

# Organic compounds containing Oxygen

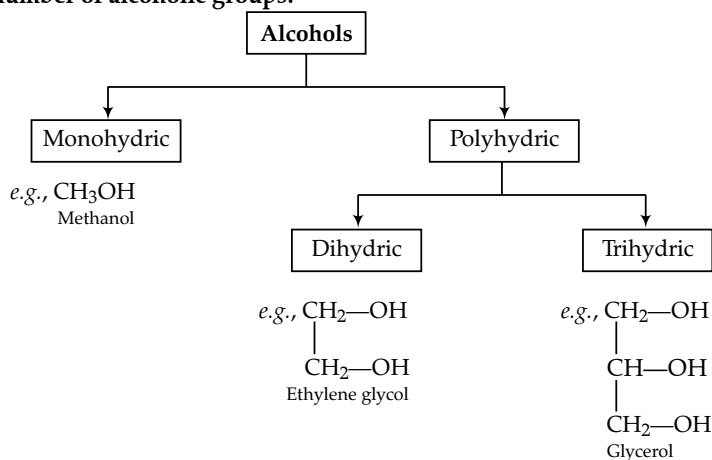
## Topic 1 Alcohols

### Revision Notes

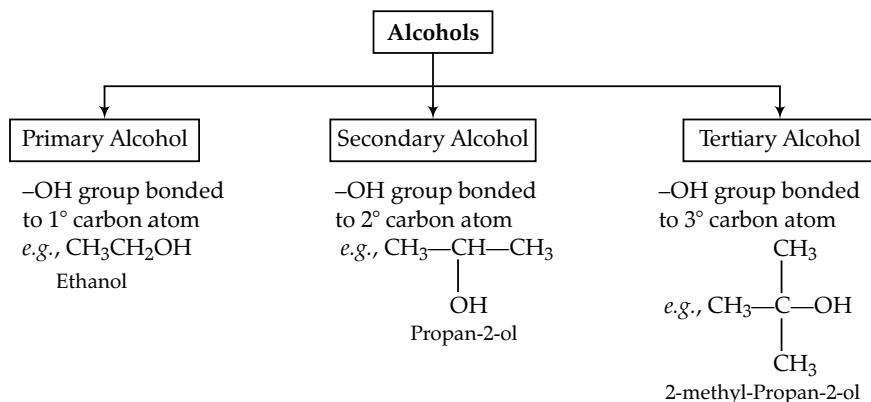
► **Alcohols:** When one hydrogen in alkane is replaced by hydroxyl group to give compound of general formula  $C_nH_{2n+1}OH$  is called alcohol.

► **Classification of Alcohols:**

On the basis of number of alcoholic groups:



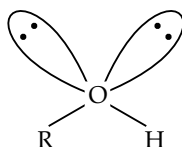
On the basis of alcoholic group attached to which type of carbon:



► **Nomenclature:** In common system → Alkyl alcohol  
In IUPAC system → Alkanol

| Formula  | Common Name              | IUPAC Name              |
|--|--------------------------|-------------------------|
| CH <sub>3</sub> CH <sub>2</sub> OH   | Ethyl alcohol            | Ethanol                 |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH   | <i>n</i> -Propyl alcohol | Propan-1-ol             |
| CH <sub>3</sub> CHOHCH <sub>3</sub>  | Iso-propyl alcohol       | Propan-2-ol             |
| CH <sub>3</sub> CH <sub>2</sub> CHOHCH <sub>3</sub>  | Sec-Butyl alcohol        | Butan-2-ol              |
| (CH <sub>3</sub> ) <sub>3</sub> C—OH   | Tert. Butyl alcohol      | 2-Methyl propan-2-ol    |
| $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$                                   | Ethylene glycol          | Ethane-1, 2-diol        |
| $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$ | Glycerol or Glycerine    | Propane, 1, 2, 3 -triol |

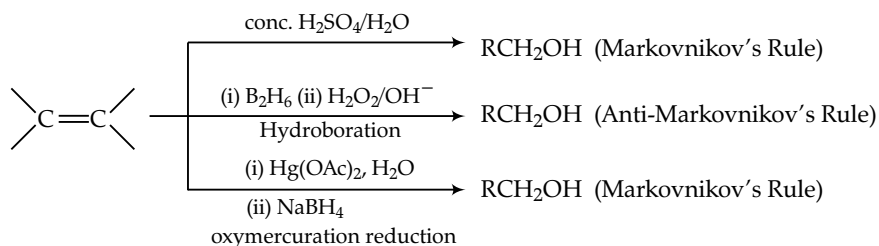
► **Structure:** Oxygen atom of hydroxyl group is attached to alkyl group. As oxygen atom contains two lone pairs of electrons along with two bond pairs of electrons, thus its structure is as follows:



#### ► Method of preparation

**From haloalkanes:**  $\text{R-X} + \text{KOH}_{(aq)} \longrightarrow \text{ROH} + \text{KX}$

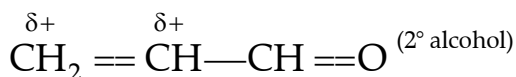
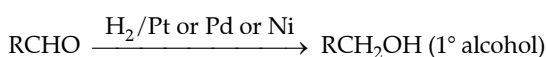
**From alkenes:**



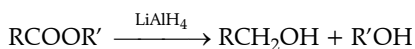
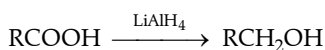
**From Grignard reagent:**



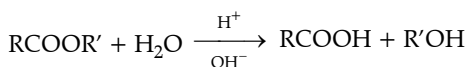
**From reduction of aldehydes and ketones:**



**By reduction of carboxylic acid and ester:**



**Hydrolysis of ester:**

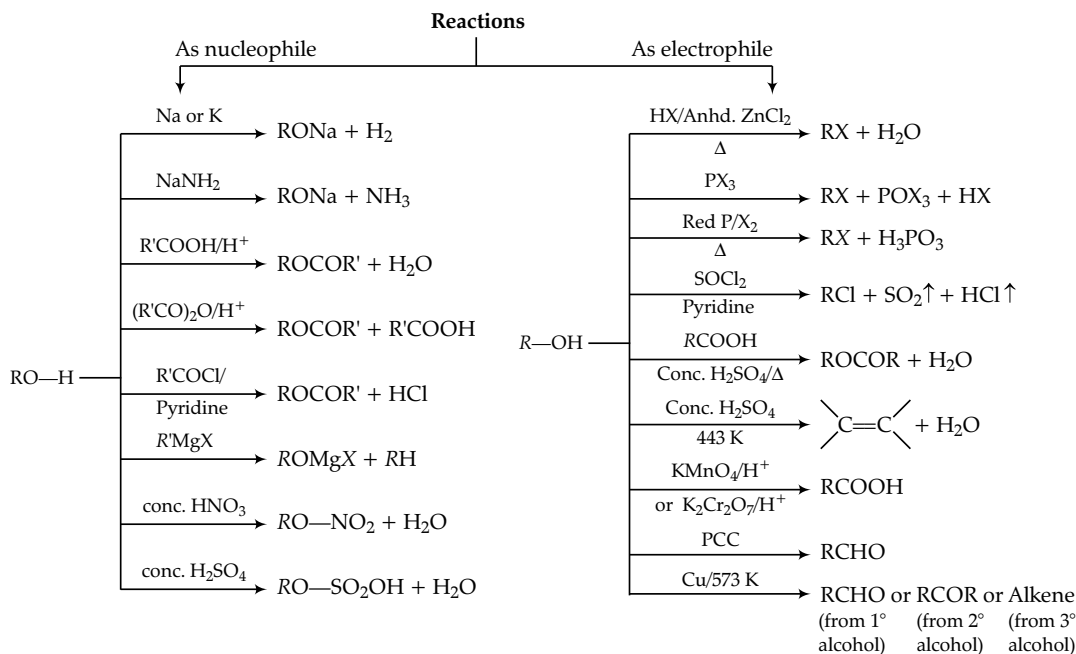


► **Properties of alcohols:** They are colourless and exist as liquid for lower order alcohols while high order alcohols exist as colourless waxy solids.

- They are soluble in water due to hydrogen bonding. Solubility decreases with increase in size of alkyl group and increases with increase in branching.

- Their boiling point increases with increase in size of alkyl group due to van der Waal's interactions and decreases with increase in branching.

► **Reactions:** They act as a nucleophile (RO<sup>-</sup>) when O—H bond is broken and act as an electrophile (R<sup>+</sup>) when C—O bond is broken.



►► **Identification of primary, secondary, and tertiary alcohols:**

**Lucas:** Lucas reagent is the solution of conc. HCl with anhydrous ZnCl<sub>2</sub>.

1° alcohol gives no cloudiness with Lucas reagent.

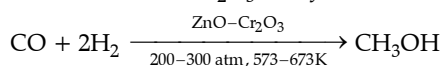
2° alcohol gives no cloudiness in 5 minutes with Lucas reagent.

3° alcohol gives no cloudiness immediately with Lucas reagent.

**Commercial Alcohols**

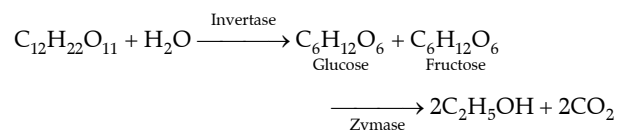
►► Some commercially important alcohols are methanol (wood spirit) and ethanol.

• Methanol is produced by catalytic hydrogenation of CO in presence of ZnO – Cr<sub>2</sub>O<sub>3</sub> catalyst.



It is highly poisonous and used as solvent in paints and varnishes.

• Ethanol is produced by fermentation of sugar.



It is used as solvent in paints and used in preparation of carbon compounds.

►► **Differentiation between methanol and ethanol:**

• **Iodoform Test:** On heating with I<sub>2</sub> and NaOH, methanol gives no reaction but ethanol gives yellow precipitate of iodoform, CHI<sub>3</sub>.

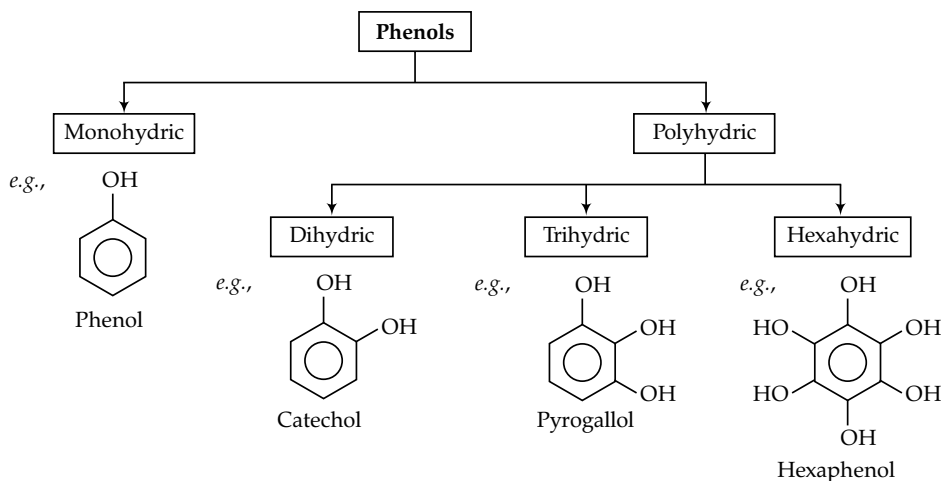
• On heating with salicylic acid and conc. H<sub>2</sub>SO<sub>4</sub>, methanol forms methyl salicylate which has characteristic odour while ethanol gives no specific odour.

## Topic 2 Phenols

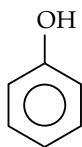
### Revision Notes

►► **Phenols:** Compounds in which hydroxy group is directly bonded to aromatic ring.

►► **Classification:** They are classified as mono and polyhydric phenols.

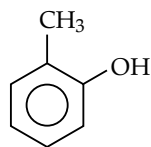


## ► Nomenclature:



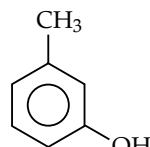
Common Name : Phenol

IUPAC : Phenol



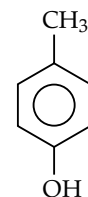
o-cresol

2-methylphenol



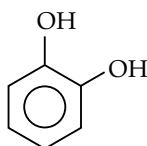
m-Cresol

3-methylphenol



p-cresol

4-methylphenol

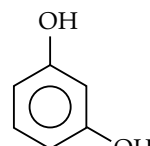


Common Name :

Catechol

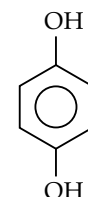
IUPAC :

Benzene-1,2-diol



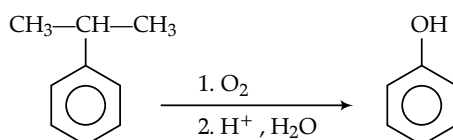
Resorcinol

Benzene-1,3-diol

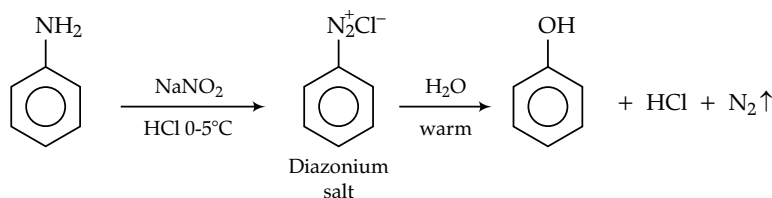

 Hydroquinone  
or quinol  
Benzene-1,4-diol

## ► General method of preparation:

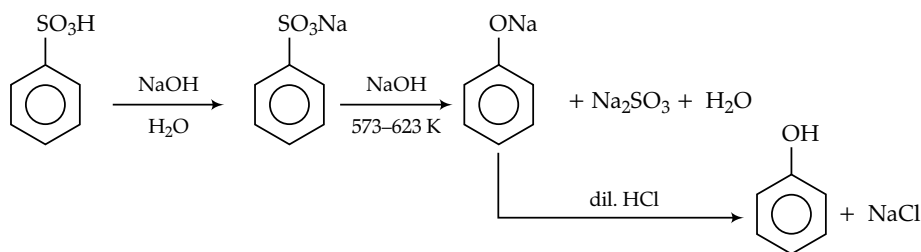
## • From cumene:



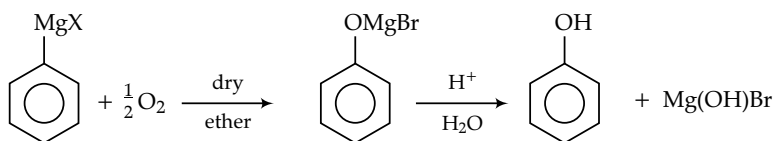
## • From diazonium salts:



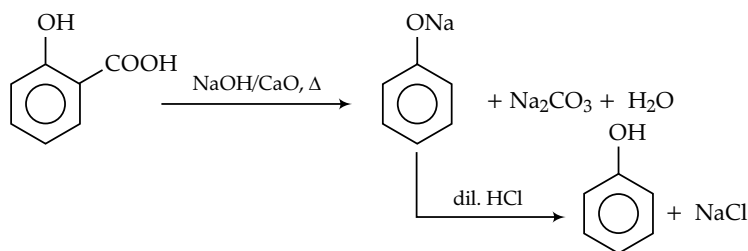
## • From benzenesulphonic acid:



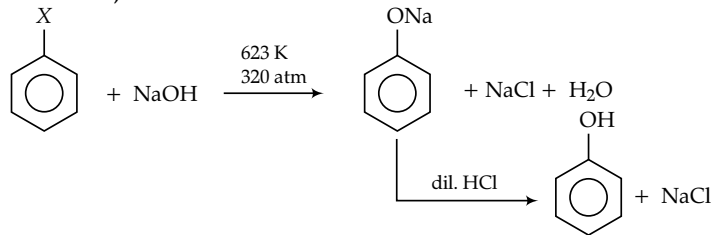
## • From phenyl magnesium bromide (Grignard reagent):



## • From salicylic acid:



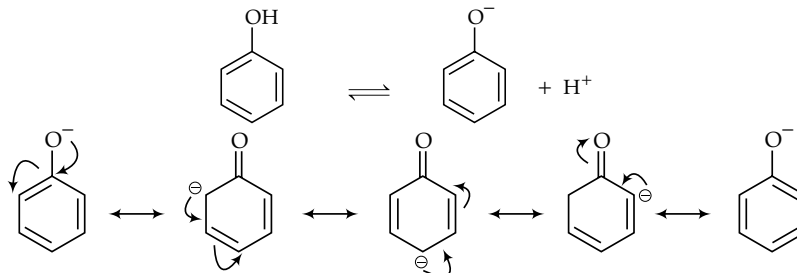
• From haloarenes (Dow's Process):



► **Properties:** Colourless, crystalline, characteristic odour, higher boiling point than their corresponding aromatic hydrocarbon and haloarenes due to hydrogen bonding. Soluble in water due to hydrogen bonding but solubility is less than the alcohols due to large hydrocarbon ring.

► **Chemical Reactions:**

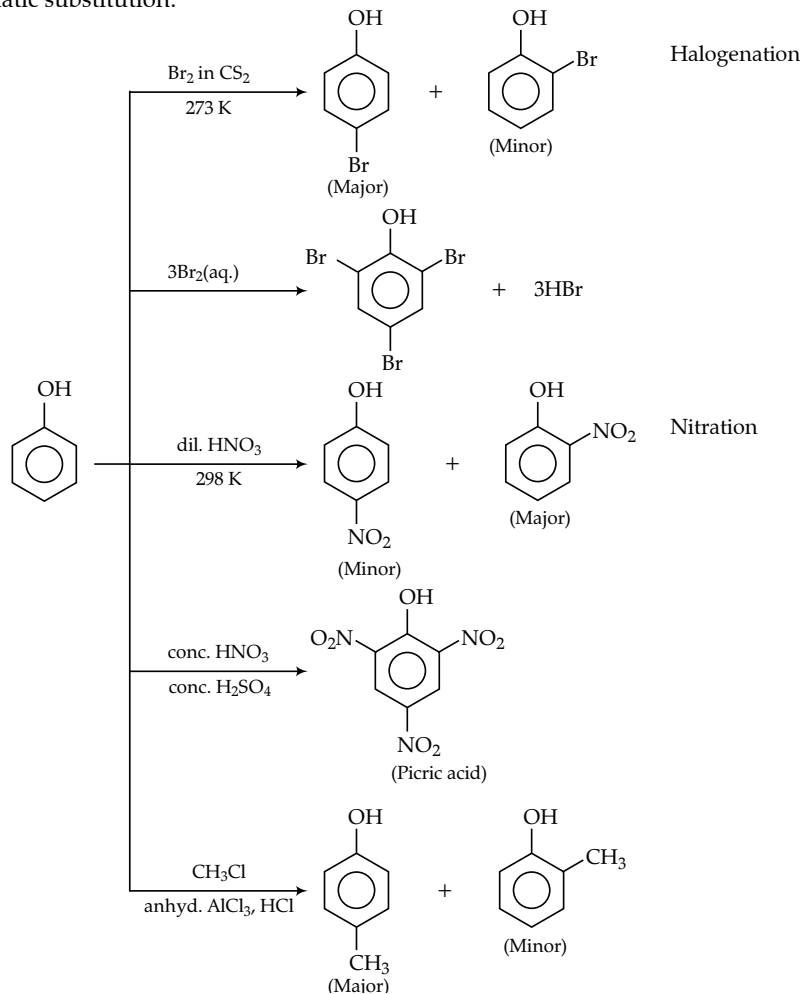
• **Acidic nature of phenol:** Phenol is acidic in nature due to resonance stabilisation of its conjugate base *i.e.*, phenoxide ion.



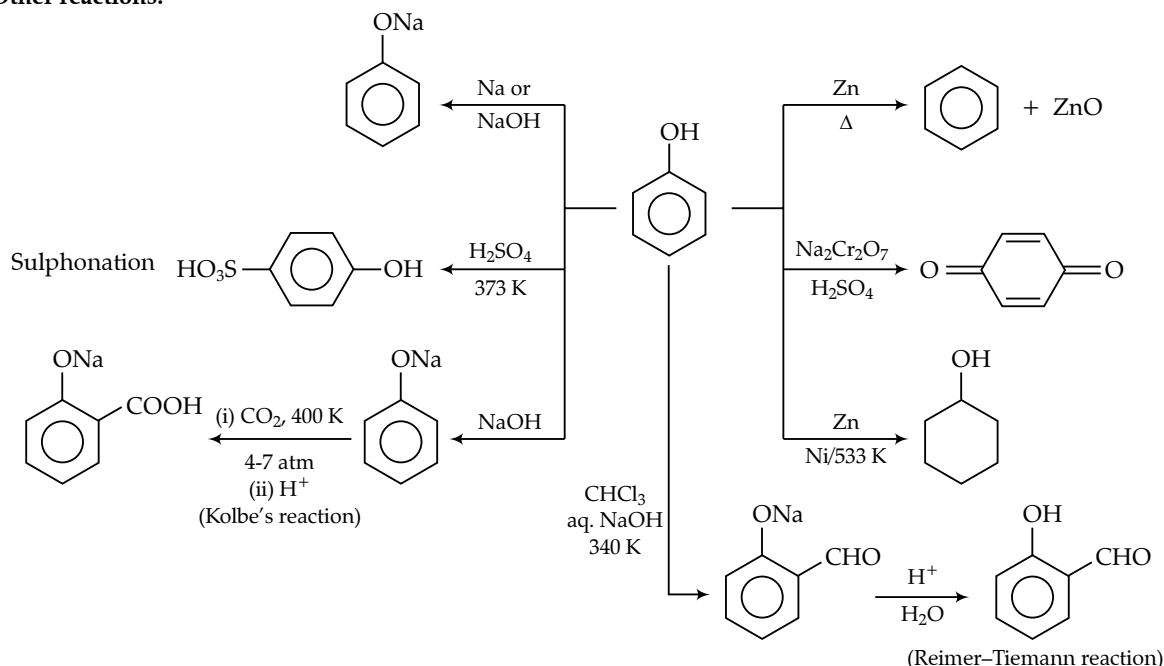
Though phenol is also resonance stabilised but in phenol there is charge separation takes place and positive charge occurs on electronegative atom, oxygen. This makes it less stable than phenoxide ion.

Electron donating group as a substituent in phenol increase the negative charge on phenoxide ion thus, destabilise it and this results in decrease in acidity of phenol. While electron withdrawing group increases the acidity of phenol.

• Electrophilic aromatic substitution.



## • Other reactions:



## Topic 3 Ethers

### Revision Notes

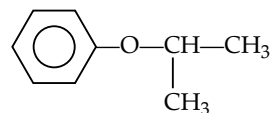
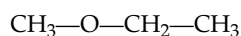
**▶ Ethers:** Compounds having general formula R—O—R' when, R and R' are same then it is symmetrical ether, otherwise it is unsymmetrical ether.

**▶ Nomenclature:**

**• Common system:** Alkyl groups are written alphabetically followed by word ether.

**• IUPAC system:** It is written as alkoxyalkane. The larger alkyl group attached to oxygen is taken as parent chain while group is written as alkoxy part of ether.

e.g.,



**Common Name :** Ethyl methyl ether  
**IUPAC :** Methoxyethane

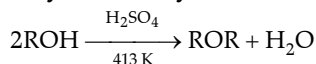
**Common Name :** Isopropyl phenyl ether  
**IUPAC :** Isopropoxy benzene

**▶ Method of preparation:**

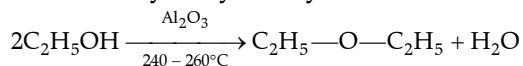
**• From alkyl halides (Williamson synthesis):**



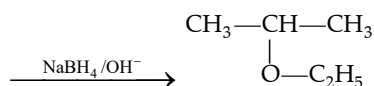
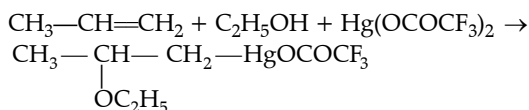
**• From alcohols by acidic dehydration:**



**• From alcohols by catalytic dehydration**



**• Addition of alcohol to alkene (Alkoxy mercuration-demercuration):**

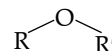


**▶ Physical properties:** They are colourless liquids except dimethyl ether and diethyl ether which are gases.

- They are polar due to bent structure.
- They have low boiling point due to absence of hydrogen bonding in ethers.
- They are slightly soluble in water due to hydrogen bonding between ether and water molecules. They are soluble in organic solvents to greater extent.

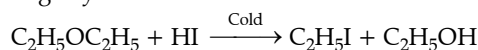
**▶ Structure of Ether:** The structure of an ether molecule is almost similar to that of a water molecule. The ethereal oxygen is in a state of sp<sup>3</sup> hybridisation.

• The two sp<sup>3</sup> hybrid orbitals of oxygen possess one unpaired electron each and overlap with the singly filled orbitals of alkyl groups to form two O—C sigma bonds. The remaining two sp<sup>3</sup> hybrid orbitals contain a lone pair of electrons.

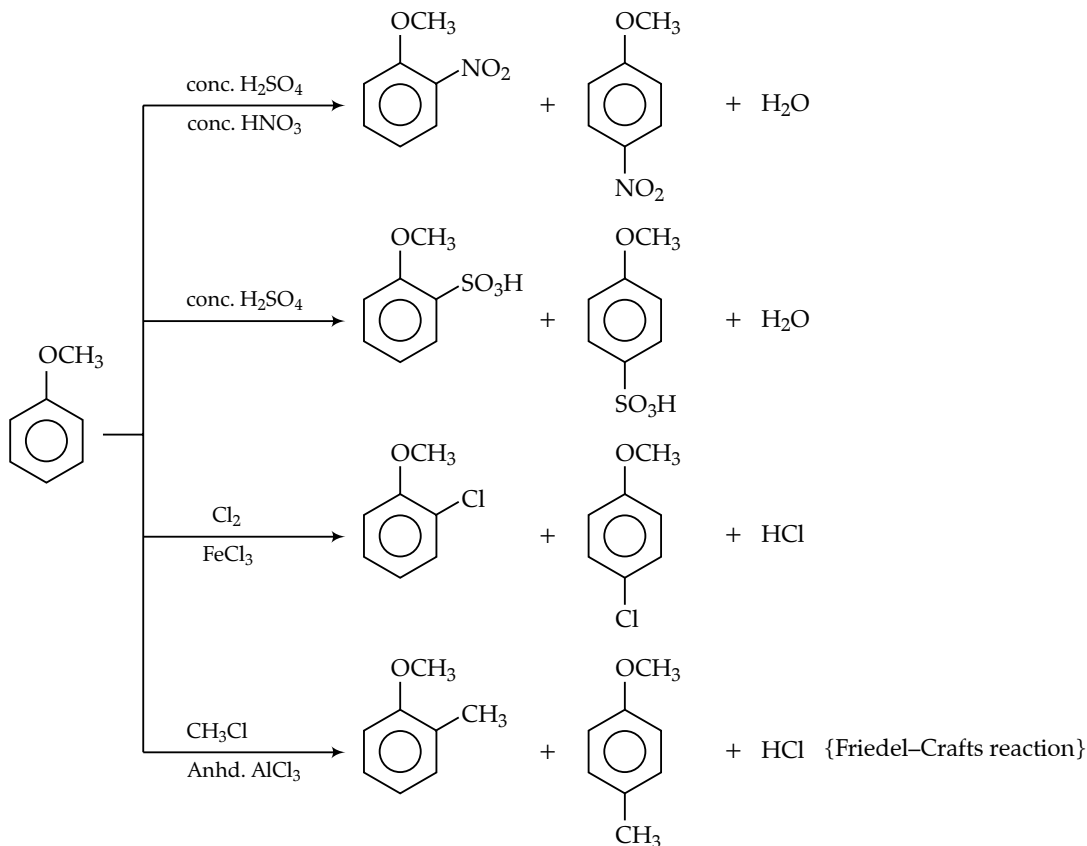


**▶ Chemical Reactions:**

- Cleavage by acid



- Reactivity of hydrogen halide  $\text{HCl} < \text{HBr} < \text{HI}$
- When  $1^\circ$  or  $2^\circ$  alkyl groups are present in ether then smaller alkyl group forms alkyl iodide.
- When one of the alkyl group is  $3^\circ$  then it forms tertiary alkyl halide.
- **Substitution in aromatic ethers**



#### ► Uses of Ethers

1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl ether is used as an anaesthesia in surgery.

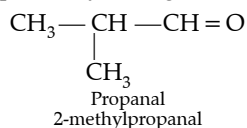
## Topic 4 Aldehydes and Ketones

### Revision Notes

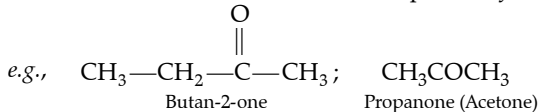
► **Aldehydes and Ketones:** Aldehydes are the compounds in which carbonyl group is either attached to two hydrogen atoms or one hydrogen and one carbon atom of alkyl or aryl group. *e.g.*,  $\text{—CH}_3\text{CHO}$ ,  $\text{HCHO}$ , etc.

Ketones are the compounds in which carbonyl group is attached to two alkyl or aryl groups. *e.g.*,  $\text{CH}_3\text{COC}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ ,  $\text{CH}_3\text{COCH}_3$ , etc.

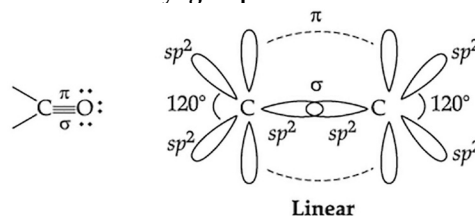
► **Nomenclature:** In IUPAC system in aldehyde the suffix 'e' of alkane is replaced by 'al'. *e.g.*,  $\text{CH}_3\text{—CH}_2\text{—CH=O}$ ;



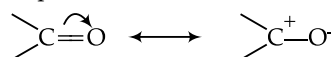
In ketones, the suffix 'e' of alkane is replaced by 'one'.



#### ► Nature of carbonyl group:



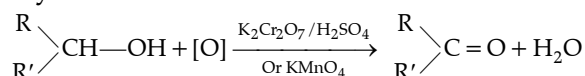
The carbonyl group is polar due to electronegativity difference between C and O. Oxygen being more electronegative pulls  $\pi$ -electrons move towards itself.



#### ► Preparation:

##### (i) Preparation of aliphatic aldehydes and ketones

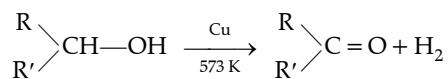
###### • By oxidation of alcohols:



When,  $\text{R}' = \text{H}$  then  $1^\circ$  alcohol to aldehyde.

$\text{R}' =$  alkyl group then  $2^\circ$  alcohol to ketone.

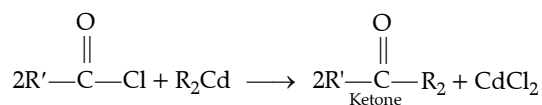
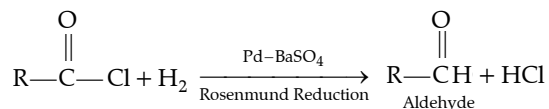
## • By dehydrogenation of alcohols:



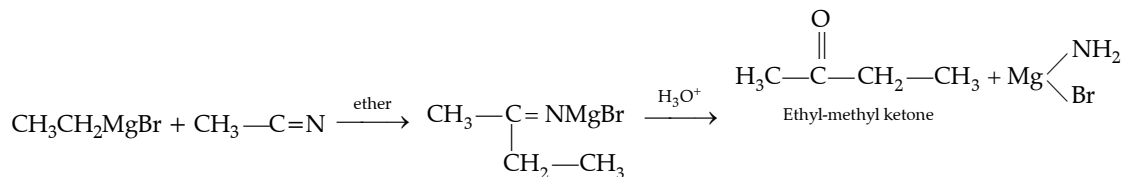
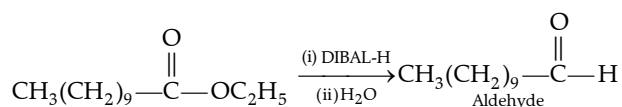
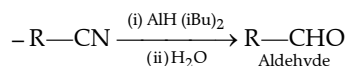
When R' = H then 1° alcohol to aldehyde.

R' = alkyl group the 2° alcohol to ketone.

## • By acid chloride

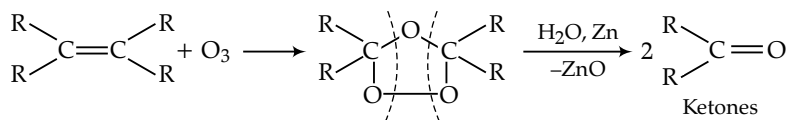
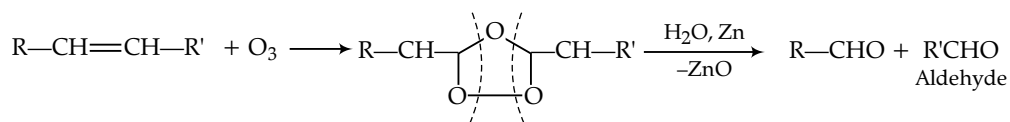


## ▶ From nitriles and esters

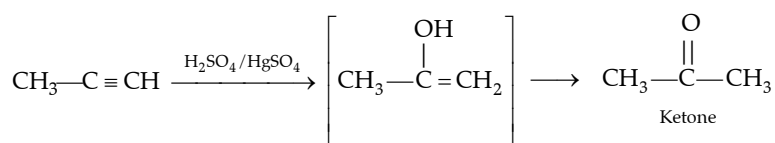
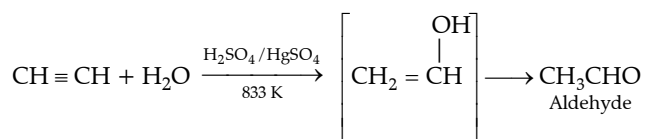


## ▶ From hydrocarbons

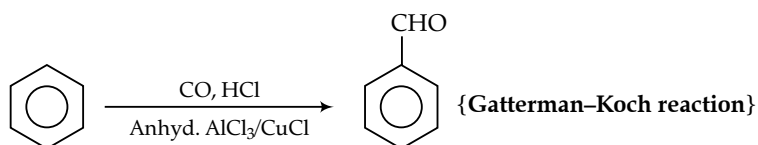
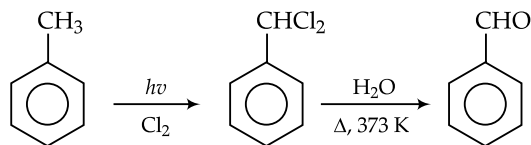
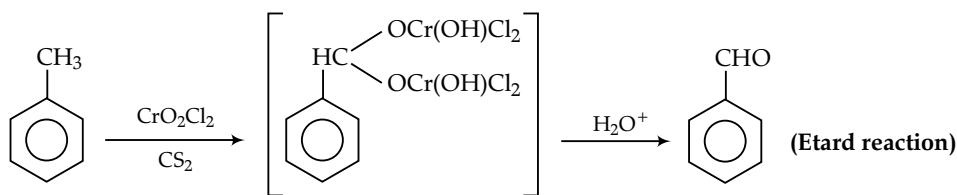
## - By ozonolysis



## - By hydration

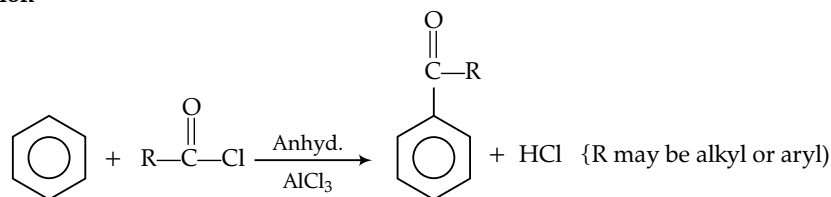


## (ii) Preparation of aromatic aldehydes

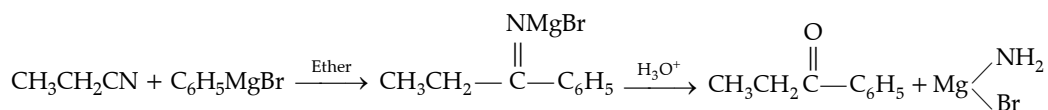


## (iii) Preparation of aromatic ketones

## Friedel crafts acylation



## From nitriles



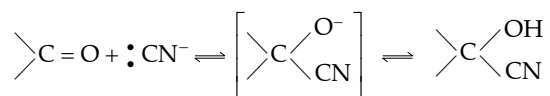
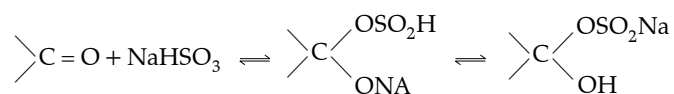
## ► Properties of Aldehydes and Ketones

- Most of the aldehydes are liquid except formaldehyde which is a gas.
- Ketones of lower order are colourless liquids and have pleasant odour.
- Aldehydes and ketones have higher b.p. than corresponding hydrocarbons but lower than the corresponding alcohols due to extensive hydrogen bonding in alcohols.
- The lower member of aldehydes and ketones are soluble in water due to hydrogen bonding while in higher members due to large alkyl groups it is difficult to dissolve in water.

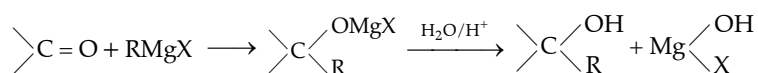
## ► Reactions of Aldehydes and Ketones

-Nucleophilic addition reaction

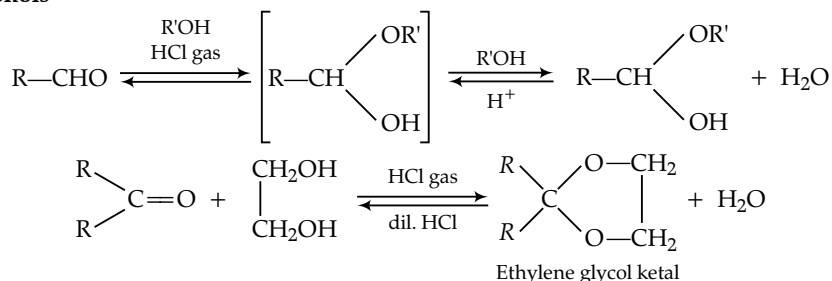
## • Addition of HCN

• Addition of NaHSO<sub>3</sub>

## • Addition of Grignard reagent

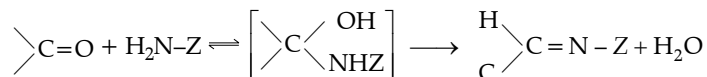


## • Addition of Alcohols



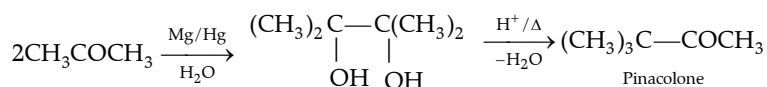
Ketones do not react with monohydric alcohol.

## • Addition of ammonia and its derivatives

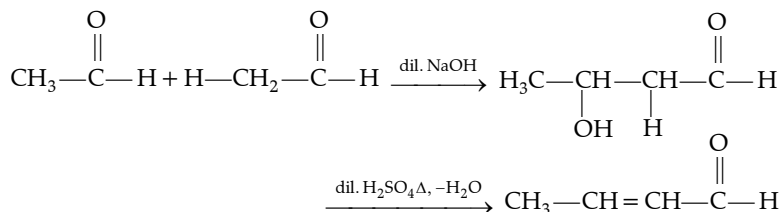


Where, Z = Alkyl, aryl, OH, NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NH, NHCONH<sub>2</sub>, etc.

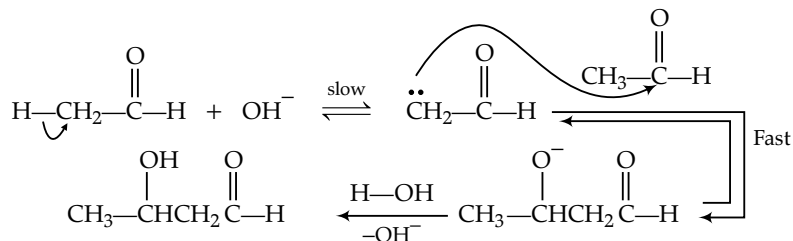
## • Pinacol pinacolone rearrangement



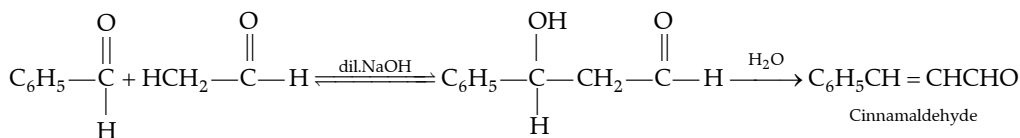
## Aldol condensation



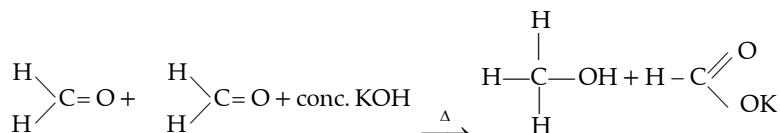
## Mechanism:



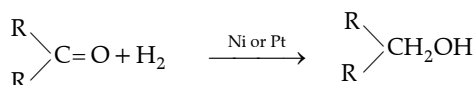
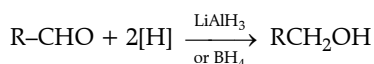
## • Cross aldol condensation



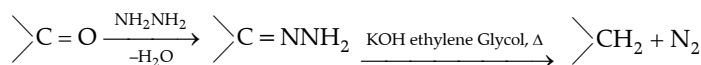
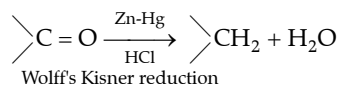
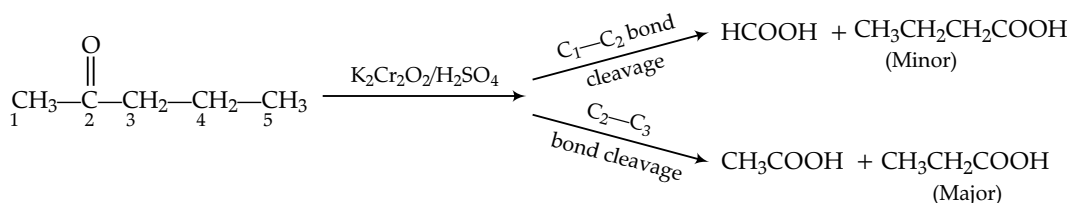
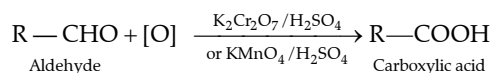
-Cannizzaro reaction: It is a self oxidation reduction reaction.



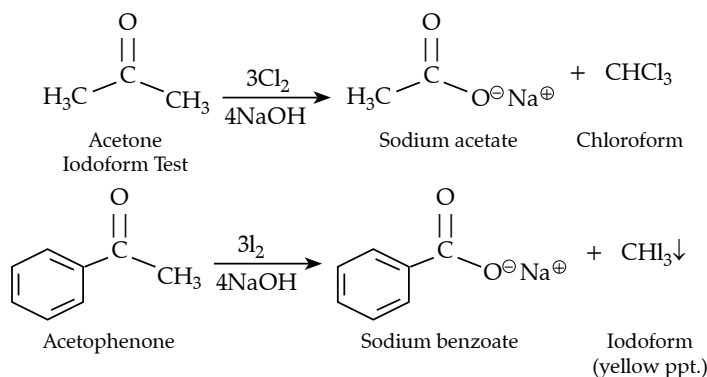
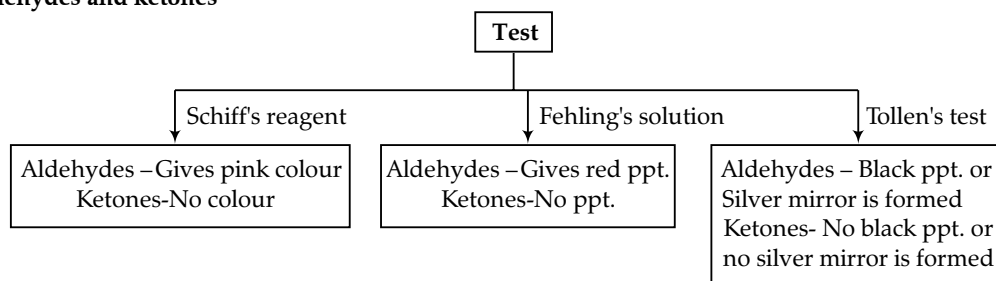
## • Reduction



Clemmensen reduction

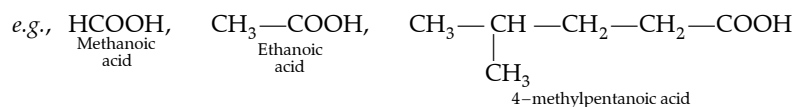
**Oxidation reaction**

**Haloform Reaction:** The aldehyde or ketone must have a methyl group next to the carbonyl since methyl has three alpha-hydrogen atoms. The reaction can be used to transform acetyl groups into carboxyl groups or to produce chloroform or iodoform. This reaction has been used in qualitative analysis to indicate the presence of a methyl ketone in which excess iodine is used to halogenate the compound. The product iodoform precipitates as a yellow-coloured substance and has a characteristic odour.

**Tests of aldehydes and ketones****Topic 5 Carboxylic Acids and their Derivatives****Revision Notes**

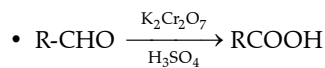
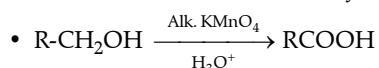
- ▶ **Carboxylic Acids:** These are the compounds with  $\text{—C(=O)—OH}$  group
- ▶ **Nomenclature:** IUPAC system - Replace suffix 'e' of alkane by 'oic acid'

While naming a compound preference will be given to carboxylic carbon.

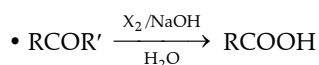


**►► Preparation:**

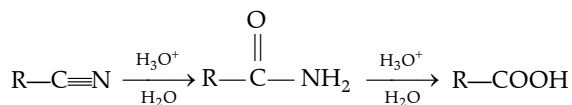
- Oxidation of alcohols and aldehydes



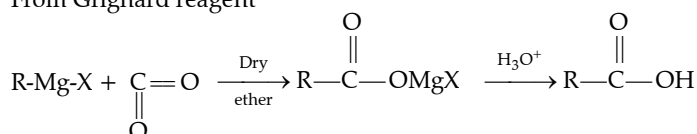
- From ketones



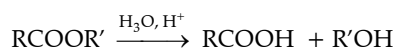
- From cyanides and amides



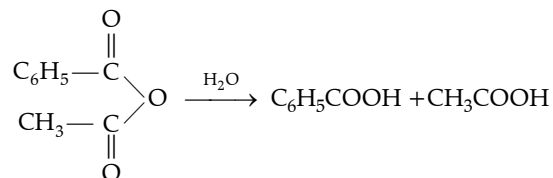
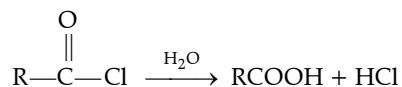
- From Grignard reagent



- Form hydrolysis of esters



- From acid halide and anhydride


**►► Properties:**

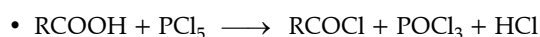
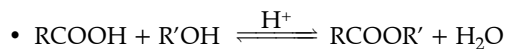
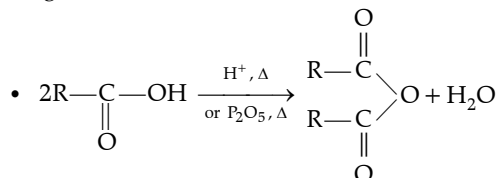
- Lower members are colourless liquid with pungent smell while higher members are odourless waxy solid.
- First four members are water soluble due to hydrogen bonding while higher acids are insoluble.
- They have higher boiling point due to their ability of form intermolecular hydrogen bonding.

**►► Chemical Reactions:**

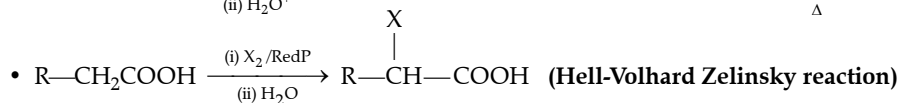
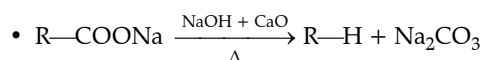
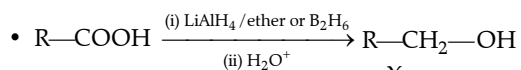
- Cleavage of O—H bond



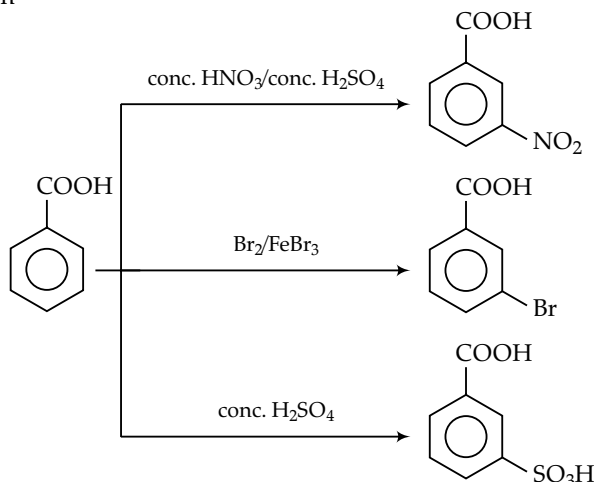
- Cleavage of C—OH bond



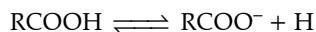
- Reduction



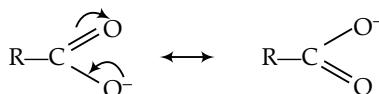
- Ring substitution reaction



### ► Acidity of carboxylic group



The conjugate base,  $\text{RCOO}^-$  is resonance stabilised thus, carboxylic acid shows acidic nature.



when R group is electron withdrawing then it disperse the negative charge on oxygen atom of carboxylic group thus, increases acidity by stabilising  $\text{R-COO}^-$  species.

When R group is electron donating then it intensify the negative charge on oxygen atom of carboxylic group thus, destabilizing  $\text{RCOO}^-$  species and hence, decreasing acidity.

The acidic strength of carboxylic acids depends on the following factors:

The induction effect of the substituent

The state of the  $-\text{COOH}$  group

The presence of electron donors or attractors

The presence of electronegative substituents near the carboxyl group

The negative induction effect of the substituent group

### ► Uses of carboxylic acids

- Methanoic acid is used in leather tanning, dyeing and finishing in textiles, manufacturing of rayon and plastic, as vinegar in cooking.

- Benzoic acid is used as food preservatives and in perfumery. ◇◇◇

## Topic 1: Previous Year's Questions

1. **Assertion A:** In Lucas test,  $3^\circ$  alcohols react immediately.

**Reason R:** An equimolar mixture of anhyd.  $\text{ZnCl}_2$  and conc.  $\text{HCl}$  is called Lucas reagent.

In the light of the above statements, choose the most appropriate answer from the options given below:

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.

(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion.

(c) Assertion is correct, reason is incorrect.

(d) Assertion is incorrect, reason is correct.

2. **Given below are two statement:**

**Statement I:** In Lucas test, primary, secondary and tertiary alcohols are distinguished on the basis of their reactivity with conc.  $\text{HCl} + \text{ZnCl}_2$ , known as Lucas Reagent.

**Statement II:** Primary alcohols are most reactive and immediately produce turbidity at room temperature on reaction with Lucas Reagent.

In the light of the above statements, choose the most appropriate answer from the options given below:

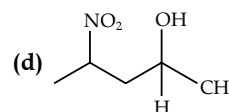
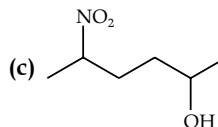
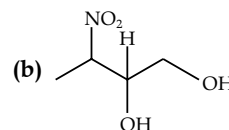
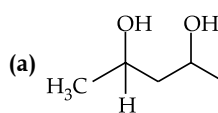
(a) Both **Statement I** and **Statement II** are correct.

(b) Both **Statement I** and **Statement II** are incorrect.

(c) **Statement I** is correct but **Statement II** is incorrect.

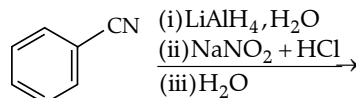
(d) **Statement I** is incorrect but **Statement II** is correct.

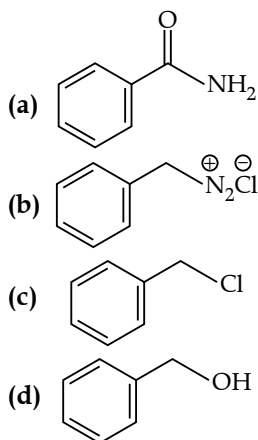
3. Which amongst the following will be most readily dehydrated under acidic conditions?



[NEET 2023]

4. The product formed from the following reaction sequence is





[NEET July 2022]

5. Match List-I with List-II:

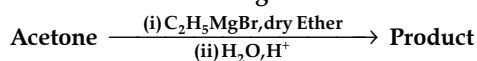
| List-I                   | List-II              |
|--------------------------|----------------------|
| (Reaction)               | (Product formed)     |
| (a) Gabriel synthesis    | (i) Benzaldehyde     |
| (b) Kolbe synthesis      | (ii) Ethers          |
| (c) Williamson synthesis | (iii) Primary amines |
| (d) Etard synthesis      | (iv) Salicylic acid  |

Choose the correct answer from the options given below:

- (a) (a) - (iii), (b) - (i), (c) - (ii), (d) - (iv)  
 (b) (a) - (ii), (b) - (iii), (c) - (i), (d) - (iv)  
 (c) (a) - (iv), (b) - (iii), (c) - (i), (d) - (ii)  
 (d) (a) - (iii), (b) - (iv), (c) - (ii), (d) - (i)

[NEET September 2022]

6. What is the IUPAC name of the organic compound formed in the following chemical reaction?



- (a) 2-methylbutan-2-ol  
 (b) 2-methylpropan-2-ol  
 (c) pentan-2-ol  
 (d) pentan-3-ol

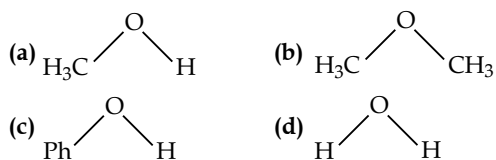
[NEET 2021]

7. Reaction between acetone and methyl magnesium chloride followed by hydrolysis will give

- (a) Sec. butyl alcohol.  
 (b) Tert. butyl alcohol.  
 (c) Isobutyl alcohol.  
 (d) Isopropyl alcohol.

[NEET 2020 Phase I]

8. The compound that is most difficult to protonate is



[NEET 2019]

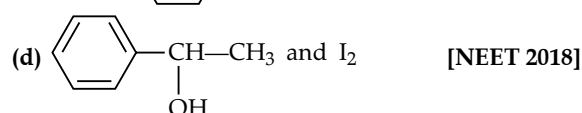
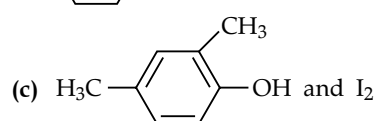
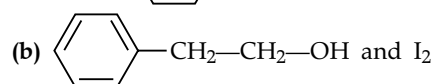
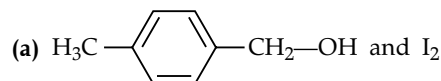
 9. The compound A on treatment with Na gives B, and with  $\text{PCl}_5$  gives C. B and C react together to give diethyl ether. A, B and C are in the order:

- (a)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$   
 (b)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{ONa}$

 (c)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{Cl}$ 

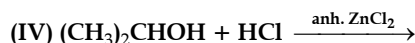
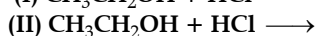
 (d)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ 

[NEET 2018]

 10. 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.


[NEET 2018]

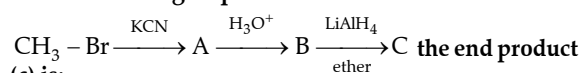
11. Which of the following reaction(s) can be used for the preparation of alkyl halides?



- (a) (I) and (II) only      (b) (IV) only  
 (c) (III) and (IV) only      (d) (I), (III) and (IV) only

[AIPMT 2015]

12. In the following sequence of reactions

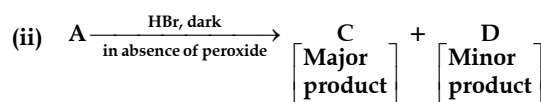
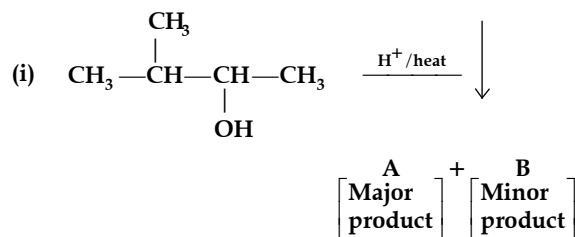


(c) is:

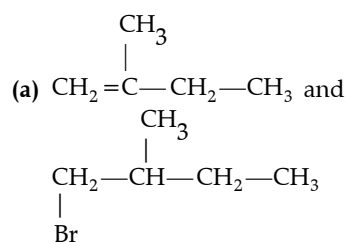
- (a) acetone      (b) methane  
 (c) acetaldehyde      (d) ethyl alcohol

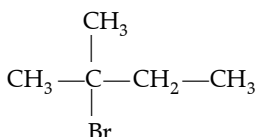
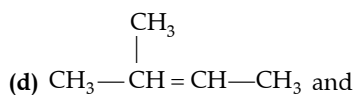
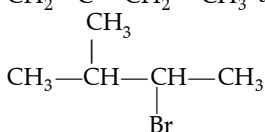
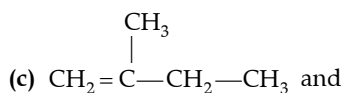
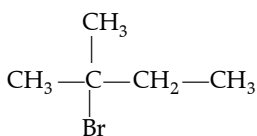
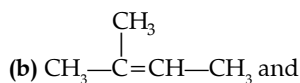
[AIPMT 2012]

13. In the following reactions:



The major products (a) and (c) are respectively:





[AIPMT 2011]

14. Following compounds are given:



Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

- (a) (i), (iii) and (iv)      (b) Only (ii)  
(c) (i), (ii) and (iii)      (d) (i) and (ii)

[AIPMT 2010]

15. When glycerol is treated with excess of HI, it produces:

- (a) 2-iodopropane      (b) allyl iodide  
(c) propene      (d) glycerol triiodide

[AIPMT 2010]

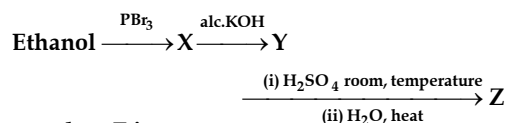
16. Match the compounds given in List I with their characteristic reactions given in List II. Select the correct option.

| List I<br>(Compounds)                            | List II<br>(Reactions)   |
|--|--|
| (a) $\text{CH}_3(\text{CH}_2)_3\text{NH}_2$      | (i) Alkaline hydrolysis  |
| (b) $\text{CH}_3\text{C}\equiv\text{CH}$         | (ii) With KOH (alcohol) and $\text{CHCl}_3$ produces bad smell |
| (c) $\text{CH}_3\text{CH}_2\text{COOCH}_3$       | (iii) Gives white ppt. with ammoniacal $\text{AgNO}_3$         |
| (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ | (iv) With Lucas reagent cloudiness appears after 5 minutes     |

- (a) a-(ii), b-(i), c-(iv), d-(iii)  
(b) a-(iii), b-(ii), c-(i), d-(iv)  
(c) a-(ii), b-(iii), c-(i), d-(iv)  
(d) a-(iv), b-(ii), c-(iii), d-(i)

[AIPMT 2010]

17. Consider the following reaction:



The product Z is:

- (a)  $\text{CH}_3\text{CH}_2\text{O}-\text{CH}_2-\text{CH}_3$   
(b)  $\text{CH}_3-\text{CH}_2-\text{O}-\text{SO}_3\text{H}$   
(c)  $\text{CH}_3\text{CH}_2\text{OH}$   
(d)  $\text{CH}_2 = \text{CH}_2$       [AIPMT 2009]

18.  $\text{HOCH}_2\text{CH}_2\text{OH}$  on heating with per-iodic acid gives:

- (a)  $2\text{HCOOH}$       (b)  $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$   
(c)  $2 \begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$       (d)  $2\text{CO}_2$       [AIPMT 2009]

19. The general molecular formula, which represents the homologous series of alkanols is:

- (a)  $\text{C}_n\text{H}_{2n+2}\text{O}$       (b)  $\text{C}_n\text{H}_{2n}\text{O}_2$   
(c)  $\text{C}_n\text{H}_{2n}\text{O}$       (d)  $\text{C}_n\text{H}_{2n+1}\text{O}$  [AIPMT 2006]

20. Ethylene oxide when treated with Grignard reagent yields:

- (a) primary alcohol  
(b) secondary alcohol  
(c) tertiary alcohol  
(d) cyclopropyl alcohol      [AIPMT 2006]

21. Which one of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

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

[AIPMT 2004]

22. *n*-propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent:

- (a)  $\text{PCl}_5$       (b) reduction  
(c) oxidation with potassium dichromate  
(d) ozonolysis.      [AIPMT 2002]

23. Which of the following is correct?

- (a) On reduction, any aldehyde gives secondary alcohol.  
(b) Reaction of vegetable oil with  $\text{H}_2\text{SO}_4$  gives glycerine.  
(c) Alcoholic iodine with NaOH gives iodoform.  
(d) Sucrose on reaction with NaCl gives invert sugar.      [AIPMT 2001]

24. Iodoform test is not given by:

- (a) ethanal      (b) ethanol  
(c) 2-pentanone      (d) 3-pentanone      [AIPMT 1998]

25. Reaction of  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$  with  $\text{RMgX}$  leads to the formation of

- (a)  $\text{RCH}_2\text{CH}_2\text{OH}$       (b)  $\text{RCHOHCH}_3$   
(c)  $\text{RCHOHR}$       (d)  $\begin{array}{c} \text{R} \\ \diagdown \\ \text{CHCH}_2\text{OH} \\ \diagup \\ \text{R} \end{array}$

[AIPMT 1998]

26. When 3-3, dimethyl-2-butanol is heated with  $\text{H}_2\text{SO}_4$ ,

the major product obtained is:

- (a) 2, 3-dimethyl-2-butene  
 (b) cis and trans isomers of 2, 3-dimethyl-2-butene  
 (c) 2, 3-dimethyl-1-butene  
 (d) 3, 3-dimethyl-1-butene. [AIPMT 1995]

27. On heating glycerol with conc.  $H_2SO_4$ , a compound is obtained which has bad odour. The compound is :

- (a) acrolein (b) formic acid  
 (c) allyl alcohol (d) glycerol sulphate

[AIPMT 1994]

28. Which one of the following on oxidation gives a ketone?

- (a) Primary alcohol (b) Secondary alcohol  
 (c) Tertiary alcohol (d) All of these

[AIPMT 1993]

29. What is formed when a primary alcohol undergoes catalytic dehydrogenation?

- (a) Aldehyde (b) Ketone  
 (c) Alkene (d) Acid [AIPMT 1993]

30. How many isomers of  $C_5H_{11}OH$  will be primary alcohols?

- (a) 5 (b) 4  
 (c) 2 (d) 3 [AIPMT 1992]

31. Methanol is industrially prepared by:

- (a) oxidation of  $CH_4$  by steam at  $900^\circ C$   
 (b) reduction of HCHO using  $LiAlH_4$   
 (c) Reaction of HCHO with a solution of NaOH  
 (d) reduction of CO using  $H_2$  and  $ZnO-Cr_2O_3$ .

[AIPMT 1992]

32. HBr reacts fastest with:

- (a) 2-Methylpropan-1-ol (b) 2-Methylpropan-2-ol  
 (c) propan-2-ol (d) propan-1-ol.

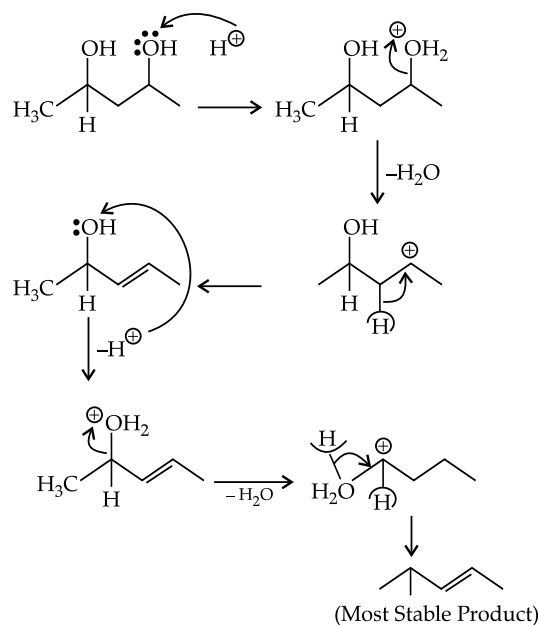
[AIPMT 1992]

## Answer Key

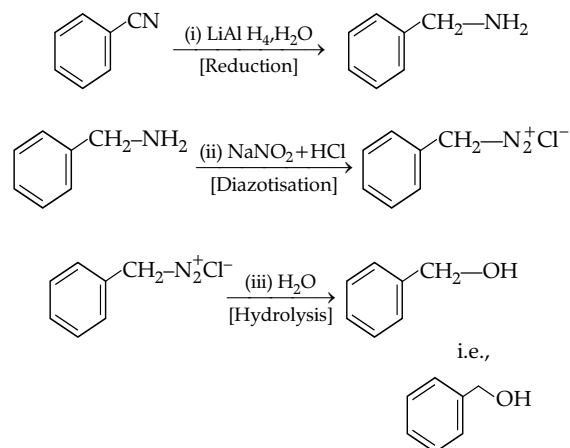
|     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (b) | 2.  | (c) | 3.  | (a) | 4.  | (d) | 5.  | (d) | 6.  | (a) |
| 7.  | (b) | 8.  | (c) | 9.  | (b) | 10. | (a) | 11. | (d) | 12. | (d) |
| 13. | (b) | 14. | (c) | 15. | (a) | 16. | (c) | 17. | (c) | 18. | (c) |
| 19. | (a) | 20. | (a) | 21. | (c) | 22. | (c) | 23. | (c) | 24. | (d) |
| 25. | (a) | 26. | (a) | 27. | (a) | 28. | (b) | 29. | (a) | 30. | (b) |
| 31. | (d) | 32. | (b) |     |     |     |     |     |     |     |     |

## Answers with Explanation

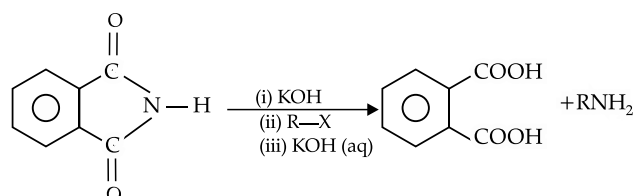
- (b) Lucas test gives positive test for alcohol.
- (c) Tertiary alcohols are most reactive and immediately produce turbidity at room temperature on reaction with Lucas reagent.
- (a) Acidic dehydration process through carbocation formation.



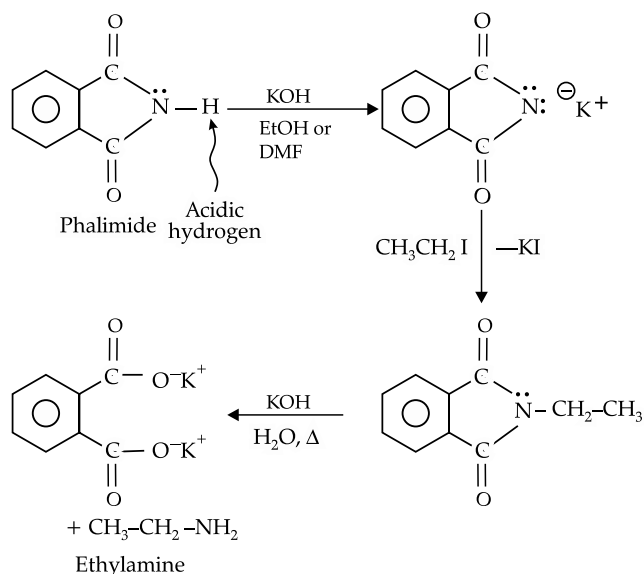
4. (d)



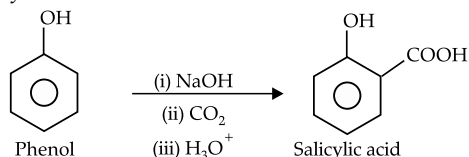
5. (d) (a) Gabriel synthesis  $\longrightarrow$  (iii) Primary amines



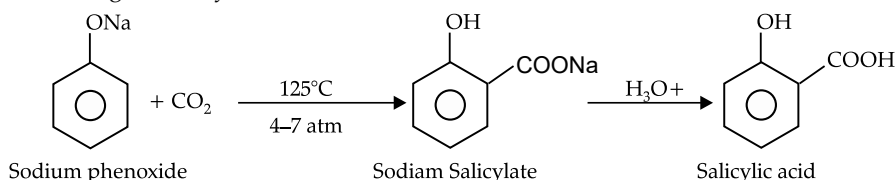
Phthalimide is alkylated with primary or unbranched secondary alkyl halides or sulphonate. The product thus obtained is hydrolysed to give primary amines.



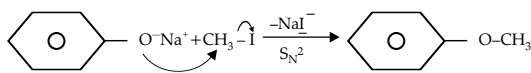
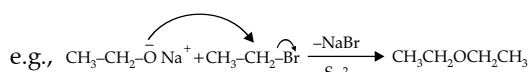
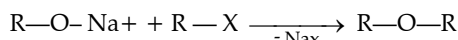
(b) Kolbe's synthesis  $\longrightarrow$  (iv) Salicylic acid.



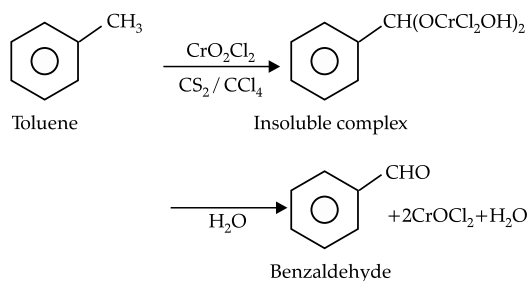
Heating of sodium phenoxide with  $\text{CO}_2$  gas under pressure produces sodium salicylate as the major product, which on further acidification gives salicylic acid.



(c) Williamson synthesis  $\longrightarrow$  (ii) Ethers



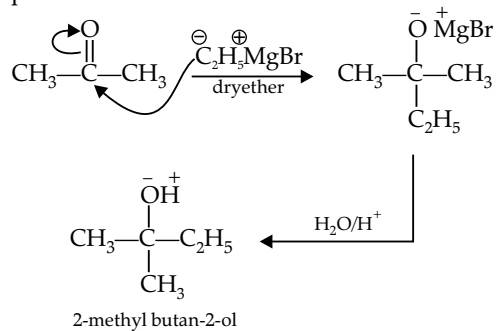
(d) Etard Reaction  $\longrightarrow$  (i) Benzaldehyde



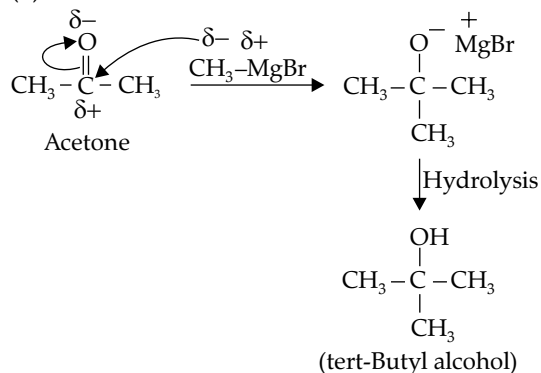
Treatment of toluene with chromyl chloride in an inert solvent like  $\text{CS}_2$  or  $\text{CCl}_4$  forms an insoluble complex  $\text{C}_6\text{H}_5\text{CH}(\text{OCrCl}_2\text{OH})_2$  which further on hydrolysis produces benzaldehyde.

6. (a)  $\text{C}_2\text{H}_5\text{MgBr}$  is a Grignard reagent in which  $\text{C}_2\text{H}_5^-$  acts as a nucleophile and gives nucleophilic addition

reaction with ketone to form tertiary alcohol as a major product.

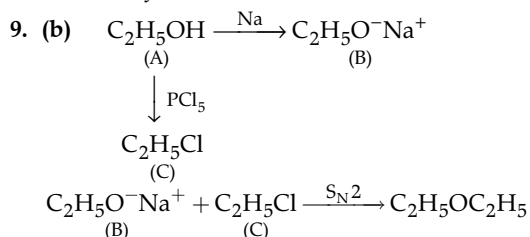


7. (b)

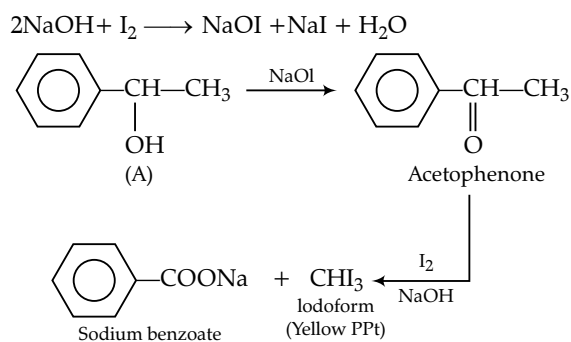


(tert-Butyl alcohol)

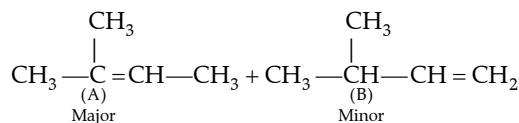
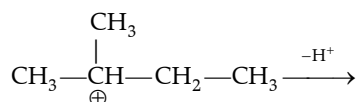
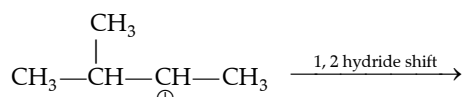
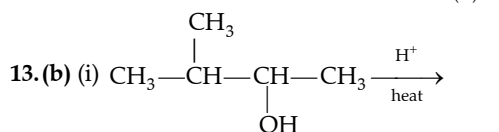
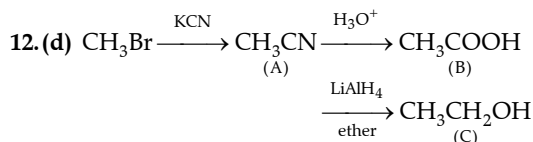
8. (c) The lone pair of electrons causes delocalisation which makes it difficult to protonate due to less availability of electrons.



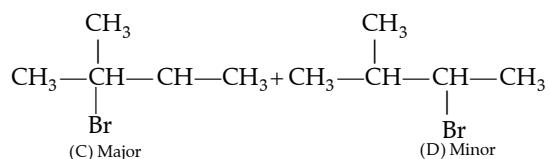
10. (a) Option (a) is secondary alcohol which on oxidation gives phenylmethyl ketone (Acetophenone). This one reaction with  $\text{I}_2$  and  $\text{NaOH}$  form iodoform and sodium benzoate.



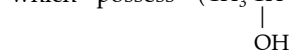
11. (d)  $1^\circ$  and  $2^\circ$  alcohols react with  $\text{HCl}$  in presence of anhydrous  $\text{ZnCl}_2$  as catalyst while in case of  $3^\circ$  alcohol  $\text{ZnCl}_2$  is not required.



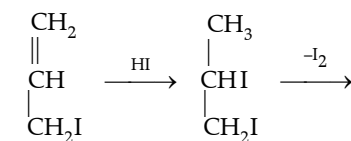
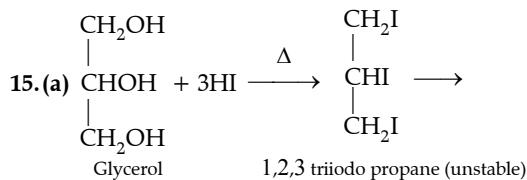
(ii) A  $\xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}}$



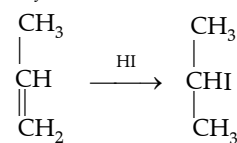
14. (c) The iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones, those alcohols which possess  $(\text{CH}_3\text{CH}-)$  group, acetophenone,



$\alpha$ -hydroxypropionic acid, keto acid, 2-aminoalkanes, etc.

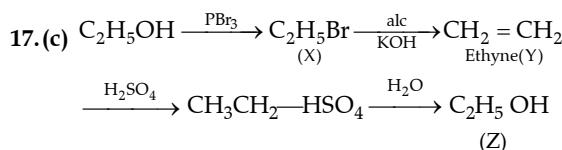
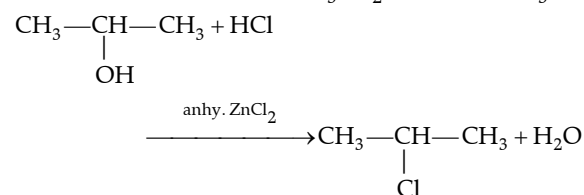
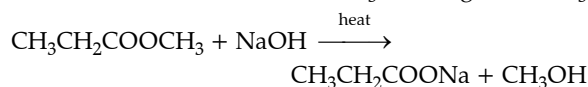
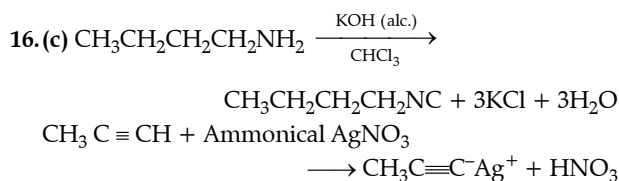


Allyl iodide

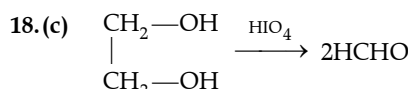


Propene

2-iodo propene

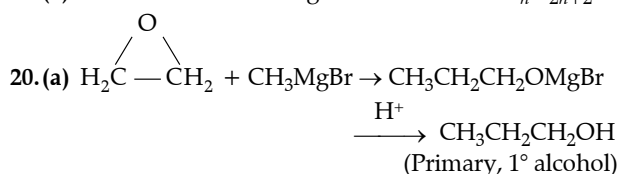


Hence Z is ethanol.



Here each alcoholic group is oxidised to carbonyl group by  $\text{HIO}_4$ .

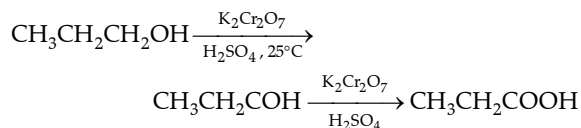
19. (a) All alcohols follow the general formula as  $\text{C}_n\text{H}_{2n+2}\text{O}$ .



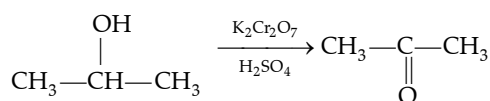
21. (c) Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones and those alcohols which possess  $(\text{CH}_3-\underset{\text{OH}}{\underset{|}{\text{C}}}-)$  group. Thus,

methyl alcohol will not give this test.

22. (c) *n*-propyl alcohol and isopropyl alcohol can be chemically distinguished by oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$ . *n*-propyl alcohol on oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  gives an aldehyde which on further oxidation gives an acid.



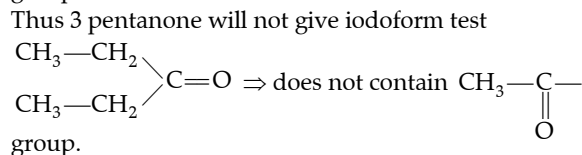
Isopropyl alcohol on oxidation gives a ketone with the same number of carbon atoms as original alcohol



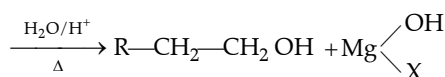
23. (c)  $\text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + \text{NaOH} \rightarrow \text{CHI}_3 + \text{NaI} + \text{HCOONa} + \text{H}_2\text{O}$

$\text{CHI}_3$  a (iodoform) is a pale yellow solid which crystallises out.

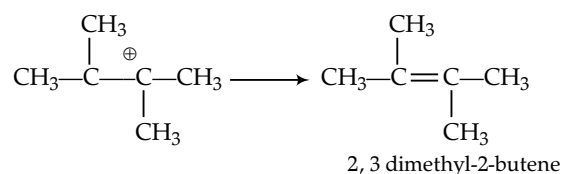
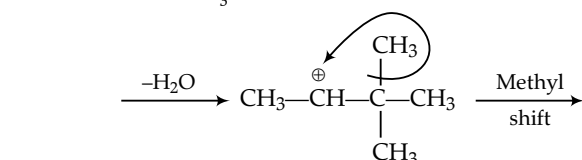
24. (d) Carbonyl compounds containing  $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-$  group shows iodoform test. Thus 3 pentanone will not give iodoform test



25. (a)  $\text{R-MgX} + \text{CH}_2=\text{CH}_2 \rightarrow \text{R-CH}_2\text{CH}_2\text{O-MgX}$



26. (a)  $\text{CH}_3-\underset{\text{OH}}{\underset{|}{\text{C}}}-\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{CH}_3-\overset{\oplus}{\text{C}}(\text{OH}_2)-\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_3$



27. (a)  $\text{CHOH}-\text{CH}_2\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{CH}_2=\text{CHCHO} + 2\text{H}_2\text{O}$   
Glycerol Acrolein

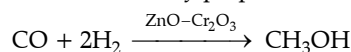
28. (b)  $2^\circ$  alcohols on oxidation gives ketones while  $1^\circ$  alcohol form aldehydes.

29. (a) Primary alcohol undergoes catalytic dehydrogenation to give aldehyde.

30. (b) There are 4 isomers of  $\text{C}_5\text{H}_{11}\text{OH}$ . They are:

- (i)  $\text{CH}_3(\text{CH}_2)_4\text{OH}$   
(ii)  $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_2\text{OH}$   
(iii)  $\text{CH}_3-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_2-\text{CH}_2\text{OH}$   
(iv)  $\text{CH}_3-\underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{OH}$

31. (d) Methanol is industrially prepared as follows.



32. (b)  $\text{CH}_3-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_3$  generates  $3^\circ$  carbocation which is very stable intermediate thus it will react more rapidly with  $\text{HBr}$  (this reaction follows  $\text{S}_{\text{N}}1$  reaction).

## Topic 2: Previous Year's Questions

1. **Assertion A:** Phenol is more reactive than benzene towards electrophilic substitution reaction.

**Reason R:** In the case of phenol, the intermediate carbocation is more resonance stabilised.

**In the light of the above statements, choose the most appropriate answer from the options given below:**

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.  
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion.  
(c) Assertion is correct, reason is incorrect.  
(d) Assertion is incorrect, reason is correct.

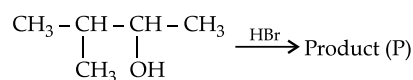
2. **Given below are two statements:**

**Statement I:** The acidic strength of monosubstituted nitro-phenol is higher than phenol because of electron withdrawing nitro group.

**Statement II:** *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol will have same acidic strength as they have one nitro group attached to the phenolic ring.

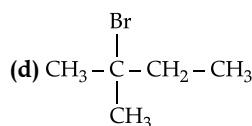
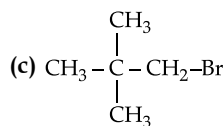
**In the light of the above statements, choose the most appropriate answer from the options given below:**

- (a) Both **Statement I** and **Statement II** are correct.  
(b) Both **Statement I** and **Statement II** are incorrect.  
(c) **Statement I** is correct but **Statement II** is incorrect.  
(d) **Statement I** is incorrect but **Statement II** is correct.
3. **Consider the following reaction and identify the product (P).**



3-Methylbutan-2-ol

- (a)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$   
(b)  $\text{CH}_3-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\underset{\text{Br}}{\underset{|}{\text{C}}}-\text{CH}_3$



[NEET 2023]

4. Match the reagents (List-I) with the product (List-II) obtained from phenol.

|     | List-I  |       | List-II          |
|-----|---|-------|------------------|
| (a) | (i) NaOH<br>(ii) CO <sub>2</sub><br>(iii) H <sup>+</sup>                        | (i)   | Benzoquinone     |
| (b) | (i) Aqueous NaOH + CHCl <sub>3</sub><br>(ii) H <sup>+</sup>                     | (ii)  | Benzene          |
| (c) | Zn duct, D  | (iii) | Salicyl aldehyde |
| (d) | Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>2</sub> SO <sub>4</sub> | (iv)  | Salicylic acid   |

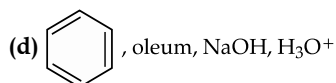
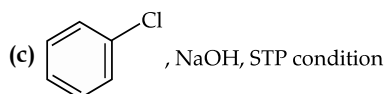
Choose the correct answer from the options given below:

- (a) (a)-(iii), (b)-(iv), (c)-(i), (d)-(ii)  
 (b) (a)-(ii), (b)-(i), (c)-(iv), (d)-(iii)  
 (c) (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)  
 (d) (a)-(iv), (b)-(ii), (c)-(i), (d)-(iii)

[NEET September 2022]

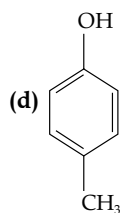
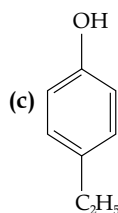
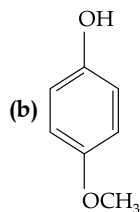
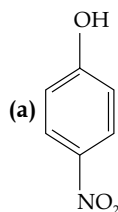
5. Which one of the following reaction sequence is incorrect method to prepare phenol?

- (a) Aniline, NaNO<sub>2</sub> + HCl, H<sub>2</sub>O, heating  
 (b) Cumene, O<sub>2</sub>, H<sub>3</sub>O<sup>+</sup>



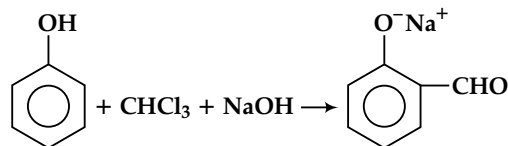
[NEET September 2022]

6. Which of the following substituted phenols is the strongest acid?



[NEET 2020 Phase II]

7. In the reaction

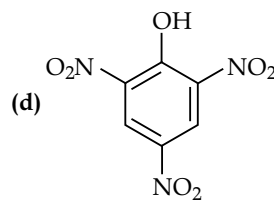
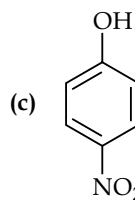
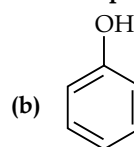
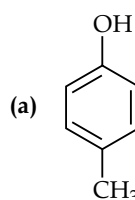


the electrophile involved is:

- (a) dichloromethyl cation ( $\text{CHCl}_2^+$ )  
 (b) formyl cation ( $\text{CHO}^+$ )  
 (c) dichloromethyl anion ( $\text{CHCl}_2^-$ )  
 (d) dichlorocarbene ( $:\text{CCl}_2$ )

[NEET 2018]

8. Which one of the most acidic compound?



[NEET 2017]

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

- (a) —COOH (b) —CHCl<sub>2</sub>  
 (c) —CHO (d) —CH<sub>2</sub>Cl [AIPMT 2015]

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

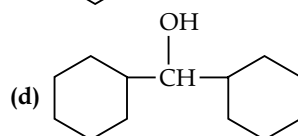
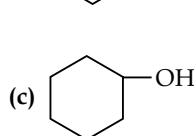
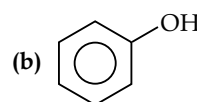
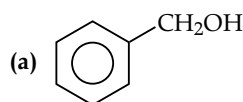
- (a) 2, 4, 6-Trinitrophenol  
 (b) Benzoic acid  
 (c) *o*-Nitrophenol  
 (d) Benzene sulphonic acid [AIPMT 2014]

11. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be:

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

[AIPMT 2010]

12. Which of the following compounds has the most acidic nature?



[AIPMT 2010]

13. Among the following four compounds

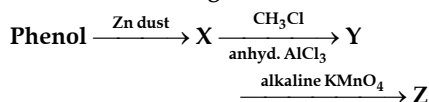
- (i) Phenol (ii) Methyl phenol  
 (iii) *Meta* nitrophenol (iv) *Para*-nitrophenol

The acidity order is:

- (a) (iv) > (iii) > (i) > (ii) (b) (iii) > (iv) > (i) > (ii)  
 (c) (i) > (iv) > (iii) > (ii) (d) (ii) > (i) > (iii) > (iv)

[AIPMT 2010]

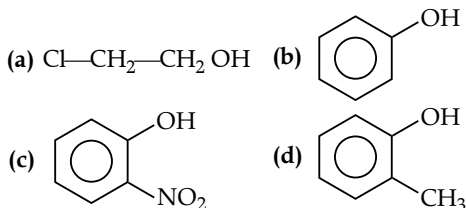
14. Consider the following reaction:



The product Z is

- (a) benzaldehyde (b) benzoic acid  
 (c) benzene (d) toluene [AIPMT 2009]

15. Which of the following compounds is most acidic?



[AIPMT 2005]

16. When phenol is treated with  $\text{CHCl}_3$  and  $\text{NaOH}$ , the product formed is:

- (a) benzaldehyde (b) salicylaldehyde  
 (c) salicylic acid (d) benzoic acid

[AIPMT 2002]

17. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is:

- (a) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol  
 (b) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol  
 (c) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol  
 (d) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol.

[AIPMT 1993]

18. When phenol is treated with excess bromine water. It gives:

- (a) *m*-bromophenol  
 (b) *o*- and *p*-bromophenols  
 (c) 2, 4-dibromophenol  
 (d) 2, 4, 6-tribromophenol

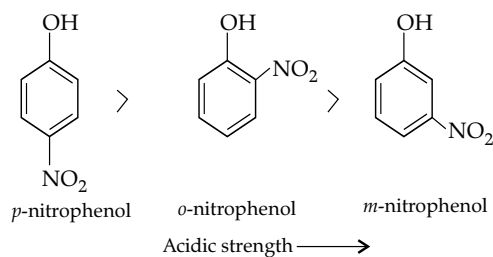
[AIPMT 1992]

## Answer Key

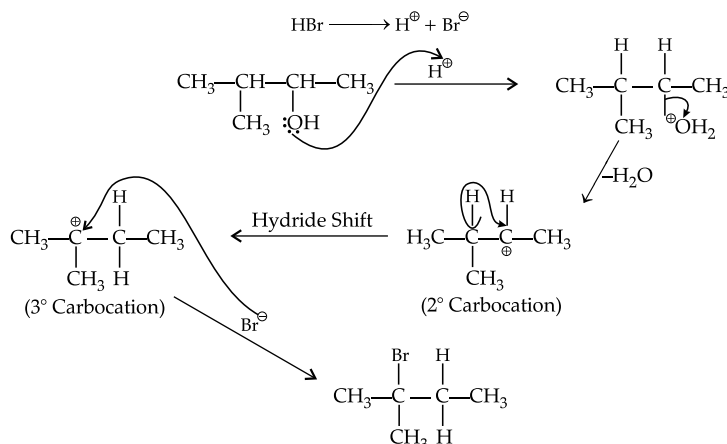
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|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (a) | 2.  | (c) | 3.  | (d) | 4.  | (c) | 5.  | (c) | 6.  | (a) |
| 7.  | (d) | 8.  | (d) | 9.  | (c) | 10. | (c) | 11. | (a) | 12. | (b) |
| 13. | (a) | 14. | (b) | 15. | (c) | 16. | (b) | 17. | (d) | 18. | (d) |

## Answers with Explanation

1. (a) The presence of lone pair on oxygen increase the electron density around the ring. This make it more reactive towards electrophilic substitution reaction and the intermediate carbocation is more resonance stabilised.
2. (c) The acidic strength of monosubstituted nitrophenol is higher than phenol because of electron withdrawing group. But, *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol have different acidic strength because of different distance of  $-\text{NO}_2$  group from the  $-\text{OH}$  group and also at *ortho* and *para* positions,  $-\text{NO}_2$  group withdraws electrons of the  $\text{O}-\text{H}$  bond towards itself by the stronger  $-\text{R}$  effect while the  $-\text{NO}_2$  group of *meta* position withdraws electrons of the  $-\text{OH}$  bond by the weaker  $-\text{I}$  effect. So, acidic strength of *ortho* and *para*-nitrophenol is greater than that of *meta* nitrophenol.

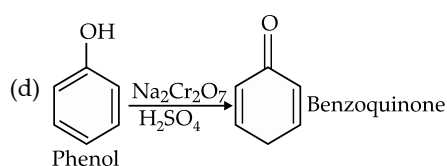
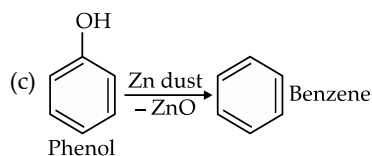
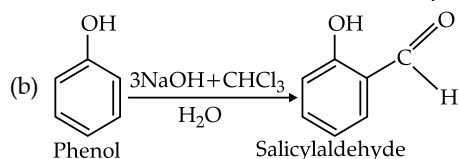
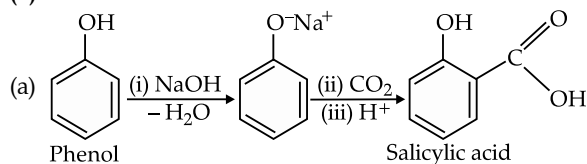


3. (d)

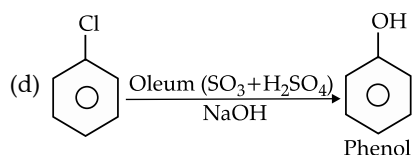
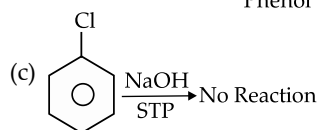
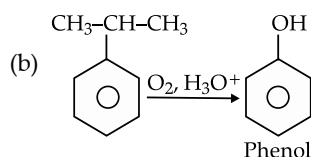
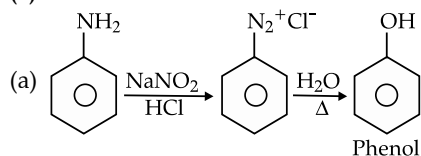


Reaction proceed through carbocation intermediate, less stable carbocation rearrange itself to more stable carbocation.

4. (c)

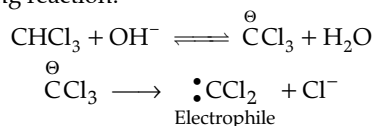


5. (c)



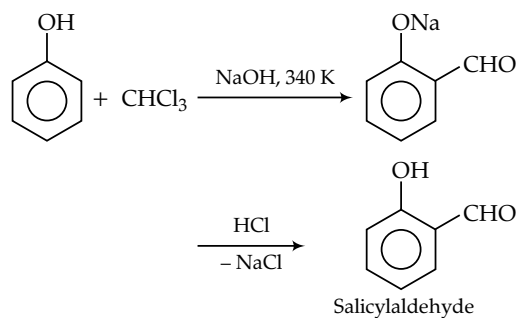
6. (a)  $\pi$ -nitrophenol has  $-\text{NO}_2$  group attached directly to ring. Due to  $-I$  and  $-M$  effect it will stabilise the phenoxide ion formed by release of  $\text{H}^+$  ion.

7. (d) It is Reimer-Tiemann reaction. The electrophile formed is:  $\text{CCl}_2$  (Dichlorocarbene) according to the following reaction:

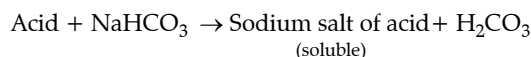


8. (d) Electron withdrawing group at  $o$  and  $p$ -position w.r.t.  $\text{OH}$  group of phenol, increase the acidic strength. Picric acid (2, 4, 6-trinitrophenol) is extremely more acidic among the given compounds due to the presence of three strong electron withdrawing groups ( $\text{NO}_2$  group) at  $ortho$  and  $para$ -positions,

9. (c) The description in the question suggests that it is a Reimer-Tiemann reaction



10. (c) Acid reacts with sodium hydrogen carbonate as follows:



Among all the given options *ortho*-nitrophenol is weaker acid than  $\text{HCO}_3^-$  hence, it does not react with  $\text{NaHCO}_3$ .

11. (a) As we know that phenols and carboxylic acids are more acidic than aliphatic alcohols thus cyclohexanol is least acidic.

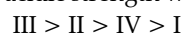
On the other hand III is more acidic than IV because of the presence of three highly electron withdrawing  $\text{NO}_2$  groups on the benzene ring which makes the  $\text{OH}$  bond extremely polarised. This facilitates the release of  $\text{H}^+$ .

In acetic acid the electron withdrawing  $\begin{array}{c} \text{—C—} \\ || \\ \text{O} \end{array}$  group

polarises the  $\text{O—H}$  bond and increases the acid strength.

Thus, acetic acid is more acidic than phenol or cyclohexanol.

Thus, the order of acidic strength will be

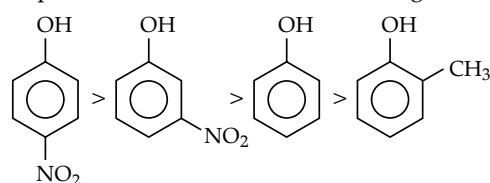


12. (b) Phenol is most acidic among the given options. In phenol, the electron withdrawing phenyl ring polarises the  $\text{O—H}$  bond thereby facilitating the release of  $\text{H}^+$ . In option (a) the  $-I$  effect of phenyl ring is diminished by  $-\text{CH}_2$  group.

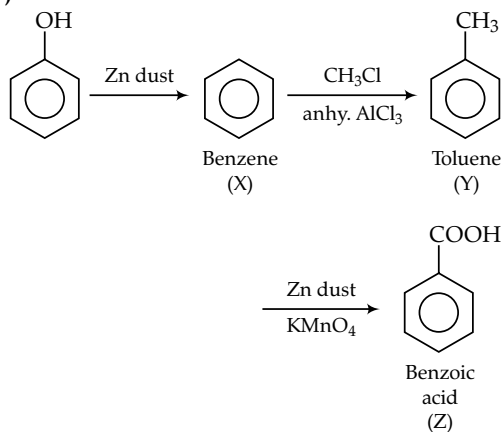
Moreover, the phenolate ion  $\left[ \text{C}_6\text{H}_5\text{O}^- \right]$  is stabilised by resonance.

13. (a) In phenols, the presence of electron releasing group decreases the acidity whereas the presence of electron withdrawing groups increases the acidity as compared to phenol.

Among *meta* and *para* nitrophenols the latter is more acidic due to presence of  $\text{NO}_2$  group at *para* position stabilises the phenoxide ion to a greater extent than at *meta* position. Thus, order of acidic strength is:

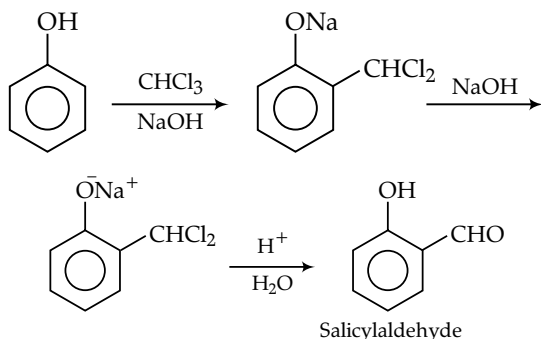


14. (b)

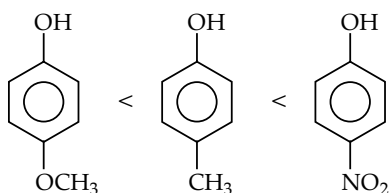


15. (c) *o*-nitrophenol is more acidic than others because  $-\text{NO}_2$  is electron withdrawing group which increase the electron density on the ring and it stabilize the phenoxide ion.

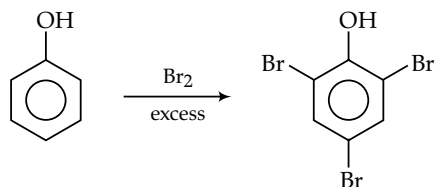
16. (b) Thus reaction is known as Reimer-Tiemann reaction.



17. (d)  $-\text{OCH}_3$ ,  $-\text{CH}_3$  are electron donating groups and decreases the acidic character of phenols. On other hand  $\text{NO}_2$ ,  $-\text{CN}$  are electron withdrawing groups which increases the acidic character. Thus, the order of acidic character is:



18. (d)



### Topic 3: Previous Year's Questions

1. **Assertion A:** Tert - Butyl methyl ether is not prepared by the reaction of ter-butyl bromide with sodium methoxide.

**Reason R:** Sodium methoxide is a strong nucleophile.

In the light of the above statements, choose the most appropriate answer from the options given below:

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.  
 (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion.  
 (c) Assertion is correct, reason is incorrect.  
 (d) Assertion is incorrect, reason is correct.

2. Given below are two statements:

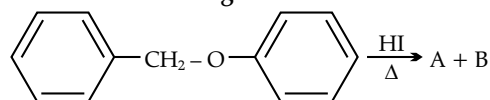
**Statement I:** Ethers do not react with sodium.

**Statement II:** Active group is present in ethers.

In the light of above statements, choose the most appropriate answer from the options given below:

- (a) Both statement I and statement II are true.  
 (b) Statement I is false but statement II is true.  
 (c) Both statement I and statement II are false.  
 (d) Statement I is true but statement II is false.

3. Consider the following reaction:



Identify products A and B.

- (a) A = c1ccc(cc1)CO and B = c1ccc(cc1)I  
 (b) A = c1ccc(cc1)CI and B = c1ccc(O)cc1  
 (c) A = c1ccc(cc1)C and B = c1ccc(I)cc1  
 (d) A = c1ccc(cc1)C and B = c1ccc(O)cc1

[NEET 2023]

4. Anisole on cleavage with HI gives:

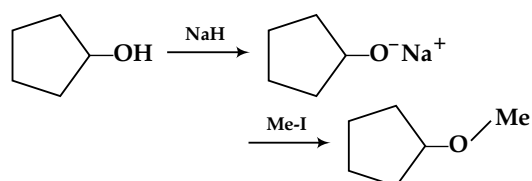
- (a) c1ccc(I)cc1 + CO    (b) c1ccc(O)cc1 + CC  
 (c) c1ccc(I)cc1 + CO    (d) c1ccc(O)cc1 + CI

[NEET 2020 Phase I]

5. The heating of phenyl-methyl ethers with HI produces:

- (a) ethyl chlorides    (b) iodobenzene  
 (c) phenol    (d) benzene [NEET 2017]

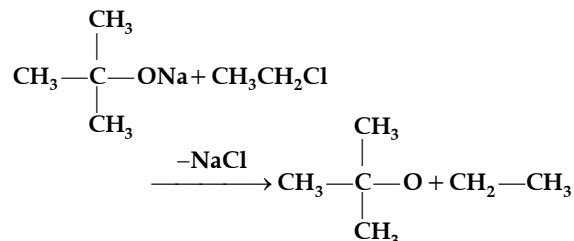
6. The reaction



can be classified as:

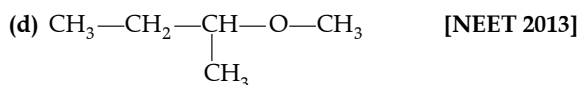
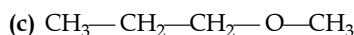
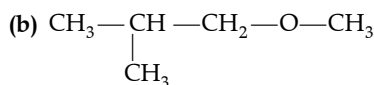
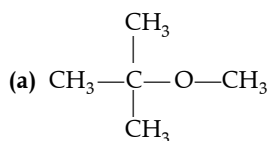
- (a) dehydration reaction  
 (b) Williamson alcohol synthesis reaction  
 (c) Williamson ether synthesis reaction  
 (d) alcohol formation reaction. [NEET 2016]

7. The reaction,

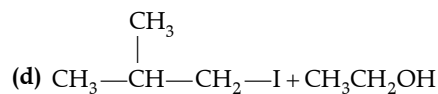
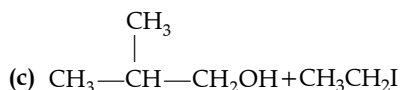
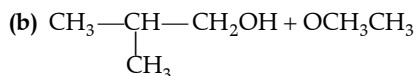
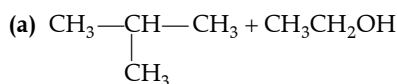
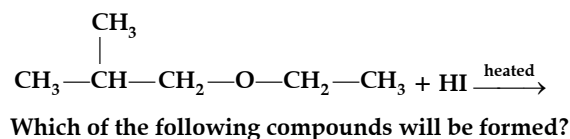


is called:

- (a) Etard reaction  
 (b) Gattermann-Koch reaction  
 (c) Williamson synthesis  
 (d) Williamson continuous etherification process. [AIPMT 2015]
8. Among the following sets of reactants which one produces anisole?  
 (a)  $\text{CH}_3\text{CHO}$ ,  $\text{RMgX}$   
 (b)  $\text{C}_6\text{H}_5\text{OH}$ ,  $\text{NaOH}$ ,  $\text{CH}_3\text{I}$   
 (c)  $\text{C}_6\text{H}_5\text{OH}$ , neutral  $\text{FeCl}_3$   
 (d)  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $\text{CH}_3\text{COCl}$ ,  $\text{AlCl}_3$  [AIPMT 2014]
9. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

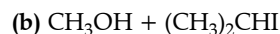
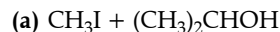


10. In the reaction:

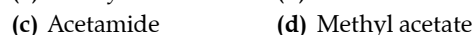


[AIPMT 2007]

11. The major organic product in the reaction is  $\text{CH}_3-\text{O}-\text{CH}(\text{CH}_3)_2 + \text{HI} \rightarrow$  products:

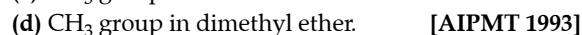
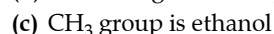
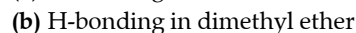
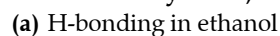


12. Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions?



[AIPMT 1998]

13. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of:



## Answer Key

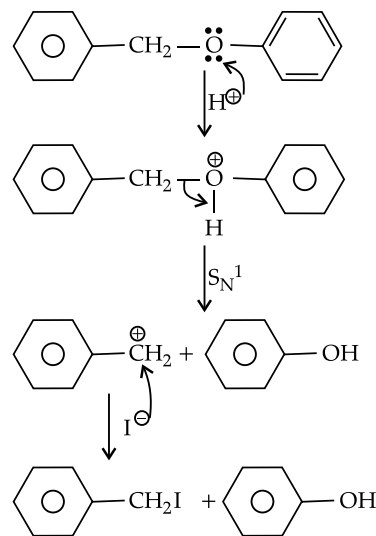
|     |     |    |     |    |     |     |     |     |     |     |     |
|-----|-----|----|-----|----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (b) | 2. | (d) | 3. | (b) | 4.  | (d) | 5.  | (c) | 6.  | (c) |
| 7.  | (c) | 8. | (b) | 9. | (a) | 10. | (c) | 11. | (a) | 12. | (a) |
| 13. | (a) |    |     |    |     |     |     |     |     |     |     |

## Answers with Explanation

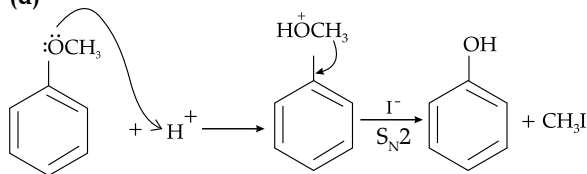
1. (b) Sodium methoxide is a strong nucleophile.

2. (d) Ethers due to absence of active group in their molecules are inert in nature. Thus, it does not react with sodium.

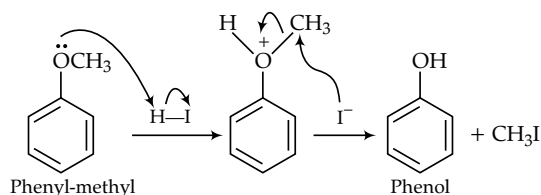
3. (b)



4. (d)



5. (c)



Phenyl-methyl ether (Anisole)

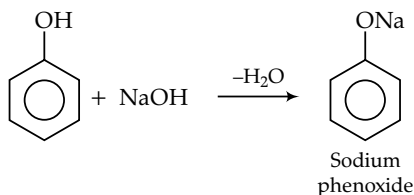
Phenol

After protonation of anisole, breaking of O—CH<sub>3</sub> bond occur but O—CH<sub>3</sub> bond is weaker and thus, it breaks to give phenol. The oxygen bonded with phenyl ring has double bond character due to sp<sup>2</sup> hybridised carbon of phenyl ring thus, it shows stronger bonding than the O—CH<sub>3</sub> bond.

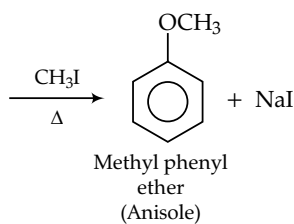
6. (c) The treatment of sodium alkoxide with a suitable alkyl halide to form an ether is called as Williamson ether synthesis reaction.

7. (c) This reaction is known as Williamson synthesis which is the best method for the preparation of ethers.

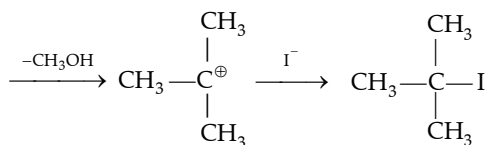
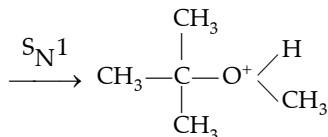
8. (b)



Sodium phenoxide



Methyl phenyl ether (Anisole)

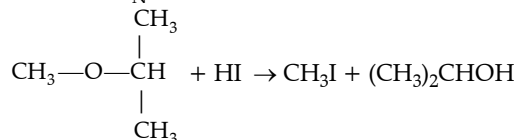
9. (a)  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{OCH}_3 + \text{HI}$  (hot and conc.)

10. (c) In this reaction the alkyl iodide produced depends on the nature of alkyl groups. If one group is CH<sub>3</sub> and other is 1° or 2° alkyl group than CH<sub>3</sub>I is produced as

it follows S<sub>N</sub>2 mechanism. Due to steric effect larger group I<sup>-</sup> attacks the smaller methyl group.

When the substrate is a methyl *t*-alkyl ether the product are *t*-RI and MeOH as it follows S<sub>N</sub>1 mechanism. The 3° carbocation is more stable than 2° or 1°.

11. (a) In case of unsymmetric ethers when treated with HI then I<sup>-</sup> attaches to smaller and less complex alkyl group as it follows S<sub>N</sub>2 mechanism



12. (a) Diethyl ether is a saturated compound, so it is resistant to nucleophilic attack by a hydroxyl ion OH<sup>-</sup>. Others have unsaturated 'C' atoms which bears partial +ve charge, therefore they undergo easy nucleophilic attack by OH<sup>-</sup> ion.

Diethyl ether ⇒ C<sub>2</sub>H<sub>5</sub>—O—C<sub>2</sub>H<sub>5</sub> (Saturated)

Acetonitrile ⇒ CH<sub>3</sub>—C≡N

Methyl acetate ⇒ CH<sub>3</sub>—C(=O)—OCH<sub>3</sub>

Acetamide ⇒ CH<sub>3</sub>—C(=O)—NH<sub>2</sub>

13. (a) The boiling point of ethanol is higher than that of dimethyl ether due to presence of intermolecular hydrogen bonding in ethanol.

## Topic 4: Previous Year's Questions

1. **Assertion A:** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

**Reason R:** This is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

**In the light of the above statements, choose the most appropriate answer from the options given below:**

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.

(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion.

(c) Assertion is correct, reason is incorrect.

(d) Assertion is incorrect, reason is correct.

2. **Given below are two statements:**

**Statement I:** Formaldehyde is a planar molecule.

**Statement II:** It contains sp<sup>2</sup> hybridised carbon atom.

**In the light of above statements, choose the most appropriate answer from the options given below:**

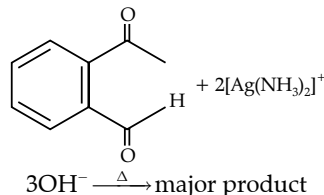
(a) Both Statement I and Statement II are true.

(b) Statement I is false but Statement II is true.

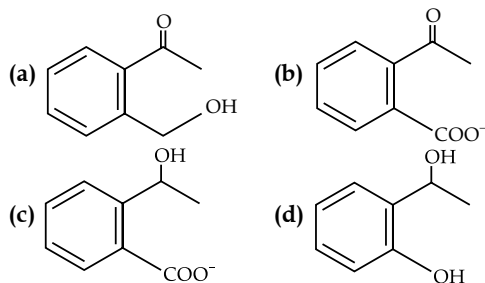
(c) Both Statement I and Statement II are false.

(d) Statement I is true but Statement II is false.

3. **Identify the major product obtained in the following reaction:**

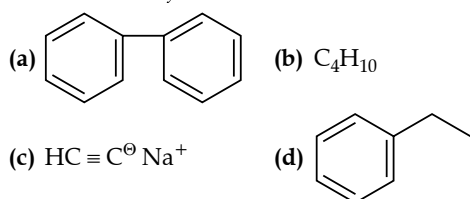
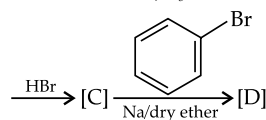
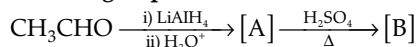


3OH<sup>-</sup>  $\xrightarrow{\Delta}$  major product



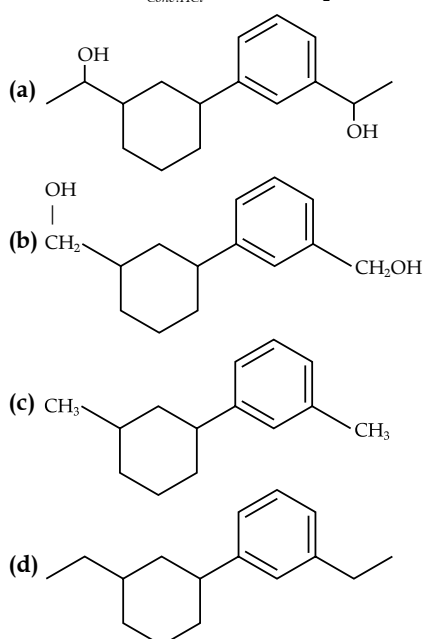
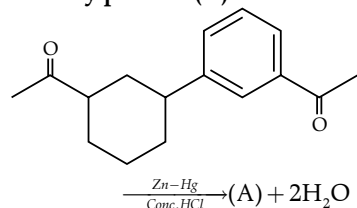
[NEET 2023]

4. Identify the final product [D] obtained in the following sequence of reactions.



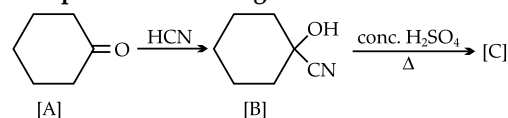
[NEET 2023]

5. Identify product (A) in the following reaction:

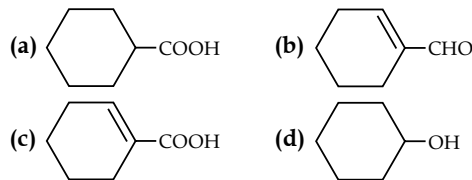


[NEET 2023]

6. Complete the following reaction:



[C] is \_\_\_\_\_.



[NEET 2023]

7. Match List-I with List-II:

| List-I<br>(Products formed) |               | List-II<br>(Reaction of carbonyl compound with) |                        |
|-----------------------------|---------------|---|------------------------|
| (a)                         | Cyanohydrin   | (i)   | $\text{NH}_2\text{OH}$ |
| (b)                         | Acetal        | (ii)  | $\text{RNH}_2$         |
| (c)                         | Schiff's base | (iii)   | alcohol                |
| (d)                         | Oxime         | (iv)  | $\text{HCN}$           |

Choose the correct answer from the options given below:

- (a) (a)-(iii), (b)-(iv), (c)-(ii), (d)-(i)  
 (b) (a)-(ii), (b)-(iii), (c)-(iv), (d)-(i)  
 (c) (a)-(i), (b)-(iii), (c)-(ii), (d)-(iv)  
 (d) (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)

[NEET July 2022]

8. Given below are two statements:

**Statements I:** The boiling points of aldehydes and ketones are higher than hydrocarbons of comparable molecular masses because of weak molecular association in aldehydes and ketones due to dipole-dipole interactions.

**Statements II:** The boiling points of aldehydes and ketones are lower than the alcohols of similar molecular masses due to the absence of H-bonding.

In the light of the above statements, choose the most appropriate answer from the options given below:

- (a) Both Statement I and Statement II are correct  
 (b) Both Statement I and Statement II are incorrect  
 (c) Statement I is correct but Statement II is incorrect  
 (d) Statement I is incorrect but Statement II is correct

[NEET July 2022]

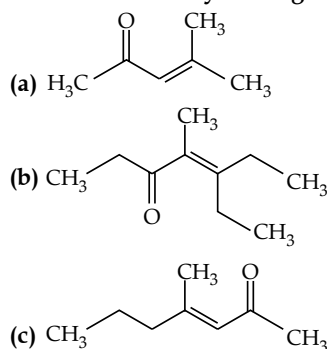
9.  $\text{RMgX} + \text{CO}_2 \xrightarrow[\text{ether}]{\text{dry}} \text{Y} \xrightarrow{\text{H}_3\text{O}^+} \text{RCOOH}$

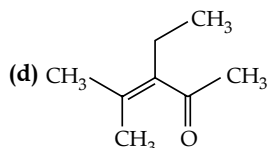
What is Y in the above reaction?

- (a)  $\text{RCOO-Mg}^+ \text{X}$  (b)  $\text{R}_3\text{CO-Mg}^+ \text{X}$   
 (c)  $\text{RCOO-X}^+$  (d)  $(\text{RCOO})_2\text{Mg}$

[NEET July 2022]

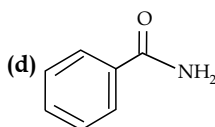
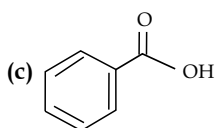
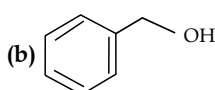
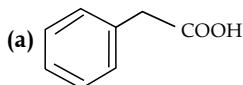
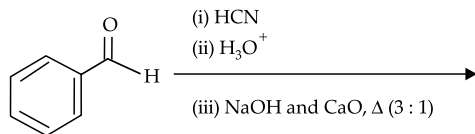
10. Which one of the following is not formed when acetone with 2-pentanone in the presence of dilute NaOH followed by heating?





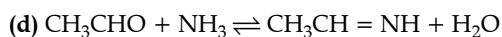
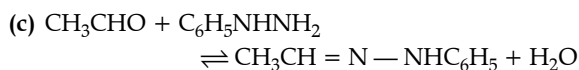
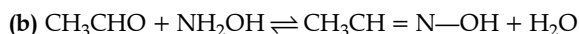
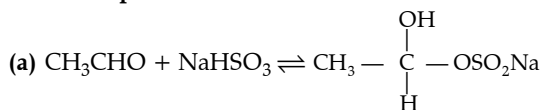
[NEET July 2022]

11. The product formed from the following reaction sequence is:



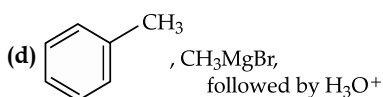
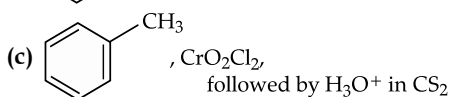
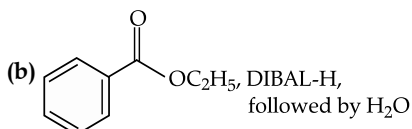
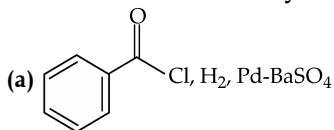
[NEET September 2022]

12. Which of the following reactions is not an example for nucleophilic addition—elimination reaction?



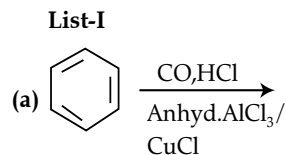
[NEET September 2022]

13. The incorrect method to synthesise benzaldehyde is:



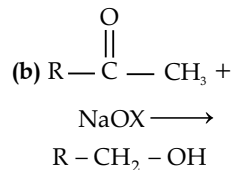
[NEET September 2022]

14. Match List-I with List-II

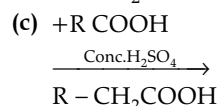


List-II

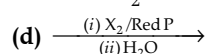
(i) Hell-Volhard-Zelinsky reaction



(ii) Gattermann Koch reaction



(iii) Haloform reaction



(iv) Esterification

Choose the correct answer from the options given below:

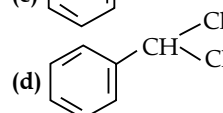
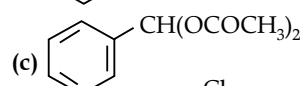
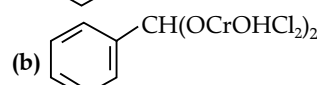
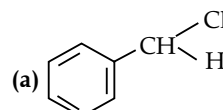
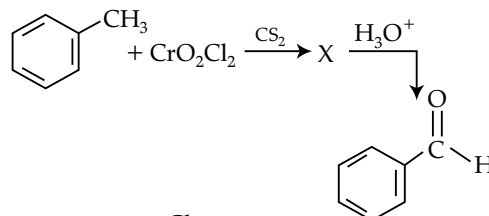
(a) (a) - (ii), (b) - (iii), (c) - (iv), (d) - (i)

(b) (a) - (iv), (b) - (i), (c) - (ii), (d) - (iii)

(c) (a) - (iii), (b) - (ii), (c) - (i), (d) - (iv)

(d) (a) - (i), (b) - (iv), (c) - (iii), (d) - (ii) [NEET 2021]

15. The intermediate compound 'X' in the following chemical reaction is:



[NEET 2021]

16. Reaction between benzaldehyde and aceto-phenone in presence of dilute NaOH is known as:

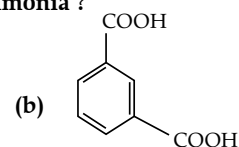
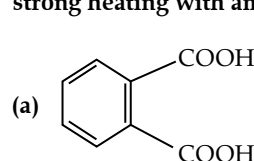
(a) Cannizzaro's reaction.

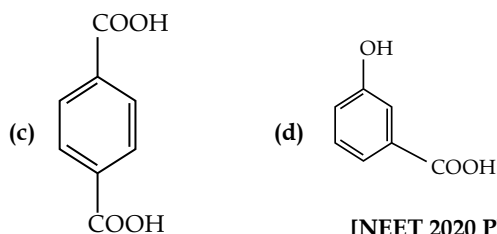
(b) Cross Cannizzaro's reaction.

(c) Cross Aldol condensation.

(d) Aldol condensation. [NEET 2020 Phase I]

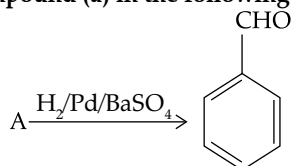
17. Which of the following acid will form an (a) Anhydride on heating and (b) Acid imide on strong heating with ammonia?





[NEET 2020 Phase II]

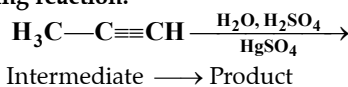
18. Identify compound (a) in the following reaction:

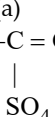
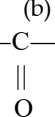
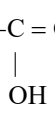

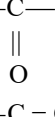





- (a) Benzoyl chloride      (b) Toluene  
 (c) Acetophenone      (d) Benzoic acid

[NEET 2020 Phase II]

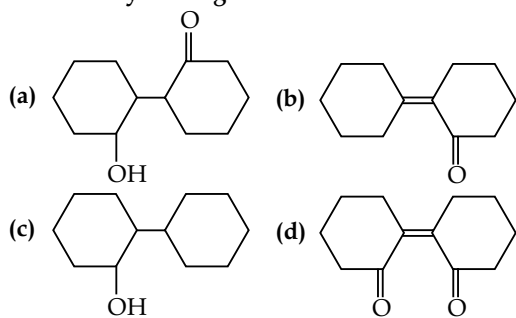
19. Predict the correct intermediate and product in the following reaction.



- (a)  $A = H_3C-C \equiv CH_2$ ,  $B = H_3C-C \equiv CH_3$   
  

- (b)  $A = H_3C-C \equiv CH_2$ ,  $B = H_2C-C \equiv CH_2$   
  

- (c)  $A = H_3C-C \equiv CH_3$ ,  $B = H_3C-C \equiv CH$   
  

- (d)  $A = H_3C-C \equiv CH_2$ ,  $B = H_3C-C \equiv CH_3$   
  


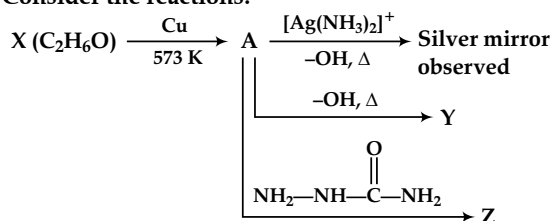
[NEET 2017]

20. Out of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?



[NEET 2017]

21. Consider the reactions:

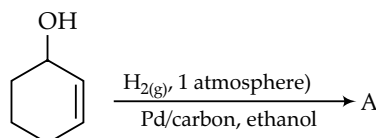


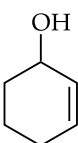
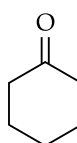
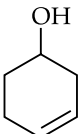
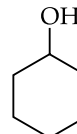
Identify A, X, Y and Z.

- (a) A-methoxymethane, X-ethanoic acid, Y-acetate ion, Z-hydrazine  
 (b) A-methoxymethane, X-ethanol, Y-ethanoic acid, Z-semicarbazide  
 (c) A-ethanal, X-ethanol, Y-but-2-enal, Z-semicarbazone  
 (d) A-ethanol, X-acetaldehyde, Y-butanone, Z-hydrazine

[NEET 2017]

22. The correct structure of the product 'A' formed in the reaction:



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

[NEET 2016]

 23. Which of the following reagents would distinguish *cis*-cyclopenta-1, 2-diol from the *trans*-isomer?

- (a)  $MnO_2$   
 (b) Aluminium isopropoxide  
 (c) Acetone  
 (d) Ozone

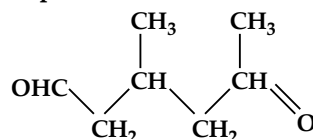
[NEET 2016]

24. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is:

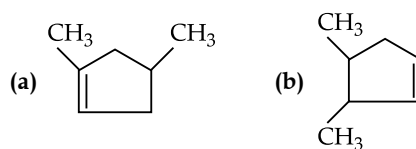
- (a) a carbonyl compound with a hydrogen atom on its alpha carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.  
 (b) a carbonyl compound with a hydrogen atom on its alpha carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.  
 (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.  
 (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

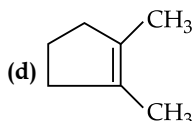
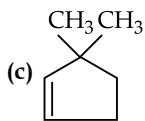
[NEET 2016]

25. A single compound of the structure



is obtainable from ozonolysis of which of the following cyclic compounds?





[AIPMT 2015]

26. Reaction of a carbonyl compound with one of the following reagent involves nucleophilic addition followed by the elimination of water. The reagents is:

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

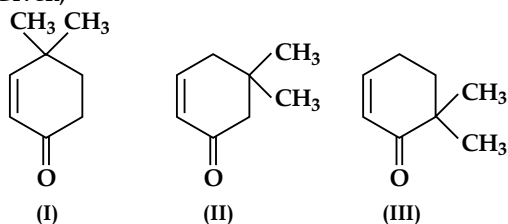
[AIPMT 2015]

27. Treatment of cyclopentanone with methyl lithium gives which of the following species?

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

[AIPMT 2015]

28. Given,



Which of the given compounds can exhibit tautomerism?

- (a) I and II  
 (b) I and III  
 (c) II and III  
 (d) I, II and III

[AIPMT 2015]

29. 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:

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

30. Reaction by which benzaldehyde cannot be prepared?

- (a) +  $CrO_2Cl_2$  and  $CS_2$  followed by  $H_3O^+$
- (b) +  $H_2$  in pressure of Pd-BaSO<sub>4</sub>
- (c) + CO + HCl in presence of anhy. AlCl<sub>3</sub>
- (d) + Zn/Hg and conc. HCl

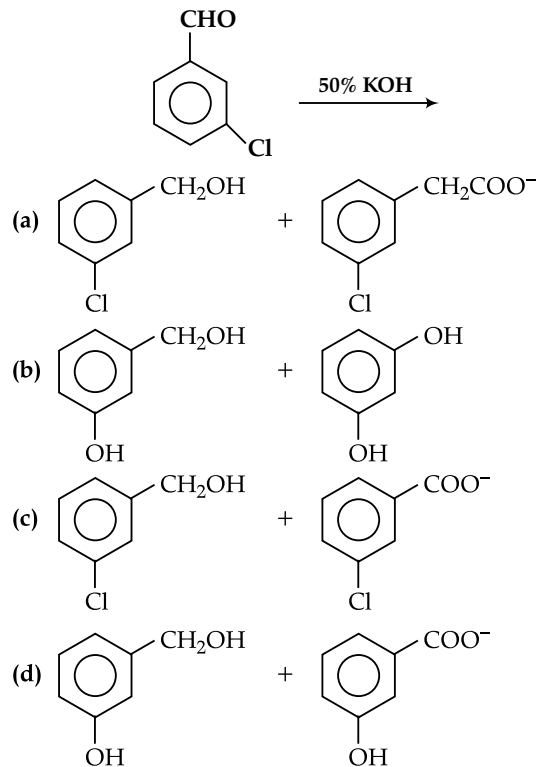
[NEET 2013]

31.  $CH_3CHO$  and  $C_6H_5CH_2CHO$  can be distinguished chemically by:

- (a) Benedict test  
 (b) Iodoform test  
 (c) Tollen's reagent test  
 (d) Fehling solution test

[AIPMT 2012]

32. Predict the products in the given reaction:



[AIPMT 2012]

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

- (a)  $CH_3CH_2CH_2-C(=O)-CH_3$
- (b)  $CH_3CH_2CH_2-C(=O)-CH_2CH_2CH_3$
- (c)  $(CH_3)_2C(OH)OC_2H_5$
- (d)  $(CH_3)_2C(OC_2H_5)_2$

[AIPMT 2012]

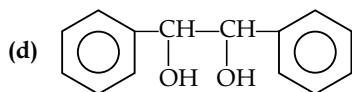
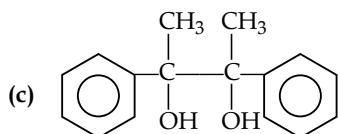
34. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

- (a) Zn-Hg with HCl  
 (b)  $LiAlH_4$   
 (c)  $H_2$  and Pt as catalyst  
 (d) Glycol with KOH

[AIPMT 2011]

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

- (a)
- (b)



[AIPMT 2008]

36. A strong base can abstract an  $\alpha$ -hydrogen from:

- (a) alkene (b) amine  
(c) ketone (d) alkane [AIPMT 2008]

37. Which one of the following on treatment with, 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?

- (a)  $C_6H_5CH_2CHO$  (b)  $C_6H_5CHO$   
(c)  $CH_3CH_2CH_2CHO$  (d)  $CH_3-C(=O)-CH_3$

[AIPMT 2007]

38. The product formed in aldol condensation is:

- (a) a beta-hydroxy acid  
(b) a beta-hydroxy aldehyde or a beta-hydroxy ketone.  
(c) an alpha-hydroxy aldehyde or ketone  
(d) an alpha, beta unsaturated ester [AIPMT 2007]

39. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called:

- (a) Clemmensen reduction  
(b) Cope reduction  
(c) Dow reduction  
(d) Wolff-Kishner reduction [AIPMT 2007]

40. Nucleophilic addition reaction will be most favoured in:

- (a)  $CH_3-CH_2-CH_2-C(=O)-CH_3$   
(b)  $(CH_3)_2C=O$   
(c)  $CH_3CH_2CHO$   
(d)  $CH_3CHO$

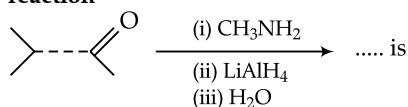
[AIPMT 2006]

41. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of  $\alpha$ -hydroxy acid. The carbonyl compound is:

- (a) acetaldehyde (b) acetone  
(c) diethyl ketone (d) formaldehyde

[AIPMT 2006]

42. The major organic product formed from the following reaction



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

[AIPMT 2005]

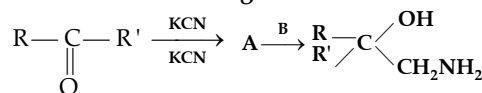
43. Which one of the following can be oxidised to the corresponding carbonyl compound?

- (a) 2-hydroxy propane  
(b) Ortho-nitro phenol

(c) Phenol

(d) 2-methyl-2, hydroxyl propane [AIPMT 2004]

44. A and B in the following reactions are:



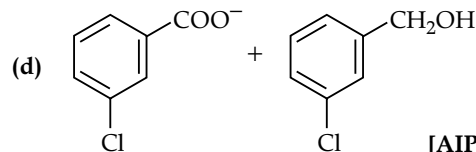
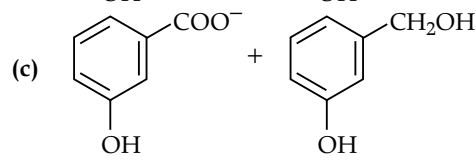
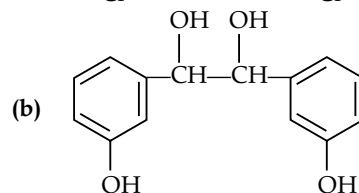
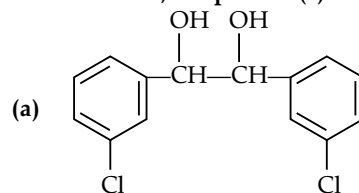
(a)  $A = RR'CH_2OH$ ,  $B = NaOH$

(b)  $A = RR'C \begin{matrix} \text{OH} \\ \text{COOH} \end{matrix}$ ,  $B = CH_3$

(c)  $A = RR'C \begin{matrix} \text{CN} \\ \text{COOH} \end{matrix}$ ,  $B = CH_3$

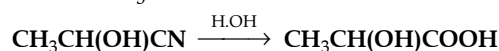
(d)  $A = RR'C \begin{matrix} \text{CN} \\ \text{OH} \end{matrix}$ ,  $B = LiAlH_4$  [AIPMT 2003]

45. When *m*-chlorobenzaldehyde is treated with 50% KOH solution, the product(s) obtained is (are):



[AIPMT 2003]

46. In this reaction  $CH_3CHO + HCN \longrightarrow$

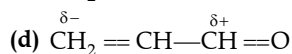
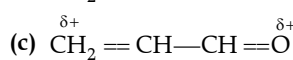
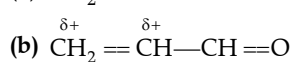
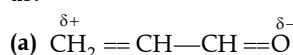


An asymmetric centre is generated. The acid obtained would be:

- (a) 50% *D* + 50% *L*-isomer  
(b) 20% *D* + 80% *L*-isomer  
(c) *D*-isomer  
(d) *L*-isomer

[AIPMT 2003]

47. Polarisation of electrons in acrolein may be written as:



[AIPMT 2000]

48. During reduction of aldehydes with hydrazine and potassium hydroxide, the first is the formation of:

- (a)  $R-CH=NH_2$  (b)  $R-C=N$   
 (c)  $R-\overset{\overset{O}{\parallel}}{C}-NH_2$  (d)  $R-CH=NH$

[AIPMT 2000]

49. Aldol condensation will not take place in:

- (a) HCHO (b)  $CH_3CHO$   
 (c)  $CH_3COCH_3$  (d)  $CH_2CH_2CHO$

[AIPMT 1999]

50. Iodoform test is not given by:

- (a) 2-pentanone (b) ethanol  
 (c) ethanal (d) 3-pentanone

[AIPMT 1998]

51. Ketones  $2 \begin{array}{c} H \\ \diagdown \\ C=O \\ \diagup \\ H \end{array}$ , where  $R = R_1 =$  alkyl group,

can be obtained in one step by:

- (a) hydrolysis of esters  
 (b) oxidation of primary alcohol  
 (c) oxidation of tertiary alcohol  
 (d) reaction of acid halide with alcohol [AIPMT 1997]

52. 1-phenyl ethanol can be prepared by the reaction of benzaldehyde with:

- (a) methyl bromide  
 (b) ethyl iodide and magnesium  
 (c) methyl iodide and magnesium  
 (d) methyl bromide and aluminium bromide

[AIPMT 1997]

53.  $[CH_3]_3C-CHO$  does not undergo alcohol condensation due to:

- (a) three electron donating methyl groups  
 (b) cleavage taking place between  $-C-CHO$  bond  
 (c) absence of alpha hydrogen atom in the molecule  
 (d) bulky  $(CH_3)_3C-$  group [AIPMT 1996]

54. Acetone reacts with iodine ( $I_2$ ) to form iodoform in the presence of:

- (a)  $CaCO_3$  (b) NaOH  
 (c) KOH (d)  $MgCO_3$  [AIPMT 1995]

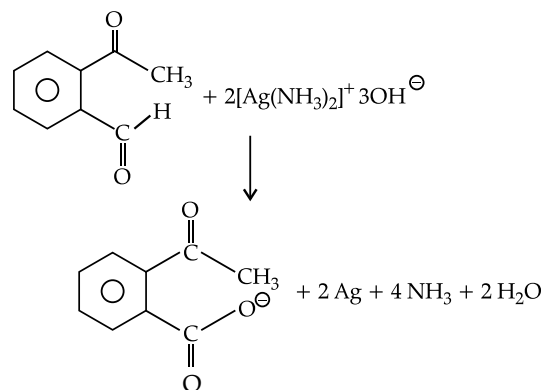
## Answer Key

|     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (a) | 2.  | (a) | 3.  | (b) | 4.  | (d) | 5.  | (d) | 6.  | (c) |
| 7.  | (d) | 8.  | (a) | 9.  | (a) | 10. | (b) | 11. | (b) | 12. | (a) |
| 13. | (d) | 14. | (a) | 15. | (b) | 16. | (c) | 17. | (a) | 18. | (a) |
| 19. | (d) | 20. | (b) | 21. | (c) | 22. | (b) | 23. | (c) | 24. | (b) |
| 25. | (a) | 26. | (b) | 27. | (a) | 28. | (d) | 29. | (c) | 30. | (d) |
| 31. | (b) | 32. | (c) | 33. | (d) | 34. | (a) | 35. | (a) | 36. | (c) |
| 37. | (b) | 38. | (b) | 39. | (a) | 40. | (d) | 41. | (a) | 42. | (b) |
| 43. | (a) | 44. | (d) | 45. | (d) | 46. | (a) | 47. | (a) | 48. | (a) |
| 49. | (a) | 50. | (d) | 51. | (c) | 52. | (c) | 53. | (c) | 54. | (b) |

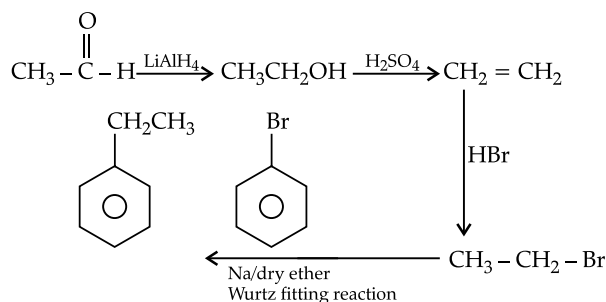
## Answers with Explanation

- (a) There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.
- (a) Formaldehyde is planer molecule with  $sp^2$  hybridisation.

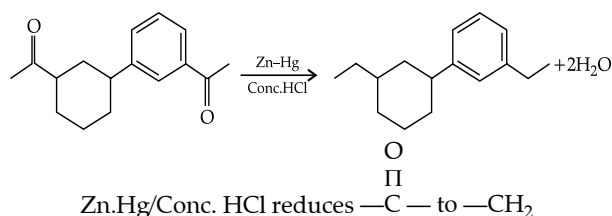
3. (b) Tollen's Reagent used to differentiate Aldehyde and Ketone and it produces silver mirror.



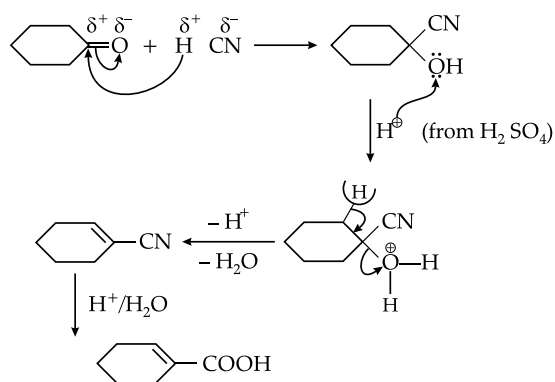
4. (d)



5. (d)

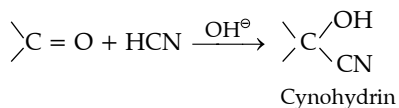


6. (c)

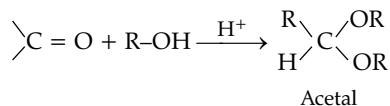


7. (d)

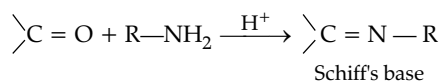
Explanation: When carbonyl group is reacted with HCN, cyanohydrin is formed as a product.



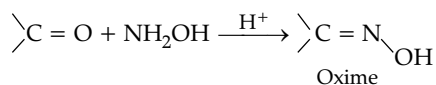
When carbonyl group is reacted with alcohol, it leads in the formation of an acetal.



On reaction with  $\text{RNH}_2$ , carbonyl compound leads to the formation of Schiff's base.

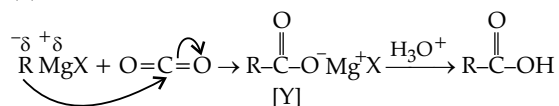


When carbonyl compound is treated with hydroxyl amine, oxime is formed.

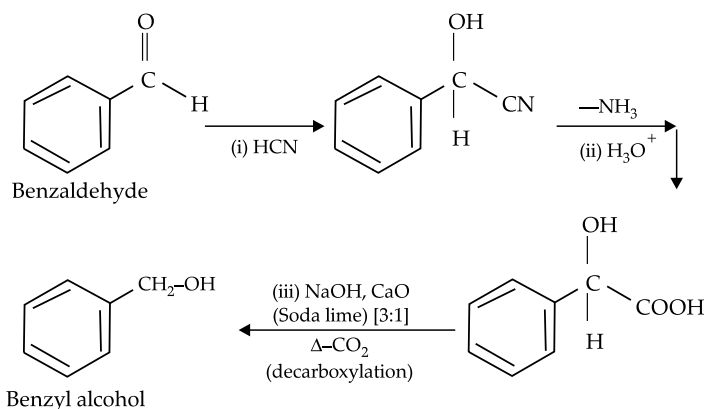


8. (a)

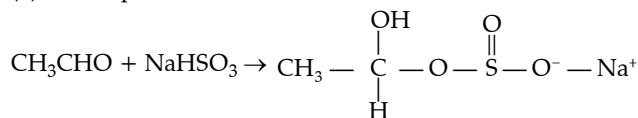
9. (a)



11. (b)

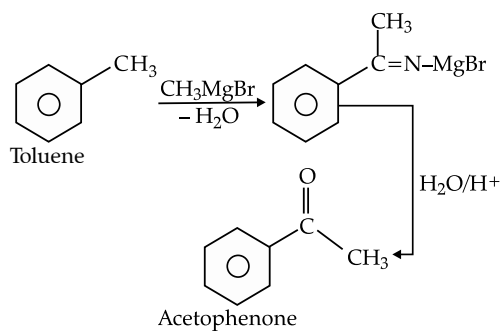


12. (a) Nucleophilic addition – elimination reaction is associated with elimination of  $\text{H}_2\text{O}$ .

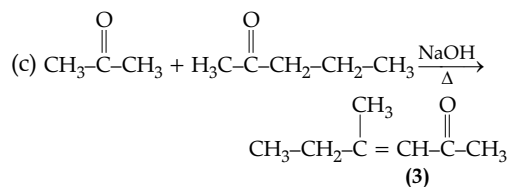
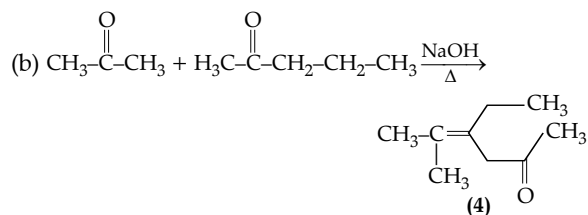
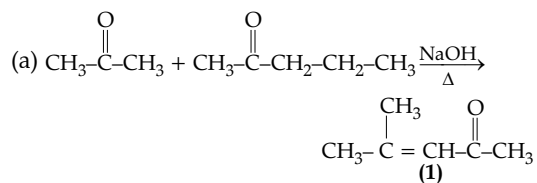
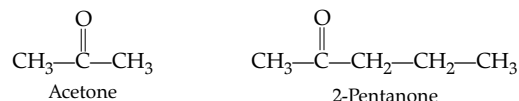


Here the above reaction is an addition reaction.

13. (d)


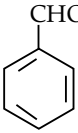


10. (b)

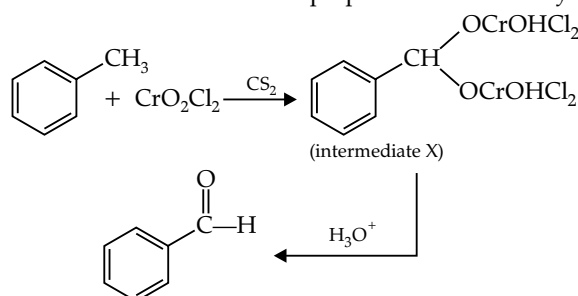


So, product (2) is not formed.

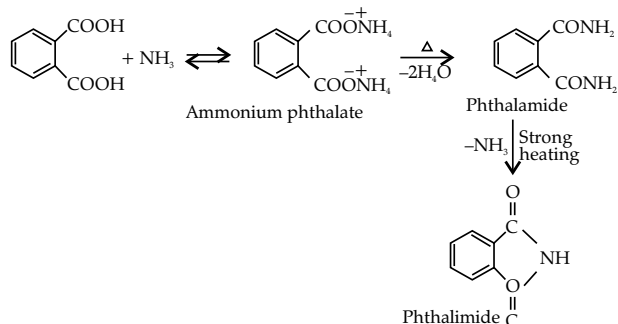
14. (a)

|     |   |       |                                |
|-----|---|-------|--------------------------------|
| (a) |  $\xrightarrow[\text{anhyd AlCl}_3/\text{CuCl}]{\text{CO, HCl}}$  | (ii)  | Gattermann Koch reaction       |
| (b) | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{NaOX} \longrightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CX}_3$   | (iii) | Haloform reaction              |
| (c) | $\text{R}-\text{CH}_2-\text{OH} + \text{R}'\text{COOH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{R}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$   | (iv)  | Esterification                 |
| (d) | $\text{R}-\text{CH}_2\text{COOH} \xrightarrow[\text{H}_2\text{O}]{\text{X}_2/\text{Red P}} \text{R}-\underset{\text{X}}{\text{CH}}-\text{COOH}$   | (i)   | Hell Volnard Zelinsky reaction |

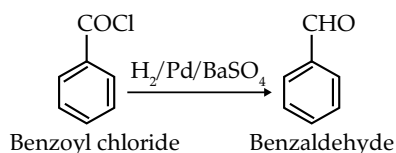
15. (b) The given reaction is Etard's reaction which is used to prepare aromatic aldehyde.

16. (c) In the presence of dil.  $\text{OH}^-$ , benzaldehyde and acetophenone will react to undergo cross-aldol condensation.

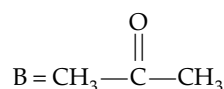
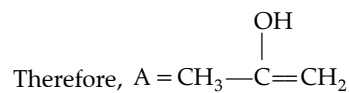
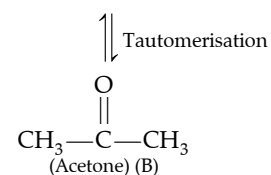
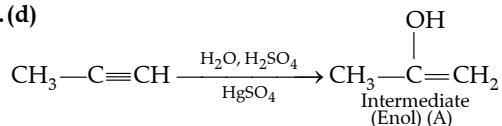
17. (a) Phthalic acid undergoes dehydration on heating to form acid anhydride and on heating with ammonia it forms ammonium phthalate which further forms phthalamide by dehydration and on strong heating further it finally forms Phthalimide.



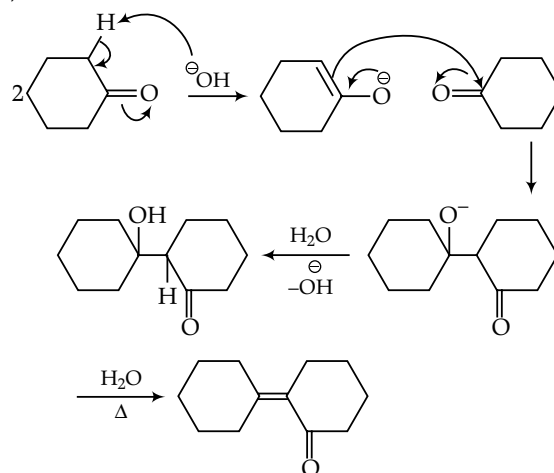
18. (a) Rosenmund reaction (partial-reduction).



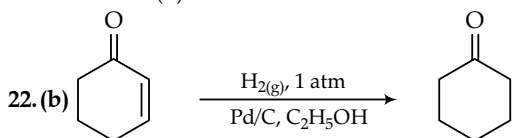
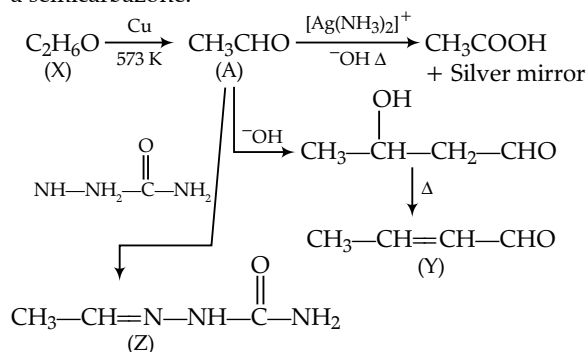
19. (d)



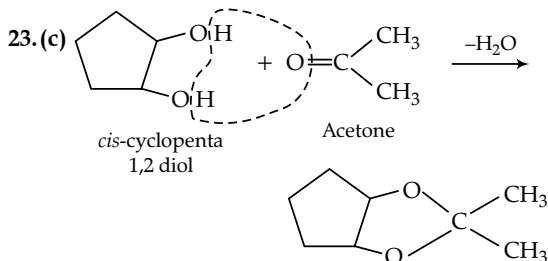
20. (b)

21. (c) 'A' gives silver mirror test thus, it must be an aldehyde or  $\alpha$ -hydroxyketone. 'X' must be an alcohol which reduces it to give an aldehyde 'A'.

'A' on treatment with base followed by heating will give alcohol condensation product. This indicates that 'A' must be an aldehyde and not a ketone. 'Z' must be a semicarbazone.

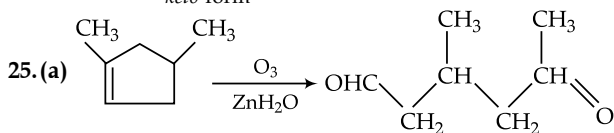
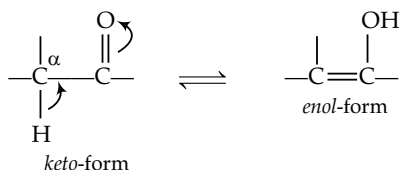


When  $\text{H}_2$  Pd/C catalyst is used then  $\text{C}=\text{C}$  is reduced at faster rate than  $\text{C}=\text{O}$  bond.

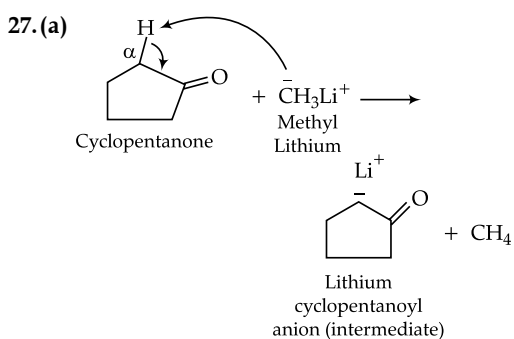


Trans isomer does not react with acetone as removal of  $\text{H}_2\text{O}$  molecule is difficult.

24. (b) Keto-enol tautomerism is as follows:

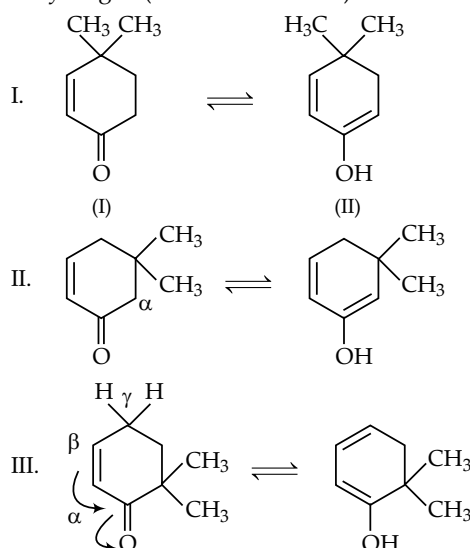


26. (b) Reaction of carbonyl compounds with ammonia derivatives give addition product followed by the elimination reaction. Slightly acidic medium generate a nucleophilic centre for the attack of weak base like ammonia derivatives.



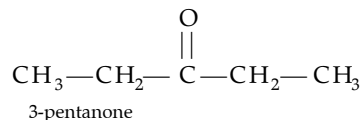
Here  $\text{CH}_3\text{Li}^+$  abstract active proton.

28. (d) In keto-enol tautomerism keto form should have  $\alpha$ -hydrogen (structure I and II).

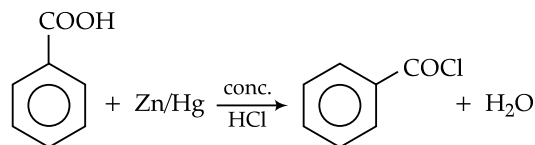


29. (c) As the compound X yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test so it must contain a  $\text{C}=\text{O}$  group but neither a methyl ketone nor in aldehyde.

Thus, the structure of X will be

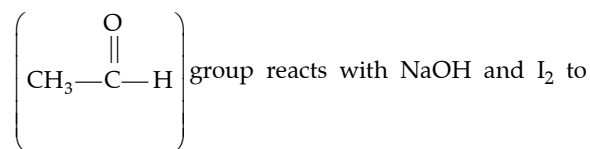


30. (d)

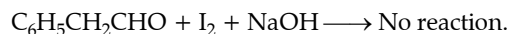
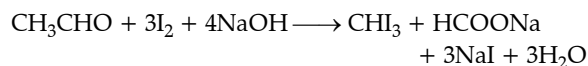


Rest all in options benzaldehyde is obtained.

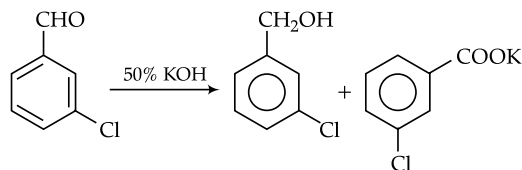
31. (b)  $\text{CH}_3\text{CHO}$  due to the presence of



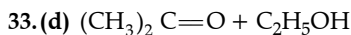
give yellow crystals of iodoform while  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$  does not react with it.



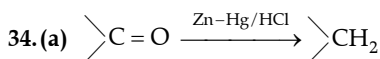
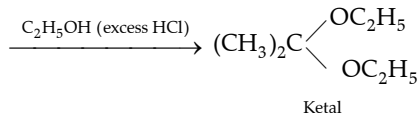
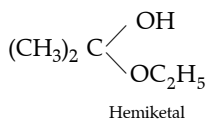
32. (c)



This reaction is called cannizzaro's reaction.

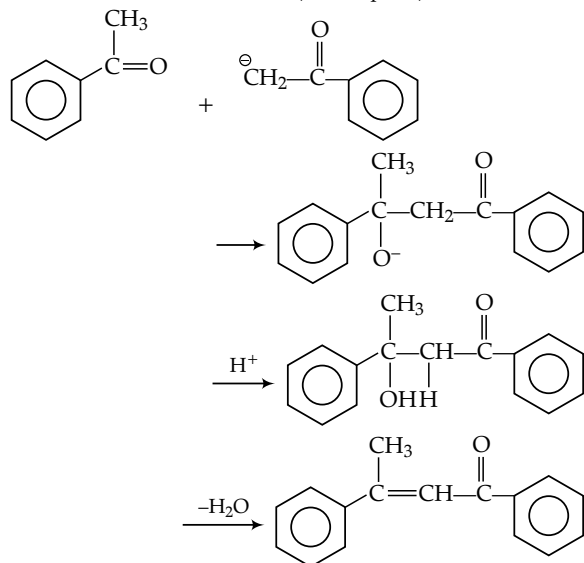
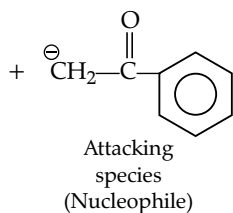
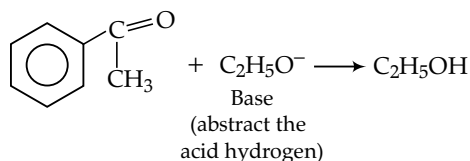
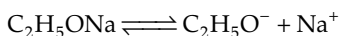


Acetone  
(2-propanone)



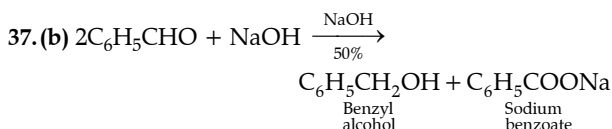
This is called as clemmensen reduction.

35. (a) This reaction is known as aldol condensation



36. (c) As the carbonyl carbon is electron deficient so most susceptible to attack by nucleophilic reagent or base.

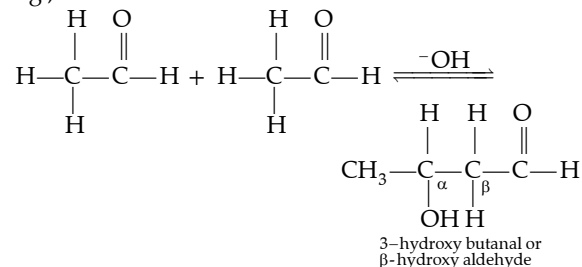
Thus  $\alpha$ -hydrogen is the easily obstructed from ketones by a base.



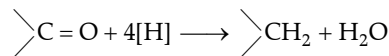
This reaction is called cannizzaro reaction.

38. (b) In aldol condensation when both molecules are same then it is called as self aldol condensation.

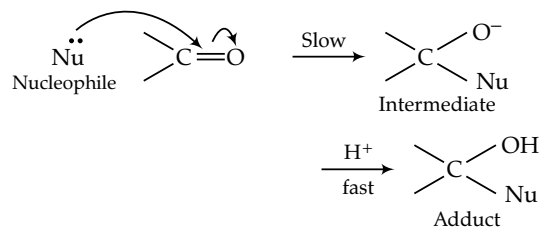
e.g.,



39. (a) **Clemmensen reduction:** Aldehydes and ketones are reduced to the corresponding alkanes by means of amalgamated Zinc and HCl.



40. (d)

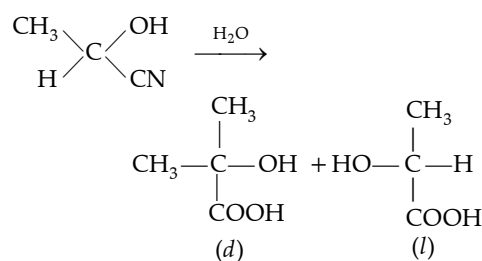
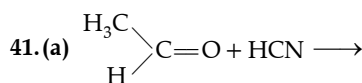
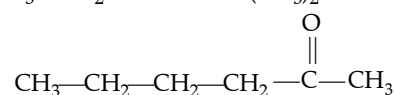
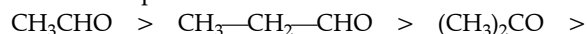


Aldehydes are more reactive than ketones towards nucleophiles. The addition of nucleophiles is based upon the positive charge present on carbon atom of

$\text{>C}=\text{O}$  group. In aldehyde  $\text{>C}=\text{O}$  group is present

with at least one alkyl group (except formaldehyde) which has +I effect and which decreases the positive charge of carbon, thereby making the attack to nucleophilic in ketones having minimum of two alkyl groups.

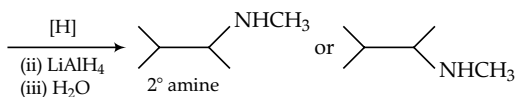
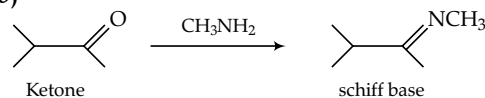
Thus nucleophilic addition order is:



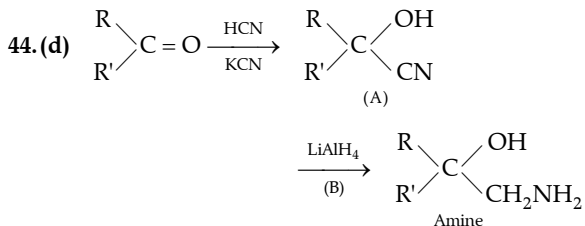
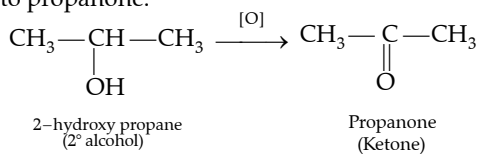
Racemic mixture

Rest all other options gives optically inactive compounds.

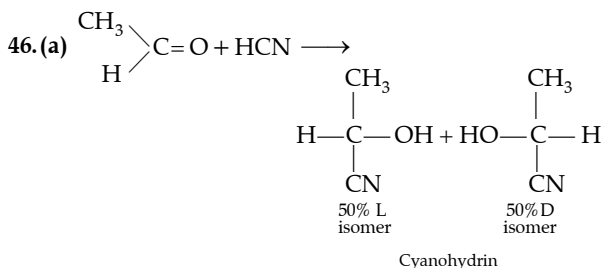
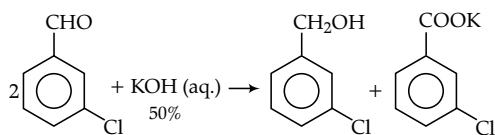
42. (b)



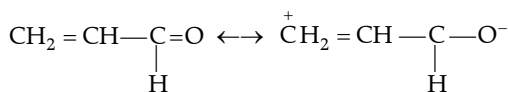
43. (a) 2-hydroxy propane or secondary alcohol is oxidised into propanone.



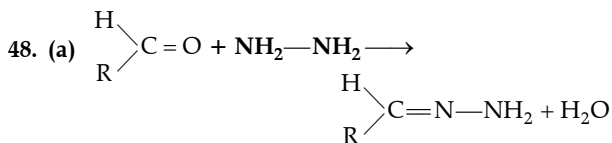
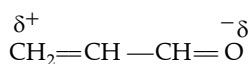
45. (d) Due to absence of  $\alpha$ -hydrogen m-chloro benzaldehyde gives cannizzaro reaction



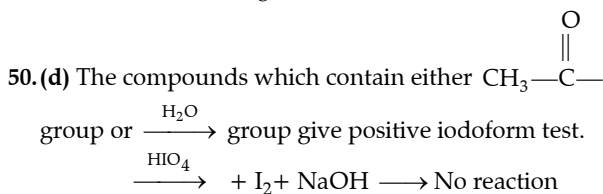
47. (a) In  $\text{CH}_2 = \text{CH}-\text{CHO}$  due to  $-M$  effect of  $-\text{CHO}$  group, polarisation of electron takes place as follows:



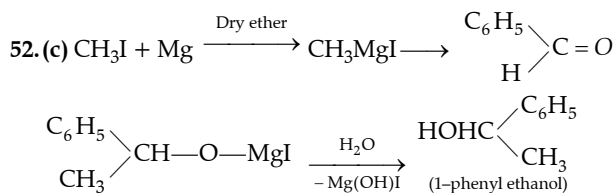
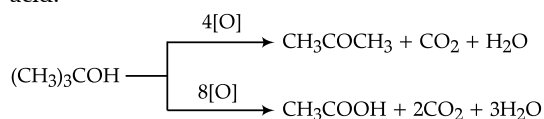
Hence partial polarisation is represented as:



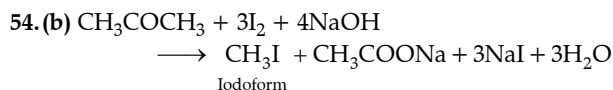
49. (a) Those aldehydes which do not have  $\alpha$ -hydrogen atom like  $\text{HCHO}$ , does not give alcohol condensation reaction.



51. (c) By oxidation of tertiary alcohol with stronger oxidising agent can yield ketones along with carboxylic acid.



53. (c)  $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CHO}$  does not undergo alcohol condensation because it does not contain  $\alpha$ -hydrogen atom.

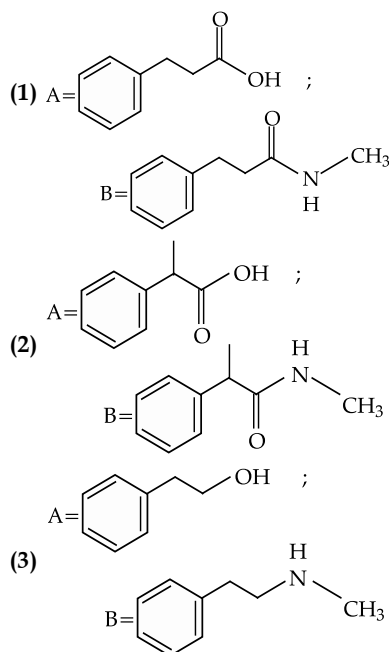
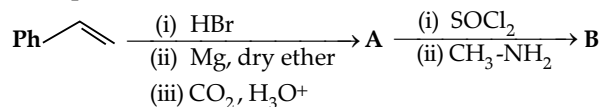


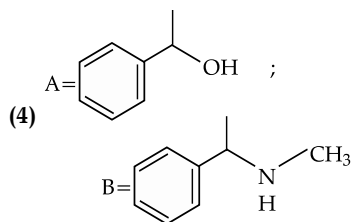
## Topic 5: Previous Year's Questions

- Assertion A:** Compounds containing  $-\text{CHO}$  group are easily oxidised to corresponding carboxylic acids.  
**Reason R:** Carboxylic acids can be reduced to alcohols by treatment with  $\text{LiAlH}_4$   
**In the light of the above statements, choose the most appropriate answer from the options given below:**

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.  
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion.  
(c) Assertion is correct, reason is incorrect.  
(d) Assertion is incorrect, reason is correct.

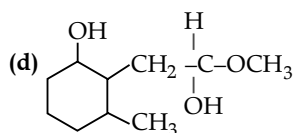
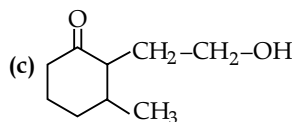
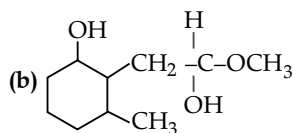
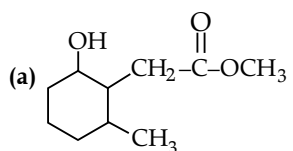
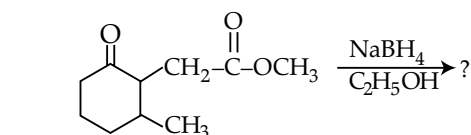
2. The products **A** and **B** in the following reaction sequence are:





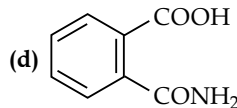
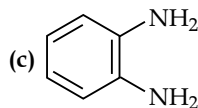
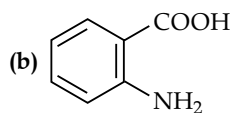
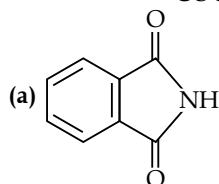
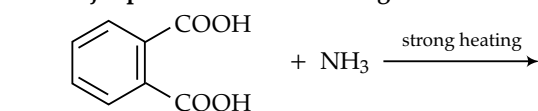
[NEET September 2022]

3. The product formed in the following chemical reaction is



[NEET 2021]

4. The major product of the following reaction is:



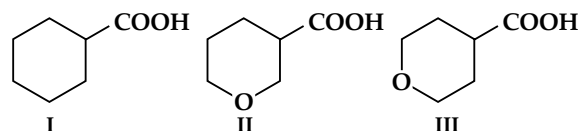
[NEET 2019]

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

- (a) More extensive association of carboxylic acid via van der Waals force of attraction  
 (b) Formation of carboxylate ion  
 (c) Formation of intramolecular H-bonding  
 (d) Formation of intermolecular H-bonding

[NEET 2018]

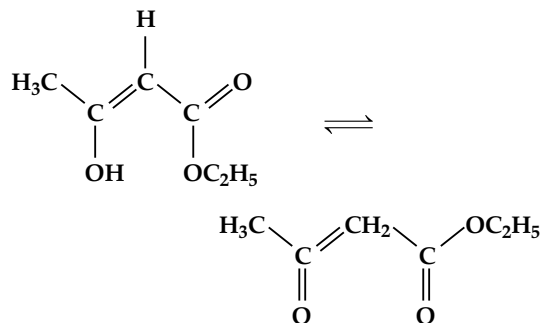
6. The correct order of strengths of the carboxylic acids:



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

[NEET 2016]

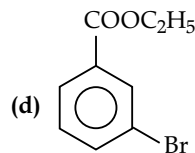
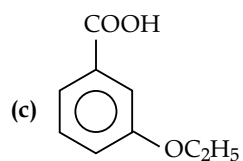
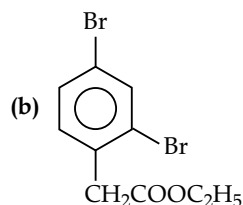
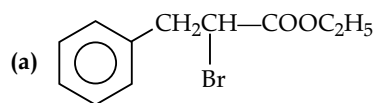
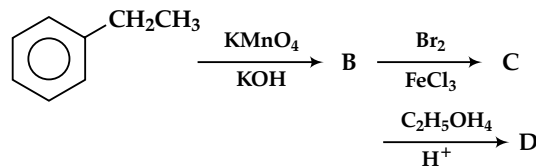
7. The enolic form of ethyl acetoacetate as below has:



- (a) 18σ bonds and 2π bonds  
 (b) 16σ bonds and 1π bond  
 (c) 9σ bonds and 2π bonds  
 (d) 9σ bonds and 1π bond

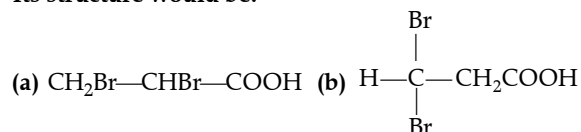
[AIPMT 2015]

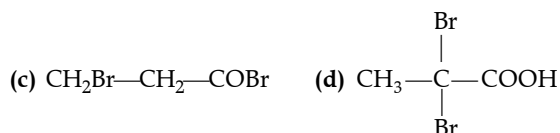
8. In a set of reaction, ethyl benzene yields a product D.



[AIPMT 2010]

9. Propionic acid with Br<sub>2</sub>/P yields a dibromo product. Its structure would be:





[AIPMT 2009]

10. The relative reactivity of acyl compounds towards nucleophilic substitution are in the order of:

- (a) acyl chloride > acid anhydride > ester > amide  
 (b) ester > acyl chloride > amide > acid anhydride  
 (c) acid anhydride > amide > ester > acyl chloride  
 (d) acyl chloride > ester > acid anhydride > amide

[AIPMT 2008]

11. Which of the following represents the correct order of acidity in the given compounds?

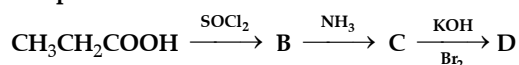
- (a)  $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$   
 (b)  $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH}$   
 (c)  $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{CH}_3\text{COOH}$   
 (d)  $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} < \text{FCH}_2\text{COOH}$

[AIPMT 2007]

12. Self condensation of two moles of ethyl acetate in the presence of sodium ethoxide yields:

- (a) ethyl butyrate      (b) acetoacetic ester  
 (c) methyl acetoacetate      (d) ethyl propionate

13. In a set of reactions propionic acid yielded a compound D.

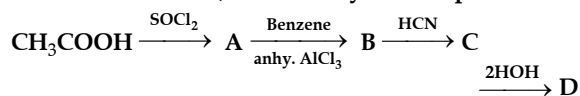


The structure of D would be:

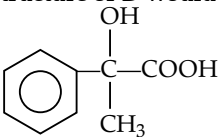
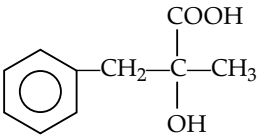
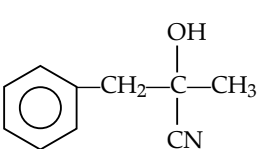
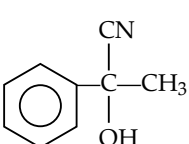
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$       (b)  $\text{CH}_3\text{CH}_2\text{CONH}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{NHCH}_3$       (d)  $\text{CH}_3\text{CH}_2\text{NH}_2$

[AIPMT 2006]

14. In a set of reactions, acetic acid yielded a product D.



The structure of D would be:

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

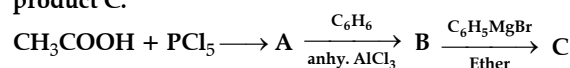
[AIPMT 2005]

15. Which one of the following order of acidic strength is correct?

- (a)  $\text{RCOOH} > \text{HOH} > \text{HC} \equiv \text{CH} > \text{ROH}$   
 (b)  $\text{RCOOH} > \text{HC} \equiv \text{CH} > \text{HOH} > \text{ROH}$   
 (c)  $\text{RCOOH} > \text{ROH} > \text{HOH} > \text{HC} \equiv \text{CH}$   
 (d)  $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH}$

[AIPMT 2003]

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

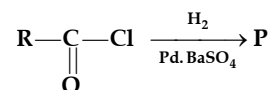


Product C would be:

- (a)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$       (b)  $\text{CH}_3-\overset{\text{C}_2\text{H}_5}{\text{C}}(\text{OH})\text{C}_6\text{H}_5$   
 (c)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$       (d)  $\text{CH}_3\text{COC}_6\text{H}_5$

[AIPMT 2003]

17. In the following reaction, product P is overlap:



- (a)  $\text{RCH}_2\text{OH}$       (b)  $\text{RCOOH}$   
 (c)  $\text{RCHO}$       (d)  $\text{RCH}_3$

[AIPMT 2002]

18. Benzoic acid may be converted into ethyl benzoate by reaction with:

- (a) sodium ethoxide      (b) ethyl chloride  
 (c) dry HCl,  $\text{C}_2\text{H}_5\text{OH}$       (d) ethanol

[AIPMT 2000]

19. Reduction by  $\text{LiAlH}_4$  of hydrolysed product of an ester gives:

- (a) two acids  
 (b) two aldehydes  
 (c) one molecule of alcohol and another of carboxylic acid  
 (d) two alcohols

[AIPMT 2000]

20. Which one of the following esters cannot undergo Claisen self-condensation?

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$   
 (b)  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$   
 (d)  $\text{C}_6\text{H}_{11}\text{CH}_2\text{COOC}_2\text{H}_5$

[AIPMT 1998]

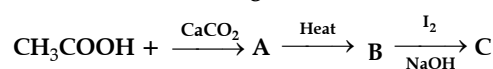
21. An ester (a) with molecular formula  $\text{C}_9\text{H}_{10}\text{O}_2$  was treated with excess of  $\text{CH}_3\text{MgBr}$  and the complex so formed was treated with  $\text{H}_2\text{SO}_4$  to give an olefin (b). Ozonolysis of (b) gave a ketone with molecular formula  $\text{C}_8\text{H}_8\text{O}$  which shows positive iodoform test.

The structure of (a) is:

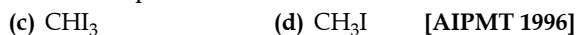
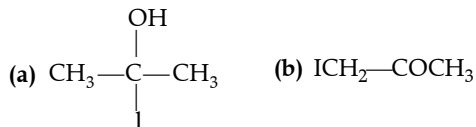
- (a)  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$       (b)  $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$   
 (c)  $\text{H}_3\text{CCOOC}_6\text{H}_5$       (d)  $p\text{-H}_3\text{COC}_6\text{H}_4\text{COCH}_3$

[AIPMT 1998]

22. Consider the following transformations



The molecular formula of C is:



23. An ester is boiled with KOH. The product is cooled and acidified with conc. HCl. A white crystalline acid separates. The ester is:

- (a) methyl acetate      (b) ethyl acetate  
(c) ethyl formate      (d) ethyl benzoate

[AIPMT 1994]

24. Schotten Baumann reaction is a reaction of phenols with:

- (a) benzoyl chloride and NaOH  
(b) acetyl chloride and NaOH  
(c) salicylic acid and conc.  $\text{H}_2\text{SO}_4$   
(d) acetyl chloride and conc.  $\text{H}_2\text{SO}_4$       [AIPMT 1994]

25. The preparation of ethyl acetoacetate involve:

- (a) Wittig reaction      (b) Cannizzaro's reaction  
(c) Reformatsky reaction      (d) Claisen condensation

[AIPMT 1994]

26. Formic acid is obtained when:

- (a) calcium acetate is heated with conc.  $\text{H}_2\text{SO}_4$   
(b) calcium formate is heated with calcium acetate  
(c) glycerol is heated with oxalic acid at 373 K  
(d) acetaldehyde is oxidised with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$

[AIPMT 1994]

27. Among acetic acid, phenol and *n*-hexanol which one of the following compounds will react with  $\text{NaHCO}_3$  solution to give sodium salt and  $\text{CO}_2$ ?

- (a) Acetic acid      (b) *n*-hexanol  
(c) Acetic acid and phenol      (d) Phenol

28. Sodium formate on heating yields:

- (a) Oxalic acid and  $\text{H}_2$   
(b) Sodium oxalate and  $\text{H}_2$   
(c)  $\text{CO}_2$  and NaOH  
(d) Sodium oxalate

[AIPMT 1993]

29. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore, X and Y are respectively.

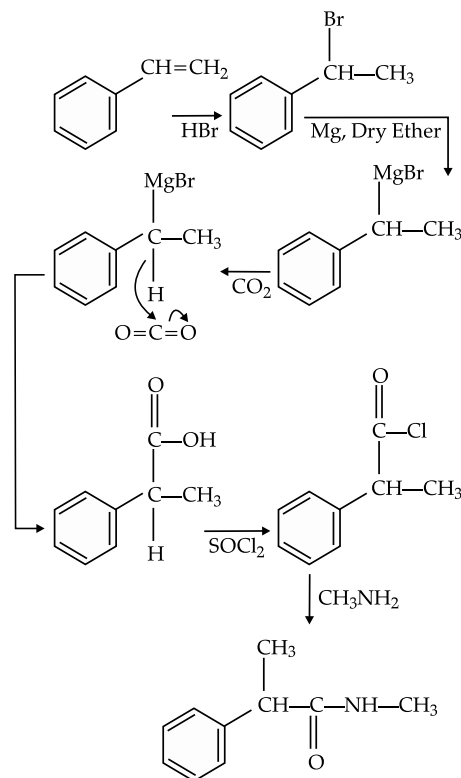
- (a) soda lime and copper  
(b) Zn dust and NaOH  
(c) Zn dust and soda lime  
(d) soda lime and zinc dust

[AIPMT 1992]

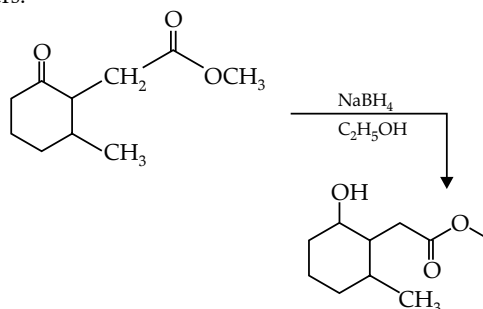
## Answers with Explanation

1. (b) Compounds containing  $-\text{CHO}$  group are easily oxidised to corresponding carboxylic acids.

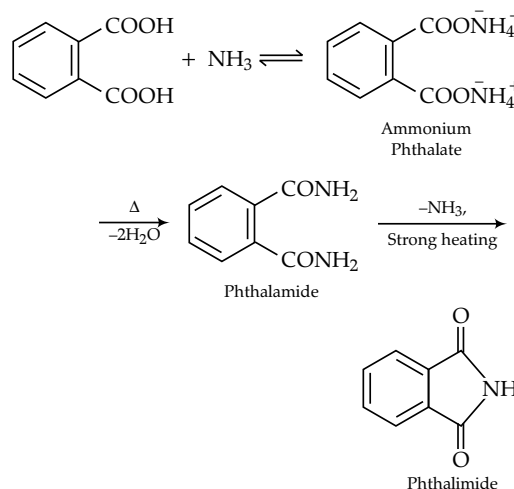
2. (b)



3. (a)  $\text{NaBH}_4$  is a weak reducing agent which can reduce carbonyl group into alcohol but does not reduce esters.



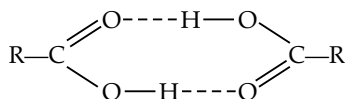
4. (a)



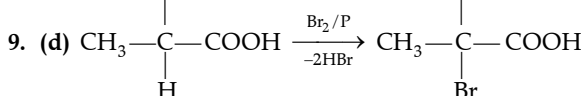
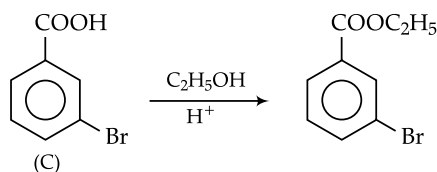
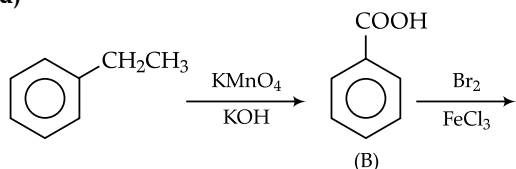
## Answer Key

|     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (b) | 2.  | (b) | 3.  | (a) | 4.  | (a) | 5.  | (d) | 6.  | (b) |
| 7.  | (a) | 8.  | (d) | 9.  | (d) | 10. | (a) | 11. | (c) | 12. | (b) |
| 13. | (d) | 14. | (a) | 15. | (d) | 16. | (b) | 17. | (c) | 18. | (c) |
| 19. | (d) | 20. | (b) | 21. | (a) | 22. | (c) | 23. | (d) | 24. | (a) |
| 25. | (d) | 26. | (c) | 27. | (a) | 28. | (b) | 29. | (d) |     |     |

5. (d) Due to formation of intermolecular H-bonding in carboxylic acid, association occurs. Hence boiling point increases and become more than the boiling point of aldehydes, ketones and alcohols of comparable molecular masses.

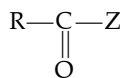


6. (b) As we know that  
Acidic strength  $\propto$  -I effect  
As oxygen is more electron withdrawing (II) and (III) shows greater -I effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of oxygen increases from  $-\text{COOH}$  group, acidic strength decreases.
7. (a) The given structure has  $18\sigma$  bonds and  $2\pi$  bonds.
8. (d)



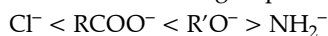
This reaction is called as Hell-Volhard Zelinsky (HVZ) reduction.

10. (a) In acyl compounds the reactivity depends upon the nature of group Z (i.e.  $\text{Cl}^-$ ,  $\text{RCOO}^-$ ,  $\text{R}'\text{O}^-$ ,  $\text{NH}_2^-$  etc)

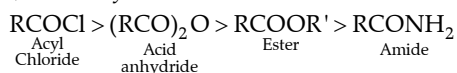


If group Z is a weak base, then it is a strong leaving agent and its reactivity towards nucleophilic substitution is high.

The order of basic nature of Z group is

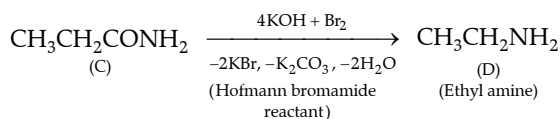
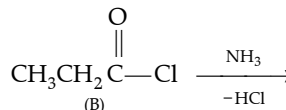
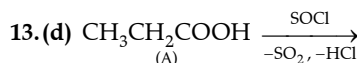
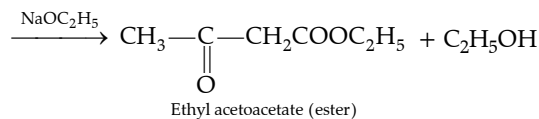
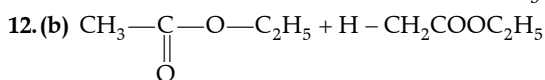
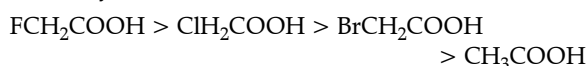


Thus, reactivity order is

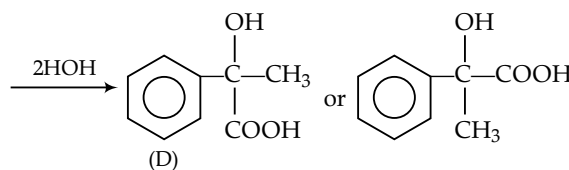
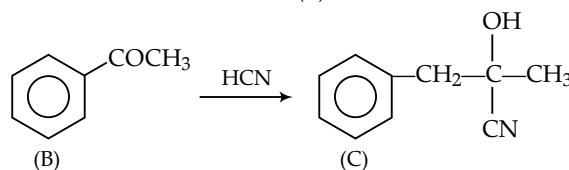
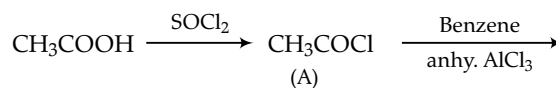


11. (c) The acidity of halogenated acid increases with increase in electronegativity of the halogen present.

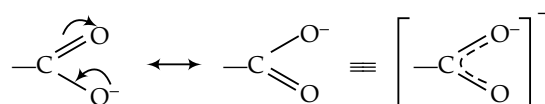
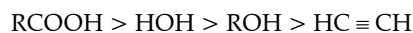
$\therefore$  Acidity order will be:



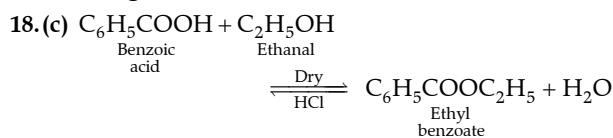
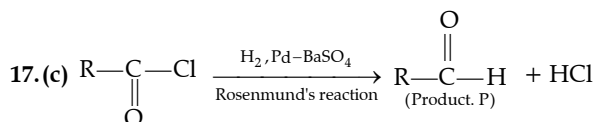
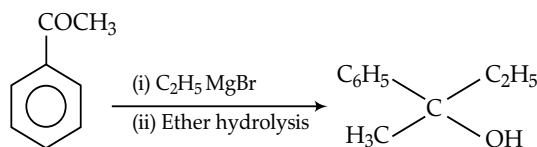
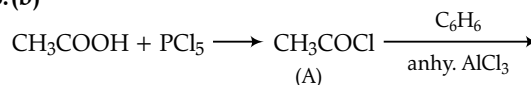
14. (a)



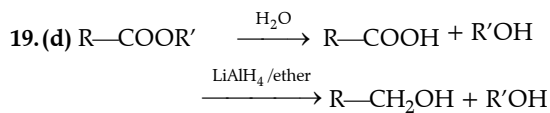
15. (d) Carboxylic acid is stronger acid than alcohol and water because after removal of proton carboxylate ion is stabilised by resonance.



16. (b)

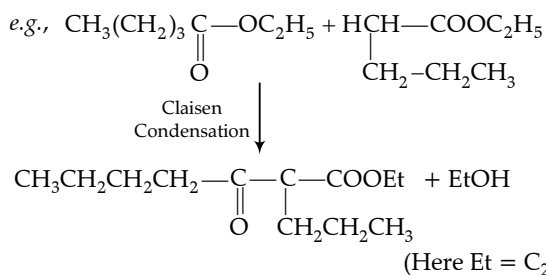


Here  $H_2O$  is continuously removed from reaction so that reaction always proceeds to product formation *i.e.*, ethyl benzoate.

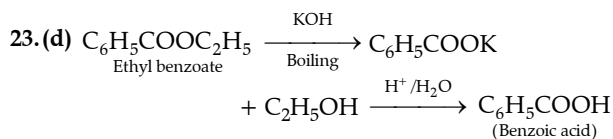
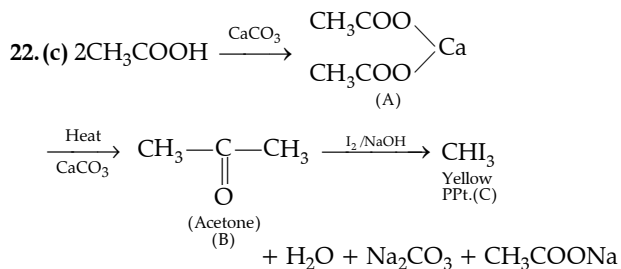
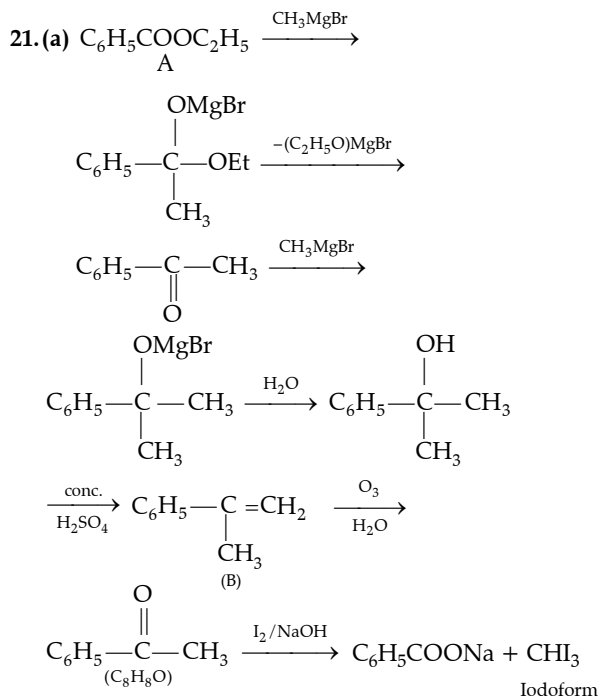


Thus, two molecules of  $R'OH$  is produced on reduction of hydrolysed product of ester.

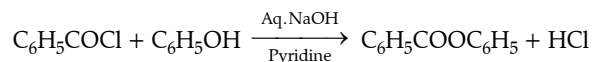
20. (b) The ester which contain  $\alpha$ -hydrogen atom undergoes Claisen self-condensation.



But in case of  $C_6H_5COOC_2H_5$ , it does not contain  $\alpha$ -hydrogen thus it does not undergo Claisen condensation.



24. (a) Schotten-Boumann reaction



25. (d) Preparation of ethyl acetoacetate involves Claisen condensation.

