

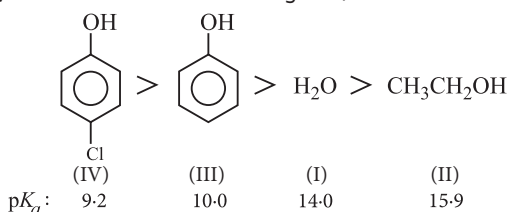
EXAM
DRILL

Alcohols, Phenols and Ethers

ANSWERS

1. (i) (d)

(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.

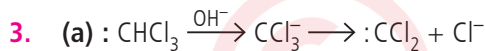
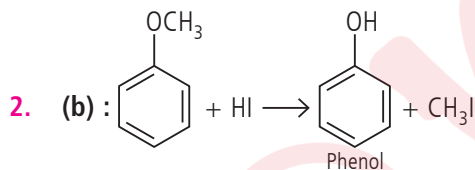
$-I$ effect order : – NO₂ > – OCH₃ > – Cl.

– CH₃ has $+I$ effect.

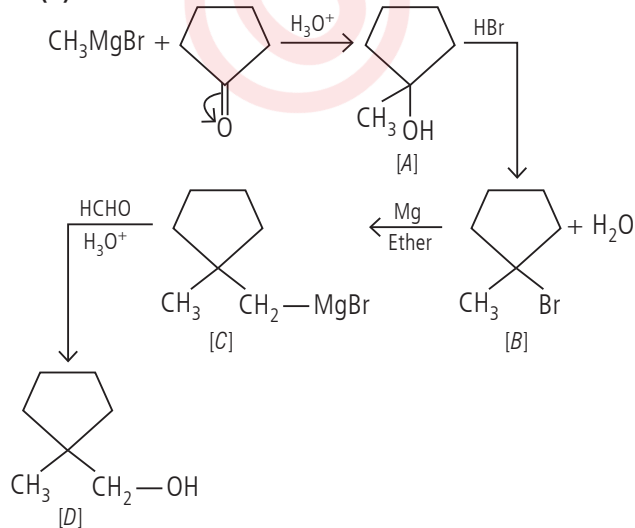
So, correct order is option (a).

(iv) (d) : Phenol (carboic acid) is a weaker acid than carbonic acid (H₂CO₃) and does not liberate CO₂ on treatment with aqueous sodium bicarbonate solution.

(v) (c) : –NO₂ exhibits both $-I$ and $-R$ influence to stabilise the corresponding phenoxide. In *ortho* derivative, intermolecular H-bonding lowers the acidity.



4. (d) :

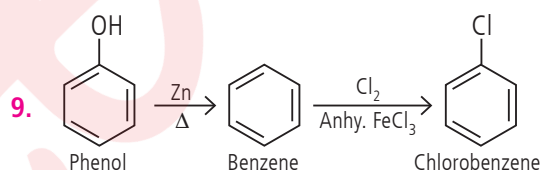


5. (c) : When chlorine is passed in boiling toluene, substitution inside chain takes place and benzyl chloride is obtained which on hydrolysis give benzyl alcohol.

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.

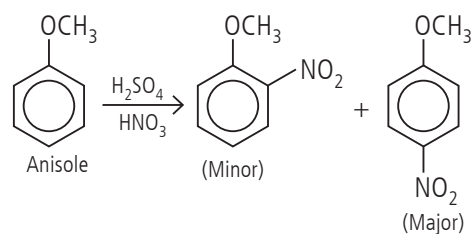
13. (a) Due to intermolecular hydrogen bonding in alcohols, they have higher boiling point than ethers of similar molecular masses.

(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.



(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.

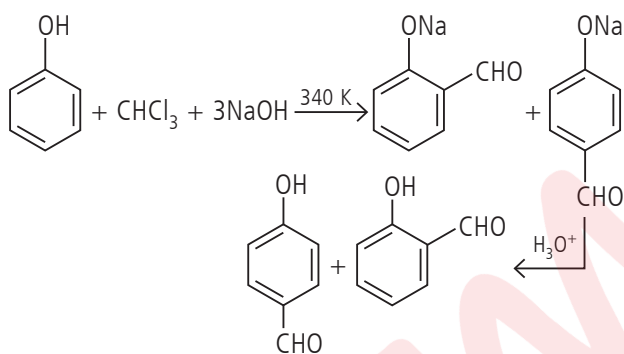
(iii) It is because phenoxide ion is stabilised by resonance, whereas methoxide ion is not.

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) SOBr_2 ; Thionyl bromide will react with secondary alcohols and give a reasonable percent yield of the corresponding bromide.

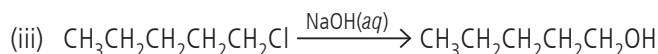
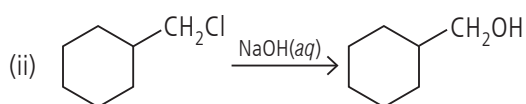
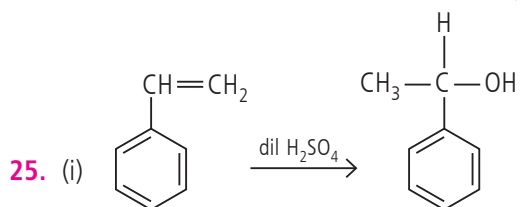
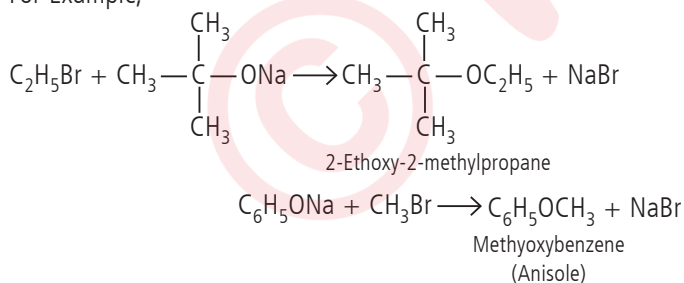
(c) Corey's reagent or pyridinium chlorochromate (PCC, $\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ or $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$). It oxidises >CHOH to >C=O without carrying out oxidation of double bond.

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,



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 $(\text{CH}_3)_3\text{C}^+$ (*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 bromide derivative so, it may be written as *R* - Br.

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

i.e., $\text{C}_n\text{H}_{2n+1} = 43$

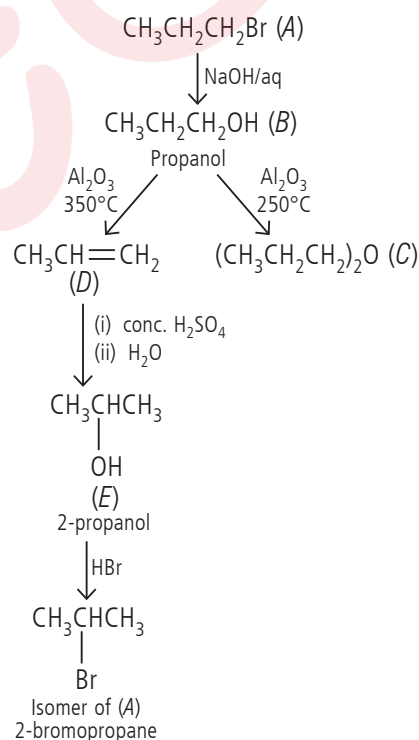
or $12n + 2n + 1 = 43$

or $n = 3$

$A = \text{C}_3\text{H}_7\text{Br}$

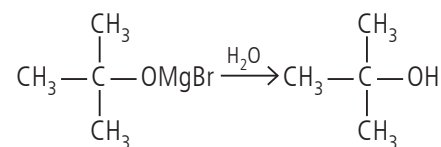
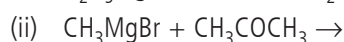
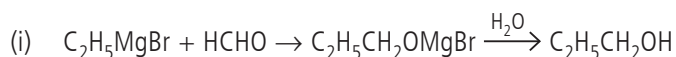
So, the possible structure of (*A*) are $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$.

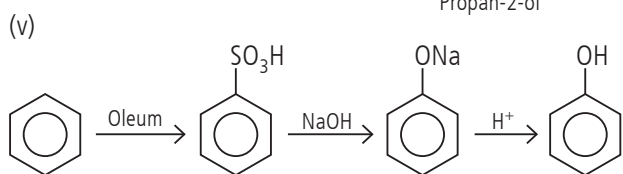
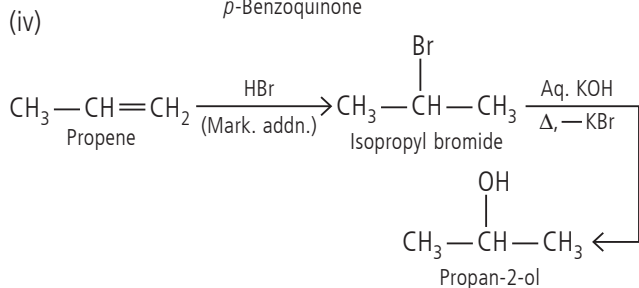
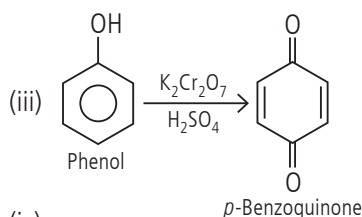
The reactions are as follows:



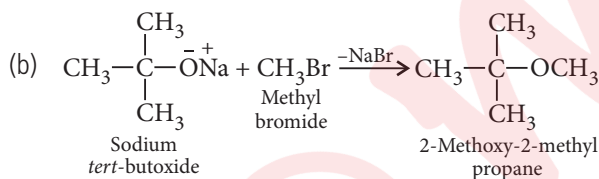
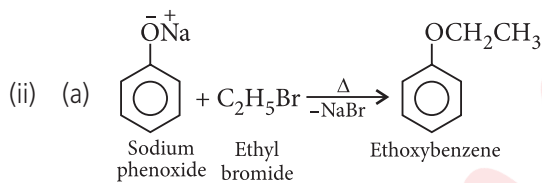
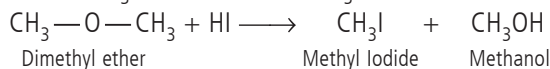
Since (*D*) gives an isomer of (*A*) on HBr addition, hence (*A*) is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and not $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$.

OR

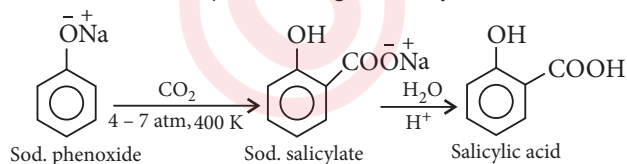




28. (i) When $\text{CH}_3-\text{O}-\text{CH}_3$ is heated with HI then methyl iodide (CH_3I) and methanol (CH_3OH) are formed.



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



29. (a) $\text{C}_6\text{H}_5\text{OH} < p\text{Cl}-\text{C}_6\text{H}_4\text{OH} < m\text{-Cl}-\text{C}_6\text{H}_4\text{OH}$

[Chlorine causes $-I$ effect which decreases with increasing distance between $-\text{Cl}$ and $-\text{OH}$. The *meta*-position is more closer than the *para*-position.]

(b) $\text{C}_6\text{H}_5\text{OH} < m\text{-NO}_2\text{C}_6\text{H}_4 < p\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$

[$-\text{NO}_2$ 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 $-\text{OH}$ group.]

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

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

30. (a) $-\text{NO}_2$ 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 $A > C > D > B$.

