}$
 (3) $\text{SOCl}_2, \text{CH}_3\text{-Li}, \text{NH}_2\text{-NH}_2/\text{OH}^\ominus$
 (4) $\text{Cd}(\text{CH}_3)_2, \text{SOCl}_2, \text{NH}_2\text{-NH}_2/\text{OH}^\ominus$



The product 'B' is :-

- (1)  (2) 
- (3)  (4) 

EXERCISE-II (Previous Year Questions)

ANSWER KEY

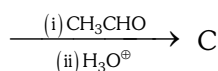
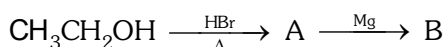
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	1	3	1	3	1	1	1	1	4	1	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	1	2	3	2	1	1	4	2	1	4	3	1	3	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	2	3	3	2	2	4	1	1	4	1	2	2	2	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	2	4	1	2	1	1	1	1	2	1	2	1	4	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73		
Ans.	4	4	1	1	3	1	1	1	1	1	2	1	1		

EXERCISE-III (Analytical Questions)

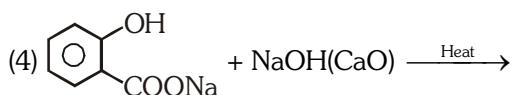
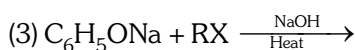
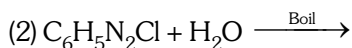
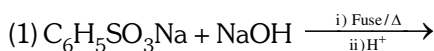
- Methanol can be distinguished from ethanol by the following except
 (1) Reaction with iodine and alkali
 (2) Reaction with salicylic acid and H_2SO_4
 (3) Reaction with Lucas reagent
 (4) Boiling point

- Ethanol on heating with acetic acid in the presence of a few drops of sulphuric acid gives the smell of
 (1) Oil of wintergreen (2) Oil of mustard
 (3) An ester (4) Oil of bitter almonds

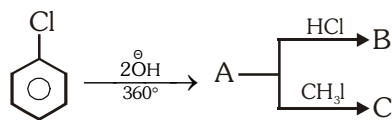
- The compounds A, B and C in the reaction sequence are given by the set :-



- (1) $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{MgBr}$, $(\text{CH}_3)_3\text{C}-\text{OH}$
 (2) $\text{CH}_3\text{CH}_2\text{Br}$, $(\text{CH}_3\text{CH}_2)_2\text{Mg}$, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
 (3) $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{MgBr}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (4) CH_3CHBr_2 , $\text{CH}_3\text{CH}(\text{MgBr})_2$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- Which of the following reactions will not lead to a phenol :-

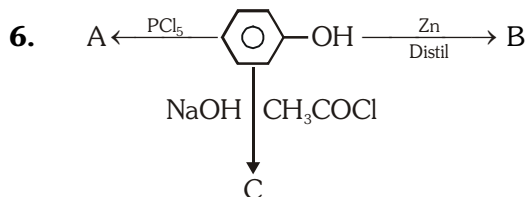


- The structures of the compounds / ions A, B and C in the reaction sequence are given by the set :-



- (1) $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_3$
 (2) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{OCH}_3$
 (3) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{I}$
 (4) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{I}$

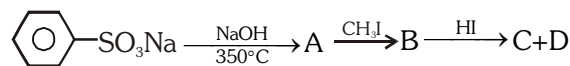
Check Your Understanding



The compounds A, B and C in the above reaction sequence are :-

- (1) Chlorobenzene, benzene, methyl benzoate
 (2) Triphenyl phosphate, benzene, phenyl acetate
 (3) Benzyl chloride, benzene, phenyl acetate
 (4) Benzyl chloride, benzene, phenylacetyl chloride

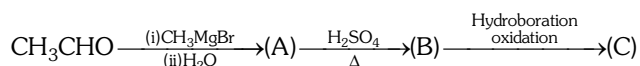
- In the reaction sequence —



A, B, C and D are given by the set :-

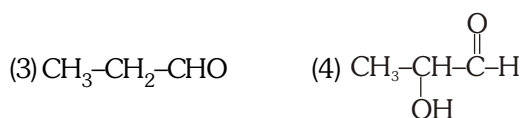
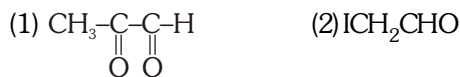
- (1) Sodium phenate, anisole, $\text{C}_6\text{H}_5\text{I}$, CH_3OH
 (2) Sodium phenate, phenetole, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{OH}$
 (3) Sodium phenate, anisole, $\text{C}_6\text{H}_5\text{OH}$, CH_3I
 (4) Sodium phenate, phenetole, $\text{C}_6\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{OH}$

- Compound A and C in the following reaction are



- (1) Identical (2) Functional isomer
 (3) Positional isomer (4) Optical isomer

- Which of the following aldehydes does not form iodoform on heating with iodine and alkali :-



- A carbonyl compound gives pink colour with Schiff's reagent and a yellow precipitate when boiled with iodine and caustic alkali. It also gives a red precipitate with Fehling's solution. It is likely to be:-
 (1) Formaldehyde (2) Propionaldehyde
 (3) Acetaldehyde (4) Crotonaldehyde

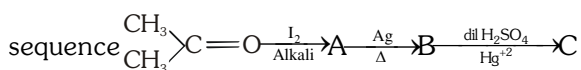
11. A carbonyl compound gives a positive iodoform test but does not reduce Tollen's reagent or Fehling's solution. It forms a cyanohydrin with HCN, which on hydrolysis gives a hydroxy acid with a methyl side chain. The compound is :-

- (1) Acetaldehyde
- (2) Propionaldehyde
- (3) Acetone
- (4) Crotonaldehyde

12. Which of the following statement is wrong :-

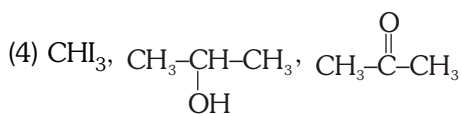
- (1) All methyl ketones give a positive iodoform test
- (2) Acetaldehyde is the only aldehyde that gives iodoform test
- (3) All secondary alcohols give positive iodoform test
- (4) Any alcohol that can be oxidised to an acetyl group gives a positive iodoform test

13. The compounds A, B and C in the reaction

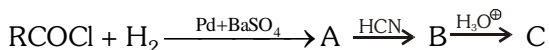


are given by the set :-

- (1) CHI_3 , $\text{H}_2\text{C}=\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{-OH}$
- (2) CHI_3 , $\text{HC}\equiv\text{CH}$, CH_3CHO
- (3) CHI_3 , $\text{CH}_3\text{-C}\equiv\text{CH}$, CH_3COCH_3



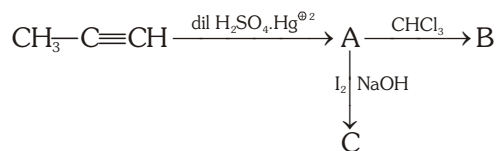
14. In the reaction sequence



A, B and C are given by the set :-

- (1) RCHO , $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{CH}_2\text{NH}_2$
- (2) RCHO , $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{COOH}$
- (3) RCHO , $\text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$
- (4) RCHO , $\text{R-CH}_2\text{-CN}$, $\text{R-CH}_2\text{-COOH}$

15. In the reaction sequence



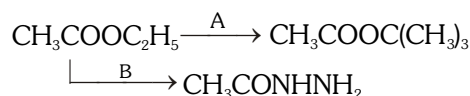
A, B and C are given by the set :-

- (1) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, CHI_3
- (2) CH_3COCH_3 , $\text{CCl}_3\text{-C}(=\text{O})\text{-CH}_3$, CHI_3
- (3) CH_3COCH_3 , $\text{CCl}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, CHI_3
- (4) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CCl}_3\text{-CH}(\text{OH})\text{-CH}_2\text{-CH}_3$, CHI_3

16. Match the reactions given in column-I with the suitable reagent given in column-II

Column-I	Column-II
(i) Benzophenone → Diphenylmethane	(a) LiAlH_4
(ii) Benzaldehyde → 1-Phenyl ethanol	(b) Dibal-H
(iii) Cyclohexanone → Cyclohexanol	(c) Zn(Hg)/conc. HCl
(iv) Phenylbenzoate → Benzaldehyde	(d) CH_3MgBr
(1) (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)	
(2) (i)-(c), (ii)-(d), (iii)-(b), (iv)-(a)	
(3) (i)-(d), (ii)-(c), (iii)-(a), (iv)-(b)	
(4) (i)-(d), (ii)-(a), (iii)-(c), (iv)-(b)	

17. The reagents A and B in the reaction sequence



are given by the set :-

- (1) $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$, $\text{H}_2\text{N-NH}_2$
- (2) $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$, $\text{H}_2\text{N-OH}$
- (3) $\text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, $\text{H}_2\text{N-NH}_2$
- (4) $\text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, $\text{H}_2\text{N-OH}$

18. Methyl amine reacts with acetyl chloride and forms :-

- (1) CH_3NH_2
- (2) CH_3NHNa
- (3) $\text{CH}_3\text{NHCOCH}_3$
- (4) $(\text{CH}_3)_2\text{NCOCH}_3$

19. Intermediates formed during reaction of



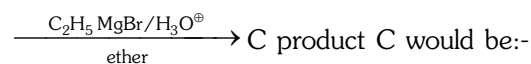
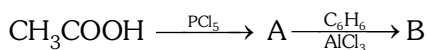
- (1) RCONHBr and RNCO
- (2) RNHCOBr and RNCO
- (3) $\text{RNH}-\text{Br}$ and RCONHBr
- (4) RCONBr_2

20. $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaCN}} \text{X} \xrightarrow{\text{Ni}/\text{H}_2} \text{Y} \xrightarrow{\text{Acetic anhydride}} \text{Z}$

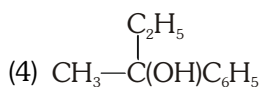
Z in the above reaction sequence is :-

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCOCH}_3$
- (2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONHCH}_3$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONHCOCH}_3$

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



- (1) $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$
- (2) $\text{CH}_3\text{COC}_6\text{H}_5$
- (3) $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$



22. CH_3CHO and CH_3COCH_3 can not be distinguished by :-

- (1) Fehling solution
- (2) Grignard reagent
- (3) Schiff's reagent
- (4) Tollen's reagent

23. When propan-1-ol is dehydrated, the product obtained is again hydrated and further oxidised to form a compound. The compound is -

- (1) $\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$
- (2) $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$
- (3) $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$
- (4) $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$

24. $\text{CH}_3\text{CH}_2\text{CH}_2-\text{C}\equiv\text{N} \xrightarrow{\text{H}_3\text{O}^+} \text{A} \xrightarrow[\Delta]{\text{NH}_3} \text{B}$

Product 'B' is :-

- (1) $\text{CH}_3-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$
- (2) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NC}$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$

25. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is :-

- (1) Ethyl chloride
- (2) Ethyl ethanoate
- (3) Diethyl ether
- (4) 2-Butanone

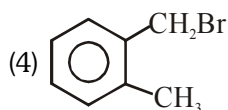
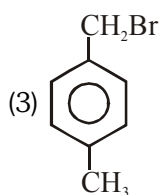
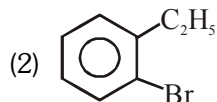
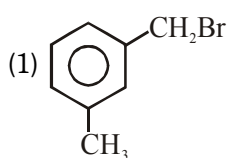
26. Phenol is heated with a solution of mixture of KBr and KBrO_3 . The major product obtained in the above reaction is :-

- (1) 4-Bromophenol
- (2) 2,4,6-Tribromophenol
- (3) 2-Bromophenol
- (4) 3-Bromophenol

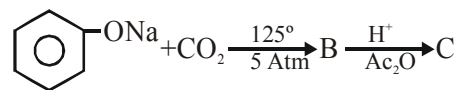
27. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is:-

- (1) 2,2,2-Trichloropropanol
- (2) Chloroform
- (3) 2,2,2-Trichloroethanol
- (4) Trichloromethanol

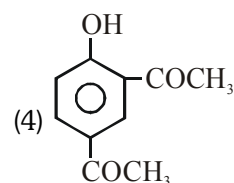
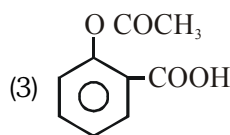
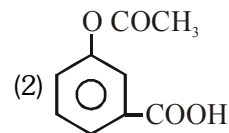
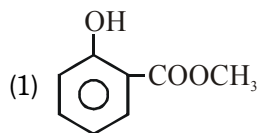
28. Compound (A), C_8H_9Br , gives a yellow precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A):



29. Sodium phenoxide when heated with CO_2 under pressure at $125^\circ C$ yields a product which on acetylation produces C



The major product C would be :



EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	3	3	2	2	3	3	3	3	3	3	2	2	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	1	3	3	1	1	4	2	2	4	2	2	3	4	3	

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** Chlorobenzene and benzyl chloride can be distinguished by treatment with AgNO_3 .
Reason :- Chlorobenzene does not give white ppt with AgNO_3 due to resonance.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzyl alcohol turns blue litmus red.
Reason :- Benzyl alcohol is not an isomer of p-cresol.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenol is stronger acid than alcohols.
Reason :- Phenol is stabilized by resonance whereas alcohols are not.
 (1) A (2) B (3) C (4) D
- Assertion :-** Addition of CH_3OH to phenyl magnesium bromide gives benzene.
Reason :- CH_3OH is a stronger acid than benzene.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ethers behave as bases in the presence of mineral acids.
Reason :- Ethers have lone pairs of electrons on oxygen.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenols give o- and p-Nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.
Reason :- -OH group in phenol shows -M effect.
 (1) A (2) B (3) C (4) D
- Assertion :-** Formic acid is a stronger acid than benzoic acid.
Reason :- pK_a of formic acid is higher than that of benzoic acid.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ketones on reaction with Grignard reagents, followed by hydrolysis yield tertiary alcohols.
Reason :- All ketones show haloform reaction.
 (1) A (2) B (3) C (4) D
- Assertion :-** $>\text{C}=\text{O}$ group is present both in aldehydes and acid derivatives.
Reason :- Aldehydes give nucleophilic addition across $>\text{C}=\text{O}$ bond but acid derivatives do not exhibit such reactions.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzamide and methyl benzoate are derivatives of benzoic acid.
Reason :- Benzamide is less easily hydrolysed as compared to methyl benzoate.
 (1) A (2) B (3) C (4) D
- Assertion :-** Dehydration of alcohols always takes place in basic medium.
Reason :- OH^- is a good leaving group
 (1) A (2) B (3) C (4) D
- Assertion :-** Acetamide on reaction with KOH and bromine gives acetic acid.
Reason :- Bromine catalyses hydrolysis of acetamide.
 (1) A (2) B (3) C (4) D
- Assertion :-** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason :- Benzaldehyde is a stronger electrophile than acetaldehyde.
 (1) A (2) B (3) C (4) D

14. Assertion :- Acetophenone shows aldol condensation.

Reason :- Acetophenone contains carbonyl group.

(1) A (2) B (3) C (4) D

15. Assertion :- Benzyl phenyl ether forms phenol and benzyl iodide with HI

Reason :- Because benzyl carbocations is more stable than phenyl carbocation.

(1) A (2) B (3) C (4) D

16. Assertion :- m-Nitrophenol is less acidic than p-nitrophenol.

Reason :- p-Nitrophenol has intermolecular-H-bonding.

(1) A (2) B (3) C (4) D

17. Assertion :- Benzene sulphonic acid on heating with NaOH gives phenoxide.

Reason :- Sulphonic group is a poor leaving group.

(1) A (2) B (3) C (4) D

18. Assertion :- Acetamide on reaction with Br_2/NaOH give $\text{CH}_3\text{-NH}_2$.

Reason :- Carbon of amide functional group becomes part of Na_2CO_3 .

(1) A (2) B (3) C (4) D

19. Assertion :- $\text{Ph-O-C}_2\text{H}_5$ can be prepared from PhONa and ethyl iodide.

Reason :- Aryl halides are less reactive substrates for nucleophilic substitution reaction.

(1) A (2) B (3) C (4) D

20. Assertion :- $\text{C}_6\text{H}_5\text{CH(OH)CH}_3$ gives benzoic acid with NaOBr followed by hydrolysis.

Reason :- First dehydration occur then oxidation

(1) A (2) B (3) C (4) D

21. Assertion :- Ethyl acetoacetate forms butane-1,4-diol with NaBH_4 .

Reason :- NaBH_4 can reduces ketone and esters group.

(1) A (2) B (3) C (4) D

22. Assertion :- Methoxy ethane has less boiling point than propanol.

Reason :- Methoxy ethane is more polar than propanol.

(1) A (2) B (3) C (4) D

23. Assertion :- Isopropyl benzene reacts with O_2 and acid gives phenol.

Reason :- Initially isopropyl benzene converts into 2-phenyl propan-2-ol.

(1) A (2) B (3) C (4) D

24. Assertion :- Benzaldehyde with alkaline CuSO_4 gives red-brown precipitate.

Reason :- Red precipitate is due to Cu_2O .

(1) A (2) B (3) C (4) D

25. Assertion :- Methoxy ethane has more boiling point than propanol.

Reason :- Attraction is more in methoxy ethane than propanol.

(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	4	2	1	1	4	3	3	2	2	4	4	3	2	1
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	2	3	1	1	3	4	3	3	4	4					