Alcohols, Phenols and Ethers

ANSWERS

1. (i) (d)

EXAM

DRILL

(ii) (b) : The order of acidic strength is,



(iii) (a) : Weaker acids have higher pK_a .

- OCH₃ at *meta*-position exerts only -I effect, hence increases the acidity.

-I effect order : $-NO_2 > -OCH_3 > -CI$.

 $- CH_3$ has +/ effect.

So, correct order is option (a).

(iv) (d) : Phenol (carbolic acid) is a weaker acid than carbonic acid (H_2CO_3) and does not liberate CO_2 on treatment with aqueous sodium bicarbonate solution.

(v) (c) : $-NO_2$ exhibits both -I and -R influence to stabilise the corresponding phenoxide. In ortho derivative, intermolecular H-bonding lowers the acidity.



5. (c) : When chlorine is passed in boiling toluene, substitution inside chain takes place and benzyl chloride is obtained which on hydrolysis give benzyl alcohol.

6. (c) : Ethers being Lewis bases form etherates with Lewis acids.

7. (b) : Dehydration of alcohol proceeds through the formation of carbonium ion. The carbonium ion can lose a proton to form alkene. The carbonium ion may be attacked by a fresh molecule of alcohol and form an oxonium ion which can then lose a proton to form ether. Usually, secondary and tertiary alcohols form alkene.

8. (b) : Low pK_a value corresponds to more acidic compound. Acetic acid ($pK_a = 4.76$) is more acidic than phenol ($pK_a = 9.98$). It is due to the fact that carboxylate ion is more stabilized due to resonance because its resonating structures are equivalent.



10. Benzene-1, 3-diol

- 11. Propan-2-ol or 2-propanol
- 12. Isopropyl benzene.

13. (a) Due to intermolecular hydrogen bonding in alcohols, they have higher boiling point than ethers of similar molecular masses.

(b) Due to the formation of hydrogen bonds with water molecules lower alcohols are soluble in water.

OR

The correct order of decreasing acid strength is b > d > a > c > e. *p*-Nitrophenol is most acidic and *p*-methoxy phenol is least acidic. When an electron withdrawing group is *para* to OH group, the acidity is maximum. When an electron releasing group is *para* to OH group, the acidity is minimum.

14. (a) Anisole reacts with a mixture of conc. sulphuric acid and conc. nitric acid forming *ortho* nitro anisole and *para* nitro anisole.



(b) Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution and hence undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.

15. Various steps involved in the suggested mechanism are :(a) Protonation of hydroxyl group

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3}C - \begin{array}{c} C - CH - CH_{3} \\ H_{3}C - \begin{array}{c} C - CH - CH_{3} \end{array} \xrightarrow{H^{+}} H_{3}C - \begin{array}{c} CH_{3} \\ C - CH - CH_{4} \\ H_{3}C - \begin{array}{c} CH_{3} \\ H_{3}C - CH_{3} \end{array} \xrightarrow{H^{+}} H_{3}C - \begin{array}{c} CH_{3} \\ H_{3}C - CH_{3} \\ H_{3}C - CH_{4} \\ H_{3}C \\ H_$$

(b) Removal of H_2O to form a secondary (2°) carbonium ion.

$$\begin{array}{c} CH_{3}\\ H_{3}C-C-CH-CH_{3}\\ H_{3}CH_{3}\\ CH_{3}\\ \end{array}$$
 (2°) secondary carbonium ion.

(c) The conversion of secondary (2°) carbonium ion to stable tertiary (3°) carbonium ion by shift of $-CH_3$ group.

$$\begin{array}{c} \begin{array}{c} CH_3 \\ I \\ H_3C - \begin{array}{c} C - \begin{array}{c} CH \\ - \end{array} \\ CH_3 \\ CH_3 \\ (2^\circ) \end{array} \xrightarrow{} \begin{array}{c} CH_3CH_3 \\ + \begin{array}{c} I \\ - \end{array} \\ CH_3CH_3 \\ CH_3CH_3 \\ (3^\circ) \end{array} \end{array}$$

(d) The removal of H⁺ to form a double bond.



(ii)
$$CH_3 - CH - CH_2OH \xrightarrow{Conc. H_2SO_4} CH_3 - C = CH_2 + 3H_2O$$

2-Methylpropanol 2-Methylpropene

17. *n*-Butanol gives the following reaction in which the colour
of KMnO₄ changes to brown. The brown colour is due to MnO₂.
$$CH_3CH_2CH_2CH_2OH + KMnO_4 \longrightarrow$$

n-Butanol (Purple)
 $CH_3CH_3COOK + MnO_2 + KOH$

$$CH_3CH_2CH_2COOK + MINO_2 + KC$$

(Soluble in water) (Brown)

tert-Alcohols are not oxidised easily and so there is no change in purple colour of $KMnO_4$.





19. (i) Due to -I and -R effect of $-NO_2$, *p*-nitrophenoxide ion is more stable than *p*-methyl phenoxide ion (+/ effect of $-CH_3$ group). (ii) It is due to sp^2 hybridisation (double bond due to resonance) in phenol than single bond (sp^3 hybridisation) in methanol. (iii) Tert. halide undergoes β -elimination reaction with strong nucleophile to form alkene and not ether.

MtG100PERCENT Chemistry Class-12



22. (i) In phenol, the — OH group is attached to sp^2 hybridised carbon which is more electronegative, hence the — OH bond becomes more polar.

(ii) Due to resonance in phenol, oxygen gets a positive charge and this increases the polarity of the O-H bond.

(iii) Delocalisation of negative charge in phenoxide ion makes phenoxide ion more stable than phenol favouring the ionisation of phenol.

Alcohols, Phenols and Ethers

(i) It is because branched chain alcohols have minimum surface area, therefore, minimum force of attraction, hence, they have lower boiling point.

(ii) It is due to +ve charge on 3 out of 5 resonating structures of phenol. It cannot be protonated easily.

(iii) It is because phenoxide ion is stabilised by resonance, whereas methoxide ion is not.

23. (a) Phenol forms stable phenoxide ion, which is stabilised by resonance. Conjugate base of phenol is less stable than conjugate base of cyclohexanol.

(b) SOBr₂; Thionyl bromide will react with secondary alcohols and give a reasonable percent yield of the corresponding bromide.

(c) Corey's reagent or pyridinium chlorochromate (PCC, CrO_3 . $C_5H_5N.HCl$ or $C_5H_5NH^+CrO_3Cl^-$). It oxidises CHOH to C=O without carrying out oxidation of double bond.

24. (i) Reimer-Tiemann reaction : Phenols, when treated with chloroform in presence of aqueous alkali at 340 K, followed by hydrolysis, give *o*-hydroxybenzaldehyde (salicylaldehyde) as the major product.



(ii) Williamson's ether synthesis : When alkyl halide reacts with sodium alkoxide, ethers are formed.

For Example, $C_2H_5Br + CH_3 - C - ONa \rightarrow CH_3 - C - OC_2H_5 + NaBr$ $C_1H_3 - C - OK_2H_5 + NaBr$ $CH_3 - C - OC_2H_5 + NaBr$ $CH_3 - C - OH$



(iii)
$$CH_3CH_2CH_2CH_2CH_2CI \xrightarrow{NaOH(aq)} CH_3CH_2CH_2CH_2CH_2OH$$

26. (i) It is because phenoxide ion is more stable than methoxide ion.

(ii) It is because ethanol is associated with intermolecular H-bonding, whereas methoxymethane is not.

(iii) It is because $(CH_3)_3C^+$ (*tert.* carbocation) is more stable, it reacts with I⁻ to form tert. butyl iodide.

27. Molecular weight of $A = (0.369 \times 22.4 \times 1000)/67.2 = 123$ (*A*) is a bromido derivative so, it may be written as R - Br.

 $M_{RBr} = 123$, So, R = 43 (:: Atomic mass of Br = 80)

i.e.,
$$C_n H_{2n+1} = 43$$

or $12n + 2n + 1 = 4$
or $n = 3$

 $A = C_3 H_7 Br$

So, the possible structure of (A) are $CH_3CH_2CH_2Br$ or $CH_3CH(Br)CH_3$. The reactions are as follows :



Since (*D*) gives an isomer of (*A*) on HBr addition, hence (*A*) is $CH_3CH_2CH_2Br$ and not $CH_3CH(Br)CH_3$.

OR

(i) $C_2H_5MgBr + HCHO \rightarrow C_2H_5CH_2OMgBr \xrightarrow{H_2O} C_2H_5CH_2OH$

(ii) $CH_3MgBr + CH_3COCH_3 \rightarrow$





 $CH_3 \longrightarrow O \longrightarrow CH_3 + HI \longrightarrow$ CH3I +CH³OH Dimethyl ether Methanol Methyl Iodide ŌŇa OCH₂CH₃ (ii) (a) C_2H_5Br Sodium Ethyl Ethoxybenzene phenoxide bromide CH₃ CH₃ $ONa + CH_3Br - NaBi$ (b) CH₃ OCH₃ Methyl CH CH₃ bromide Sodium 2-Methoxy-2-methyl tert-butoxide propane

(iii) **Kolbe's reaction**: When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



MtG100PERCENT Chemistry Class-12

29. (a) $C_6H_5OH < pCI - C_6H_4OH < m-CI C_6H_4OH$

[Chlorine causes –/ effect which decreases with increasing distance between –Cl and –OH. The *meta*-position is more closer than the *para*-position.]

(b) $C_6H_5OH < m-NO_2C_6H_4 < p-NO_2C_6H_4OH$

 $[-NO_2 \text{ group is electron withdrawing and acid strengthening.}$ Its resonance effect (which occurs from *o*- and *p*-positions) predominates over inductive effect.]

(c) p-bromophenol < m-bromophenol < o-bromophenol [Acidity decreases as the distance of electron withdrawing substituent increases from -OH group.]

(d) phenol < *p*-nitrophenol < carbonic acid < benzoic acid.

(e) m-cresol < phenol < m-chlorophenol < m-nitrophenol.

30. (a) $-NO_2$ is electron – withdrawing group and acid strengthen by both inductive effect and resonance. Its resonance effect is effective from only the *ortho* and *para* positions to about an equal extent. It predominates over the inductive effect which operates from all positions but at decreasing effectiveness with increasing separation of NO_2 and OH. Hence all the nitrophenols are more acidic than phenol with *m*-nitrophenol being the weakest of the three. Since the inductive effect from the closer *o*-positions is the strongest, one might expect *o*-nitrophenol to be stronger than *p*-nitrophenol. However, the intramolecular H-bond in *o*-nitrophenol must be broken and this requires some energy. So, the decreasing order of acidity is

D > B > C > A.

(b) Phenols are more acidic than ethanol. Although Cl is electron donating by resonance, but electron – withdrawing from inductive it is effect that decreases with increasing separation of Cl and OH making all the chlorophenols more acidic than phenol. The decreasing order is

B>C>D>A>E.

(c) Methyl has electron donating inductive effect from all positions and hyperconjugative effect at the *ortho* and *para* positions. The three isomers are weaker acids than phenol. *m*-Cresol is the strongest because its acidity is not weakened by hyperconjugation. The decreasing order of acidity is A > C > D > B.

BEST SELLING BOOKS FOR CLASS 12 MtG **A B B M** 👧 🙆 🧕 🔜 🚥 🔍 🙆 🔍 📖 100 PERCENT 00 100 PERCENT 12 MATHEMATICS NCERT. NCERT. NCERT. **F**•NGERTIPS **F**•NGERTIPS FUNGERTIPS - 🛯 🏹 Sand Sand - 1 CBSE CBSE CHEMISTRY PHYSICS MATHEMATICS A 🕲 🔕 🔍 🔿 🙆 🖃 🔍 🔍 🔕 🖳 Concerning of CONCERCE. NCERT NCERT NCERT. **F**+NGERTIPS **F**•NGERTIPS **F** NGERTIPS NCERT NCERT NCERT रसायन विज्ञान भौतिकी जीव विज्ञाल 2 **OUESTION BANK OUESTION BANK** QUESTION BANK 0 PHYSICS CHEMISTRY - 1 MATHEMATICS 0 -NTA HTA NTA Ξ 3 AIN MAI **CHAMPION** CHAMP ON CHAMP ON PHYSICS CHEMISTRY MATHEMATICS CHAPTERWISE CHAPTERWISE TOPICWISE HAPTERWISE 2021-2012 2021-3013 76 MATHEMATICS CHEMISTRY PHYSICS 11.000 MASED ON L ASED ON LAS LASED ON LATEST PALTERN (\mathbf{X}) X Y DAYS DAYS DAYS MAIN MAIN MAIN **JEE MAIN JEE**MAIN **JEE**MAIN MATHEMATICS CHEMISTRY CHEMISTRY PHYSICS MATHEMATICS 000 JEE MAIN JEE MAIN JEEMAIN CHAPTERWISE SOLUTIONS CHAPTERWISE SOLUTIONS CHAPTERWISE SOLUTIONS / 4/ 44+20 4+2 И --ICED ICED MATHEMATICS PHYSICS CHEMISTRY MATHEMATICS PHYSICS CHEMISTRY **58**93 JEE MAIN EXPLORER NEW 2021 PATTERN TSA JEE MAIN 2022 MATHEMATICS B ADVANCED **POWER GUIDE** 9 **EXPLORER** 10 JEE MAIN 21 PRIVATE - INCOMPTENT - MATHEMATICS

Visit www.mtg.in for complete information