

OCOCH₃

meta-fluorobenzoic acid

Daily Tutorial Sheet 3

JEE Advanced [Archive]

Due to strong +M effect, phenol is more reactive towards electrophilic substitution. Thus statement-I is correct.

Due to +M effect of -OH group, the intermediate arenium ion generated is also more stabilised. Thus statement-II is also correct and explains statement-I as well.

53.
$$\begin{array}{c|c} Br & OH \\ \hline Mg & (i) CH_3CHO \\ \hline ether & (ii) H^+/H_2O \end{array} \\ \hline & CH - CH_3 \\ \hline \\ & Br \\ \hline & Br \\ \hline & Br \\ \hline & & Ring expansion \\ \hline \end{array}$$

54. (i)
$$\frac{1. \text{ NaOH}}{2. \text{ COO}_{2}}$$

$$\frac{1. \text{ NaOH}}{2. \text{ COOH}}$$

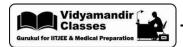
$$\frac{1. \text{ NaNOH}}{2. \text{ COOH}}$$

$$\frac{1. \text{ NaOH}}{2. \text{ COOH}}$$

$$\frac{1$$

55.(A) $C_2H_5O^-$ (as a strong base) will first abstract a proton from phenol to give a phenoxide ion (a resonance stabilised ion). It will attack the methyl carbon of alkyl iodide to from $C_6H_5OC_2H_5$ (S_N2). However if $C_2H_5O^-$ is in excess, then $C_2H_5OC_2H_5$ will be formed because $C_2H_5O^-$ is a better nucleophile than $C_6H_5O^-$.

OH



56.
$$CH_{2} = CH - O - CH(CH_{3})_{2} \xrightarrow{H^{+}} CH_{3} - \overset{+}{C}H - \overset{-}{O} - CH(CH_{3})_{2} \longleftrightarrow CH_{3}CH = \overset{+}{O} - CH(CH_{3})_{2}$$

$$(CH_{3})_{2}CHOH \xrightarrow{1. H_{2}O} (CH_{3})_{2}\overset{+}{C}H + CH_{3}CHO \overset{-}{\longleftrightarrow} (CH_{3})_{2}$$

$$(CH_{3})_{2}CHOH \xrightarrow{1. H_{2}O} (CH_{3})_{2}\overset{+}{C}H + CH_{3}CHO \overset{-}{\longleftrightarrow} (CH_{3})_{2}\overset{+}{\longleftrightarrow} (CH_{3})_{2}\overset{+}$$

- ▶ Both P and Q respond positively to iodoform test.
- Note: (i) When π e's are in conjugation with lone pair over O [Vinylic ethers], then visualise the above pathway to form a stable carbocation and subsequent formation of carbonyl compound.
 - (ii) The above reaction is faster because of formation of highly stable carbocations as compound to poorly stable $CH_3CH_2^+(1^\circ)$ from ethylene.
- **57.(B)** Concentrated HCl, HBr and HCl+ $ZnCl_2$ all are nucleophiles that convert alcohols to alkyl halide. Conc. H_3PO_4 is a dehydrating agent which will give alkene.

$$\mathbf{58.(B)} \begin{picture}(200,10) \put(0,0){\line(1,0){100}} \put(0,0){\l$$

59.(C) 1, 4-dihydroxy benzene shows highest boiling point among the given compounds due to formation of strong intermolecular H-bonding.

Order of H-bonding among the isomers - o < m < p

Thus order of boiling point is: IV < I < II < III.

60-62. 60.(B) 61.(C) 62.(C)

Refer to module for mechanism of Riemer-Tiemann reaction.

64.(D) Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to stronger aryl-oxygen bond. The reaction yields phenol and alkyl halide. Thus,

65.(B) If the lone pair is conjugated with π -bond and conditions are anhydrous (which do not support cleavage easily), visualise the following pathway.



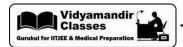
The above reaction is Reimer Tiemann Reaction, where intermediate formed is \$CCl2 carbene.

- **67.(D)** Phenol is weaker acid than carbonic acid (H_2CO_3) and does not liberate CO_2 on treatment with aqueous sodium bicarbonate solution.
- **68.(B)** It is an example of *ipso* substitution
 - Refer to Solution of Q.87

$$\mathbf{Q}:$$
 ONa $\frac{\operatorname{EtBr}}{\operatorname{S}_{N}2}$ OEt

R:
$$\frac{1. \text{ Hg(OAC)}_2}{2. \text{ NaBH}_4}$$
 OH (Markovnikov's addn)

70.(C) Acidic hydrolysis of benzylic ethers follow S_N1 pathway and rate of S_N1 reaction depends on the stability of carbocation. When two phenyl rings are replaced by group, the carbocation will be more stabilized due +M effect of -OMe group.



71.(D) In Dye-test, phenolic –OH groups is converted to –O⁻ which activates the ring towards EAS (Electrophilic aromatic substitution).

72.(ACD)

C₄H₁₀O is monohydric alcohol, i.e., C₄H₉OH. Its isomeric alcohols are

(A)
$$\begin{array}{c} {}^{3}\mathrm{CH_{3}} \\ \downarrow \\ \mathrm{CH_{3}} - {}^{2}\mathrm{C} - \mathrm{OH} \\ \downarrow \\ {}^{1}\mathrm{CH_{3}} \\ \end{array}$$
 (C)
$$\begin{array}{c} {}^{4} \ {}^{3} \ {}^{2} \ {}^{1} \\ \mathrm{CH_{3}CH_{2}CH_{2}CH_{2}OH} \\ \mathrm{Butan-1-ol\ (n-butanol)} \\ \end{array}$$

(D)
$${^{3}\text{CH}_{3}} - {^{2}\text{CH}} - {\text{CH}_{2}\text{OH}}$$
2-Methylpropan-1-ol (iso-butylalcohol)

p, q and r are suitable positions as per strongly activating nature of (electronic effect) –OH group via +M effect. Due to steric effect of the tert-butyl group, the bulky electrophiles are less likely to attack positions q and r. Hence, only position p is suitable for I_2 , positions p and r are suitable for Br_2 and Cl_2 being smaller can attack on all p, q and r positions.

74.(B) Observe that all three reactions involved are S_N2 and proceed via inversion of configuration. So the correct structure of X is :

Enantiomerically pure product after several substitution reaction, is only possible when each reaction is stereospecific in nature which confirms the pathway used is $S_N 2$ in nature.