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Aryl Halides and Phenols

Objective Questions I (Only one correct option)

1 What will be the major product when *m*-cresol is reacted with propargyl bromide ($HC{\equiv}C{-}CH_2Br$) in presence of K_2CO_3 in acetone? **(2019 Main, 12 April II)**

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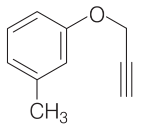

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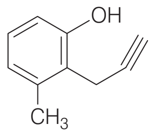

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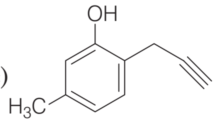

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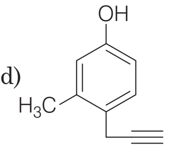

2. Increasing rate of S_N1 reaction in the following compounds is

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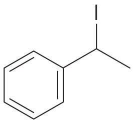

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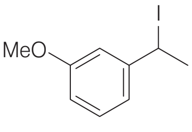

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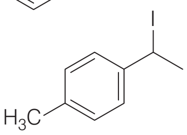

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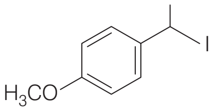
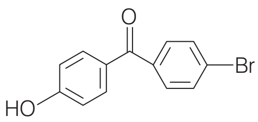


(2019 Main, 10 April I)

(a) (A) < (B) < (C) < (D)
(b) (B) < (A) < (C) < (D)
(c) (A) < (B) < (D) < (C)
(d) (B) < (A) < (D) < (C)

3. *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives **(2019 Main, 9 April II)**

(a)


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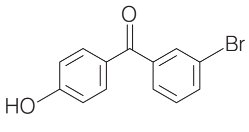

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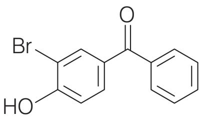

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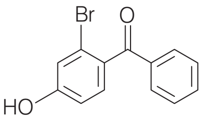
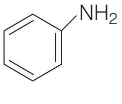


4. The organic compound that gives following qualitative analysis is **(2019 Main, 9 April I)**

Test	Inference
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2 /water	Decolourisation

(a)


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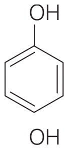

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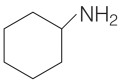

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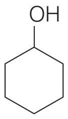

5. Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution **(2019 Main, 11 Jan II)**

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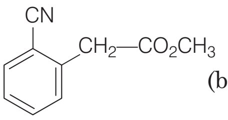

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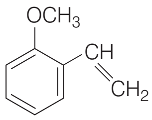

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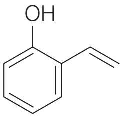

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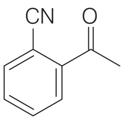

6. Which of the following compounds will produce a precipitate with $AgNO_3$? **(2019 Main, 11 Jan I)**

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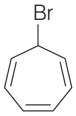

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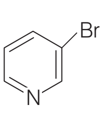

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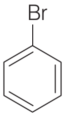

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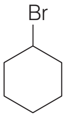
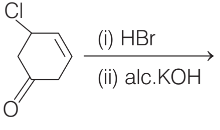
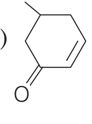


7. The major product of the following reaction is



(2019 Main, 11 Jan I)

(a)


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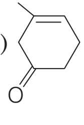

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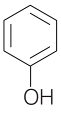
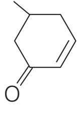
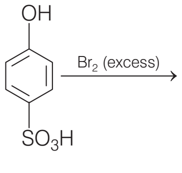
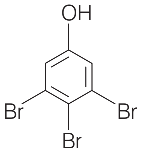


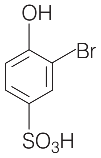
(d)


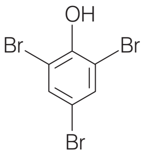
8. The major product of the following reaction is

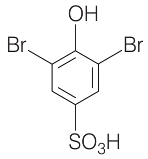


(2019 Main, 11 Jan I)

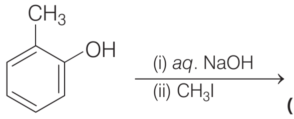
(a) 

(b) 

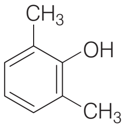
(c) 

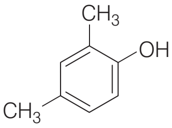
(d) 

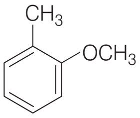
9. The major product of the following reaction is

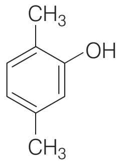


(2019 Main, 10 Jan II)

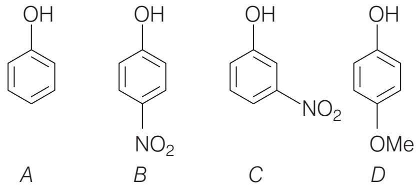
(a) 

(b) 

(c) 

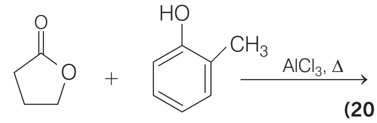
(d) 

10. The increasing order of the pK_a values of the following compounds is **(2019 Main, 10 Jan I)**

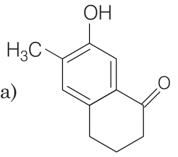


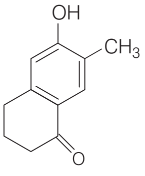
(a) $D < A < C < B$ (b) $B < C < A < D$
(c) $C < B < A < D$ (d) $B < C < D < A$

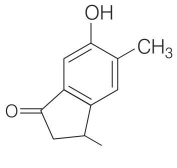
11. The major product of the following reaction is

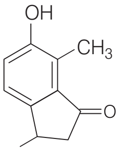


(2019 Main, 9 Jan II)

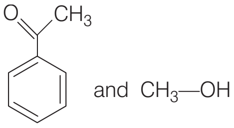
(a) 

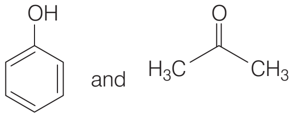
(b) 

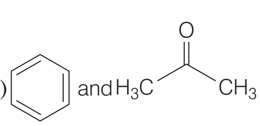
(c) 

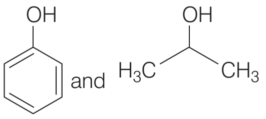
(d) 

12. The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are **(2019 Main, 9 Jan II)**

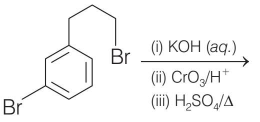
(a) 

(b) 

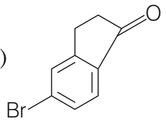
(c) 

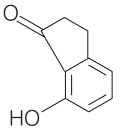
(d) 

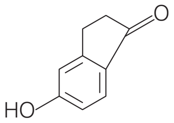
13. The major product of the following reaction is

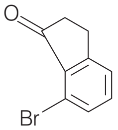


(2019 Main, 9 Jan I)

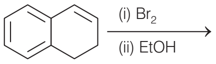
(a) 

(b) 

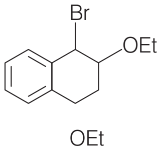
(c) 

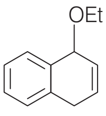
(d) 

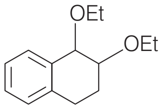
14 The major product of the following reaction is

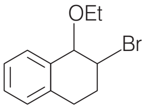


(2019 Main, 9 Jan I)

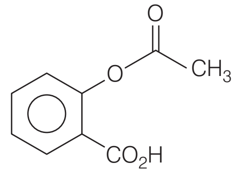
(a) 

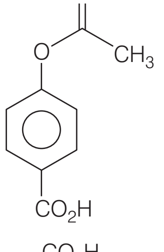
(b) 

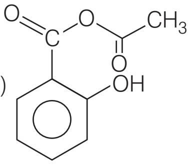
(c) 

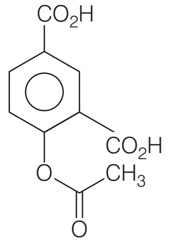
(d) 

15. Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces: **(2018 Main)**

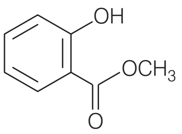
(a) 

(b) 

(c) 

(d) 

16. Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively **(2018 Main)**

(a)


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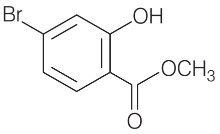

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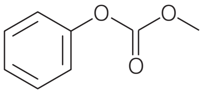

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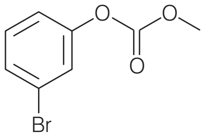

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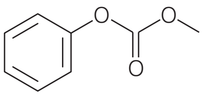
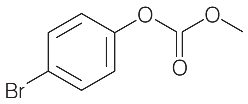


and


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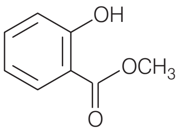

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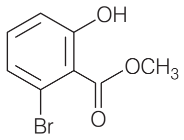
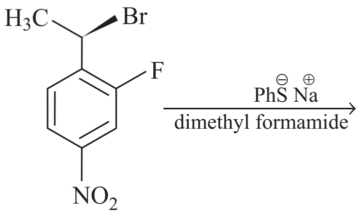


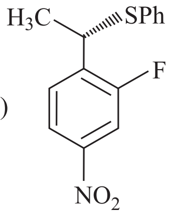
17. For the identification of β-naphthol using dye test, it is necessary to use **(2014 Adv.)**

(a) dichloromethane solution of β-naphthol
(b) acidic solution of β-naphthol
(c) neutral solution of β -naphthol
(d) alkaline solution of β-naphthol

18. The major product of the following reaction is



(2008, 3M)

(a)


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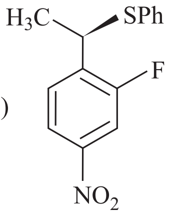

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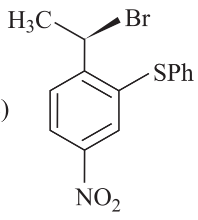

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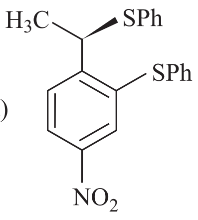
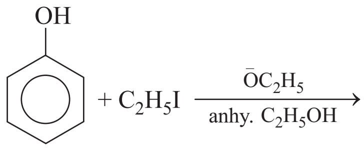


19.



(2003, 1M)

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

20. In the reaction of *p*-chlorotoluene with KNH_2 in liq. NH_3, the major product is **(1997, 1M)**

(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloroaniline

21. Phenol reacts with bromine in carbon disulphide at low temperature to give **(1988, 1M)**

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol
(c) *p*- bromophenol (d) 2, 4, 6-tribromophenol

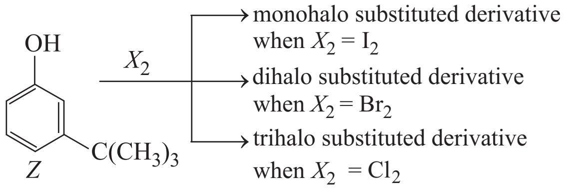
22. When phenol is treated with excess of bromine water, it gives **(1984, 1M)**

(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol

Objective Questions II

(One or more than one correct option)

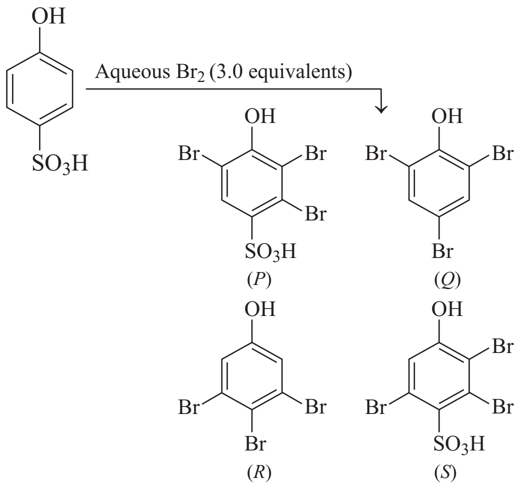
23. The reactivity of compound *Z* with different halogens under appropriate conditions is given below



The observed pattern of electrophilic substitution can be explain by

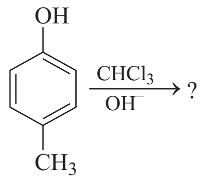
(a) the steric effect on the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group

24. The major product(s) of the following reaction is/are **(2013 Adv.)**

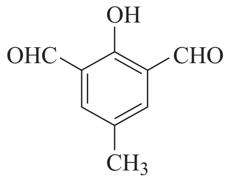


(a) *P* (b) *Q* (c) *R* (d) *S*

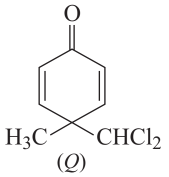
25. In the following reaction, the product (s) formed is/are



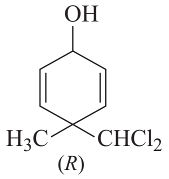
(2013 Adv.)



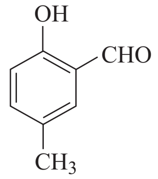
(*P*)



(*Q*)



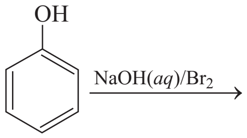
(*R*)



(*S*)

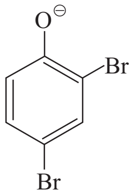
(a) *P* (major) (b) *Q* (minor) (c) *R* (minor) (d) *S* (major)

26. In the reaction,

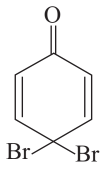


the intermediate(s) is/are **(2010)**

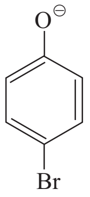
(a)



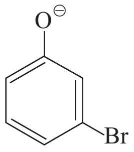
(b)



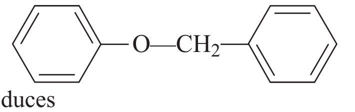
(c)



(d)

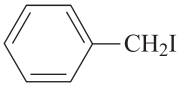


27. The ether

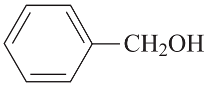


,when treated with HI produces **(1999, 3M)**

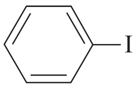
(a)



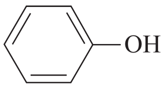
(b)



(c)

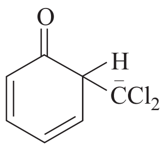


(d)

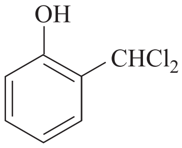


28. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediates ? **(1995, 2M)**

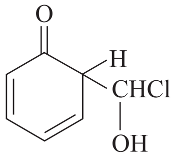
(a)



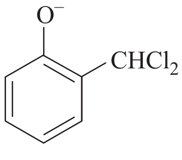
(b)



(c)



(d)



29. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to **(1990, 1M)**

(a) the formation of less stable carbonium ion
(b) resonance stabilisation
(c) longer carbon halogen bond
(d) sp^2-hybridised carbon bonded to halogen

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I
(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct

30. **Statement I** Bromobenzene, upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product.

Statement II In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **(2008, 3M)**

31. **Statement I** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Statement II In the case of phenol, the intermediate carbocation is more resonance stabilised. **(2000, M)**

32. **Statement I** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement II Cyanide (CN^-) is a strong nucleophile. **(1998, 2M)**

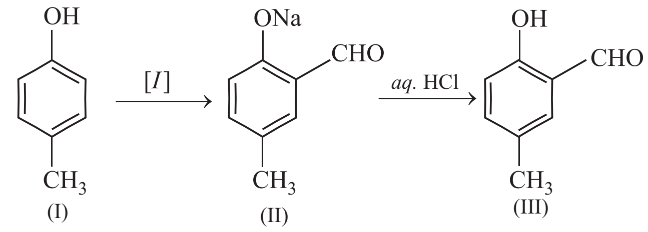
33. **Statement I** Aryl halides undergo nucleophilic substitution with ease.

Statement II The carbon halogen bond in aryl halides has partial double bond character. **(1991, 2M)**

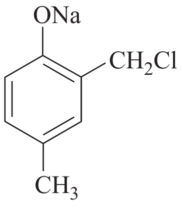
Passage Based Problems

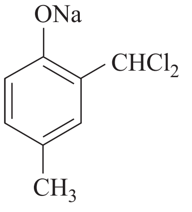
Passage 1

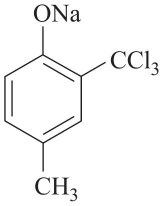
Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.

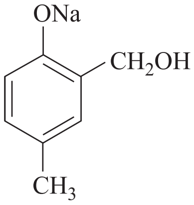


34. The structure of the intermediate I is

(a)


(b)


(c)


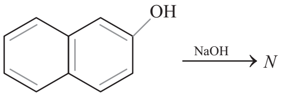
(d)


35. The electrophile in this reaction is
(a) $:CHCl$ (b) $^{+}CHCl_2$ (c) $:CCl_2$ (d) $^{\bullet}CCl_3$

36. Which one of the following reagents is used in the above reaction ?
(a) *aq* NaOH + CH_3Cl (b) *aq* NaOH + CH_2Cl_2
(c) *aq* NaOH + $CHCl_3$ (d) *aq* NaOH + CCl_4

Integer Type Questions

37. The number of resonance structures for N is **(2015, Adv.)**



Fill in the Blanks

38. Amongst the three isomers of nitrophenol, the one that is least soluble in water is ……… **(1992, 1M)**

39. Phenol is acidic due to resonance stabilisation of its conjugate base, namely …… **(1990, 1M)**

40. Formation of phenol from chlorobenzene is an example of ……… aromatic substitution. **(1989, 1M)**

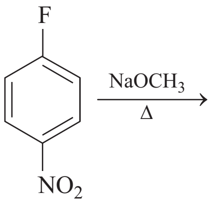
41. The acidity of phenol is due to the ……… of its anion. **(1984, 1M)**

Subjective Questions

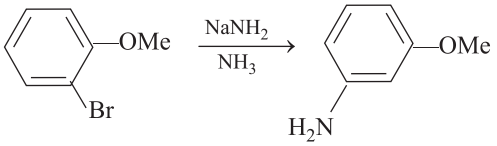
42. Carry out the following conversions.
(i) Phenol to aspirin
(ii) Benzoic acid to *meta*-fluorobenzoic acid in not more than three steps. **(2003)**

43. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **(2001, 5M)**

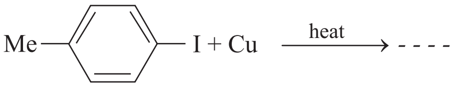
44. What would be the major product in the following reaction?



45. Explain briefly the formation of the products giving the structures of the intermediates.



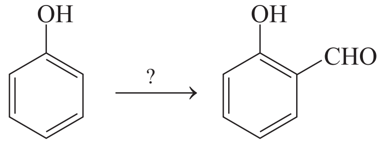
46. Complete the following, giving the structures of the principal organic products



47. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps) ? **(1996, 2M)**

48. Explain the following in one or two sentences only :
"Phenol is an acid, but it does not react with sodium bicarbonate." **(1987, 1M)**

49. Complete the following with appropriate structures :



(1986, 1M)

50. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolve in dilute NaOH solution and gives a characteristic colour with $FeCl_3$. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound. **(1985, 2M)**

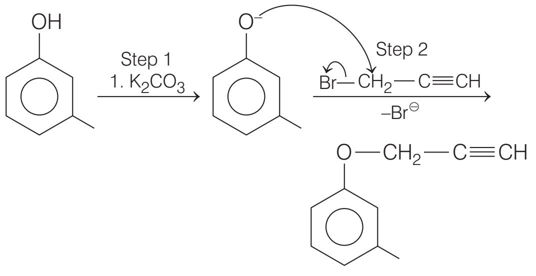
51. Give reason in one or two sentences for the following :
"*o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not." **(1985, 1M)**

Answers

1. (a) **2.** (b) **3.** (c) **4.** (b)
5. (c) **6.** (a) **7.** (c) **8.** (c)
9. (c) **10.** (b) **11.** (c) **12.** (b)
13. (a) **14.** (d) **15.** (a) **16.** (c)
17. (d) **18.** (a) **19.** (a) **20.** (b)
21. (c) **22.** (d) **23.** (a,b,c) **24.** (b)
25. (b,d) **26.** (b,c) **27.** (a, d) **28.** (a,d)
29. (b,d) **30.** (c) **31.** (a) **32.** (d)
33. (d) **34.** (b) **35.** (c) **36.** (c)
37. (9) **38.** *ortho*-nitrophenol
39. phenoxide ion **40.** nucleophilic **41.** phenoxide ion

Hints & Solutions

1 The major product when *m*-cresol reacts with propargyl bromide ($HC \equiv C—CH_2Br$) in presence of K_2CO_3 in acetone is given in the following reaction:



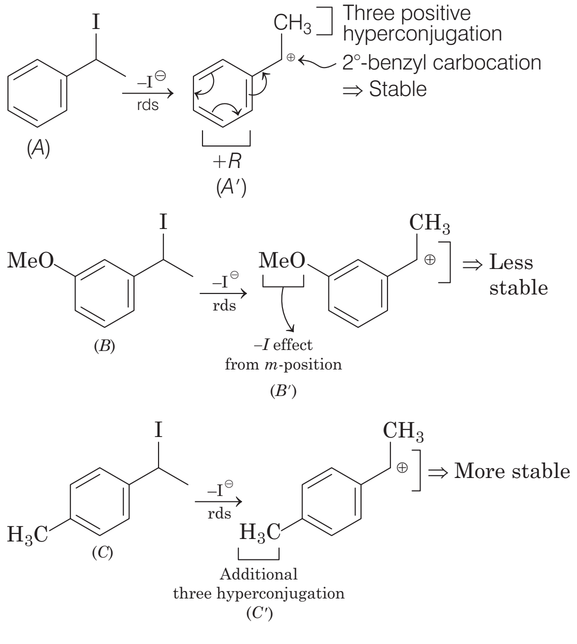
Major product

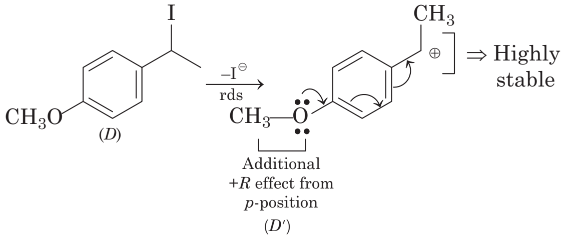
In **step 1** K_2CO_3 act as a base and abstract H-atom from —OH group. This leads to the formation of substituted phenoxide ion (highly stable).

In **step 2** substituted phenoxide ion on reaction with $Br—CH_2—C \equiv CH$ gives the required product.

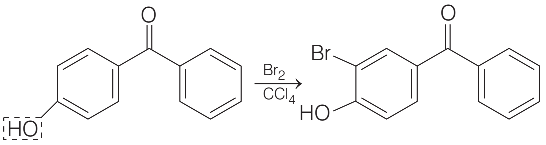
2. More stable the carbocation intermediate, higher will be the rate of S_N1 reaction.

The reaction involving carbocation intermediate formation for the given compounds are as follows:

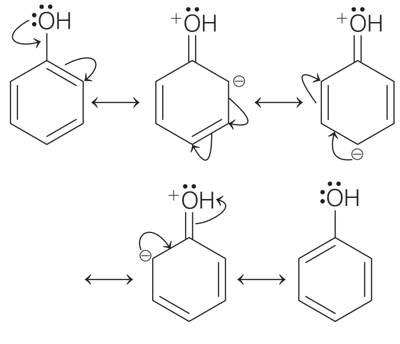




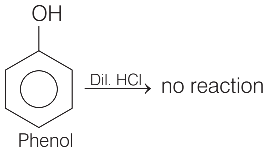
3. *p*-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.



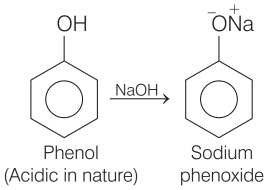
—OH group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions. —OH group also exhibit –I group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of —Br occur at *ortho* position. Resonating structures are as follows:

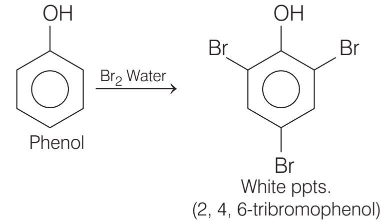


4. Phenol (ArOH) is insoluble in dil. HCl and readily soluble in NaOH solution. It reacts with Br_2/water to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of Br_2 water. Reactions involved are as follows :

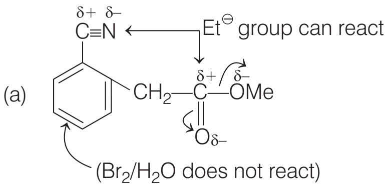
- 

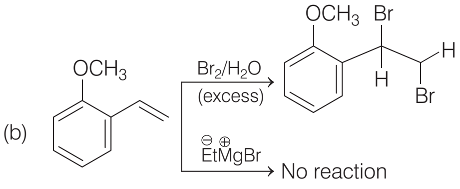
Phenol
(Acidic in nature)

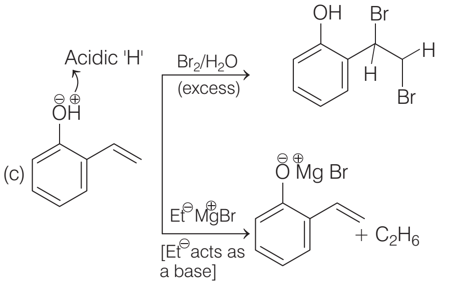
- 

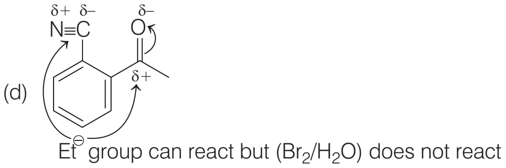
- 

5. Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes $C_2H_5^-$ [$C_2H_5^-\overset{\oplus}{M}gBr$ in ether/aprotic medium] which can act as nucleophile as well as strong base. Bromine water (Br_2/H_2O, red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as $\gt C{=}C\lt$ is present outside the ring (aliphatic, not aromatic).

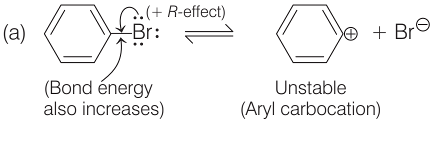


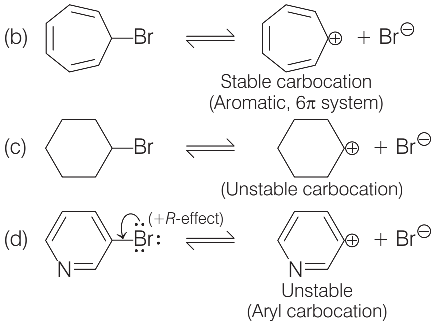


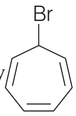




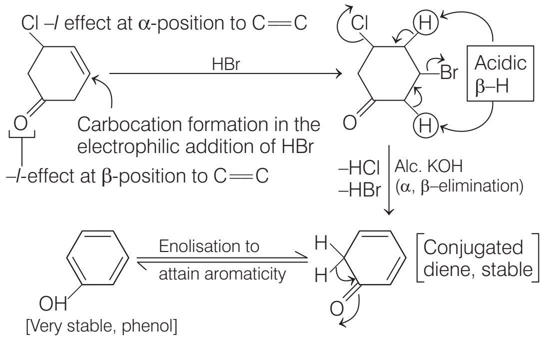
6. Only ionic halides (X^-) give precipitate of AgX with $AgNO_3$ solution. So, an organic bromide able to produce $R^{\oplus}$ (stable carbocation) and Br^- in aqueous solution will give precipitate of AgBr with $AgNO_3$.

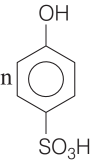


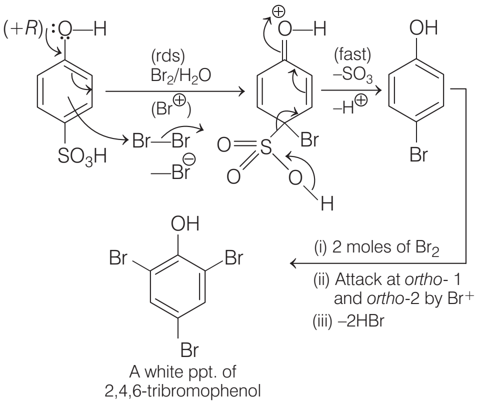


So, only  produces a precipitate of AgBr with $AgNO_3$ solution.

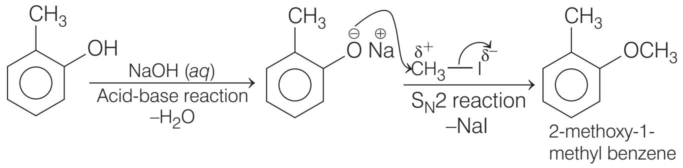
7. In presence of HBr, reactant containing $\gt C{=}C\lt$ undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc. KOH, α,β-elimination takes place that give corresponding diene. The diene undergoes enolisation to give stable product (phenol).



8. In  ipso-substitution takes place with the carbon bearing —SO_3H group. After the attack of the electrophilic Br^+ in the rate determining step (rds) of the ArS_E2 pathway desulphonation (—SO_3) takes place with a faster rate.



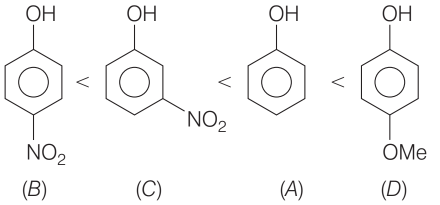
9. Substituted phenols react with *aq.*NaOH to form sodium phenoxides which on reaction with CH_3I undergoes S_N2 reaction to give 2-methoxy-1-methyl benzene.



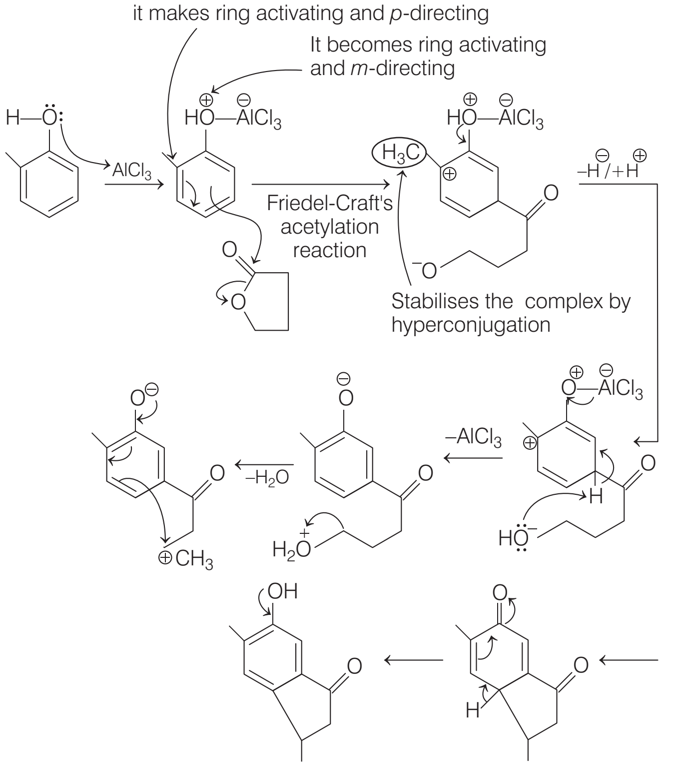
10. Acidic strength is inversely proportional to pK_a value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol. Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol. Electron withdrawing groups ($-NO_2$) increases the acidic strength of phenol whereas electron donating group ($-OCH_3$) decreases the acidic strength of phenol. In case of $-NO_2$ group attached to phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

Thus, order of acidic strength of nitrophenol is:

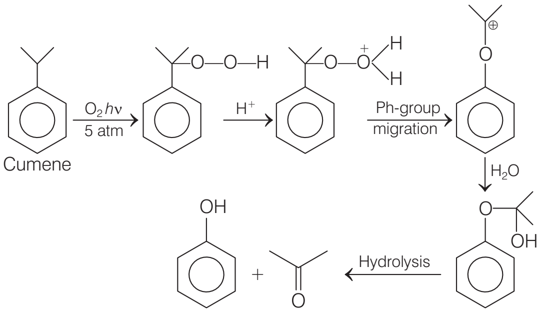
p-nitrophenol > *o*-nitrophenol and the correct order of the pK_a values of give option is



11. It is an aromatic electrophilic substitution reaction (ArS_E2). The reaction follows $Ar\,S_E2$ (Aromatic electrophlic substitution pathway) as shown below :4

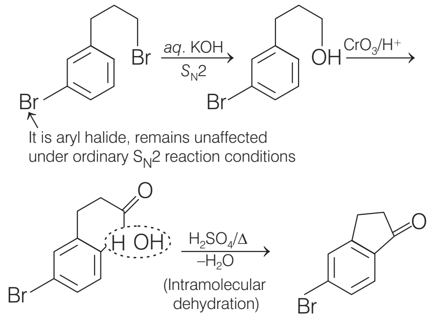


12 The given process is cumene process (Hock process) to synthesise phenol and acetone industrially.
In Hock p rocess, Ph — group migrate and release H_2O.

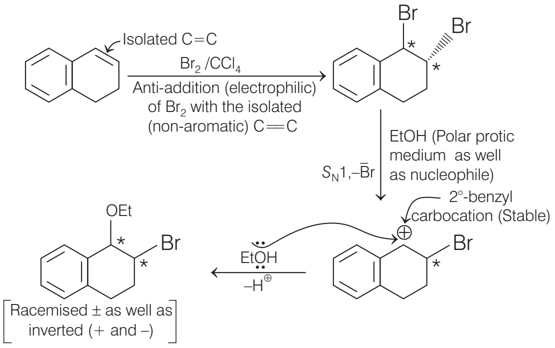


13. **Key Idea** The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step 1.

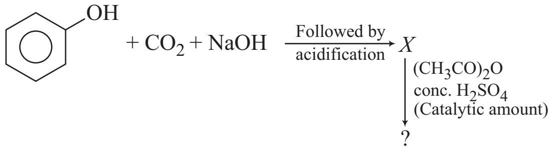
The road map of the given reaction is as follows:



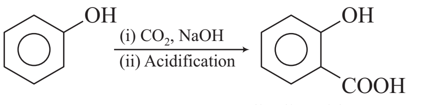
14 The road map of the given reaction is :



15.

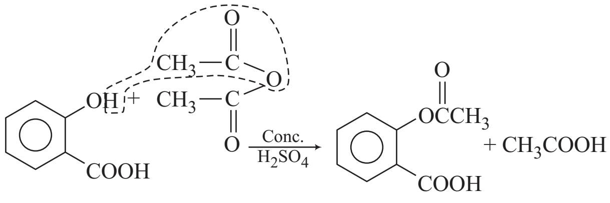


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as



Salicylic acid
(*X*)

The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as



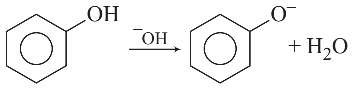
Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Pain killer).

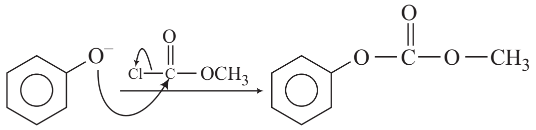
16. Given,

In the above road map, first reaction appears as acid base reaction followed by S_NAE (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

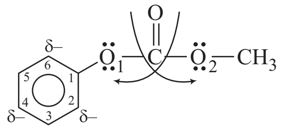
(i) **Acid base reaction**



(ii) **S_NAE**

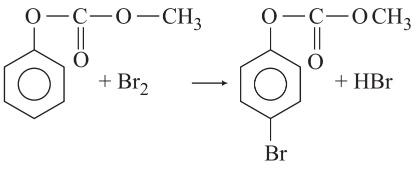


In the product of S_NAE the attached group is *ortho* and *para*-directing due to following cross conjugation



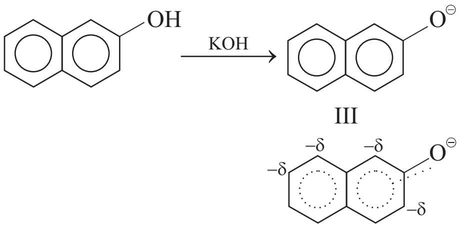
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group $—O—\underset{\underset{O}{\|}}{C}—O—CH_3$ is bulky.

Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product i.e.



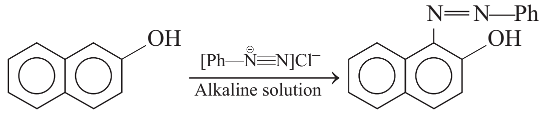
17. **PLAN** This problem can be solved by using the concept of synthesis of dye using electrophilic aromatic substitution reaction.

In basic (alkaline) solution naphthol exists as naphthoxide ion which is a strong *o*, *p*-directing group.



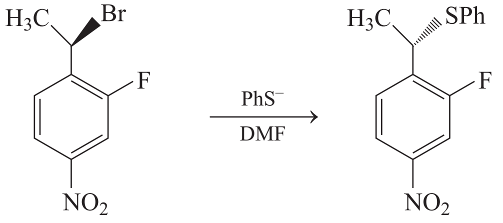
III

Thus, formation of dye can be shown as



Thus, (d) is the correct choice.

18.

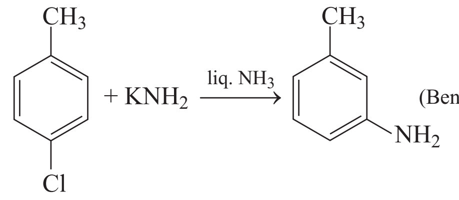


S_N2 reaction bring about inversion of configuration.

19. $C_6H_5OH + C_2H_5O^- \longrightarrow C_6H_5O^-$

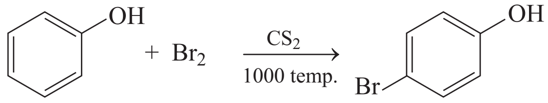
$$\xrightarrow{C_2H_5I} C_6H_5—OC_2H_5$$

20.



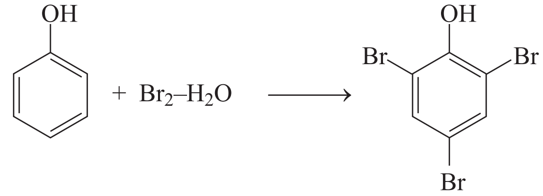
(Benzyne mechanism)

21.



In carbon disulphide, no phenoxide ion exist, therefore only monobromination takes place.

22.



precipitate

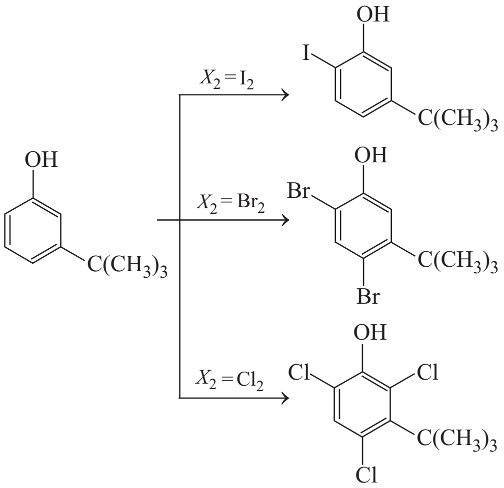
$$Br_2 + H_2O \longrightarrow HBrO + HBr$$

It is a reversible reaction, but equilibrium is significantly shifted to left, also indicated as $Br_2(aq)$.

23. **PLAN** This problem includes concept of effect of steric and electronic effect on reactivity of organic compounds.

Steric effect of halogens are as follows $Cl_2 < Br_2 < I_2$

Electronic effect of phenolic group directs the approaching electrophile towards *ortho* and *para* positions. Tertiary butyl group has large size so it causes steric effect around aromatic nucleus. On the basis of above factors the products of the given reactions are as follows:



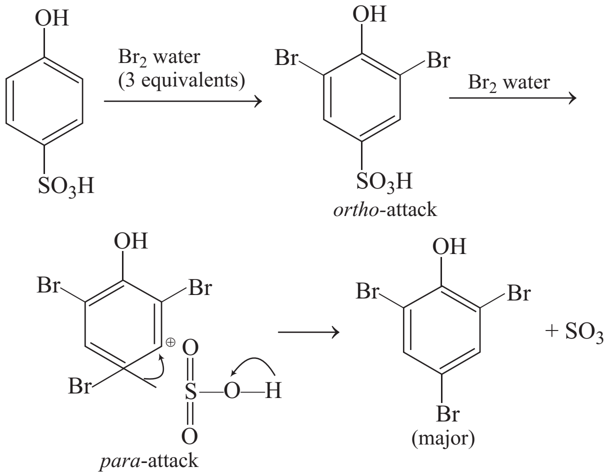
Hence, orientation in electrophilic substitution reaction is decided by

(a) The steric effect of the halogen
(b) The steric effect of the *tert*-butyl group
(c) The electronic effect of the phenolic group

So, (a), (b) and (c) are correct choices.

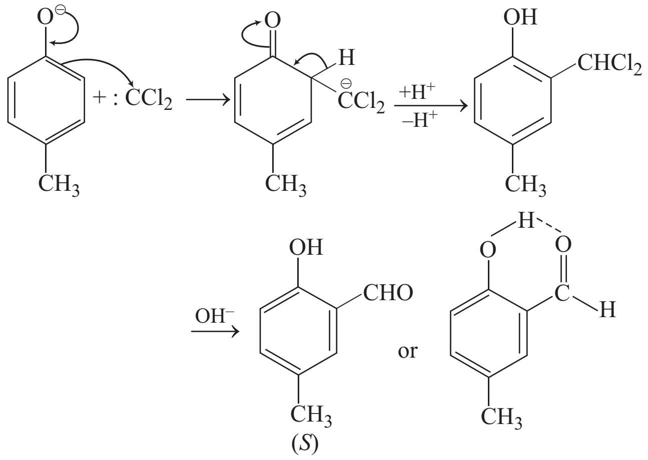
24. **PLAN** —OH group is activating group and is *o*- and *p*-directing.

Also, —SO_3H is a better leaving group and is knocked out by Br^-.

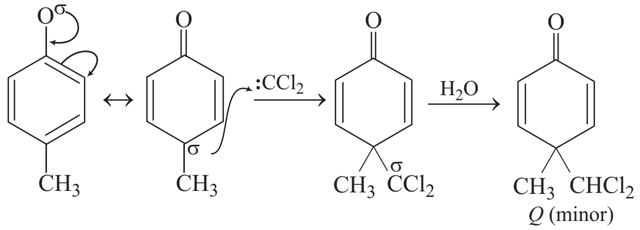


25. **PLAN** Phenolic compounds in alkaline solution react with chloroform ($CHCl_3$) at a temperature lower than that of $CHCl_3$ to form *ortho*-isomer as the major product (due to greater stability resulting from intramolecular hydrogen bonding).

$$\overset{-}{HO} + H—CCl_3 \rightleftharpoons H_2O — \overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^-} \underset{\text{dichloro carbene}}{:CCl_2}$$

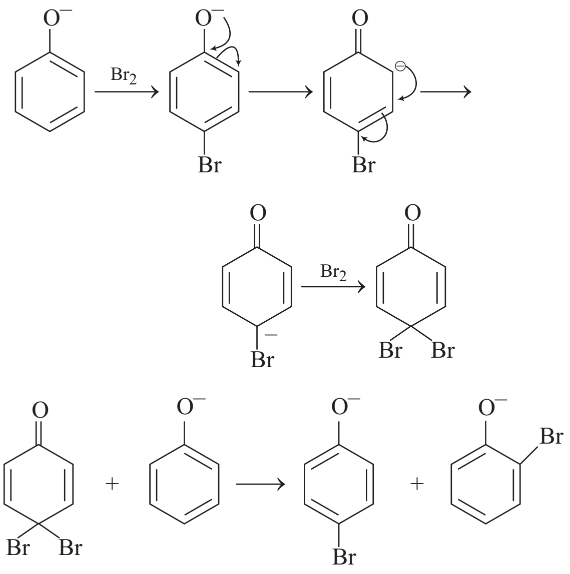


Major as stable due to intramolecular H-bonding.

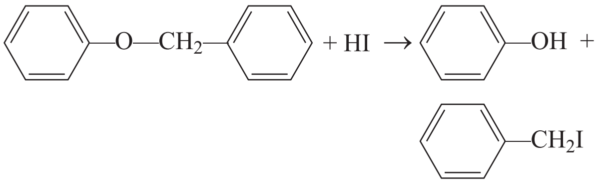


Thus, (b) and (d) are correct.

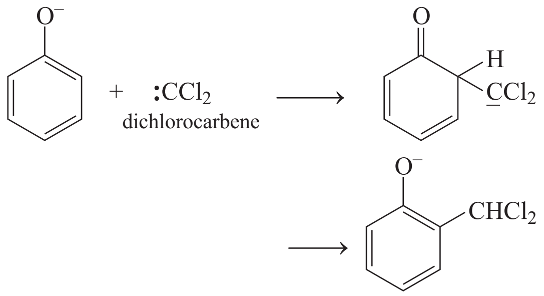
26. —OH in phenol is *ortho/para* directing group.



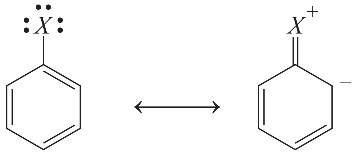
27.



28.



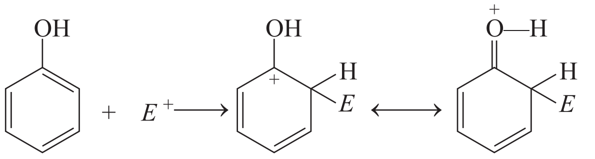
29.



Above resonance makes *X*- a poor leaving group. Also, the carbon bearing *X* is sp^2- hybridised.

30. Bromo group is deactivating due to dominance of inductive effect over resonance effect. However, orientation is determined by mesomeric effet of —Br.

31.

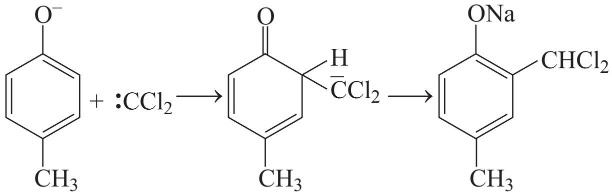


resonance stabilisation of intermediate carbocation

32. Statement I is incorrect, aryl halides do not undergo nucleophilic substitution reaction with ease. Cyanide ion (CN^-) is a strong nucleophile.

33. Statement I is incorrect, aryl halides do not usually undergo nucleophilic substitution with ease. Statement II is correct, resonance introduces partial double bond character to C—*X* bond.

34.

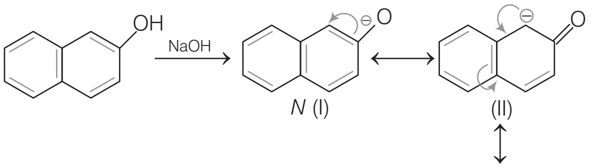


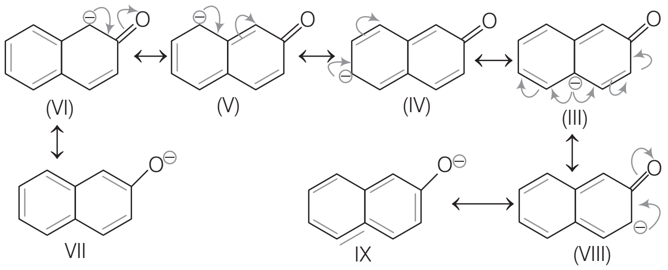
Intermediate

35. Dichlorocarbene is the electrophile as shown above.

36. $CHCl_3 + NaOH \longrightarrow \underset{\text{electrophile}}{:CCl_2}$ (Dichlorocarbene)

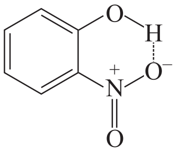
37.





All the above shown nine resonance structures are different.

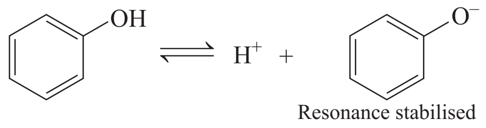
38. *Ortho*-nitrophenol : Due to intramolecular H-bonding.



Intramolecular H-bonding in *ortho*-nitrophenol

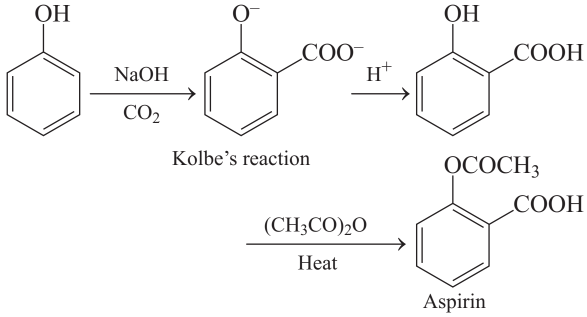
39. Phenoxide ion **40.** Nucleophilic

41. Phenoxide ion :

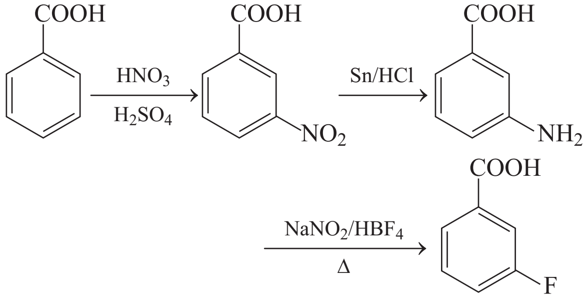


Resonance stabilised conjugate base

42. (i)

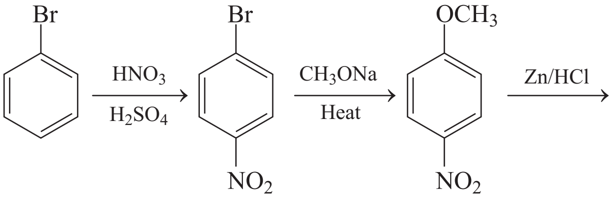


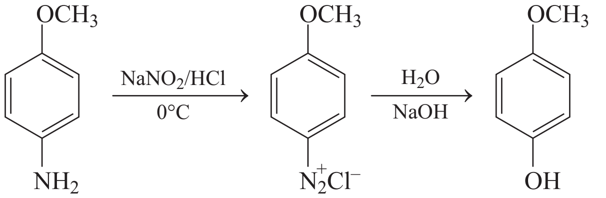
(ii)



meta-fluorobenzoic acid

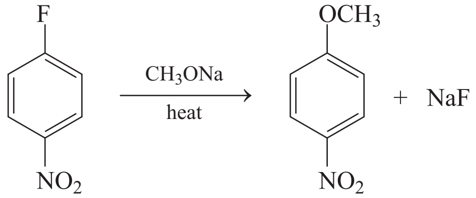
43.





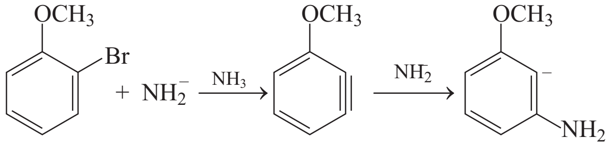
4-methoxyphenol

44.

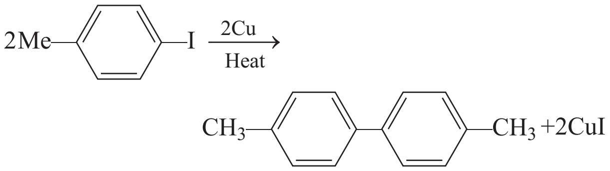


Nucleophilic aromatic substitution occur which is assisted by electron withdrawing —NO_2 group from *para* position.

45.

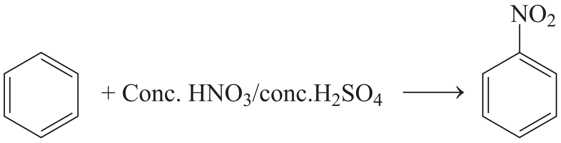


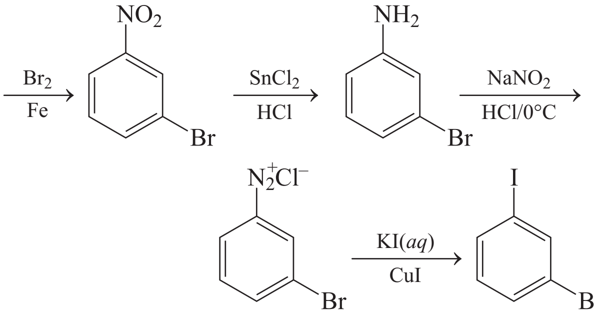
46.



Ullmann's reaction

47.

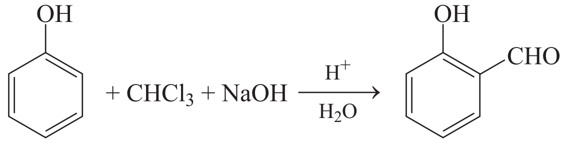




m-bromoiodo-benzene

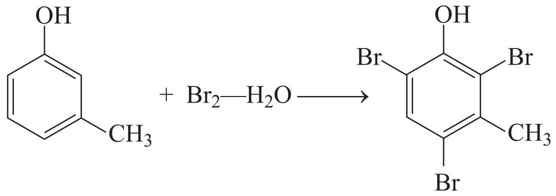
48. Phenol is weaker acid than carbonic acid.

49.

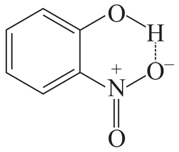


Reimer-Tiemann reaction

50. The compound must contain a hydroxy group on the ring with all three *ortho/para* positions vacant :



51. Intramolecular H-bonding in *ortho*-nitrophenol lowers its boiling point. No such intramolecular H-bonding is possible with *p*-nitrophenol and rather it is associated together by intermolecular H-bonding which increases the boiling point.



ortho-nitrophenol