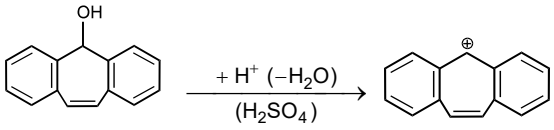
HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

3. 

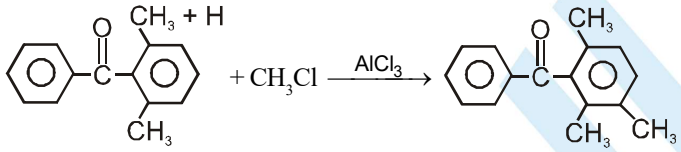
(Aromatic carbocation)

5. In the presence of +M effect, the rate of mononitration is increase and in the presence of – M effect, the rate of mononitration is decrease.

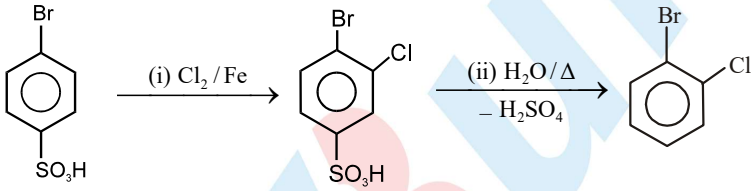
7. In presence of +M effect rate of mononitration increase and in presence of –M effect rate will decreases.

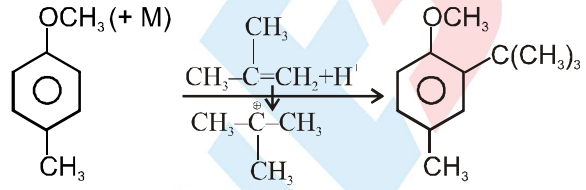
10. Benzene $+CH_3Cl \xrightarrow{\text{An hydrous } AlCl_3}$ gives toluene.

24. Highly deactivating and highly activating rings do not undergo Friedel craft acylation.

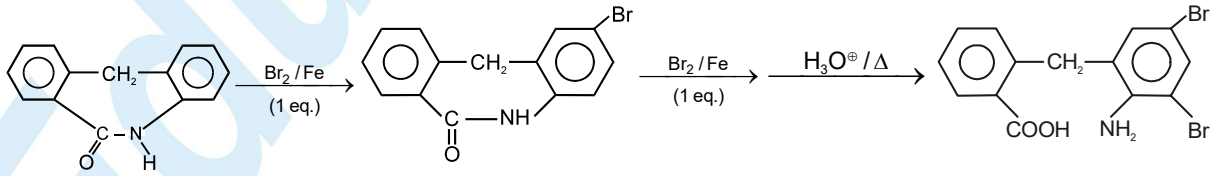
25. 

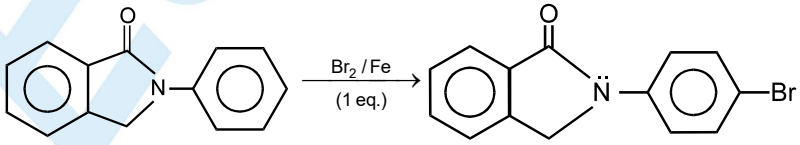
26. Rate of electrophilic substitution ∝ Stability of arenium ion.

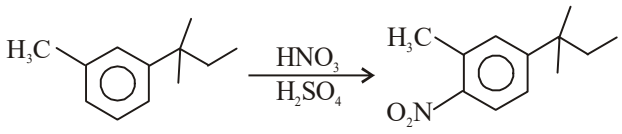
27. 

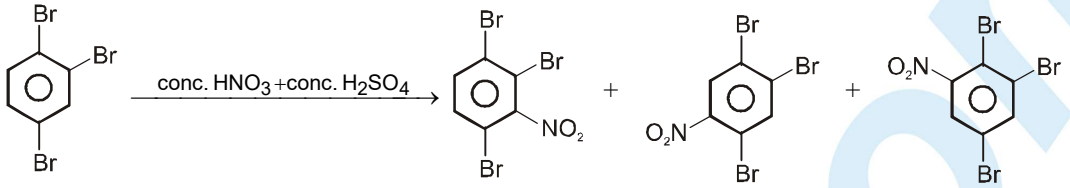
28. 

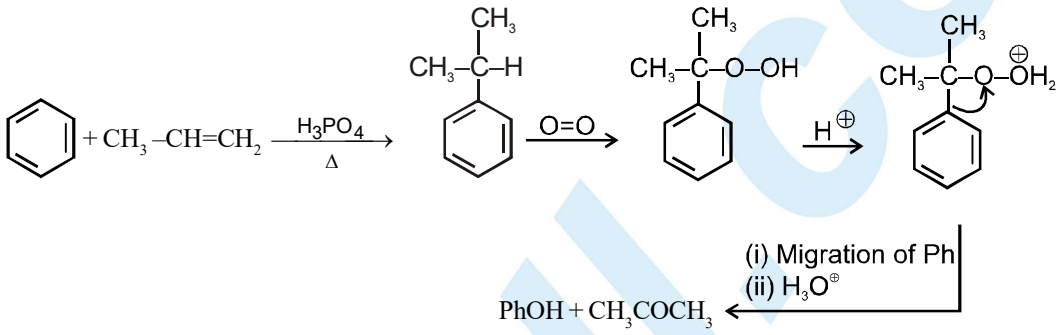
29. If both +M group are present on benzene ring then electrophilic attack in the influence of more +M group.

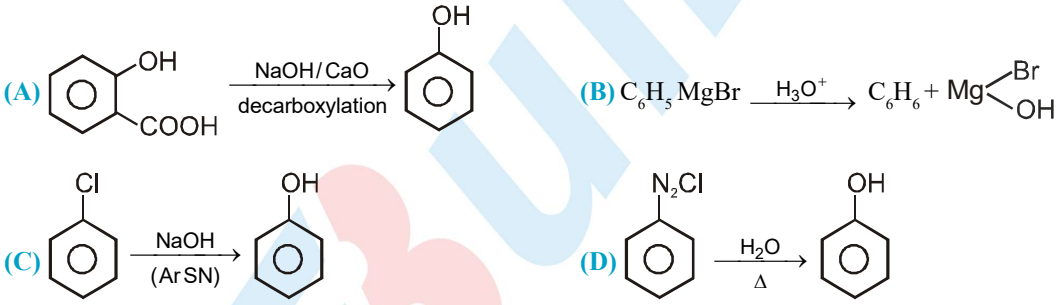
30. 

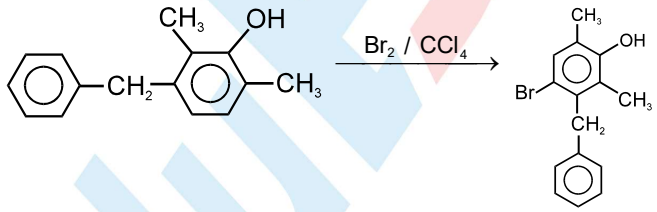
31. 

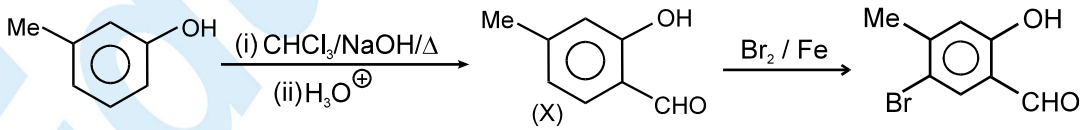
35. 

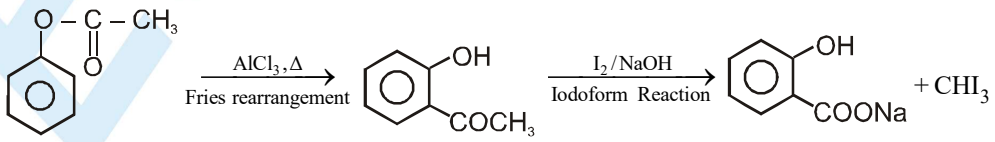
36. 

38. 

39. 

41. 

42. 

46. 

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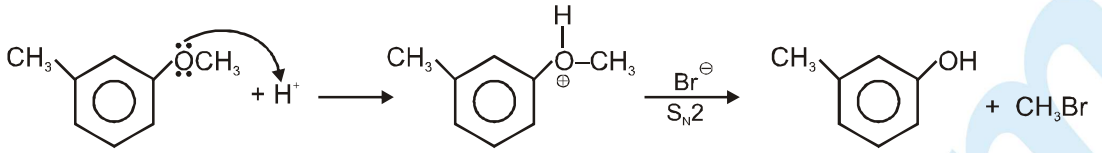


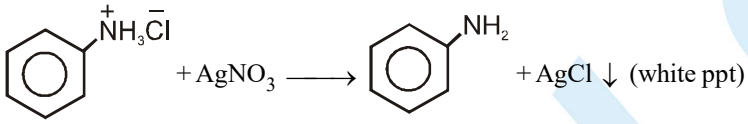
50. $C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2+HCl} C_6H_5\overset{\oplus}{N_2}\overset{\ominus}{Cl} \xrightarrow[KCN]{CuCN} C_6H_5CN \xrightarrow{H^+/H_2O} C_6H_5COOH$

51. $Ph-NH_2 + CH_3COCl \xrightarrow{Pyridine} Ph-NH-COCH_3$ (acetanilide)

52. $Ph-NH_2 \xrightarrow[CHCl_3]{KOH} Ph-N\equiv C$

$CH_3COCH_3 \xrightarrow{Cl_2/Ca(OH)_2} (CH_3COO)_2Ca + CHCl_3$

53.



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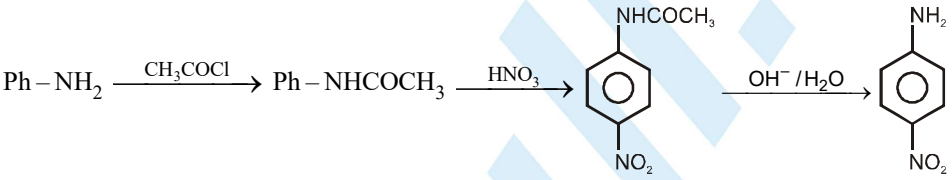

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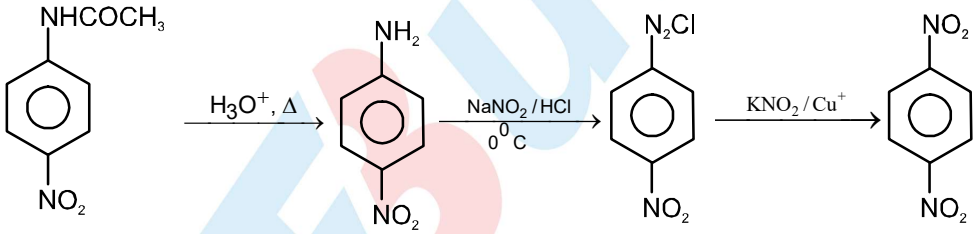

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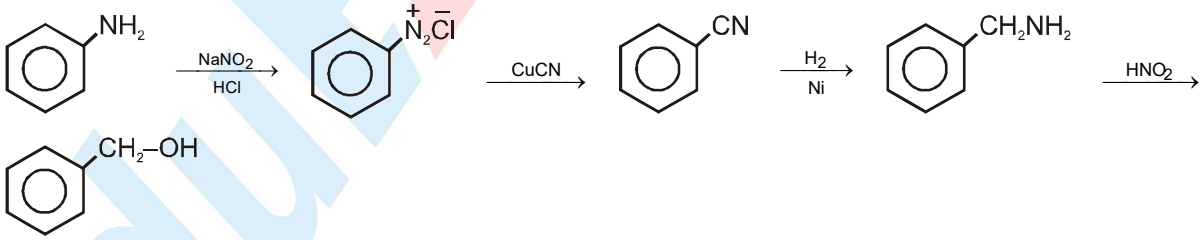
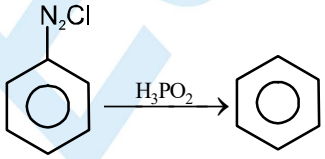
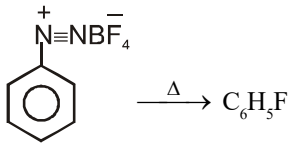
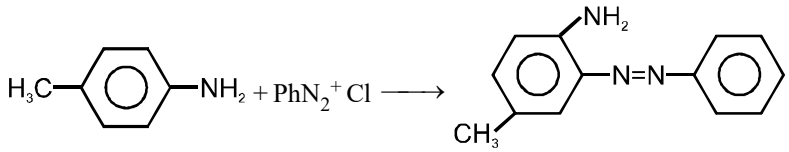


60. $C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2+HCl} C_6H_5N_2Cl \xrightarrow[\Delta]{H_2O} C_6H_5OH$

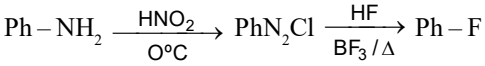
61.

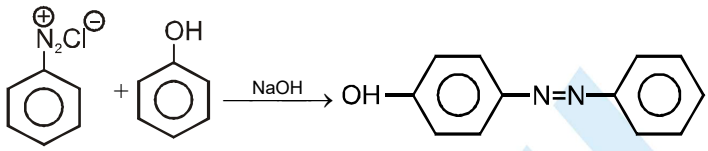


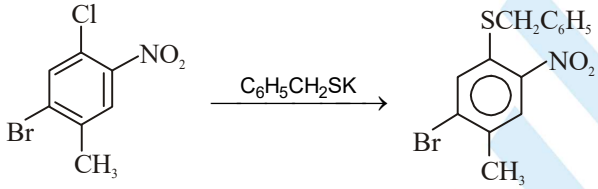
62. 

64. 

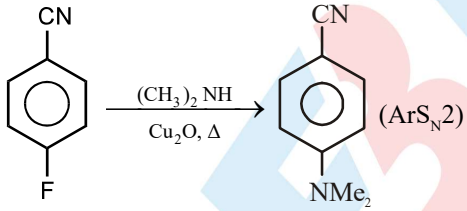
66. Phenol prefer coupling in sligtly basic medium.

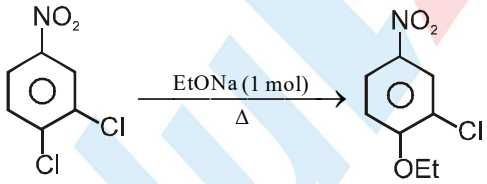
67. 

69. 

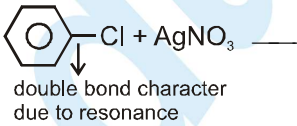
70. 

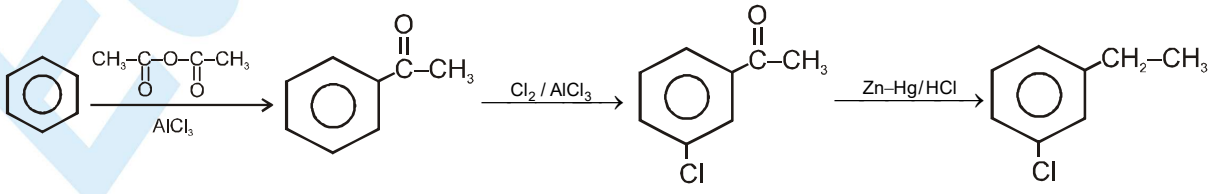
74. Because rate of S_N2 Ar is – F > – Cl > – Br > – I

75. 

76. 

[– M effect of $-NO_2$ group at para position]

79. **(A)** 

80. 

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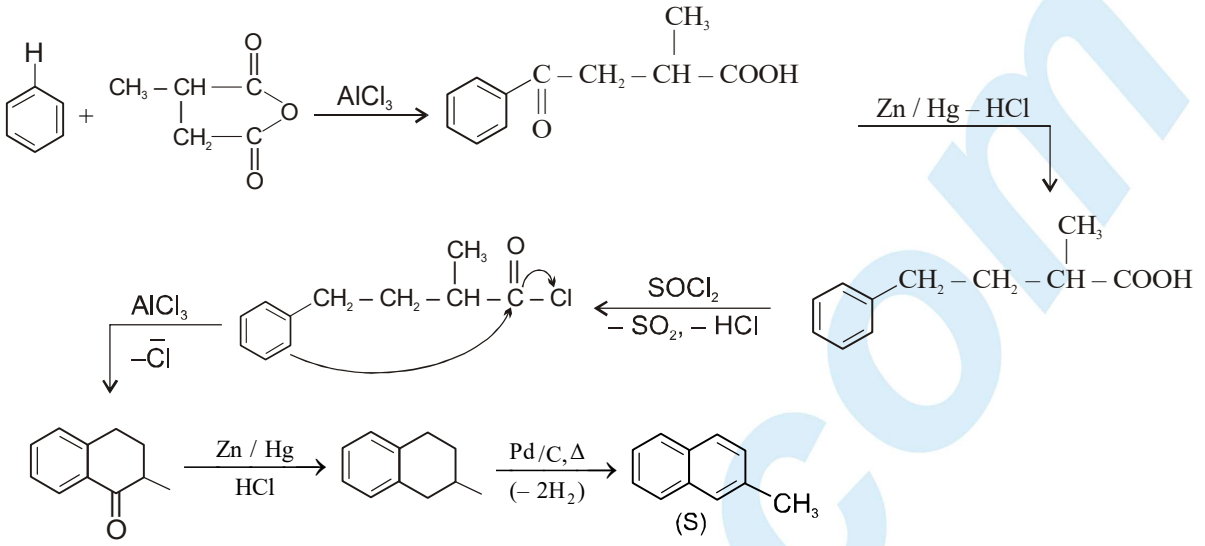

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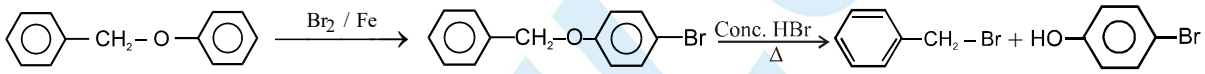
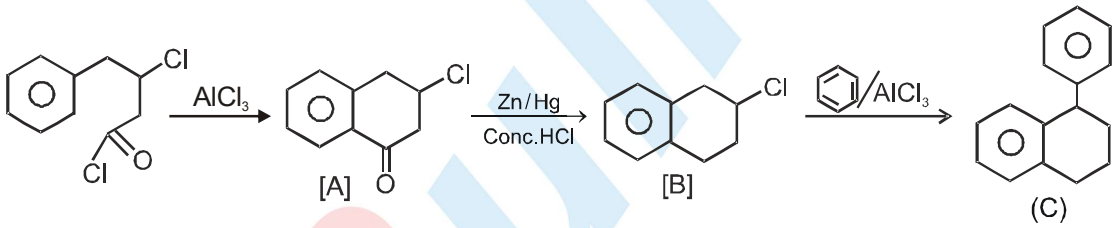
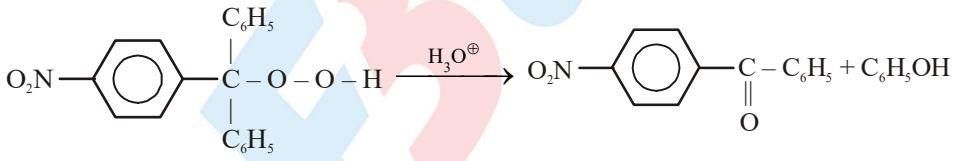


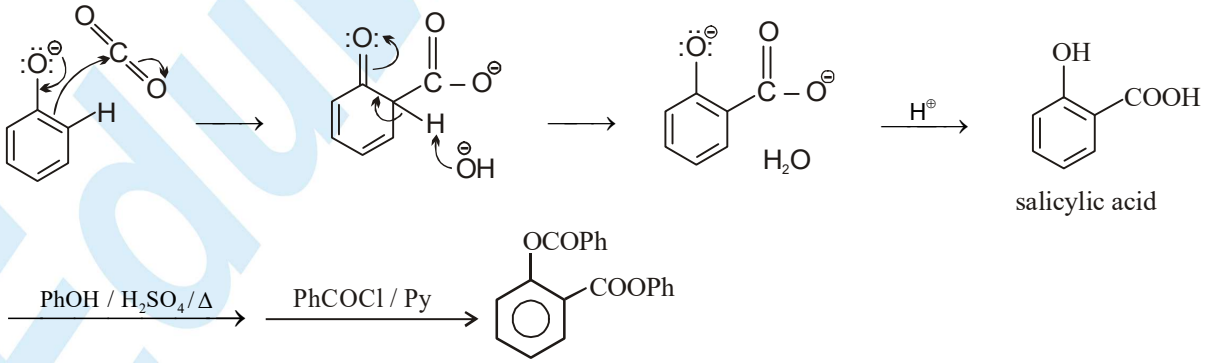
83.



84.

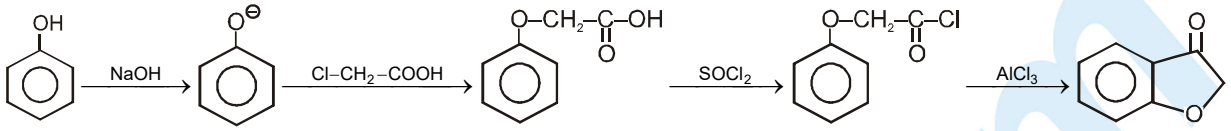


85.

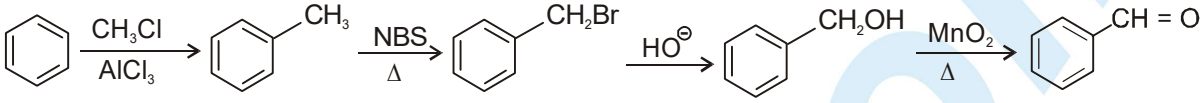


Phenoxide ions are so strongly activated that they undergo electrophilic aromatic substitution with CO_2, a weak electrophile.

86.



87.



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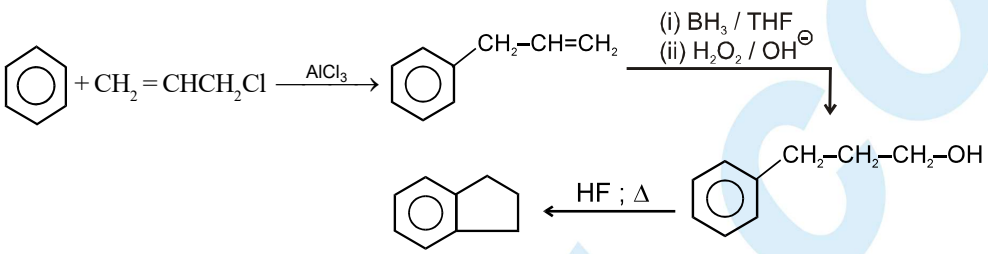

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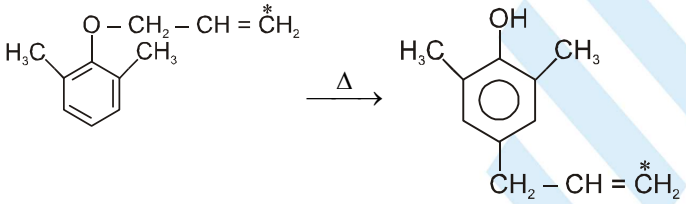

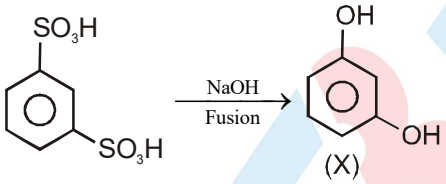

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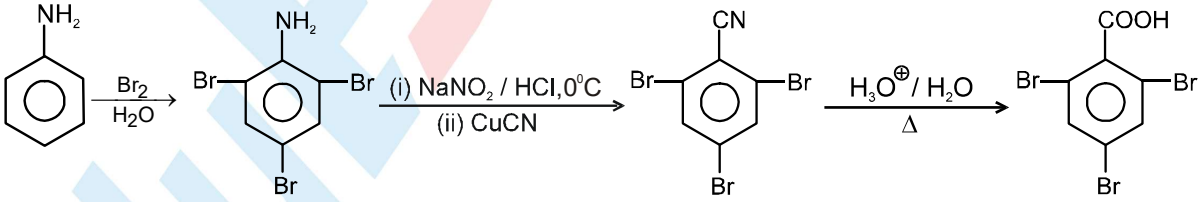

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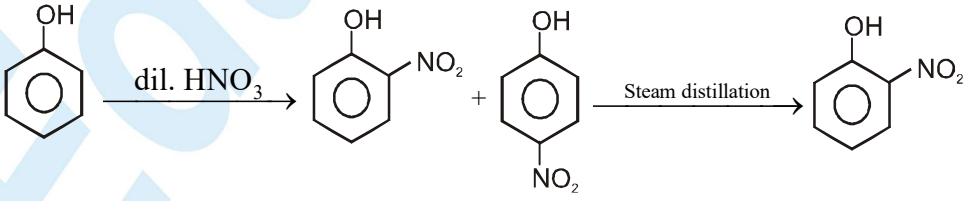
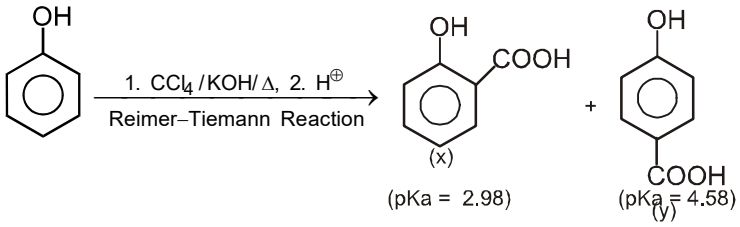


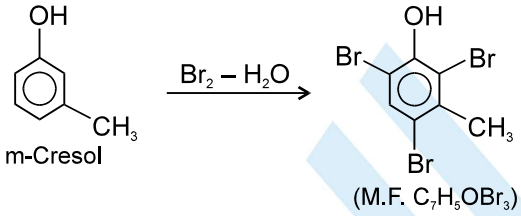
[X] [Y] [Interamolecular H–Bonding low B.P.]

94. **(D)**



(Ka) = x > y (Carboxylate anion stabilized By H-bonding)
(Sol.) = y > x (Intermolecular H-bonding in y)
(Vol.) = x > y (Intramolecular H-bonding in x)
(MP) = y > x (More Symmetrical Structure of y)

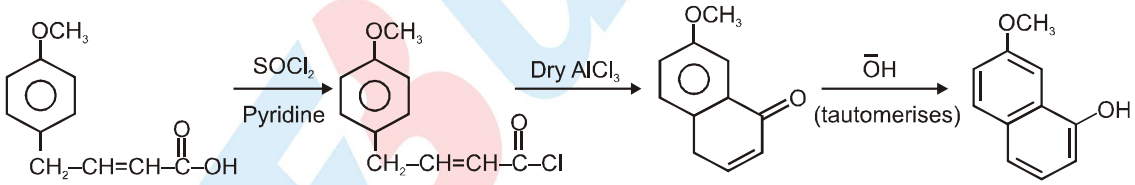
96. Since the compound dissolves in NaOH, and gives a characteristic colour with $FeCl_3$, it must be a phenol. Now three phenols having the M.F. C_7H_8O are o-, m- or p-cresol. Since the compound on treatment with Br_2 gives a tribromoderivative, therefore, two o- and one p-position w.r.t. OH group must be free. That is the phenol is m-cresol.



98. Nitrobenzene reduced into aniline by metal/acid and electrolytic reduction.

99. $C_1 - C_2$ - is shorter because it is double bond in two of three resonance strucutre ; $C_2–C_3$ is a single bond in two of three resonance strucutres.

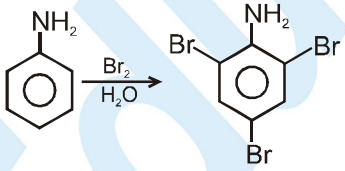
100.



101. Mustard oil reaction given by 1° amines because it has 2 active -H atoms.

102. Substitution reaction of benzene diazonium salt.

103.

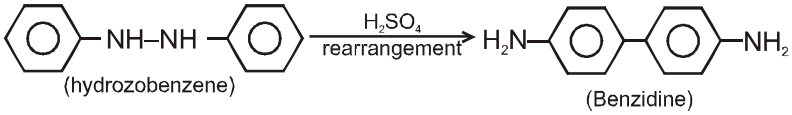


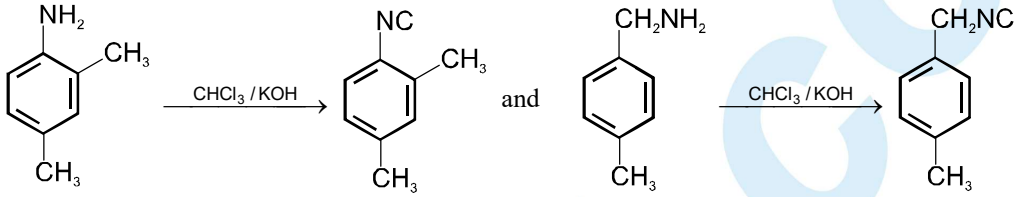
104. $CH_3N \equiv C \xrightarrow{H_2O/H^+} CH_3NH_2 + HCOOH$

105. For **(A)** → Kinetic isotopic effect is present in sulfonation.
(B) Heating p-Xylene with $AlCl_3$ and HCl results in the conversion of the majority of it into more stable m-Xylene
(C) Electron withdrawing group retards the Fries rearrangement.

106. $NaNO_2 + HCl \xrightarrow[(-NaCl)]{} HNO_2 \xrightarrow{H^+} H-\overset{\oplus}{O}(H)-N=O \longrightarrow \overset{\oplus}{N}=O + H_2O$

$Ph-NH_2 \xrightarrow[HCl\ (0-5°C)]{\oplus NO} Ph\overset{\oplus}{N}_2\overset{\ominus}{Cl}$

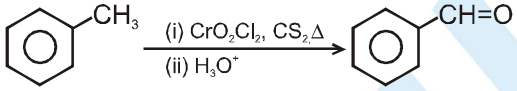
107. 

108. 

109. $R-\overset{+}{C}=\ddot{O} \longleftrightarrow R-C\equiv\overset{+}{O}$
(A) (B)

These ions are stabilized by a cannonical form containing a triple bond **(B)**, though the positive charge is principally located on the carbon, so that **(A)** contributer more than **(B)**.

110. Etard reaction.



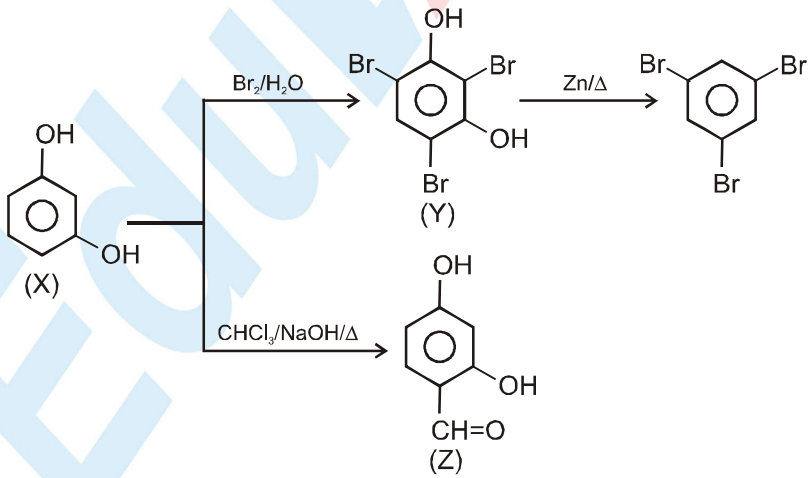
111. Nitration of benzene takes place by electrophilic substitution (Electrophile is $\overset{\oplus}{N}O_2$)

112. Ion formed by dissociation of C–H bond in toluene, is resonance stabilised.

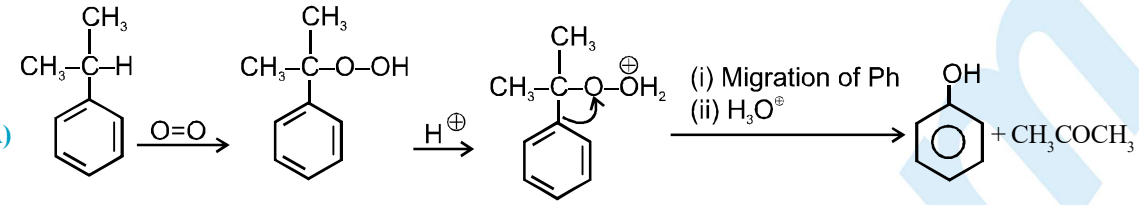
EXERCISE - 2

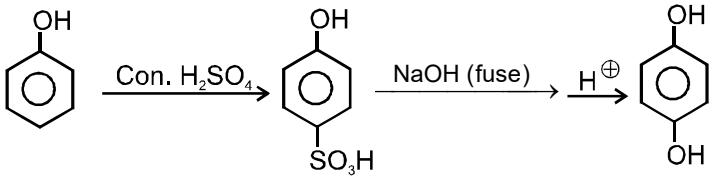
Part # I : Multiple Choice

2.

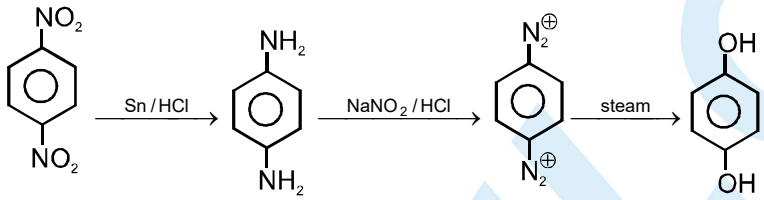


3. (A)

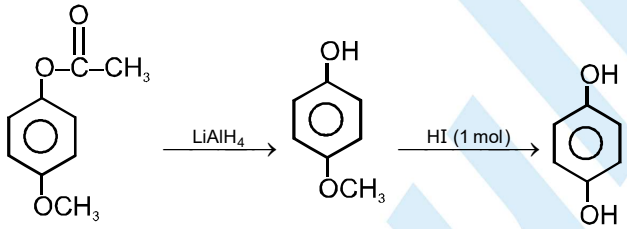




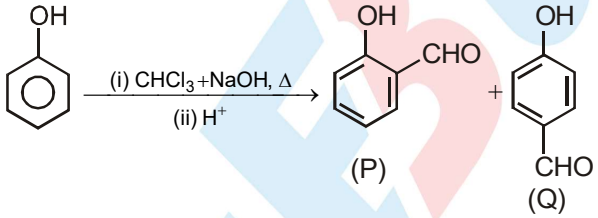
(C)



(D)



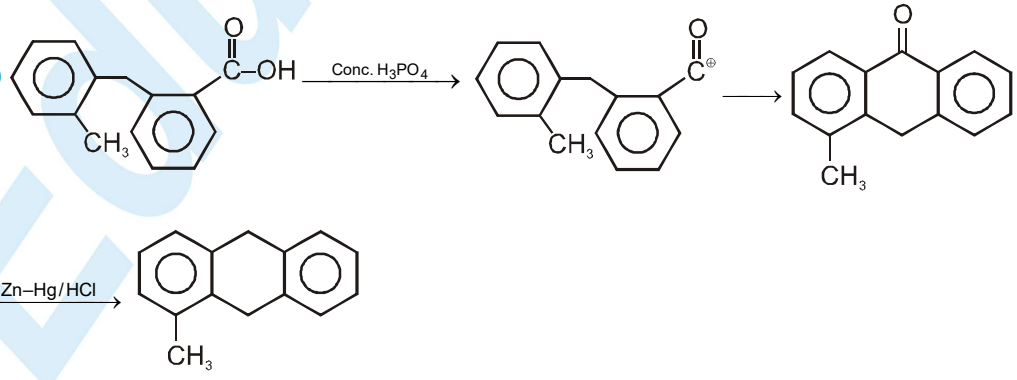
4.



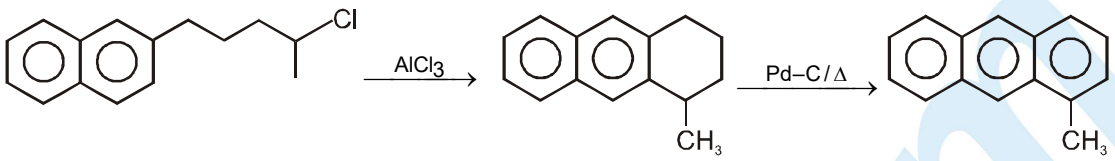
EXERCISE - 3

Part # I : Matrix Match Type

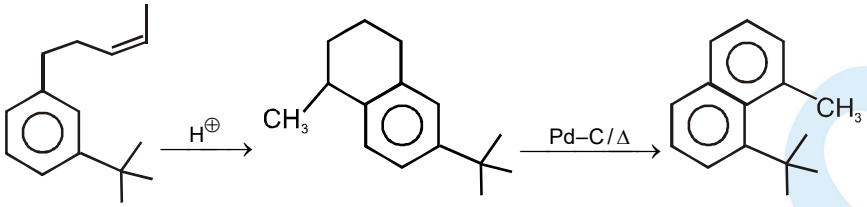
1. (A)



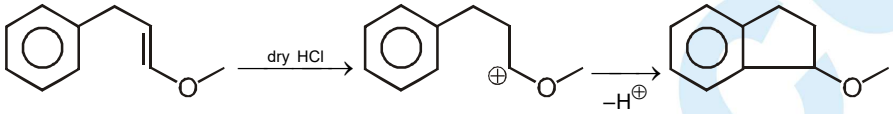
(B)



(C)



(D)

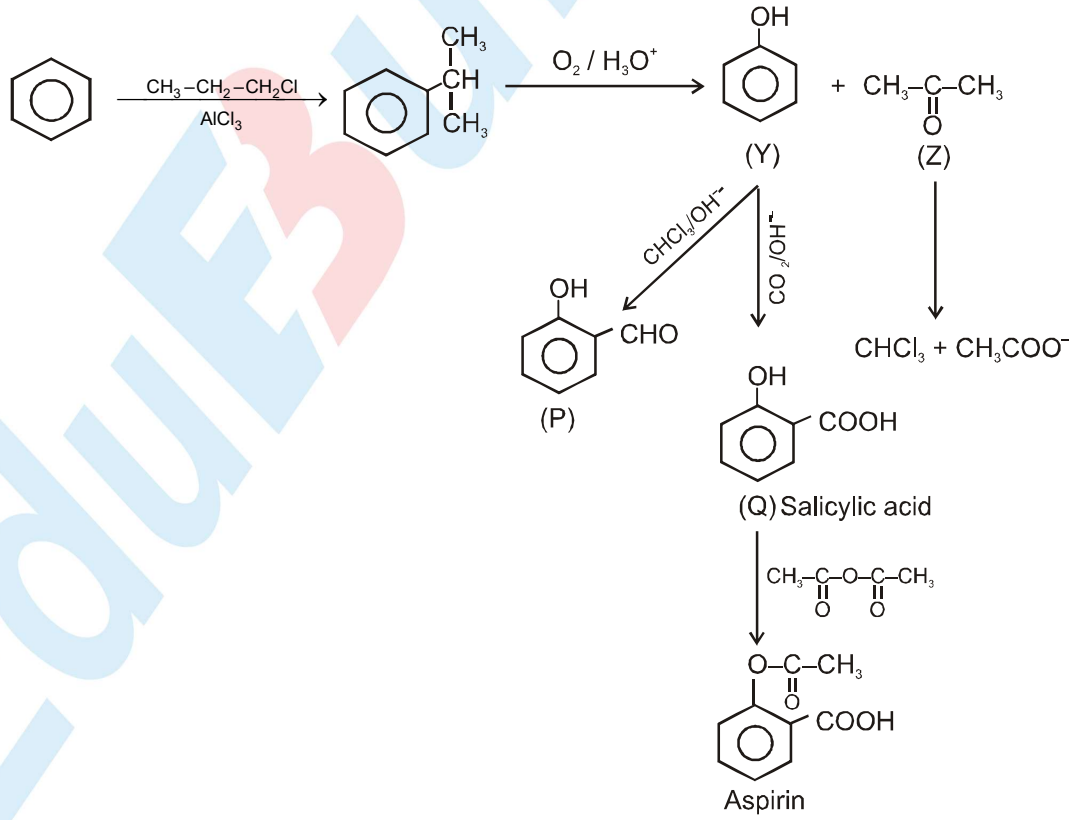


2. **(A)** –CH=CHCOOH is deactivating due to –I of –COOH group, but o,p-directing due to stability of carbocation.
(B) $-CCl_3$ is electron withdrawing group due to –I nature.
(C) –OH is electron donating due to +m.
$-NO_2$ is electron withdrawing due to –m.

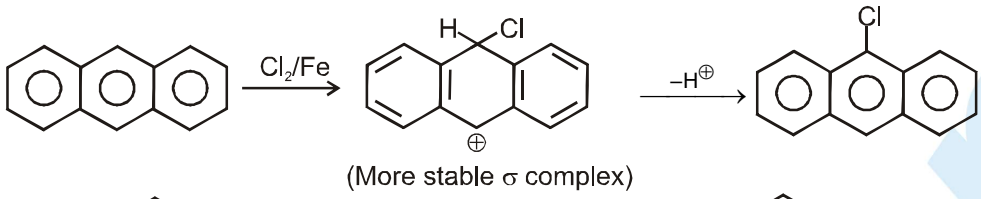
Part # II : Comprehension

Comprehension # 1 :

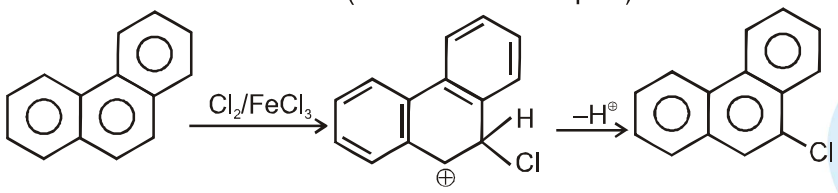
Sol. (1 to 3)

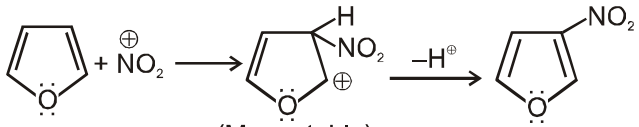


Comprehension # 2 :

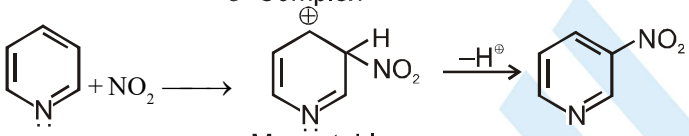
1. 

(More stable σ complex)

2. 

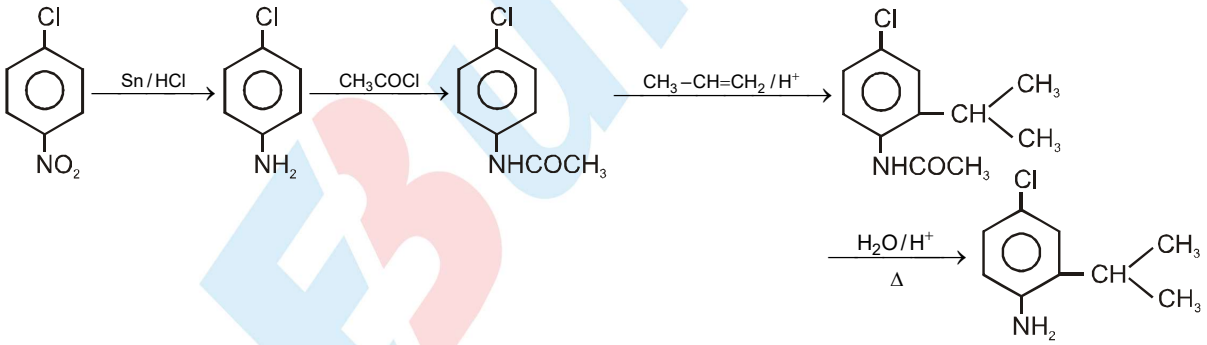
3. 

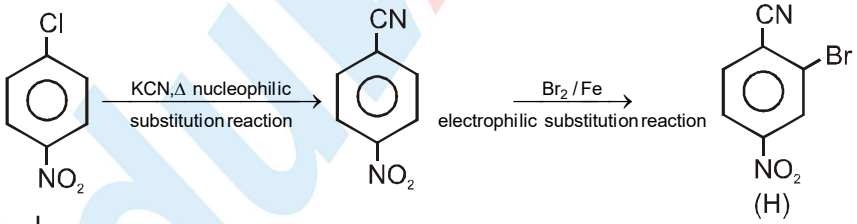
(More stable)
σ–Complex

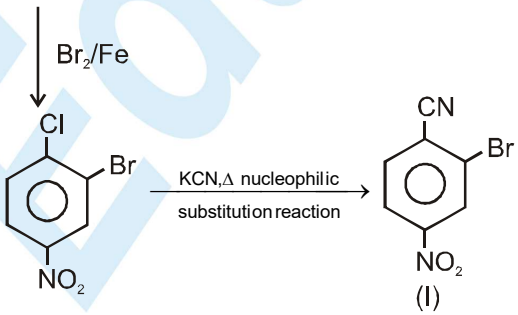
4. 

More stable
(σ –Complex)

Comprehension # 3 :

3. 



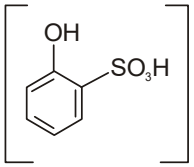
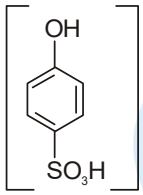


EXERCISE - 4

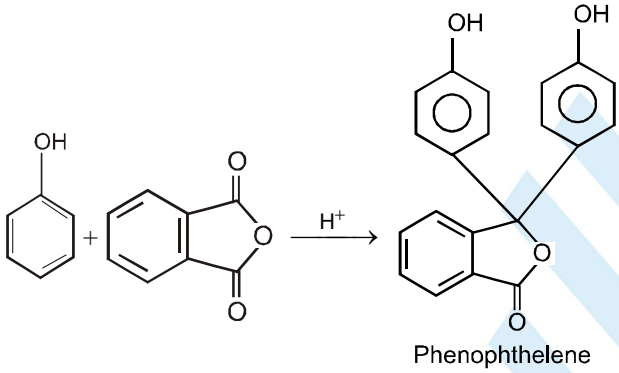
Subjective Type

3. Position (1) is most nucleophilic as well as least stearically hindered.

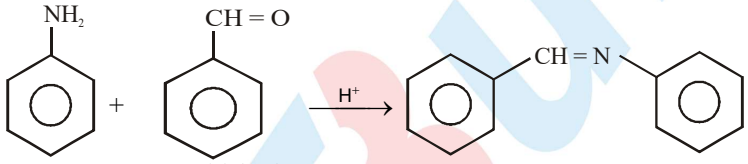
5. An aromatic electrophilic substitution reaction with $NaNO_2$ / HCl will be observed in those compound which have +I, +M, HC group. Due to more electron density.

7.  o-isomer is formed at low temperature, and the  p- isomer at high temperature.

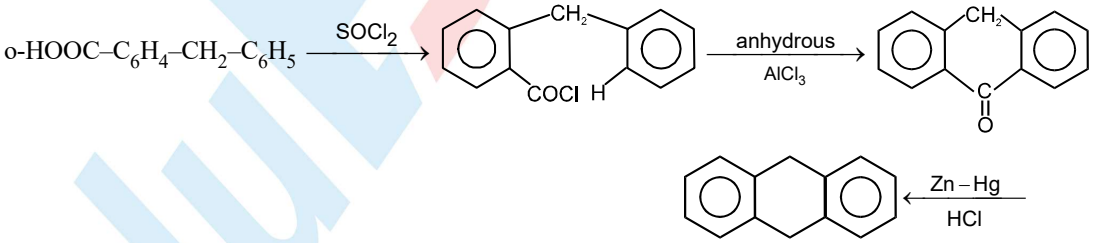
Reason : Sulfonation is reversible. At higher temperature the rate controlled ortho product reverts to phenol which then reacts to give the thermodynamically controlled para product.

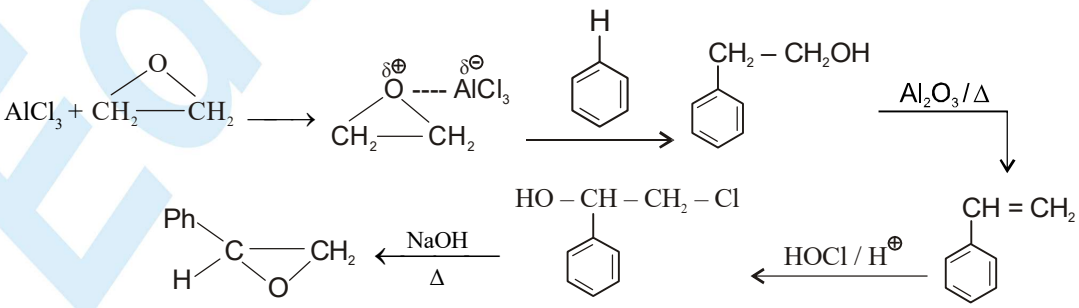
8. 

Phenophthelene

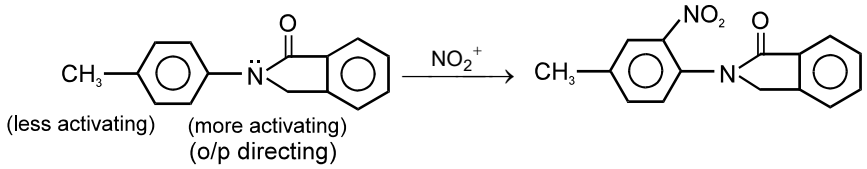
10. 

Aniline Benzaldehyde Benzalaniline (schiff's base)

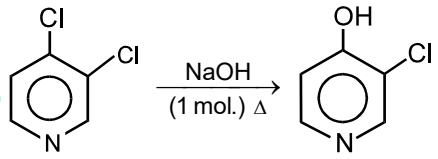
12. 

13. 

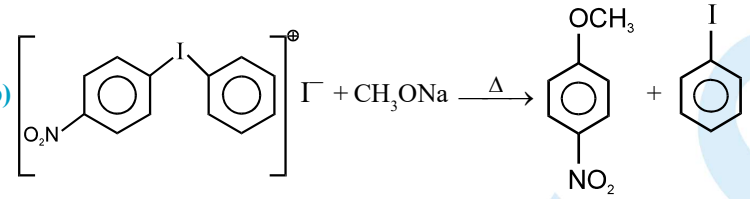
16.



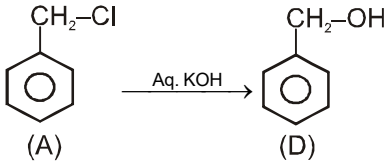
19. **(a)**

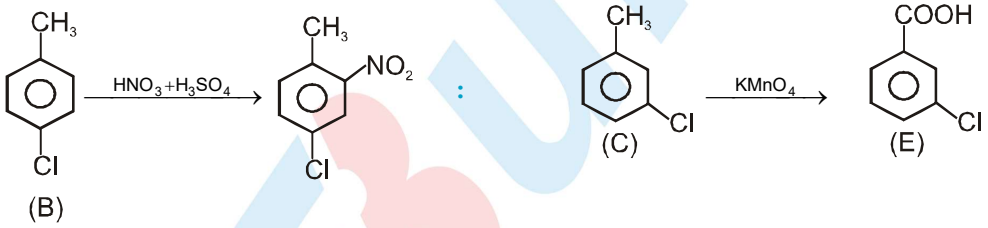


(b)



20.

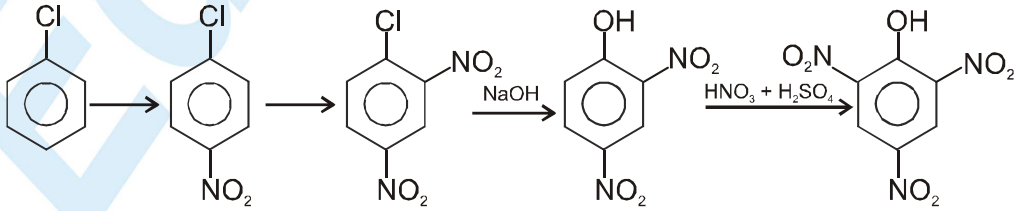




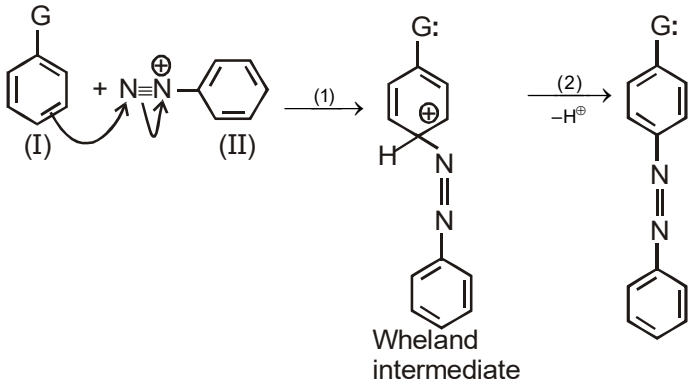
21. Cl is o-, p-directing but deactivating group, hence nitration before S_N reaction will decrease extent of nitration hence, further yield of picric acid is decreased in path I. By S_N reaction –OH group. introduced will activate benzene ring for nitration hence path II would give better yield.

22.

25.



28.



ERG in I and EWG in II will increase the rate of reaction.

32. Phenol $\xrightarrow[\text{distillation}]{\text{Zinc}}$ Benzene $\xrightarrow[\text{Conc.}H_2SO_4\text{ at }60^\circ C\text{ (electrophilic substitution)}]{\text{Conc.}HNO_3}$ Nitrobenzene $\xrightarrow[\text{NaOH (Reduction)}]{\text{Zn}}$ hydrazobenzene

EXERCISE - 5

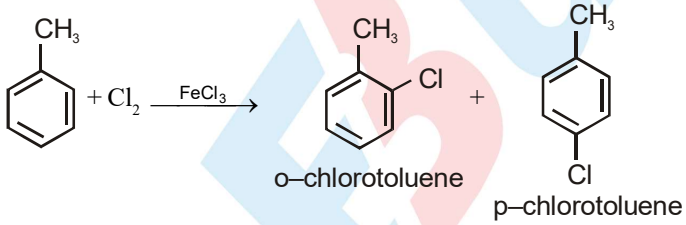
Part # I : AIEEE/JEE-MAIN

1. In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N reaction.

2.

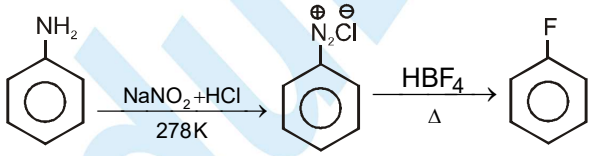
3. $-NO_2$ group in benzene ring shows – I and – M effect, which deactivates the ring towards electrophilic substitution but activates towards nucleophilic substitution.

4.

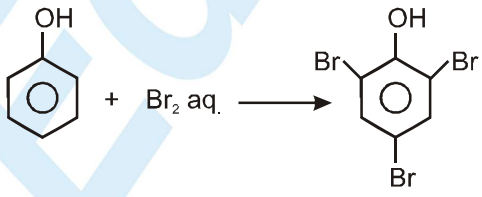


The reaction proceeds by electrophilic substitution mechanism. The CH_3 group is o/p directing.

8.

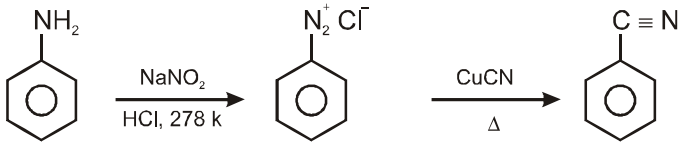


9. $KBr\,(aq.) + KBrO_3\,(aq.) \longrightarrow Br_2\,(aq.)$



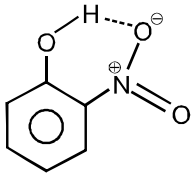
2, 4, 6-tribromophenol

10.



Benzene diazonium chloride (A) Benzonitrile (B)

11.

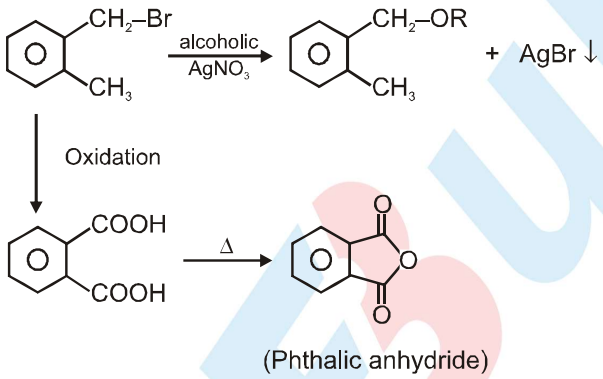


intra-molecular H-bonding.

12. By reaction with one mole of $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ with one $-NH_2$ group the molecular mass increases with 42 unit. Since the mass increases by (390 – 180) = 210 hence the number of $-NH_2$ groups is 5.

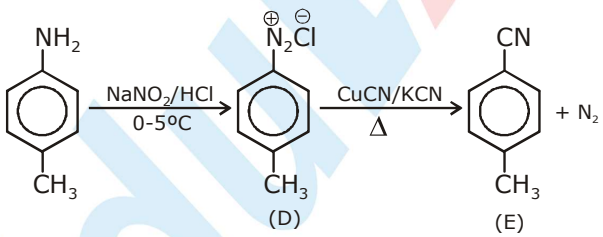
$$R-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[(-HCl)]{} R-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

13.

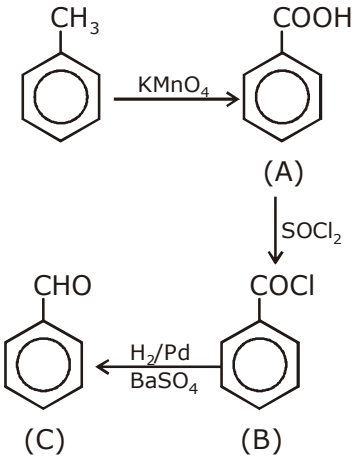


(Phthalic anhydride)

14.



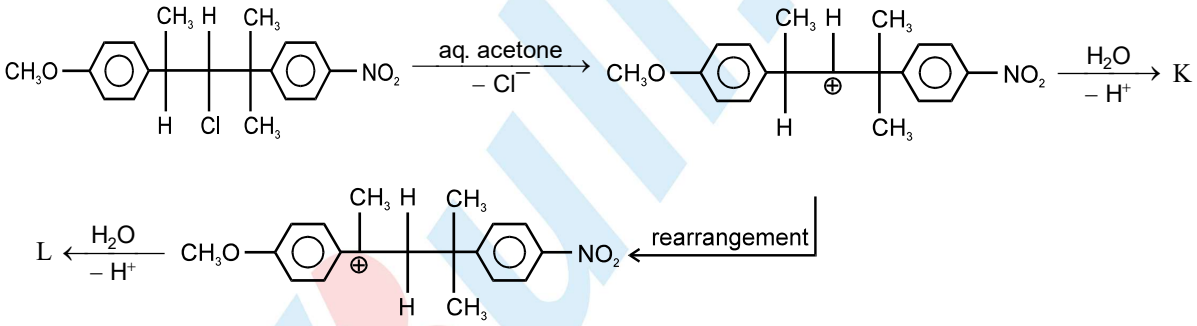
15.



Part # II : IIT-JEE ADVANCED

2. It is ArS_E2 reaction, N has lone pair so it is activating and subtitutions accurs at most activated position.

3.



4. **(A)** Due to presence of p-NO_2 group, (– I, -m group) the S_N2 Ar reaction is accelerated (due to stabilization of intermediate carbanion). In the second case NO_2 can not exert its – m effect to stabilize the carbanion.

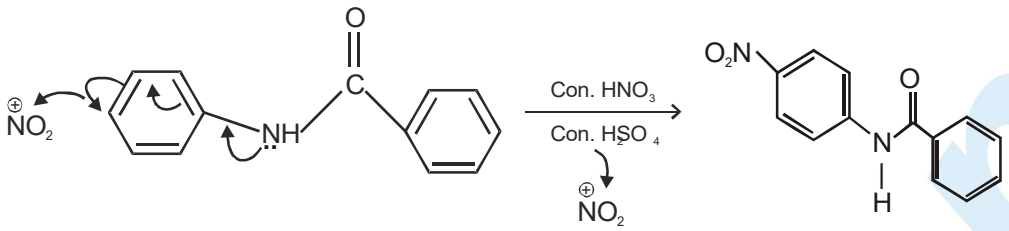
5. Reaction involved are

(1) A ⟶ B

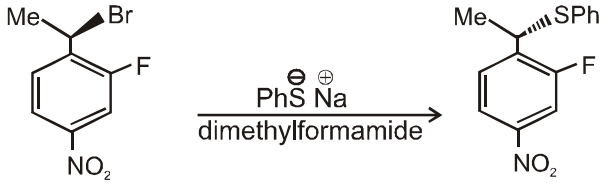
$$3H_2SO_4 + 2NaBr + MnO_2 \longrightarrow Br_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$
(A) (B)

(2) A ⟶ C

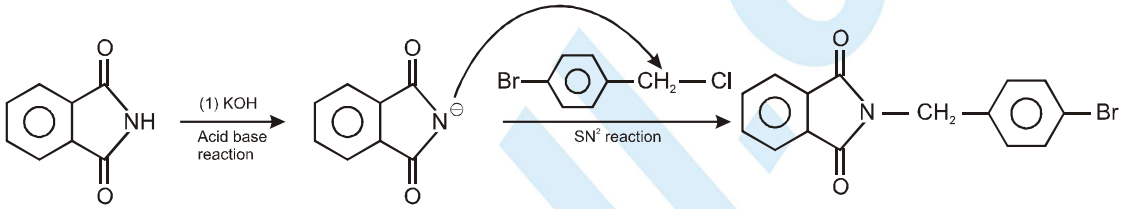
$$2H_2SO_4 + H-O-N=O \longrightarrow (H-\overset{+}{O}(H)-N=O + HSO_4^- + H_2SO_4) \longrightarrow H_3O^{\oplus} + \overset{\oplus}{N}O_2 + 2HSO_4^{\ominus}$$

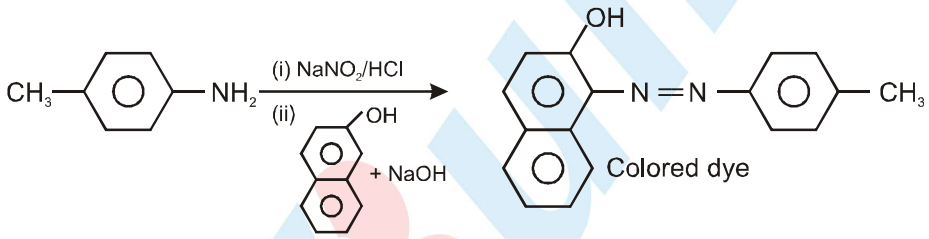
6. 

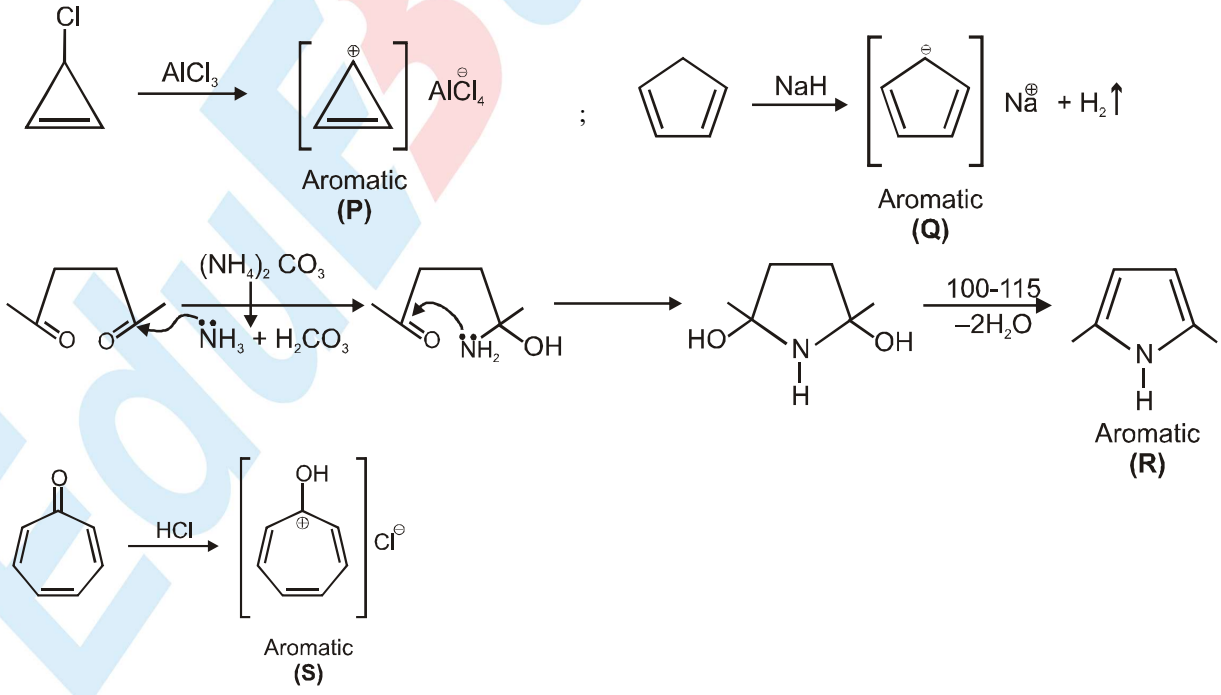
Note : (–NH– part is p-directing).

7. 

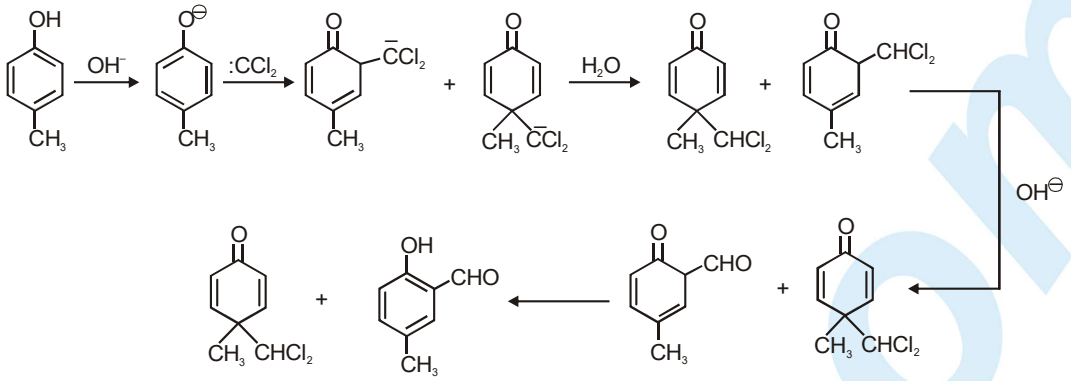
It is S_N2 reaction so back side attack is possible.

8. 

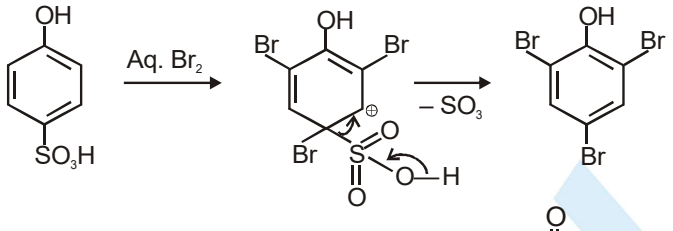
9. 

10. 

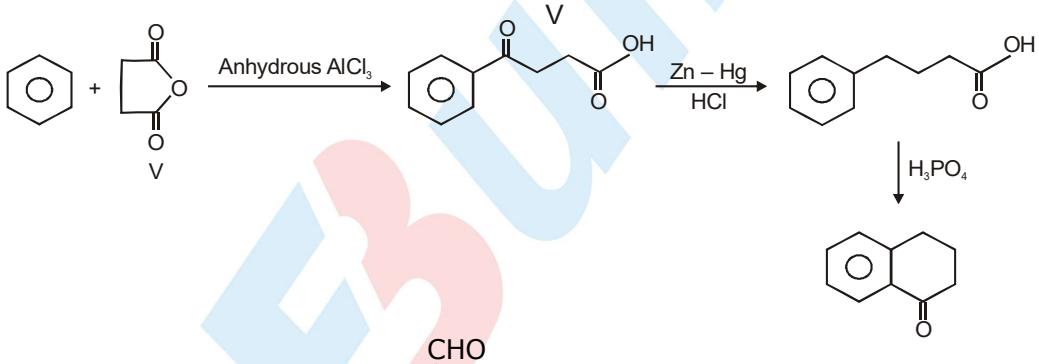
11.



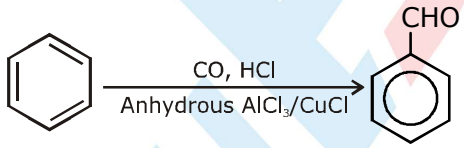
12.



13. HOOC–CH=CH–COOH (Q) $\xrightarrow[\Delta]{H_2/Ni}$ V

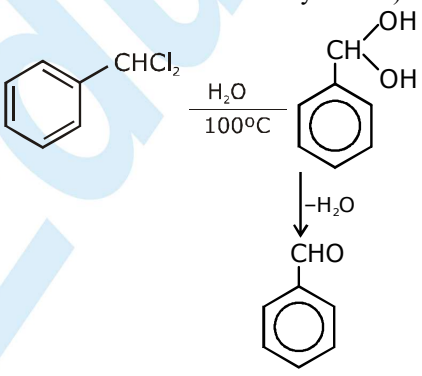


14. I.

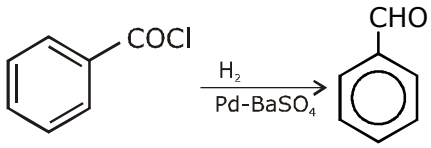


(Gatterman Koch. synthesis)

II.

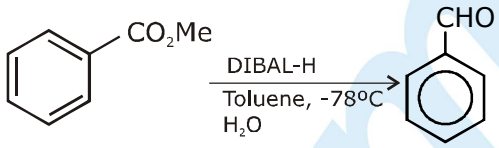


III.



(Rosenmund)

IV.



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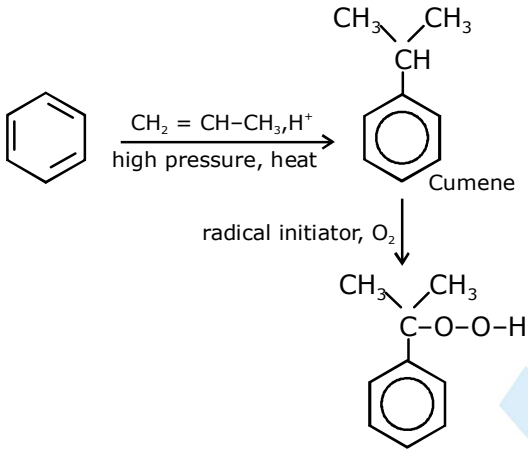
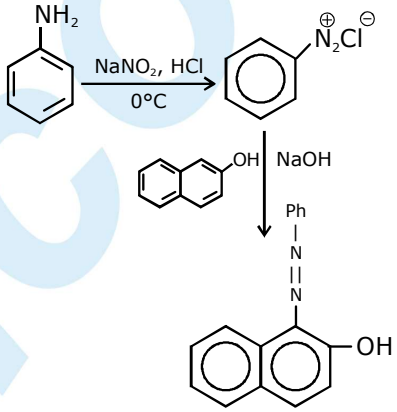
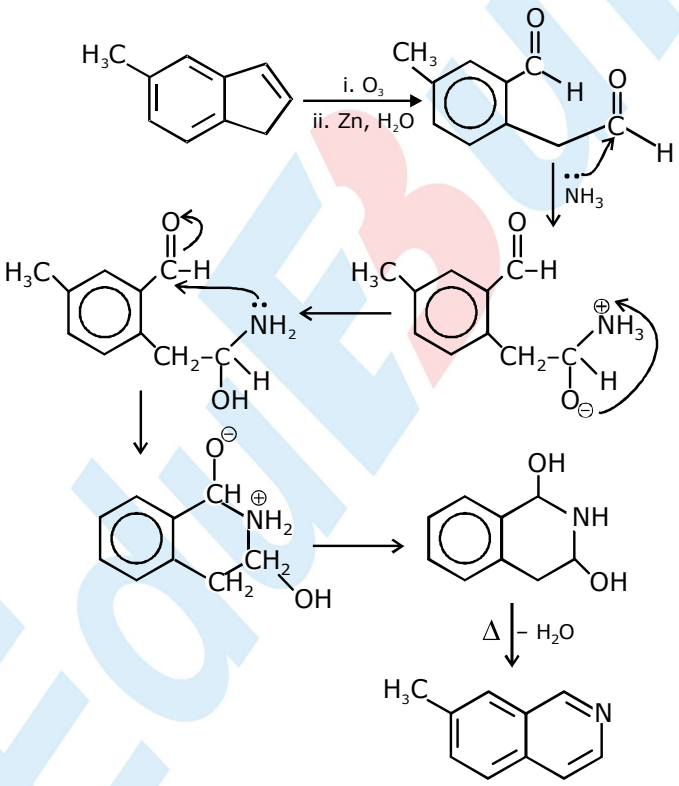


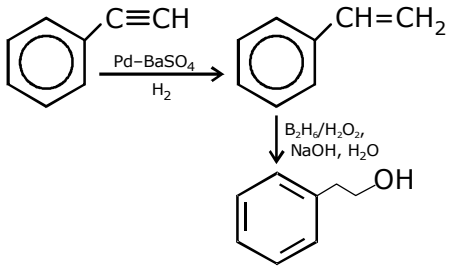
16.



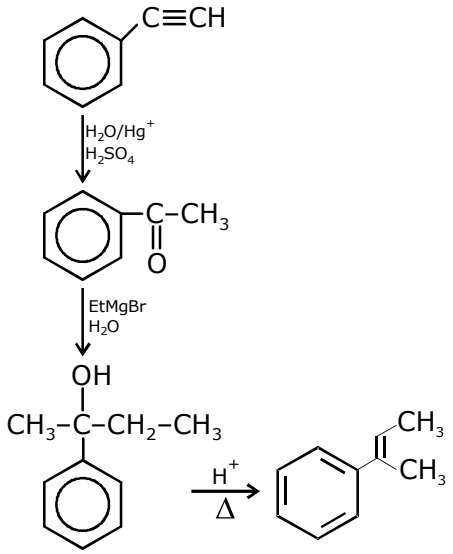
17.



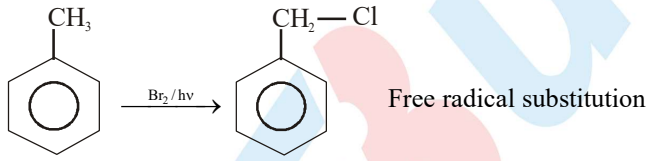
18.



19.

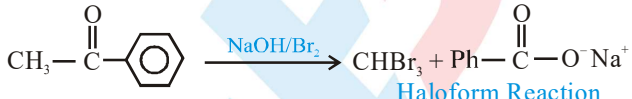


25.



Free radical substitution

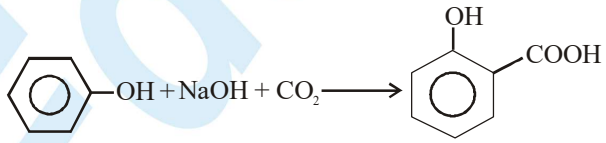
26.



Acetophenone — Haloform Reaction

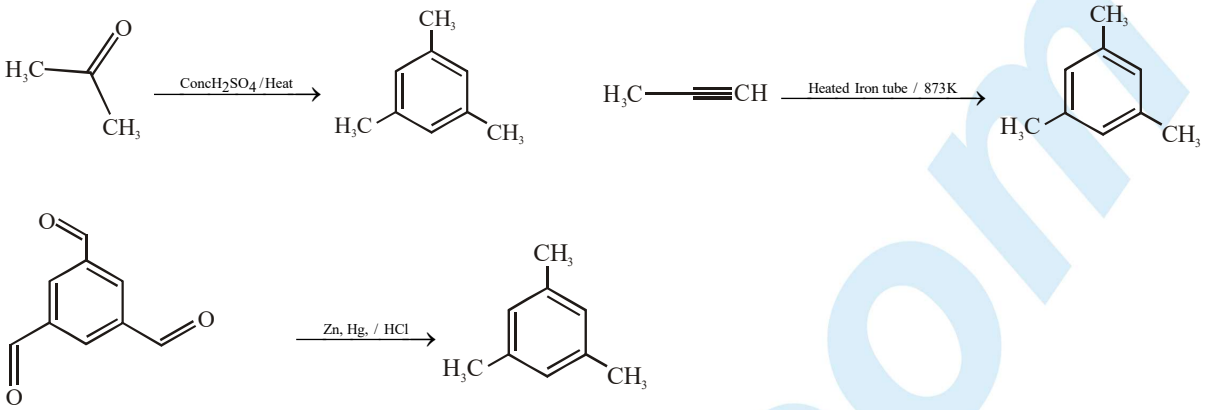
27.

Benzaldehyde — cis and trans (Perkin's reaction)

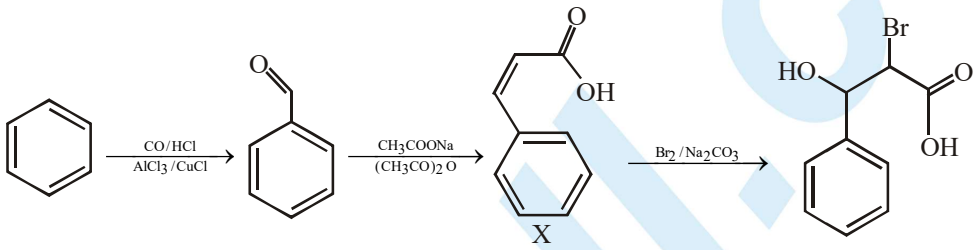


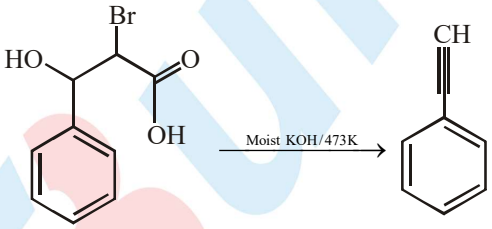
Kolbe-schmidt reaction

28.

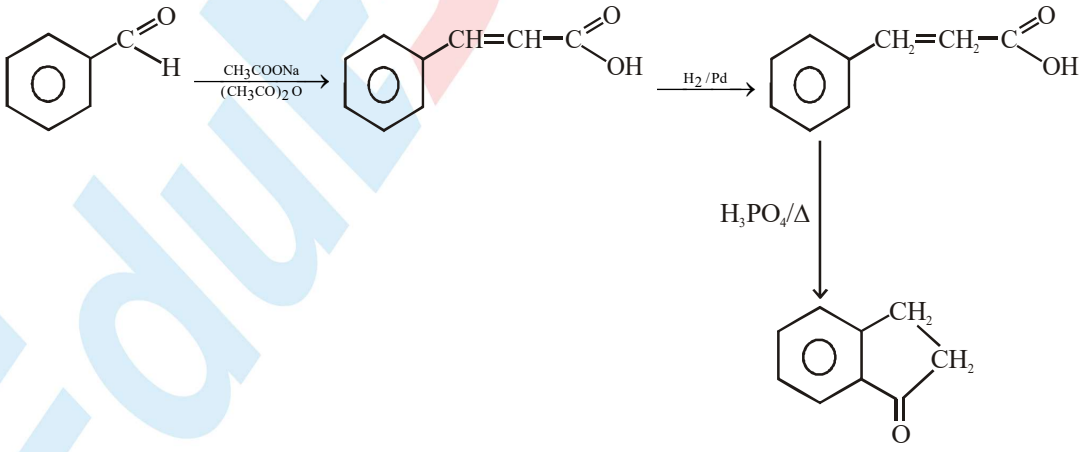

H3C
O
CH3
Conc H2SO4 / Heat
CH3
H3C
CH3
H3C
CH
Heated Iron tube / 873K
CH3
H3C
CH3
O
O
O
Zn, Hg, / HCl
CH3
H3C
CH3

29.


CO/HCl
AlCl3 /CuCl
O
CH3COONa
(CH3CO)2 O
O
OH
X
Br2 /Na2CO3
Br
HO
O
OH

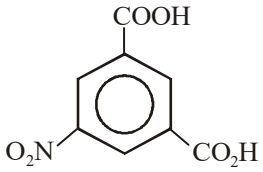

Br
HO
O
OH
Moist KOH/473K
CH

30.

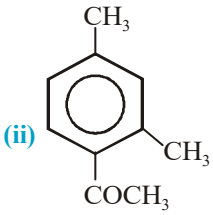

O
C
H
CH3COONa
(CH3CO)2 O
CH=CH—C
O
OH
H2 /Pd
CH2=CH2—C
O
OH
H3PO4/Δ
CH2
CH2
O

MOCK TEST

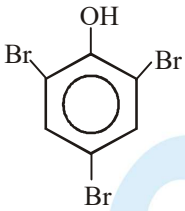
23. **(i)**



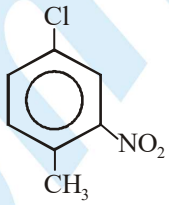
(ii)



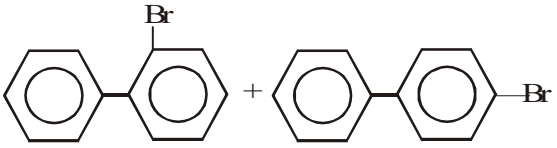
(iii)



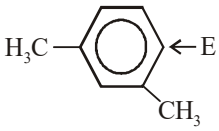
(iv)



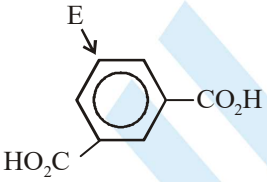
(v)



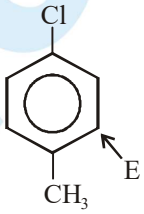
24. **(i)**



(ii)



(iii)



25. **(i)** ; because $-CH_3$ is an activating group hence toluene is most reactive.