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Alcohols, Phenols and Ethers





Preparation and Properties of Alcohols



1. The major product of the following reaction is:

[Sep. 05, 2020 (II)]

$$\begin{array}{c} \text{HO} \\ \text{CH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$$

(c)
$$CH = CH_2$$

 When neopentyl alcohol is heated with an acid, it slowly converted into an 85: 15 mixture of alkenes A and B, respectively. What are these alkenes? [Sep. 04, 2020 (I)]

(a)
$$H_3C$$
 H_3C and H_3C CH_3 CH_3

(b)
$$H_3C$$
 CH_3 and H_3C CH_3 CH_5

(c)
$$CH_3$$
 CH_3 CH_3 CH_3 CH_2 CH_2

(d)
$$H_3C$$
 CH_3 H_3C H_3C CH_2 and H_3C

3. The number of chiral centres present in [B] is

$$CH - C \equiv N \xrightarrow{(i) C_2H_3MgBr} [A]$$

$$CH_3 \xrightarrow{(i) CH_3MgBr} [B]$$

4. The major product of the following reaction is:

[Jan. 08, 2020 (I)]

$$H_3C$$
 OH $dil. H_2SO_4$ H_3C

Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives X as the major product. Reaction of X with Hg (OAc),/H2O followed by NaBH4 gives Y as the major product. Y is: [April 12, 2019 (II)]

OH

-CH3 cannot be prepared by:

[Jan. 12, 2019 (I)]

- (a) CH₃CH₂COCH₃+PhMgX
- (b) PhCOCH₂CH₃+CH₃MgX
- (c) PhCOCH3+CH3CH2MgX
- (d) HCHO+PhCH(CH3)CH2MgX

7.
$$CH_2 - C - OCH_3 \xrightarrow{NaBH_4} X$$

[Jan. 10, 2019 (I)]

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(a)
$$CH_2 - C - H$$

$$\begin{array}{c} \text{OH} & \text{O} \\ \text{(d)} & \text{CH}_2 - \text{C} - \text{OCH}_2 \end{array}$$

Which is the most suitable reagent for the following transformation? [Jan. 10, 2019 (II)]

$$CH_3 - CH = CH - CH_2 - CH - CH_3 \longrightarrow$$

- $CH_3 CH = CH CH_2CO_2H$
 - (b) I₂/NaOH
- (a) Tollen's reagent (c) CrO,Cl,/CS,
- (d) alkaline KMnO₄
- The gas evolved on heating CH₃MgBr in methanol is:

[Online April 9, 2016]

- (a) Methane
- (b) Ethane
- (c) Propane
- (d) HBr
- The most suitable reagent for the conversion of

$$R - CH_2 - OH \rightarrow R - CHO$$
 is: [2014]

- (a) KMnO.
- (b) K, Cr, O,
- (c) CrO₂
- (d) PCC (Pyridinium chlorochromate)
- 11. Which one of the following statements is not correct?

[Online April 11, 2014]

- (a) Alcohols are weaker acids than water
- (b) Acid strength of alcohols decreases in the following $RCH_3OH > R_3CHOH > R_3COH$
- (c) Carbon-oxygen bond length in methanol, CH₂OH is shorter than that of C - O bond length in phenol.
- (d) The bond angle / in methanol is 108.9°.
- 12. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively: [Online April 12, 2014]
 - (a) Red, colourless, blue (b) Red, blue, colourless
 - (c) Colourless, red, blue (d) Red, blue, violet
- 13. An unknown alochol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism: [2013]

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- (a) secondary alcohol by S_N1
- (b) tertiary alcohol by S_N1
- (c) secondary alcohol by S_N2
- (d) tertiary alcohol by S_N2
- 14. Rate of dehydration of alcohols follows the order:

[Online April 9, 2013]

- (a) 2°>1°> CH₃OH>3° (b) 3°>2°>1°> CH₃OH
- (c) $2^{\circ} > 3^{\circ} > 1^{\circ} > \text{CH}_3\text{OH}$ (d) $\text{CH}_3\text{OH} > 1^{\circ} > 2^{\circ} > 3^{\circ}$
- Amongst the following alcohols which would react fastest with conc. HCl and ZnCl₂? [Online April 22, 2013]
 - (a) pentanol
- (b) 2-methyl butanol
- (c) 2-pentanol
- (d) 2-methyl butan-2-ol
- Reagent used to convert allyl alcohol to acrolein is [Online May 19, 2012]
 - (a) MnO₂
- (b) H_2O_2
- (c) OsO,
- (d) KMnO₄
- 17. Consider thiol anion (RS°) and alkoxy anion (RO°). Which of the following statements is correct? [2011RS]
 - (a) RS° is less basic but more nucleophilic than RO°
 - (b) RS[⊕] is more basic and more nucleophilic than RO[⊕]
 - (c) RS^o is more basic but less nucleophilic than RO^o
 (d) RS^o is less basic and less nucleophilic than RO^o
- 18. From amongst the following alcohols, the one that would react fastest with conc. HCl and anhydrous ZnCl₂, is
 - (a) 2-Butanol
- (b) 2- Methylpropan-2-ol
- (c) 2-Methylpropanol
- (d) 1-Butanol

[2010]

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19. The main product of the following reaction is $C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{conc.H_2SO_4}$? [2010]

(a)
$$H_5C_6 \sim C = C < H_{CH(CH_3)_2}$$

(b)
$$C_6H_5CH_2 C = C CH_3 CH_3$$

(c)
$$C_6H_5CH_2CH_2$$

 H_3C $C = CH_2$

(d)
$$C_6H_5$$
 $C = C CH(CH_3)_2$

20. In the following sequence of reactions,

 $CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow{Mg} B \xrightarrow{HCHO} B$

ether
$$C \xrightarrow{\text{H}_2\text{O}} D$$

the compound D is

- (a) propanal
- (b) butanal
- (c) n-butyl alcohol
- (d) n-propyl alcohol.
- 21. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is [2006]

 CH_3

- (a) CH₃ CHCH₂OH
- (b) PhCHOHCH₂
- (c) CH₃CH₂CH(OH)CH₂CH₃
- (d) C₆H₅CH₅CH₅OH
- 22. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is [2005]
 - (a) Pyridinium chlorochromate
 - (b) Chromic anhydride in glacial acetic acid
 - (c) acidic dichromate
 - (d) Acidic permanganate
- 23. Among the following compounds which can be dehydrated very easily? [2004]

(a) CH₃CH₂-C-CH₂CH₃

- (b) CH₃CH₂CH₂CHCH₃
- (c) CH₃CH₂CH₂CH₂CH₂OH
- (d) CH₃CH₂CHCH₂CH₂OH

- During dehydration of alcohols to alkenes by heating with conc. H₂SO₄, the initiation step is [2003]
 - (a) formation of carbocation
 - (b) elimination of water
 - (c) formation of an ester
 - (d) protonation of alcohol molecule

POPIC 2 Preparation and Properties of Phenols



25. A solution of phenol in chloroform when treated with aqueous NaOH gives compound P as a major product. The mass percentage of carbon in P is ______. (to the nearest integer) (Atomic mass: C = 12; H = 1; O = 16)

[NV, Sep. 06, 2020 (II)]

26. The increasing order of boiling points of the following compounds is: [Sep. 05, 2020 (II)]



- (a) I < III < IV < II
- (b) I < IV < III < II
- (c) IV < I < II < III
- (d) III < I < II < IV
- [Sep. 03, 2020 (II)]
- 27. Consider the following reaction:

$$(iv) \bigoplus O \longrightarrow CH_3$$

$$O \bigoplus (ii)$$

$$O \bigoplus_{(i)} O$$

The product 'P' gives positive ceric ammonium nitrate test. This is because of the presence of which of these -OH group(s)? [Sep. 03, 2020 (II)]

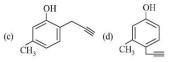
- (a) (ii) only
- (b) (iii) and (iv)
- (c) (iv) only
- (d) (ii) and (iv)
- The major product of the following reaction is:

[Sep. 02, 2020 (II)]

$$CH_{3} \xrightarrow{OH} \underbrace{\begin{array}{c} conc. \ HNO_{3} + conc. \\ H_{2}SO_{4} \end{array}}_{NO_{2}}$$

$$(c) \begin{array}{c} OH \\ NO_2 \end{array} \\ NO_2 \\ NO_2 \end{array} \\ (d) \begin{array}{c} OH \\ NO_2 \\ NO_2 \end{array}$$

- 29. Arrange the following compounds in increasing order of C - OH bond length: methanol, phenol, p-ethoxyphenol [Jan. 08, 2020 (I)]
 - (a) methanol < p-ethoxyphenol < phenol
 - (b) phenol < methanol < p-ethoxyphenol
 - (c) phenol < p-ethoxyphenol < methanol
 - (d) methanol < phenol < p-ethoxyphenol
- 30. What will be the major product when m-cresol is reacted with propargyl bromide (HC = C - CH₂Br) in presence [April 12, 2019 (II)] of K2CO3 in acetone?



31. The major product of the following reaction is:

[Jan. 11, 2019 (I)]

$$(c)$$
 (d) (d)

32. The major product of the following reaction is:

$$\xrightarrow{\mathrm{OH}} \xrightarrow{\mathrm{Br}_2 \; (\mathrm{excess})} \\ \mathrm{SO}_3 \mathrm{H}$$
 [Jan. 11, 2019 (I)]

$$(a) \begin{tabular}{|c|c|c|c|c|} \hline OH & OH \\ Br & (b) & OH \\ \hline SO_3H \\ \hline \end{tabular}$$

$$(c) \ \underset{Br}{\overset{OH}{\underset{Br}{\longrightarrow}}} \ Br \qquad (d) \ \underset{SO_3H}{\overset{OH}{\underset{Br}{\longrightarrow}}} \ Br$$

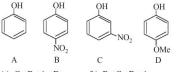
The major product of the following reaction is:

[Jan. 11, 2019 (II)]



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(d) 34. The increasing order of the pK_a values of the following compounds is: [Jan. 10, 2019 (I)]



- (a) C < B < A < D
- (b) B < C < D < A
- (c) $D \le A \le C \le B$
- (d) B < C < A < D

35. The major product of the following reaction is:

$$\begin{array}{c}
\text{CH}_{3} \\
\text{OH} \\
\hline
\begin{array}{c}
\text{(i) aq.NaOH} \\
\text{(ii) CH}_{3}\text{I}
\end{array}$$

[Jan. 10, 2019 (II)]

(a)
$$CH_3$$
 OH CH_3 OCH CH_3 OCH CH_3 OH

36. The products formed in the reaction of cumene with O₂ followed by treatment with dil. HCl are:

[Jan. 9, 2019 (II)]

37. Phenol on treatment with CO₂ in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with (CH₃CO)₂O in the presence of catalytic amount of H₂SO₄ produces:

[2018

(a)
$$CO_2H$$
 (b) CO_3H

(c)
$$OH$$
 (d) CO_2F CO_3F

38. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br₂ to form product B. A and B are respectively: [2018]

(a)
$$OCH_3$$
 and OCH_3 OCH_4





39. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine? [2017]

40. The major product of the following reaction is:

[Online April 8, 2017]

41. Sodium phenoxide when heated with CO₂ under pressure at 125 °C yields a product which on acetylation produces C [2014]

$$ONa + CO_2 \xrightarrow{125^{\circ}} B \xrightarrow{H^+} Ac_2O \rightarrow C$$

The major product C would be

12. The following reaction

$$OH \longrightarrow + HCl + HCN \xrightarrow{Anhyd.} OH$$

$$CHC$$

is known as:

[Online April 11, 2014]

- (a) Perkin reaction
- (b) Gatterman-Koch Formylation
- (c) Kolbe's reaction
- (d) Gattermann reaction
- 43. Which one of the following substituents at para-position is most effective in stabilizing the phenoxide

- (a) CH₃
- (b) -OCH₃
- (c) -COCH₃ (d) -CH₂OH
- 44. Which one of the following compounds will not be soluble in sodium bicarbonate? [Online April 19, 2014]
 - (a) 2, 4, 6 Trinitrophenol (b) Benzoic acid
 - (c) o-Nitrophenol (d)
- (d) Benzene sulphonic acid
- 45. Arrange the following compounds in order of decreasing acidity: [2013]

$$\begin{picture}(200,0)(0,0) \put(0,0){\ovalpha} \put(0,0){\ov$$

- (a) II>IV>I>III
- (b) I>II>III>IV
- (c) III>I>II>IV
- (d) IV > III > I > II
- 46. What is the structure of the major product when phenol is treated with bromine water? [Online April 22, 2013]

(a)
$$\xrightarrow{Br}$$
 \xrightarrow{OH} \xrightarrow{Br} \xrightarrow{Br} \xrightarrow{Br} \xrightarrow{Br} \xrightarrow{Br}



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- The reaction of phenol with benzoyl chloride to give phenyl benzoate is known as: [Online April 23, 2013]
 - (a) Claisen reaction
 - (b) Schotten-Baumann reaction
 - (c) Reimer-Tiemann reaction
 - (d) Gatterman-Koch reaction
- 48. The major product in the following reaction is:

[Online April 25, 2013]







(d)
$$OH$$

Phenol on heating with CHCl3 and NaOH gives salicylaldehyde. The reaction is called:

[Online April 25, 2013]

- (a) Reimer Tiemann reaction
- (b) Claisen reaction
- (c) Cannizzaro's reaction
- (d) Hell Volhard Zelinsky reaction
- 50. The correct order of acid strength of the following compounds: [2011RS]
 - (A) Phenol
- (B) p-Cresol (D) p-Nitrophenol
- (C) m-Nitrophenol
- (a) D>C>A>B
 - (b) B>D>A>C
- (c) A>B>D>C
- (d) C > B > A > D
- 51. Consider the following reaction:

 $C_2H_5OH + H_2SO_4 \longrightarrow Product$

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

- (a) Ethylene
- (b) Acetylene
- (c) Diethyl ether
- (d) Ethylhydrogen sulphate
- 52. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is [2009]
 - (a) salicylaldehyde
 - (b) salicylic acid
 - (c) phthalic acid
 - (d) benzoic acid
- Phenol, when it reacts first with concentrated sulphuric acid and then with concentrated nitric acid, gives [2008]
 - (a) 2, 4, 6-trinitrobenzene
 - (b) o-nitrophenol
 - (c) p-nitrophenol
 - (d) nitrobenzene
- 54. The structure of the compound that gives a tribromo derivative on treatment with bromine water is







15.
$$OH + CHCl_3 + NaOH \longrightarrow CHO$$
The electrophile involved in the above reaction is [2006]

- (a) trichloromethyl anion (CCl₂)
- (b) formyl cation
- (c) phenoxide ion
- (d) dichlorocarbene
- Picric acid is:

[2002]

COOH



Preparation and Properties of Ethers



57. The major product [B] in the following reactions is:

[Sep. 04, 2020 (II)]

$$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{CH_3} - \operatorname{CH_2} - \operatorname{CH} - \operatorname{CH_2} - \operatorname{OCH_2} - \operatorname{CH_3} \\ \xrightarrow{\operatorname{HI}} [\operatorname{A}] \operatorname{alcohol} \xrightarrow{\operatorname{H_2SO_4}} [\operatorname{B}] \end{array}$$

(a) CH, = CH,

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

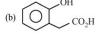
$$\begin{array}{c} CH_3 \\ \text{(c)} \quad CH_3 - CH_2 - C = CH_2 \\ \text{(d)} \quad CH_3 - CH_5 - CH = CH_7 - CH_7 \\ \end{array}$$

58. The major aromatic product C in the following reaction sequence will be: [Sep. 02, 2020 (I)]

$$\frac{\text{(i) KOH (Alc.)}}{\Delta} A \xrightarrow{\text{(i) KOH (Alc.)}} B$$

$$\frac{O_3}{Z_{\text{II}}/H_3O^+} C$$





(c)
$$O_2H$$
 (d)



An organic compound 'A' (CoH10O) when treated with conc. HI undergoes cleavage to yield compounds 'B' and 'C'. 'B' gives yellow precipitate with AgNO3 where as 'C' tautomerizes to 'D'. 'D' gives positive iodoform test. 'A' [Sep. 02, 2020 (II)] could be:

(a)
$$\sqrt{\text{O} - \text{CH}_2 - \text{CH}} = \text{CH}_2$$

(c)
$$CH_2 - CH_2 - CH = CH_2$$

(d)
$$H_3C - CH = CH$$

Among the compounds A and B with molecular formula $C_9H_{18}O_3$, A is having higher boiling point the B. The possible structures of A and B are: [Jan. 08, 2020 (II)]

$$B = H_3CO$$
 OCH₃

(d)
$$A = H_3CO$$
 OCH₃

$$OCH_3$$

$$OH$$

- 61. 1-methyl ethylene oxide when treated with an excess of HBr produces: [Jan. 07, 2020 (I)]
 - $(a) = \begin{matrix} Br \\ CH_3 \end{matrix} \qquad (b) Br \begin{matrix} Br \\ CH_3 \end{matrix}$ $(c) Br \begin{matrix} CH_3 \end{matrix} \qquad (d) \begin{matrix} Br \\ Br \end{matrix}$



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62. The major product of the following reaction is:

[April 10, 2019 (I)]

63. The major product obtained in the given reaction is:

[April 10, 2019 (II)]

$$CH_3 \xrightarrow{O} CH_2 \xrightarrow{CH} CH_3 \xrightarrow{AlCl_3} Proc$$

$$(a) \xrightarrow{H_3C} \xrightarrow{O} CH_2 \xrightarrow{CH} CH \xrightarrow{CH} CH_3$$

$$(b) \xrightarrow{H_3C} \xrightarrow{O} CH_2 \xrightarrow{CH_2} CH = CH_2$$

$$(c) \xrightarrow{H_3C} \xrightarrow{O}$$

$$(d) \xrightarrow{H_3C} \xrightarrow{O}$$

64. The major product of the following reaction is:

[April 8, 2019 (I)]

(a)
$$Br$$
 (b) OH Br $CHCH_3$ Br CH_2CH_2Br CH_2CH_2Br

65. The major product of the following reaction is:

66. The major product in the following conversion is:

[Jan. 12, 2019 (II)]

$$CH_3O$$
 $CH = CH - CH_3 \xrightarrow{HBr (excess)} ?$



(c)
$$CH_3O$$
— $CH-CH_2-CH_3$
 Br

(d)
$$CH_3O$$
— CH_2 $-CH$ $-CH_3$ Br

The major product of the following reaction is:

[Jan. 10, 2019 (I)]

$$\begin{array}{c|c} CH_3O & & \\ \hline & CH_2CI \\ \hline & \underbrace{ \begin{array}{ccc} (i) & AICI_3 \, (anhyd.) \\ \hline (ii) & H_2O \end{array}} \end{array}}$$

The major product formed in the following reaction is:

(d)

Consider the reaction sequence below:

[Online April 10, 2016]

$$\underbrace{\begin{array}{c} \text{OCH}_3\\ \text{Succinic anhydride} \\ \text{AlCl}_3 \end{array}} + A \underbrace{\begin{array}{c} \text{Clemmenson's}\\ \text{reduction} \end{array}} X, \text{ is }$$

Allyl phenyl ether can be prepared by heating:

[Online April 9, 2014]

(a)
$$C_6H_5Br + CH_2 = CH - CH_2 - ONa$$

(b)
$$CH_2 = CH - CH_2 - Br + C_6H_5ONa$$

(c)
$$C_6H_5 - CH = CH - Br + CH_3 - ONa$$

(d)
$$CH_2 = CH - Br + C_6H_5 - CH_2 - ONa$$

71. Williamson synthesis of ether is an example of:

[Online April 19, 2014]

(a) Nucleophilic addition

- (b) Electrophilic addition
- (c) Electrophilic substitution
- (d) Nucleophilic substitution
- 72. An ether (A), C₅H₁₂O, when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (A) is:

[Online April 9, 2013]

- (a) 2-ethoxypropane (b) ethoxypropane
- (c) methoxybutane (d) 2-methoxybutane
- In Williamson synthesis of mixed ether having a primary and a tertiary alkyl group if tertiary halide is used, then:

[Online April 22, 2013]

- (a) Rate of reaction will be slow due to slow cleavage of carbon-halogen bond.
- (b) Alkene will be the main product.
- (c) Simple ether will form instead of mixed ether.
- (d) Expected mixed ether will be formed.
- 74. HBr reacts with CH₂ = CH OCH₃ under anhydrous [2006] conditions at room temperature to give
 - (a) BrCH₂-CH₂-OCH₃
 - (b) H₂C CHBr OCH₂
 - (c) CH₃CHO and CH₃Br
 - (d) BrCH,CHO and CH,OH

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Hints & Solutions



(c)

3. (4)
$$CH - C = N \xrightarrow{(i) C_2H_3MgBr} CH_3$$
 CH_3

$$\begin{array}{c|c} & CH-C=O & \xrightarrow{(i) CH_3MgBr} \\ CH_3 & CH_2-CH_3 & \xrightarrow{(i) H_2O} \end{array}$$

Number of chiral centres, represented as (*) in the product (B) = 4

5. (c)

(d) Tertiary alcohol is prepared by the reaction of Grignard reagent with a ketone (formaldehyde is used to prepare primary alcohol).

$$\begin{array}{c} O \\ \parallel \\ H-C-H+PhCH(CH_3)CH_2MgX \xrightarrow{H_3O^+} \\ \\ HOCH_2-CH_2-CH-Ph \\ \mid \\ CH_3 \end{array}$$

(d) NaBH4 is a selective reducing agent, used for the reduction of aldehydes and ketones, it does not affect alk-

$$CH_2-C-OCH_3 \xrightarrow[MoDH]{OH} CH_2-C-OCH_3$$



 (b) The most suitable reagent for the given reaction is I₂/ NaOH (Iodoform reaction).

$$\begin{array}{c} \text{CH}_{3}\text{--CH} = \text{CH}\text{--CH}_{2}\text{--CH}\text{--CH}_{3} \xrightarrow{I_{2}/\text{NaOH}} \\ \text{OH} \end{array}$$

$$\begin{array}{c} \mathrm{CH_{3}\text{--}CH} = \mathrm{CH}\text{--}\mathrm{CH_{2}\text{--}C\text{--}CH_{3}} \xrightarrow{\quad L_{2}/\mathrm{NaOH} \quad } \\ \mathrm{O} \end{array}$$

9. (a)
$$CH_3MgBr + CH_3OH \longrightarrow Mg$$

$$+ CH_4 \uparrow \atop Br$$
Methane

 (d) An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC (consult Q.3 also).

$$R - CH_2 - OH \xrightarrow{PCC} R - CHO$$

- 11. (c) The C O bond length in alcohols is 142 pm and in Phenol it is 136 pm. The C – O bond length in phenol is shorter than that in methanol due to the conjugation of unshared pair of electrons on oxygen with the ring, which imparts double bond character to the C – O bond.
- 12. (b) Victor Meyer's test: The various steps involved are

(i)
$$RCH_2OH \xrightarrow{HI} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2}$$

$$\begin{array}{c}
R - C - NO_2 \xrightarrow{KOH} Blood red colour \\
NOH \\
Nitrolic acid
\end{array}$$

(ii)
$$\text{RCHOHR} \xrightarrow{\text{HI}} \overset{R}{\underset{R}{\longrightarrow}} \text{CHI} \xrightarrow{\text{AgNO}_2} \overset{R}{\underset{R}{\longrightarrow}} \text{CHNO}_2$$

$$\begin{array}{c}
R \\
R
\end{array}
\xrightarrow{H \xrightarrow{0} \text{NO}}
\xrightarrow{H_2 \text{O}}
\xrightarrow{R}
\xrightarrow{R}
\xrightarrow{NO}
\xrightarrow{KOH}$$
blue colour
$$\begin{array}{c}
NO_2 \\
Preud-onitral
\end{array}$$

(iii)
$$R_3COH \xrightarrow{HI} R_3CI \xrightarrow{AgNO_2} R_3CNO_2$$

$$\xrightarrow{\text{HNO}_2}$$
 No reaction $\xrightarrow{\text{KOH}}$ Colourless \longrightarrow

13. (b) Reaction of alcohols with Lucas reagent proceeds through carbocation formation. Further 3° carbocations (from tertiary alcohols) are highly stable thus reaction proceeds through S_N1 mechanism.

excellent reagent for oxidation of 1° alcohols to

14. (b) The order of dehydration among three type of alcohols is 3° > 2° > 1° > CH₃OH. This behaviour is related to the relative stabilities of carbocations (3° > 2° > 1°).
 15. (b) 7. (c) 1. (c) 1.

15. (d) ZnCl₂ + conc. HCl is Lucas reagent. Lucas reagent reacts fastest with tertiary alcohol.

3° alcohol + Lucas reagent = Immediate turbidity

- 16. (a) MnO₂ being a mild oxidising agent stops the oxidation of – CH₂OH group at aldehyde stage.
- 17. (a) On moving down a group, the basicity & nucleophilicity are inversely related, i.e. nucleophilicity increases while basicity decreases. i.e. RS[©] is more nucleophilic but less basic than RO[©]. This opposite behaviour is because of the fact that basicity and nucleophilicity depends upon different factors. Basicity is directly related to the strength of the H-element bond, while nucleophilicity is indirectly related to the electronegativity of the atom to which proton is attached.
- 18. (b) Tertiary alcohols react fastest with cone. HCl and anhydrous ZnCl₂ (Lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

Mechanism:

Step 1:
$$CH_3 - CH_3 - CH_3 - CH_3$$

$$CH_3 - CH_3$$
2 Methylpropane-2-ol

$$\rightleftharpoons$$
 (CH₃)₃C $-$ OH₂+Cl $^-$

Step 2:
$$(CH_3)_3C - \overset{+}{O}H_2 \rightleftharpoons (CH_3)_3C^+ + H_2O$$

3° Carbocation

Step
$$3: (CH_3)_3C^+ + Cl^- \rightleftharpoons (CH_3)_3C - Cl$$
 t -Butylchloride

19. (a) Whenever dehydration can produce two different alkenes, major product is formed according to Saytzeff rule i.e. more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amounts than the other are called regioselective; in case a reaction is 100% regioselective, it is termed as regiospecific.

In addition to being regioselective, alcohol dehydrations are **stereoselective** (a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).



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$$C_6H_5 - CH_2 - CH - CH - CH_3 \xrightarrow{Conc. H_2SO_4}$$
OH CH_3

$$\begin{array}{l} \overset{H}{\underset{(minor)}{\text{Ca}}} \overset{H}{\underset{(minor)}{\text{CH}}} \overset{H}{\underset{(CH)}{\text{CH}}} + \overset{H}{\underset{(CH)}{\text{Ca}}} \overset{C}{\underset{(major)}{\text{CH}}} \overset{CH(CH_3)_2}{\underset{(major)}{\text{CH}}{\text{CH}}} \\ \end{array}$$

20. (d)
$$CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I \xrightarrow{Mg} Ether$$

$$\begin{array}{c} \text{CH}_2\text{CH}_3\\ \text{CH}_3\text{CH}_2\text{MgI} \xrightarrow{\text{HCHO}} & \text{H-C-OMgI} \xrightarrow{\text{H}_2\text{O}} \\ \text{H} & \text{(C)} \end{array}$$

 (b) Ethanol and only those 2° alcohols which contain – CHOHCH₃ group undergo haloform reaction.

22. (a)
$$CH_3 - CH - CH = CH - CH_3 \longrightarrow$$

Pyridinium chlorochromate (PCC) oxidises 1° and 2° alcohols to aldehyde and ketones.

 (a) 3-Methyl pentan-3-ol will be dehydrated most readily since it produces a very stable, tertiary carbonium ion as intermediate.

24. (d) The dehydration of alcohol to form alkene occurs in following three steps. Step (1) is initiation step. Step (1) Formation of protonated alcohol.

$$CH_3-CH_2- \bigodot_{-H}^{\downarrow}-H+H \stackrel{\downarrow}{\longleftarrow} CH_3CH_2- \bigodot_{H}^{\downarrow}H$$
(Protonated ethanol)

Step (2) Formation of carbocation

$$CH_3\text{--}CH_2\text{--} \overset{-4}{\overset{\circ}{\bigcirc}} \overset{\leftarrow}{\underset{H}{\overset{\circ}{\bigcirc}}} \overset{H}{\overset{-\text{Slow}}{\longrightarrow}} CH_3\text{--} \overset{+}{\underset{C}{\overset{\circ}{\bigcirc}}} H_2\text{+-} H_2O$$

Step (3) Elimination of a proton to form alkene

$$H-CH_2$$
 $\stackrel{+}{C}H_2$
 $\stackrel{-}{\longleftarrow}CH_2 = CH_2 + H^+$
Ethene

25. (69)

$$OH \\ + CHCl_3 \xrightarrow{NaOH} OH \\ P (Salicylaldehyde)$$

Molecular formula of product 'P' = $C_2H_2O_3$

So, mass % of C in 'P'

$$= \frac{12 \times 7}{84 + 6 + 32} \times 100 = 68.85\% \approx 69\%$$

26. (b) (II) and (III) compounds almost have same boiling point. In the given options, option (b) will be the correct answer.

(I)
$$OH$$

$$B.P. \rightarrow 202 \, ^{\circ}C$$

(II)
$$OH$$

$$B.P. \rightarrow 279 ^{\circ}C$$

$$NO_2$$



(III)
$$OH$$

$$NH_{2}$$

$$OH$$

$$(IV) OH$$

$$B.P. \rightarrow 284 ^{\circ}C$$

$$B.P. \rightarrow 243 ^{\circ}C$$

27. (a)

Generally CAN test is done for alcohols which give pink or red colour. But for phenols and phenolic compounds it gives brown or black colour. So, this test helps to diffirentiate phenols from alcohols.

28. (c)

$$CH_3 \xrightarrow{OH} H_3C \xrightarrow{OH} NO_2$$

$$H_3C \xrightarrow{NO_2} NO_2$$

It is an example of electrophilic substitution reaction. Position of electrophile is directed by the strong ring activating group (-OH), present in the ring.

Resonance is a deciding factor to determine the order of bond length in given compounds. Phenol exhibits least C-OH bond length due to resonance, whereas methanol will show maximum bond length due to lack of resonance and p-ethoxyphenol will have some intermediate value of bond length.

30. (a)

$$\begin{array}{c} \text{OH} \\ \\ \text{H}_{3}\text{C} \\ \end{array} \xrightarrow{\begin{array}{c} \text{OK}_{2}\text{C}\\ \text{Acctons} \\ \text{CH}_{3} \\ \end{array}} \xrightarrow{\begin{array}{c} \text{OK}_{2}\text{C} = \text{CH}_{2}\text{CH}_{2} \\ \text{S}_{3}\text{C} \\ \text{H}_{3}\text{C} \\ \end{array}} \xrightarrow{\text{OCH}_{2}\text{C} = \text{CH}_{2}\text{CH}_{2}\text{C}} \xrightarrow{\text{OCH}_{2}\text{C}} = \text{CH}_{3}$$

31. (b)

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

$$\begin{array}{c}
OH \\
& OH \\
& Br
\end{array}$$

$$\begin{array}{c}
OH \\
& Br
\end{array}$$

$$\begin{array}{c}
Br
\end{array}$$

(d) (1) HC1

- (d) Electron withdrawing substituents increase the acidic strength, while electron releasing groups decrease the acidic strength.
 - \therefore Acidic strength $\propto K_a \propto \frac{1}{pK}$



33.

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 $pK_a: B < C < A < D$

35. (b) Reaction involved:

$$\underbrace{\overset{CH_3}{\overset{OH}{\underset{(i) \text{ NaOH(aq)}}{}}}} \underbrace{\overset{CH_3}{\overset{O}{\overset{Na^+_{(ii) \text{ CH}_3I}}{}}}} \underbrace{\overset{CH_3}{\overset{OCH_3}{\overset{OCH_3}{}}}}$$

36. (3) Reaction involved:

$$\begin{array}{c} O - O - H \\ CH_3 - CH - CH_3 & CH_3 - CH - CH_3 & OH \\ \hline \\ Cumene & O_2 \\ \hline \\ Cumene & Phenol \\ \end{array} \\ \begin{array}{c} O - O - H \\ O \\ H^* \\ \hline \\ CH_3 - C - CH \\ Acetone \\ \end{array}$$

37. (a)
$$CO_2$$
, NaOH $COOH$
 CO_2 , NaOH $COOH$
 CO_3 , NaOH $COOH$
 $COOH$

$$\begin{array}{c|c}
O & C \\
O - C - O - CH_3
\end{array}$$
Br
(B)

39. (a)

(b)
$$R$$
 C_6H_5 $tert-BuONa$ C_6

(d)
$$\underset{Br}{\overbrace{\hspace{1cm}}} \xrightarrow{\text{tert-BuONa}}$$



40. (a)
$$OH \xrightarrow{1. K_2CO_3}$$

41. (a)
$$ONa + CO_2 \xrightarrow{125 \, {}^{\circ}C} 5 \text{ Atm} \rightarrow$$

Sodium Phenoxide

$$\xrightarrow{\text{(CH}_3\text{CO)}_2\text{O}} \xrightarrow{\text{COOH}} \xrightarrow{\text{Aspirin}}$$

$$\text{(Acetyl salicyelic acid)}$$

42. (d)
$$HCN \xrightarrow{HCl} H > -N \xrightarrow{ZnCl_2} ZnCl_2$$

$$\begin{array}{c}
OH \\
H \\
Cl
\end{array} = N \begin{array}{c}
H \\
ZnCl_2
\end{array}$$

$$\begin{array}{cccc}
\text{OH} & \text{H} & \text{OH} \\
& & \text{NH}_2\text{CI} & \text{H}_2\text{O} \\
& & \text{NH}_4\text{CI}
\end{array}$$

Note: Gattermann Koch reaction is a variation of Gattermann reaction, and this reaction involves the use of carbon monoxide instead of HCN.

- 43. (c) Electron withdrawing group stabilises the benzene ring due to delocalisation of charge.
 - -CH₃ and -CH₂OH are electron donating group and hence decrease the stability of benzene ring -OCH3 is weaker electron withdrawing group than -COCH3. Hence -COCH3 group more stabilizes the phenoxide ion at pposition.
- (b) Due to intramolecular hydrogen bonding this will not be soluble in sodium bicarbonate.

45. (c) Electron withdrawing substituents like -NO2, -Cl increase the acidity of phenol while electron releasing substituents like - CH3, - OCH3 decrease acidity. hence the correct order of acidity will be

$$(-M, -I)$$
 $(-I > +M)$ $(+I, +HC)$ $(+M)$

(a) Phenol has activating (electron releasing) OH group and bromine water supplies Br⁺ ion easily, hence under such conditions reaction does not stop at monobromo or dibromo stage but a fully brominated (2,4,6,-tribromophenol) compound is the final product.

OH OH
$$Br$$
 Br
 Br
 $2,4,6-Tribromophenol$

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51. (b)

48. (c)

$$\begin{array}{c} & \begin{array}{c} & 433 \times \\ \text{C}_2\text{H}_5-\text{OH} \\ +\\ & +\\ \text{H}_2\text{SO}_4 \end{array} & \begin{array}{c} & \text{ethylene} \\ & 413 \times \\ & \text{H}_3\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH} \\ & \text{diethyl ether} \end{array} \\ & \begin{array}{c} & \\ & 383 \times \\ \end{array} & \begin{array}{c} \text{CH}_3\text{CH}_2\text{HSO}_4+\text{H}_2\text{O} \\ & \text{ethyl hydrogen sulphate} \end{array} \end{array}$$

Acetylene is not formed under any condition.

O'Na OH CHO

Salicylaldehyde

Electron withdrawing substituents increase the acidity of phenols; while electron releasing substituents decrease acidity. Thus the correct order is

53. (b) Phenol on reaction with conc. H₂SO₄ gives a mixture of o- and p- products (i.e., -SO₃H group occupies o-, p-position). At room temperature, o-product is more stable, which on treatment with conc. HNO₃ will yield o-nitrophenol.

54. (c) In **(c)** both groups are activativating and undergo electrophilic substitution in the same positions.

o-nitrophenol



$$\overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longrightarrow} \overset{OH}{\longrightarrow} \overset{Br_2/H_2O}{\longrightarrow} \overset{Br}{\longrightarrow} \overset{CH_3}{\longrightarrow} \overset{C$$

55. (d) This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.

$$\begin{array}{c} Cl \\ H \stackrel{\frown}{ } \stackrel{\frown}{ } \stackrel{\frown}{ } Cl + NaOH \xrightarrow{ (\alpha \text{-elimination})} \\ Cl & Cl \stackrel{\frown}{ } \stackrel{\frown}{ } Cl + NaCl + H_2Cl \\ \begin{array}{c} \text{dichlorocarbene} \end{array}$$

56. (c) 2,4,6 Trinitrophenol is also known as picric acid.

57. (b)
$$H_3C - CH_2 - CH - CH_2 - O - CH_2 - CH_3 \xrightarrow[Heat]{} H_{Eat} \rightarrow$$

$$\begin{array}{c} CH_3 \\ CH_3 - CH_2 - \underbrace{CH}_{[A]} - CH_2 - OH + CH_3CH_2 - I \xrightarrow{H_2SO_4/\Delta} \end{array}$$

$$CH_3 - CH = C - CH_3$$

$$[B]$$

58. (a)

$$\begin{array}{c} \text{OH} \\ \text{Excess} \end{array} \\ \begin{array}{c} \text{OH} \\ \text{Br} \\ \text{(A)} \\ \text{(ii) KOH (Alc.)} \\ \text{(ii) H}^{-} \end{array} \\ \text{HCHO} + \begin{array}{c} \text{CHO} \\ \text{CHO} \end{array} \\ \begin{array}{c} \text{OH} \\ \text{CHO} \end{array} \\ \begin{array}{c} \text{OH} \\ \text{Zn/H}_{3}\text{O}^{+} \end{array} \\ \begin{array}{c} \text{OH} \\ \text{(B)} \end{array}$$

59. (c)
$$\leftarrow$$
 CH_2 -O-CH=CH $_2$
 \rightarrow
 $C_0H_{10}O$

$$\begin{array}{c} & \longleftarrow \\ \text{(B)} & \longleftarrow \\ \text{CH}_2\text{-I+ CH}_2 = \\ \text{CH-OH} & \longleftarrow \\ \text{(D)} & \longleftarrow \\ \text{+ve lodoform test} \\ \text{AgNO}_3 & \longleftarrow \\ \text{CH}_2\text{-ONO}_2 \\ \end{array}$$

- 60. (a) In (A), -OH group is present, so inter-molecular Hbonding is possible while in (B), due to methoxy group there is no possibility of Inter-molecular H-bonding. So A is having higher boiling point than B.
 - 1-Methylethylene oxide

$$\begin{array}{c} \text{OH} & \text{CH}_3 & \text{Br} & \text{CH}_3 \\ \text{CH}_2 & \text{CH} & \frac{\text{HBr}}{\text{SN}^2} & \text{CH}_2 & \text{CH} \end{array}$$

62. (c)

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

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$$\begin{array}{c} & \overset{H}{\underset{\text{excess}}{\text{CH}}} \xrightarrow{\text{CH}_3} & \overset{H}{\underset{\text{hbr}}{\text{D}}} \xrightarrow{\text{CH}_3} & \overset{H}{\underset{\text{hbr}}{\text{D}}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} & \overset{H}{\underset{\text{Br}}{\text{CH}}} \xrightarrow{\text{CH}} & \overset{H}{\underset{\text{Br}}{\text{CH}}} \xrightarrow{\text{CH}} & \overset{H}{\underset{\text{CH}}{\text{CH}_3}} & \overset{H}{\underset{\text{Br}}{\text{CH}}} \xrightarrow{\text{CH}} & \overset{H}{\underset{\text{CH}}{\text{CH}_3}} & \overset{H}{\underset{\text{Br}}{\text{CH}}} \xrightarrow{\text{CH}} & \overset{H}{\underset{\text{CH}}{\text{CH}_3}} & \overset{H}{\underset{\text{CH}$$

65. (d)

66. (b)

$$\begin{array}{c} \text{CH}_3\text{O} & \begin{array}{c} \text{CH}=\text{CH}-\text{CH}_3 \\ \text{H}^+ \end{array} \\ \text{CH}_3\text{O} & \begin{array}{c} \text{CH}=\text{CH}_2-\text{CH}_3 \\ \text{Enzyl carbocation (stable)} \end{array} \\ & \begin{array}{c} \text{Br}^- \\ \text{Br} \end{array} \\ \text{H}_3\text{CO} & \begin{array}{c} \text{CH}=\text{CH}_2-\text{CH}_3 \\ \text{HBr (excess)}, \Delta \end{array} \\ \text{HO} & \begin{array}{c} \text{CH}=\text{CH}_2-\text{CH}_3 \\ \text{Br} \end{array} \end{array}$$

67. (d)

68. (d)

$$\begin{array}{c|c}
\ddot{O} & \xrightarrow{2H^+} & & \downarrow & \downarrow \\
\ddot{O} & \xrightarrow{2H^+} & & \downarrow & \downarrow \\
\downarrow & & \downarrow & \downarrow \\
OH & & + H_2\dot{C}CH_3 & \xrightarrow{2I^-} & \\
OH & & OH
\end{array}$$

69. (d)



70. **(b)**
$$C_6H_5ONa + Br - CH_2 - CH = CH_2 \longrightarrow$$

$$C_6H_5 - O - CH_2 - CH = CH_2 + NaBr$$

Allyl phenyl ether

71. (d) This method is suitable for the preparation of a wide variety of unsymmetrical ethers. The nucleophilic substitution of halides with alkoxide leads to desired product.

72. (a)

$$\begin{array}{c} \operatorname{CH_3CH_2OCH(CH_3)_2} \xrightarrow{\operatorname{Conc.\,HI}} \operatorname{CH_3CH_2I} & + & (\operatorname{CH_3)_2CHI} \\ & & & & (\operatorname{C}) \\ & & & & & (\operatorname{CH_3OH}) \\ & & & & & (\operatorname{CH_3)_2CHOH} \\ & & & & & (\operatorname{CH_3CH_2OH}) \\ & & & & & (\operatorname{CH_3)_2CO} \end{array}$$

Hence the IUPAC name of compound (A) is

 (b) The tertiary alkyl halide undergo elimination reaction to give alkenes.

$$\begin{array}{c|cccc} CH_3 & CH_3 \\ | & | \\ CH_3-C-X & + NaOC_2H_5 & CH_3-C=CH_2 \\ | & | & 2-Methyl \ propene \\ CH_3 & & \end{array}$$

74. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

$$\text{CH}_2 = \text{CH} - \text{OCH}_3 \xrightarrow{\text{HBr}} \text{CH}_3 - \text{CH} - \text{O} - \text{CH}_3$$

$$\text{Br}$$

