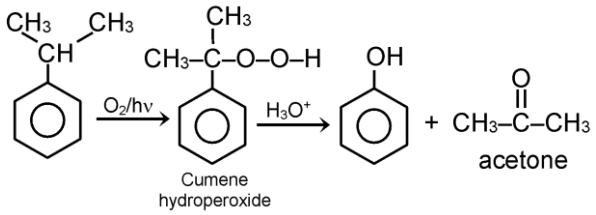
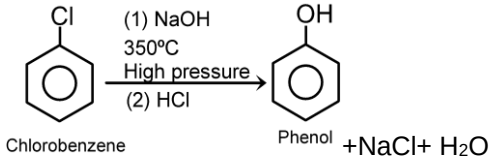
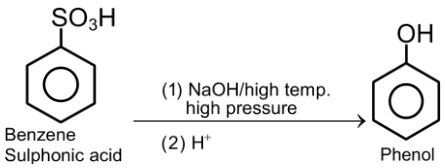
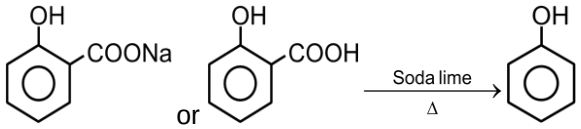
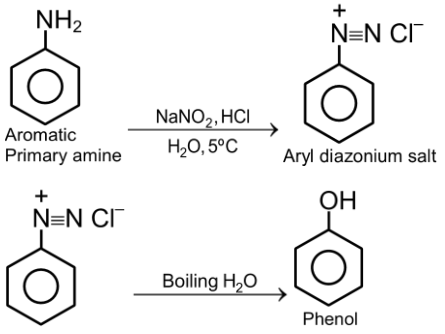
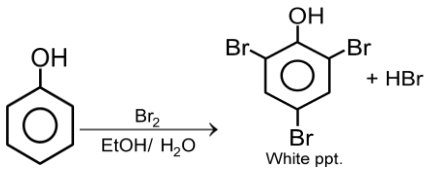
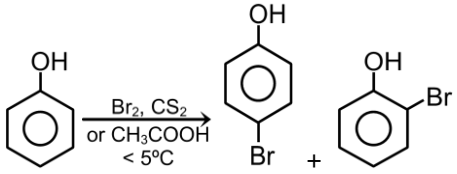
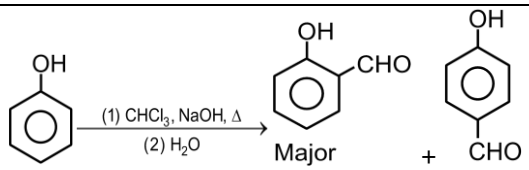
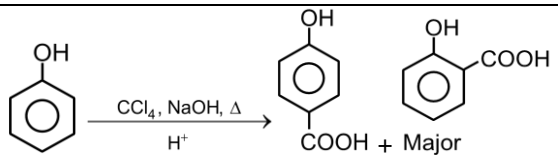
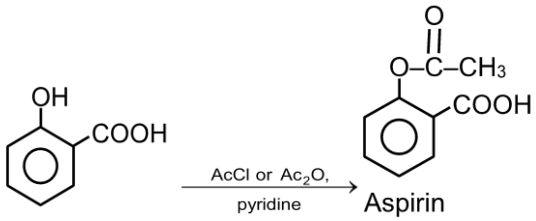
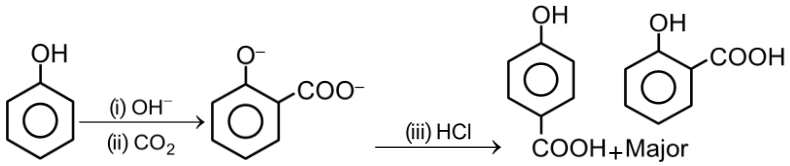
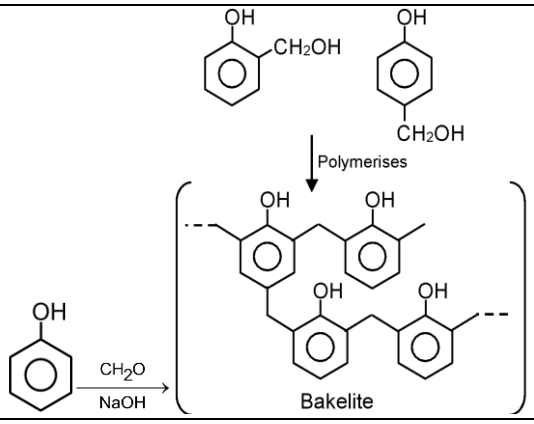
ABC-2 (Phenol & Aniline)

(A) PHENOL

Preparation of phenol (5-Methods)

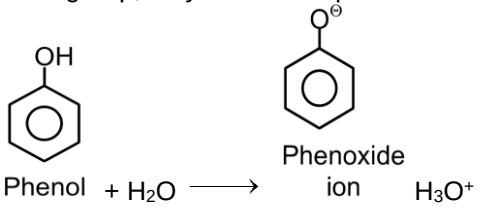
1.	**Cumene hydroperoxide method** This is an industrial process to convert cumene into phenol and acetone in the presence of oxygen from air followed by hydrolysis.	
2.	**Dow's process.** In this process chlorobenzene is heated at 350°C (under high pressure) with sodium hydroxide which yields phenol.	
3.	**Fusion of benzene sulphonic acid with concentrated NaOH** This is commercial process for synthesizing phenol. Benzene sulphonic acid is melted (fused) with sodium hydroxide at (300°C–320°C) followed by hydrolysis which yields phenol.	
4.	**Decarboxylation of salicylic acid** Distillation of salicyclic acid with soda-lime (NaOH + CaO) produces phenol.	
5.	**Hydrolysis of benzene diazonium salt** Benzene diazonium salt is prepared by reacting aromatic primary amine with $NaNO_2$, HCl at low temperature.Then this aqueous solution is heated to get phenol.	

Chemical reactions of phenol [5-Reactions]

1	**(a) Reaction with Br_2/H_2O** When bromine is added to solution of phenol in presence of ethanol or H_2O, it forms white precipitate of 2,4,6-tribromo-phenol.	
	(b) Reaction with Br_2/CS_2 In presence of non-polar solvent (like CS_2) or acids like CH_3COOH at low temperature, only monobromo product is obtained.	
2.	**Reimer Tiemann formylation** Phenol when heated with chloroform and NaOH followed by H_2O forms salicyladehyde.	
3.	**Reimer Tiemann carboxylation** Phenol when heated with CCl_4 and sodium hydroxide followed by hydrolysis forms salicylic acid.	
	Note: Salicyclic acid can be used in formation of aspirin. (Aspirin is used as painkiller)	
4.	**Kolbe's Schmidt reaction** Phenol when reacted with hydroxide ion in presence of CO_2 forms a complex which on acidification forms salicyclic acid.	
5.	**Bakelite formation** Bakelite is made by condensation reaction between phenol and formaldehyde.	

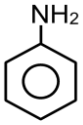
Lab test for phenol

1. Litmus test : Phenol turns blue litmus red. Phenols behave as weak acid because of presence of polar O–H group, they ionise in aqueous solution to give H^+ ions.



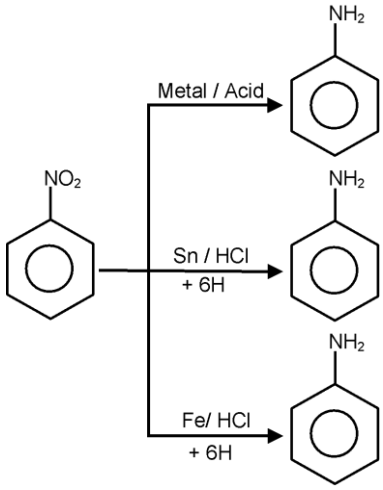
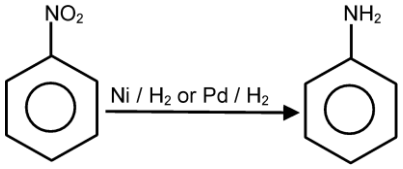
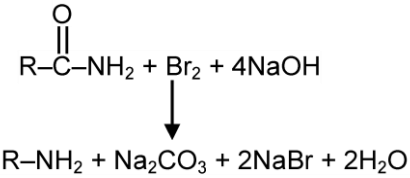
2. Neutral $FeCl_3$: Phenols give a violet-coloured water soluble complex with neutral ferric chloride.

$$6Ph–OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{Fe(OPh)_6^{3-}} + 3H^+ + 3HCl$$

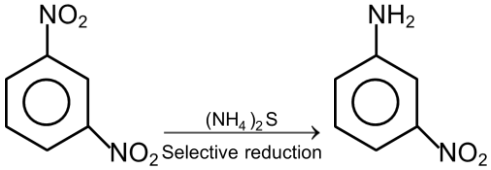


(B) ANILINE

Preparation of aniline [3-Methods]

1. Reduction by Metals	2. Reduction by H_2	3. Hofmann bromamide degradation reaction
		In this reaction an unsubstituted amides (only 1°) treated with NaOH/KOH and bromine to give a primary amine that has one carbon lesser than starting amide.  **R can be :** Alkyl or phenyl This method is used to prepar 1° aliphatic or aromatic amines.

Special :

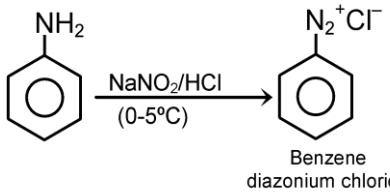


(various other sulphides can be used.)

Chemical reactions of aniline :

1. Preparation of diazonium salt:

Aniline reacts with $NaNO_2$/H+ to form diazonium salt.

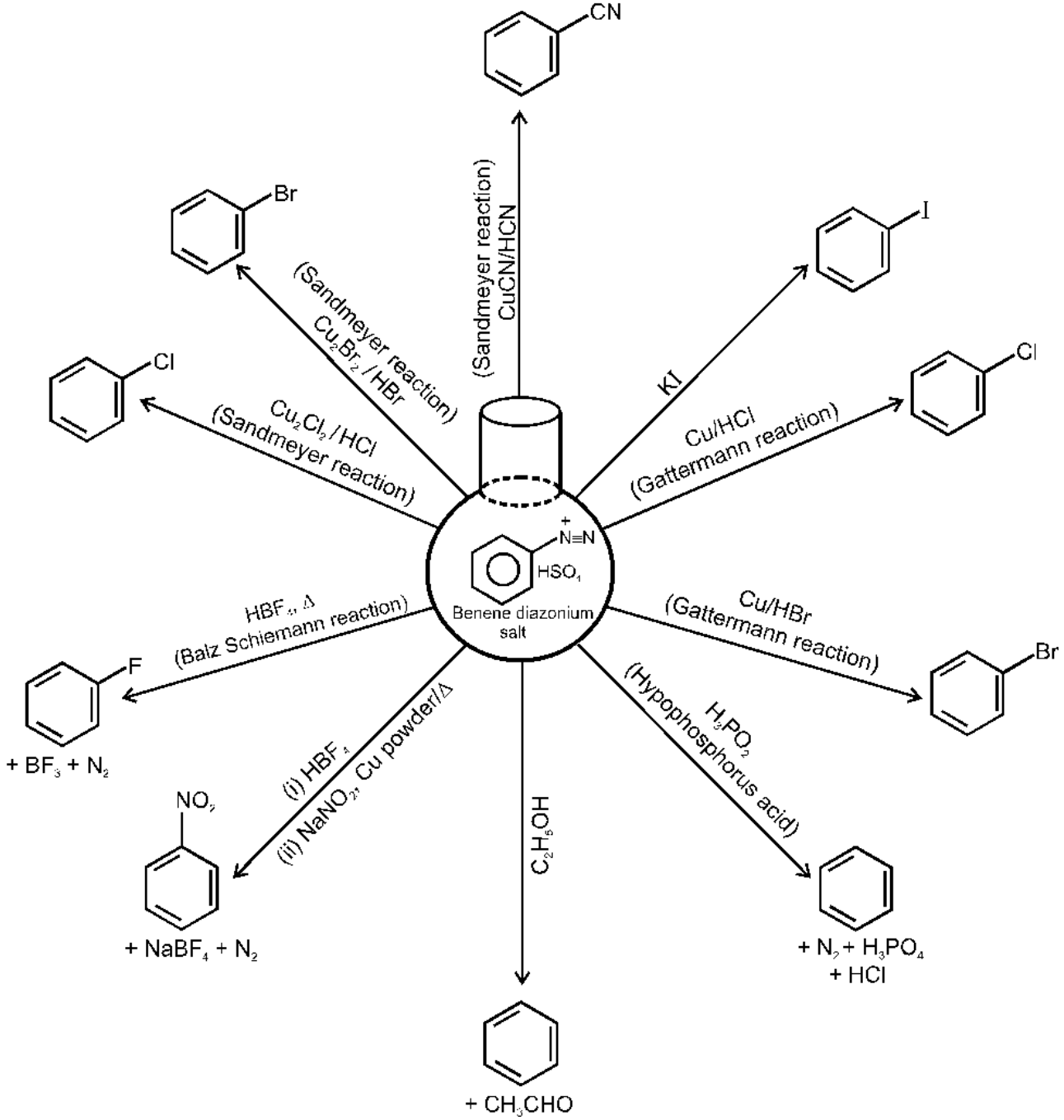


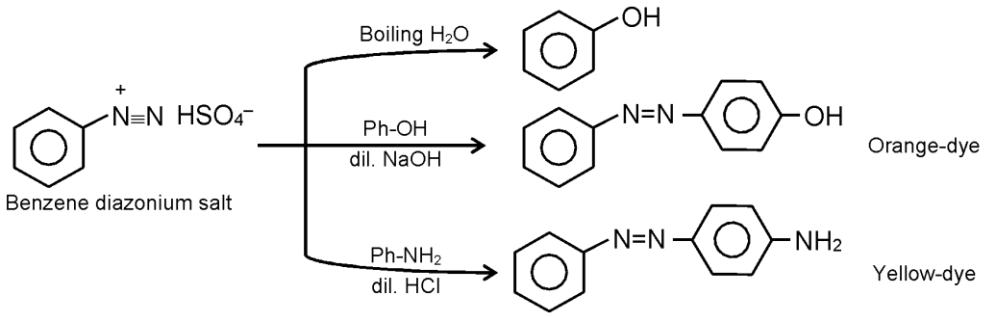
Note :

1. **Primary aliphatic amines** react with nitrous acid to form aliphatic diazonium salt which being unstable, liberate nitrogen gas.
2. Primary aromatic amines form arene diazonium salts which are stable for a short time in solution at low temperatures (273-278 K).Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

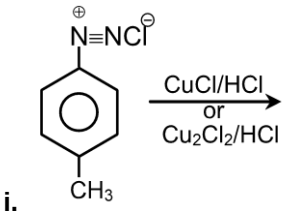
2. Chemical reactions of diazonium salt

Diazonium salt opens the way to prepare many other compounds, see following chart.

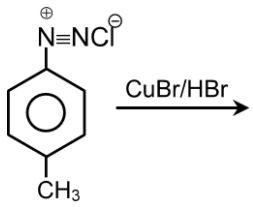




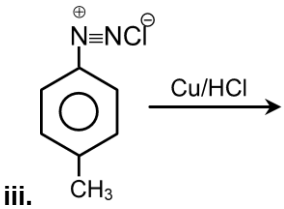
1. Complete the following reactions.



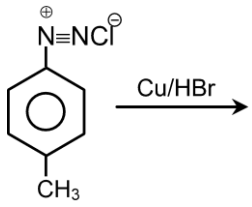
i.



ii.



iii.



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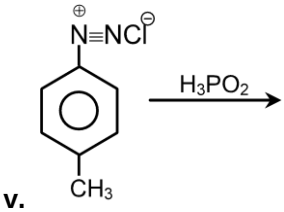
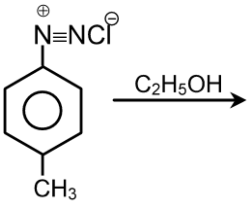
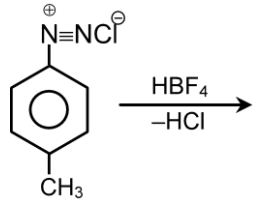


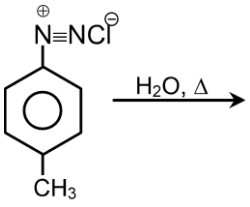
v.



vi.

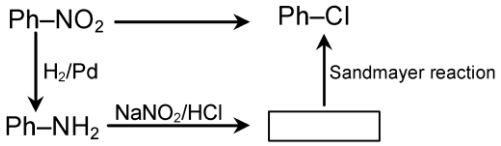


vii.



viii.

2. Conversion.



Lab test of aniline :

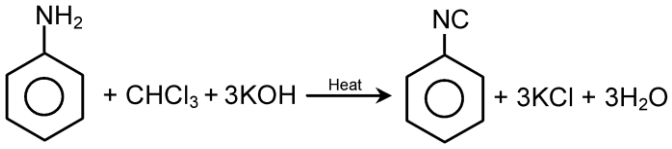
1. Carbylamine reaction

Primary amines (aliphatic as well as aromatic) react with chloroform ($CHCl_3$) on heating in the presence of ethanolic solution of KOH to form isocyanides (also called carbylamines) which are foul smelling substances. Secondary and tertiary amines do not undergo this reaction, therefore this reaction is used as a test for primary amines (aliphatic as well as aromatic).

$$R–NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R–NC + 3KCl + 3H_2O$$

Ex. $CH_3–NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} CH_3–NC + 3KCl + 3H_2O$

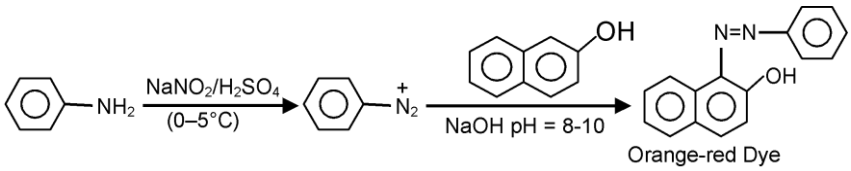
Ex.



2. Azo dye test

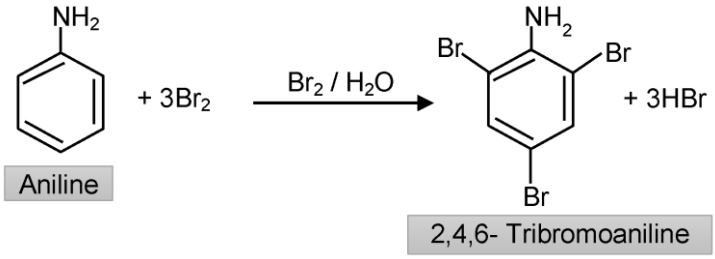
Azo compounds are usually intensely colored because of the azo linkage (–N=N–). Azo compounds, because of their intense color's and because they can be synthesized from relatively inexpensive compounds, are used extensively as dyes.

Synthesis of orange-red dye from 2-naphthol [β-naphthol] and aniline.



3. Bromine water test ($Br_2 + H_2O$):

Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline. Aniline also gives test with $Br_2 + CS_2$



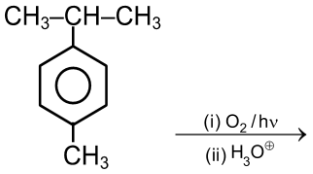
Exercise

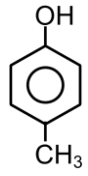
ONLY ONE OPTION CORRECT TYPE

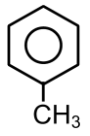
1. The process of conversion of cumene in the presence of oxygen and light followed by hydrolysis lead to the formation of _____ .

(A) Phenol (B) Aniline (C) Anisole (D) Benzene

2. Identify the product of following reaction.

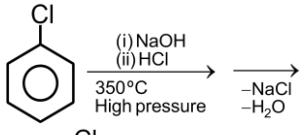


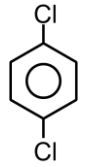
(A) 

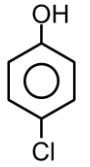
(B) 

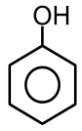
(C) 
(D) None of these

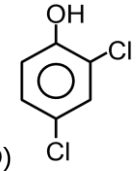
3. Identify the product of the following reaction.

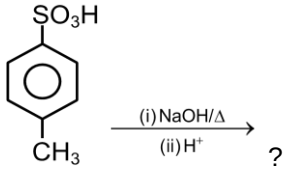


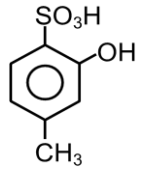
(A) 

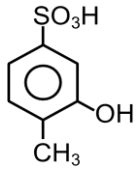
(B) 

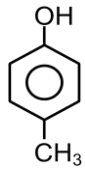
(C) 

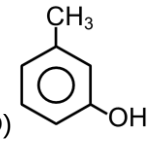
(D) 

4. 

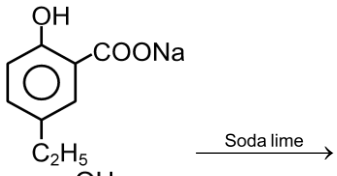
(A) 

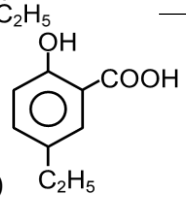
(B) 

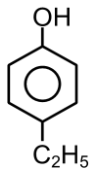
(C) 

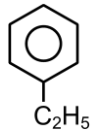
(D) 

5. Give the product for following reaction.



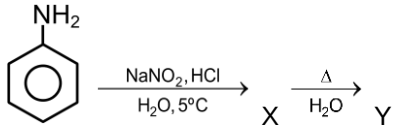
(A) 

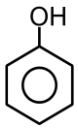
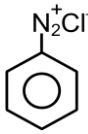
(B) 

(C) 

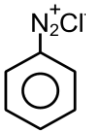
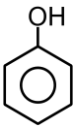
(D) None of these

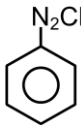
6. Identify the X and Y in the following reaction.



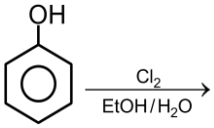
(A) X =  Y = 

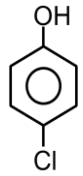
(B) X =  Y = 

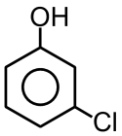
(C) X =  Y = 

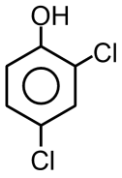
(D) X =  Y = 

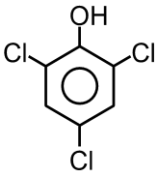
7. What will be the product of following reaction?



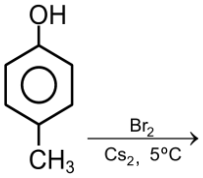
(A) 

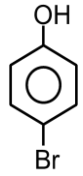
(B) 

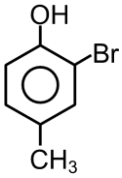
(C) 

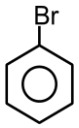
(D) 

8. Find the product for the following reaction.



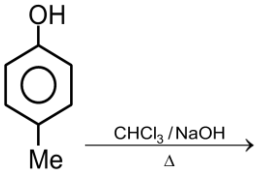
(A) 

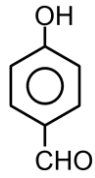
(B) 

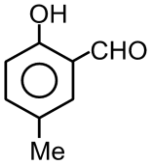
(C) 

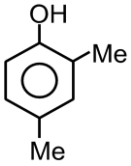
(D) None of these

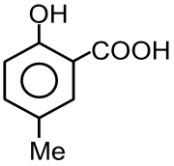
9. Give the major product for the following reaction.



(A) 

(B) 

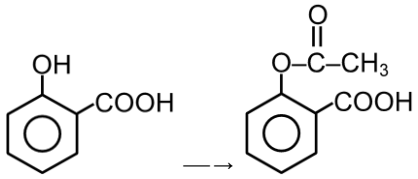
(C) 

(D) 

10. The reagent used for Reimer Tiemann carboxylation in order to form salicylic acid is _____ .

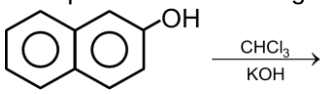
(A) $CHCl_3$ / NaOH / H^+ (B) CCl_4 / NaOH / H^+ (C) OH^- / CO_2 / HCl (D) None of these

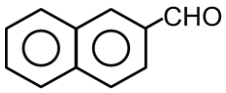
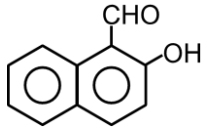
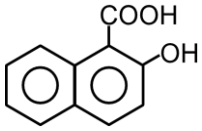
11. Aspirin can be formed from following reaction using which reagent?



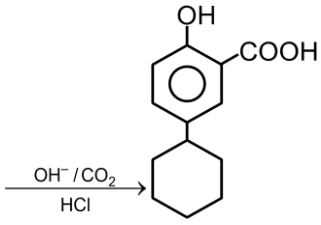
(A) $(CH_3-\overset{O}{\overset{\|}{C}}-)_2O$ / H^+ (B) $(C_2H_5-\overset{O}{\overset{\|}{C}}-)_2O$ / H^+ (C) $CHCl_3$ / NaOH (D) None of these

12. Give product for following reaction.

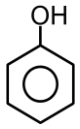
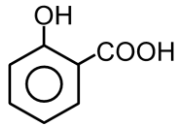
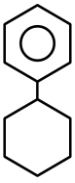


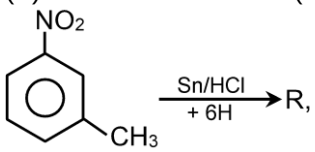
(A)  (B)  (C)  (D) None of these

13. The reactant used in the reaction is :

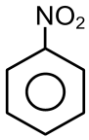
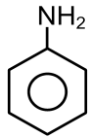
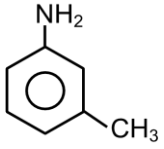
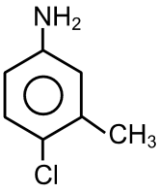


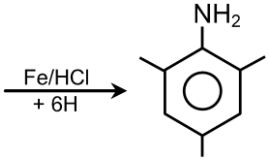
Reactant

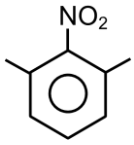
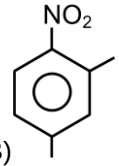
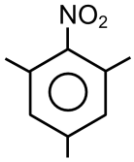
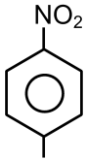
(A)  (B)  (C)  (D) 

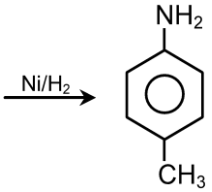
14. 

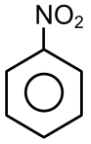
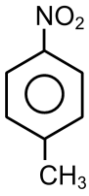
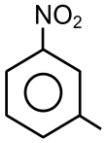
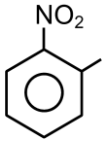
R is :

(A)  (B)  (C)  (D) 

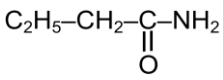
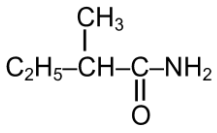
15. R  , R is :

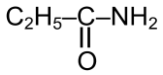
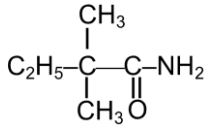
(A)  (B)  (C)  (D) 

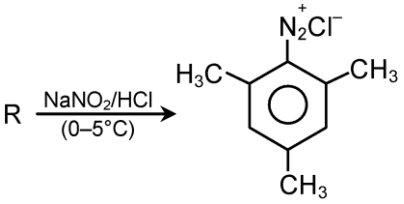
16. R  , R is :

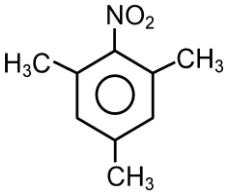
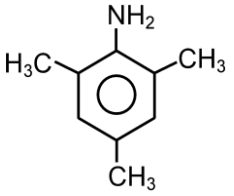
(A)  (B)  (C)  (D) 

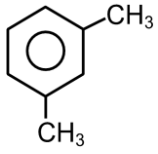
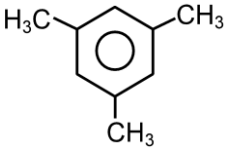
17. R $\xrightarrow{Br_2/NaOH}$ $C_2H_5–NH_2$, R is :

(A)  (B) 

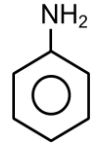
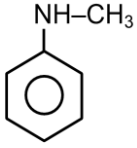
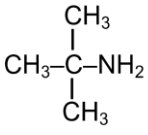
(C)  (D) 

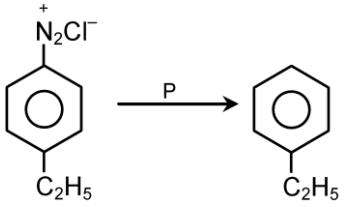
18. R  R, is-

(A)  (B) 

(C)  (D) 

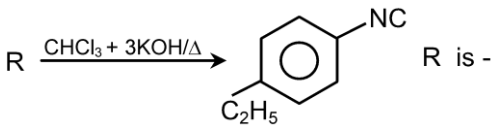
19. Which of them produces diazonium cation at 0°C ?

(A)  (B)  (C) $CH_3–CH_2–NH_2$ (D) 

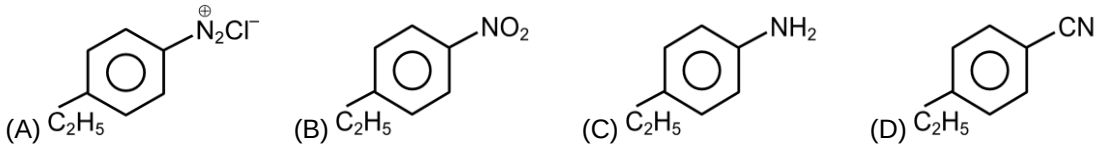
20. 

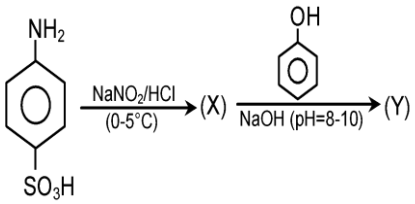
, P is :

(A) Cu_2Cl_2/HCl (B) Cu/HCl (C) C_2H_5OH (D) HBF_4

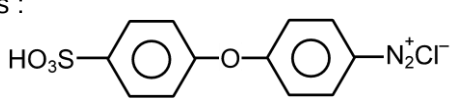
21. 

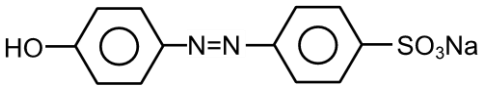
R is -

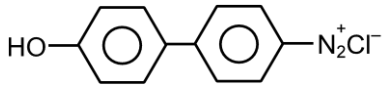


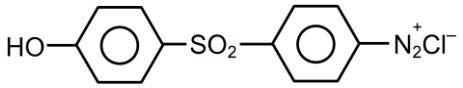
22. 

Y is :

(A) 

(B) 

(C) 

(D) 

Answers

1.	(A)	**2.**	(A)	**3.**	(C)	**4.**	(C)	**5.**	(B)
6.	(C)	**7.**	(D)	**8.**	(B)	**9.**	(B)	**10.**	(B)
11.	(A)	**12.**	(B)	**13.**	(C)	**14.**	(C)	**15.**	(C)
16.	(B)	**17.**	(C)	**18.**	(B)	**19.**	(A)	**20.**	(C)
21.	(C)	**22.**	(B)						