

AROMATIC COMPOUNDS (Phenol, Aniline & Diazonium Compounds)

CONTENTS

Particular	Page No.
Theory	01 – 12
Exercise - 1	13 – 20
Part - I : Subjective Questions	
Part - II : Only One Option Correct Type	
Part - III : Match the Columns	
Exercise - 2	20 – 29
Part - I : Only One Option Correct Type	
Part - II : Single or Double Digit Integer Type Questions	
Part - III : One or More Than One Options Correct Type	
Part - IV : Comprehensions	
Exercise - 3	29 – 43
Part - I : JEE(ADVANCED) / IIT-JEE Problems (Previous Years)	
Part - II : JEE(MAIN) / AIEEE Problems (Previous Years)	
Answers	44 – 49
Additional Problems for Self Practice (APSP)	50 – 64
Part - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))	
Part - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I	
Part - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))	
APSP Answers	65
APSP Solutions	66 – 71

JEE(Advanced) Syllabus

Phenol, Aniline & Diazonium Compounds :

Phenols : Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation); Reimer-Tieman reaction, Kolbe reaction.

Amines : Basicity of substituted anilines and aliphatic amines, preparation from nitrocompounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines. Sandmeyer and related reactions of diazonium salts; carbylamine reaction.

JEE(Main) Syllabus

Phenols : Acidic nature, electrophilic substitution reactions: Halogenation, nitration and sulphonation, Reimer-Tiemann reaction.

Organic Compounds Containing Nitrogen : General methods of preparation, properties, reactions and uses.

Amines : Structure, basic character and identification of primary, secondary and tertiary amines.

Diazonium Salts : Importance in synthetic organic chemistry.

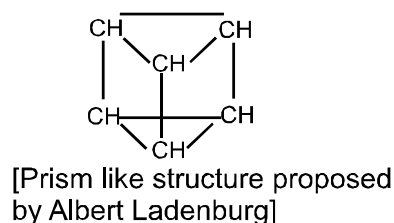
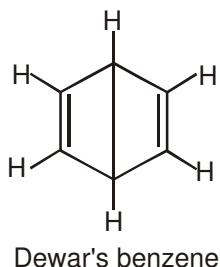
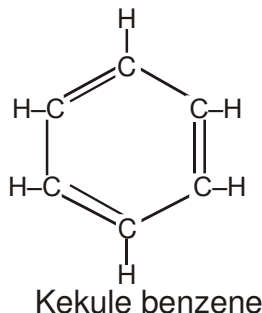


Aromatic Compounds

Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

Proposed structure of benzene :



* Benzene mostly represents by Kekule structure.

Huckel's ($4n + 2$) rule for aromaticity :

An aromatic compound must have cyclic clouds of delocalised $(4n + 2)\pi$ electrons above and below the plane of the molecule or in other words a compound which is cyclic, planar and have complete cyclic delocalisation of $2, 6, 10, \dots \pi$ electrons is an aromatic compound, according to Huckel's rule.

The following three rules are useful in predicting whether a particular compound is aromatic or non-aromatic.

- (i) Aromatic compounds are cyclic and planar.
- (ii) Each atom in an aromatic ring is sp^2 or sp hybridised.
- (iii) The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2)\pi$ electrons, i.e., 2, 6, 10, 14, π electrons. Where n = an whole number 0, 1, 2, 3,

Characteristic reaction of aromatic compounds :

* Aromatic compounds prefer **electrophilic substitution** rather than electrophilic addition reaction.

* In aromatic electrophilic substitution reaction benzene ring serve as source of electrons that is as a base or nucleophile.

* Electrophilic aromatic substitution includes a wide variety of reactions :

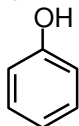
e.g. Halogenation, Nitration, Sulphonation, Friedel Crafts alkylation & acylation but reactions like Nitrosation and Diazocoupling undergoes only by rings of high reactivity.

Section (A) : Phenol

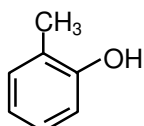
Phenol, also known as **carbolic acid**, was first isolated in the early nineteenth century from coaltar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives.

Some common examples are :

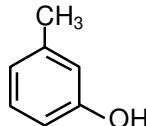
(i)



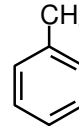
Common name : Phenol
IUPAC name : phenol



o-Cresol
2-methylphenol



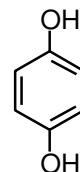
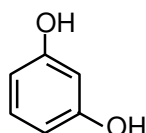
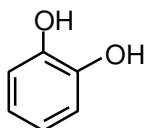
m-Cresol
3-methylphenol



p-Cresol
4-methylphenol



(ii)



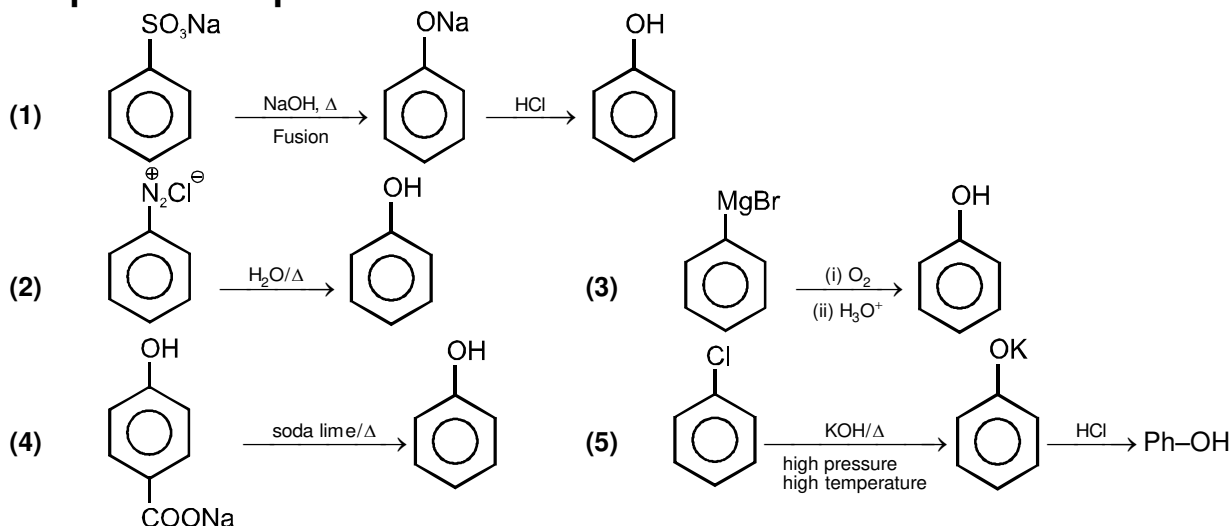
Common name : Catechol
IUPAC name : Benzene-1,2-diol

Common name : Resorcinol
IUPAC name : Benzene-1,3-diol

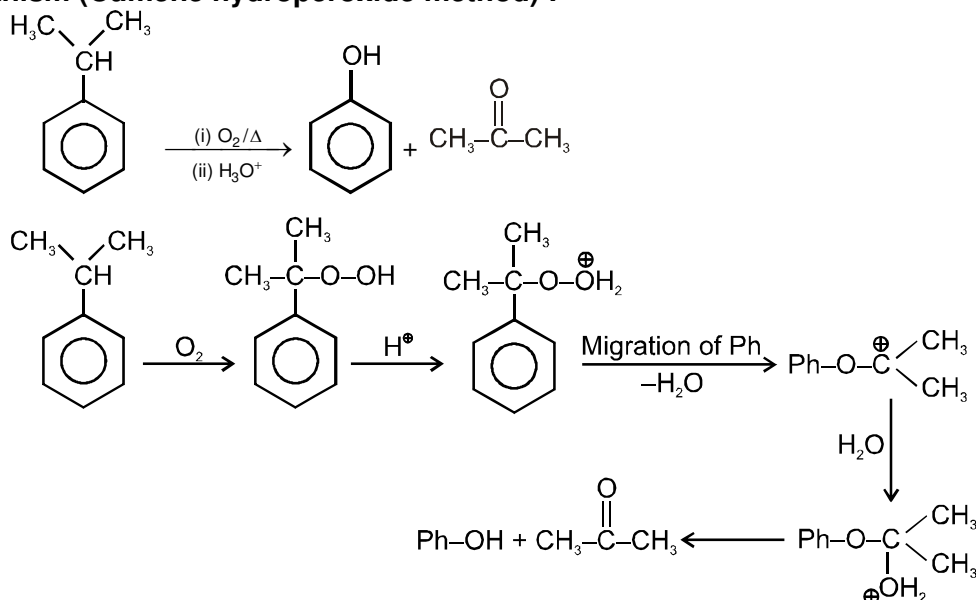
Common name : Hydroquinone or quinol
IUPAC name : Benzene-1,4-diol

Dihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.

(a) Preparation of phenol



Mechanism (Cumene hydroperoxide method) :



(b) Properties of phenol :

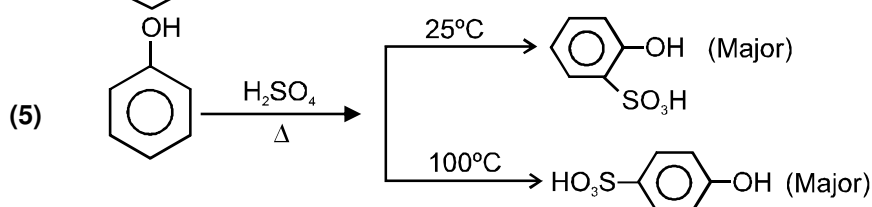
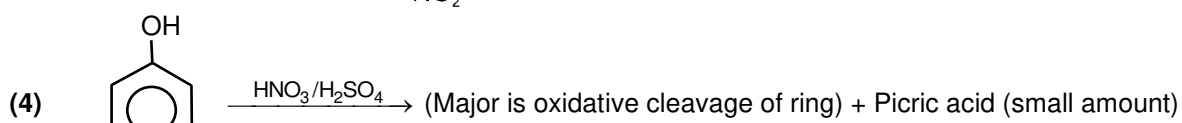
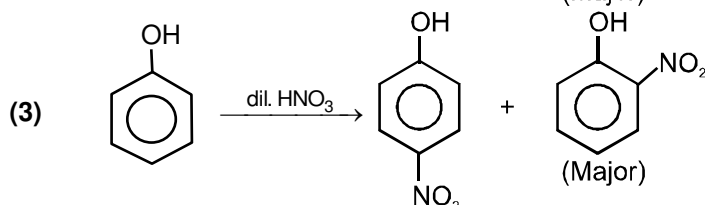
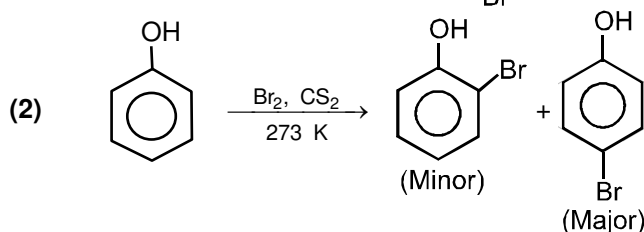
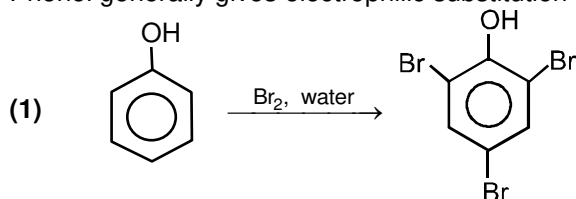
Phenol is a colourless crystalline solid, m.p. 43°C, b.p. 182°C, which turns pink on exposure to air and light.

Phenol is used as an antiseptic and disinfectant and in the preparation of dyes, drugs, bakelite, etc.

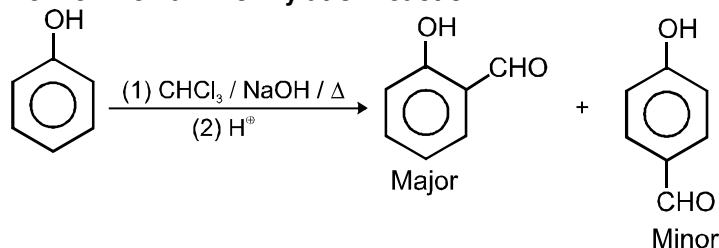


(c) Chemical reactions of phenol :

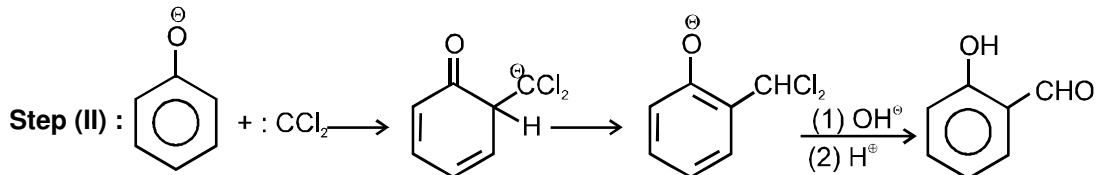
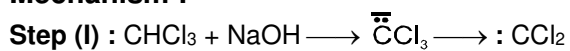
Phenol generally gives electrophilic substitution with electrophilic reagents.

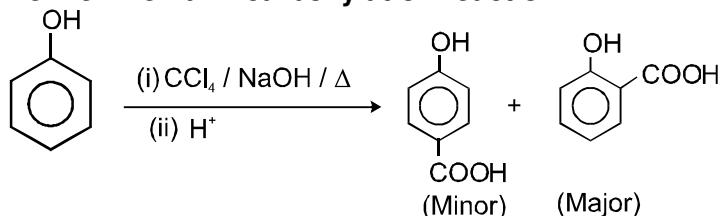
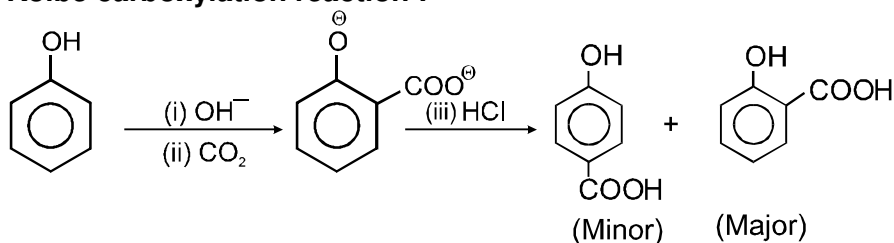
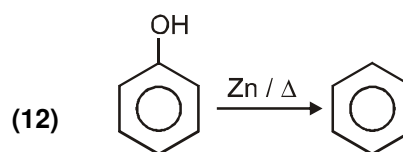
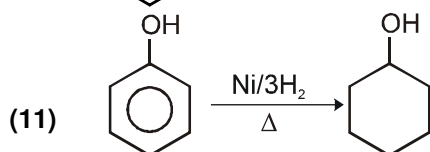
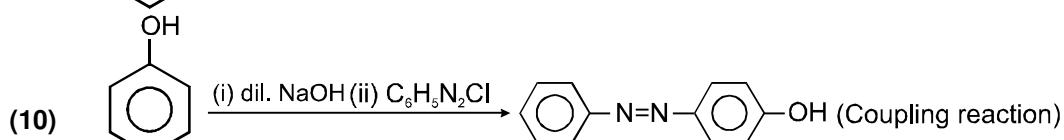
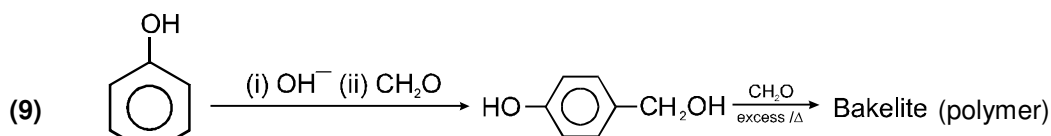
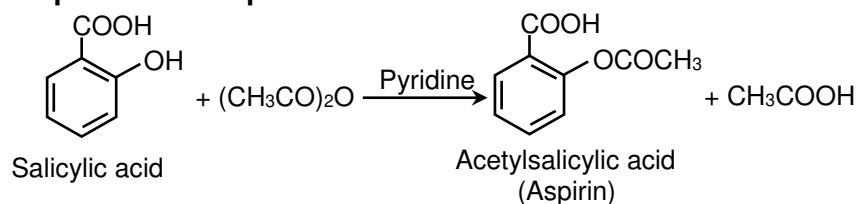
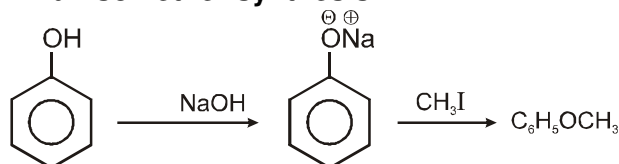
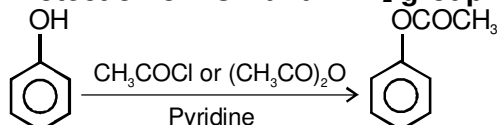


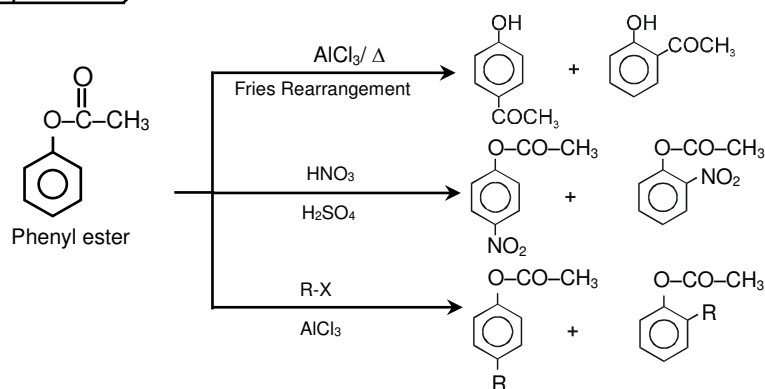
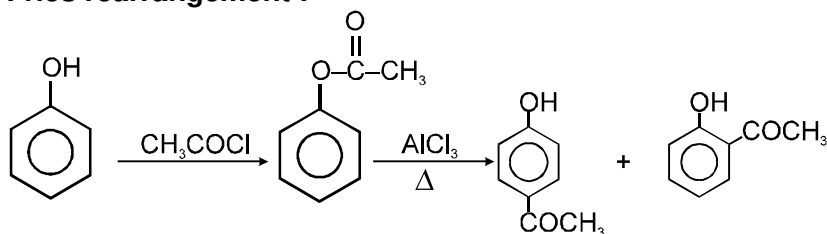
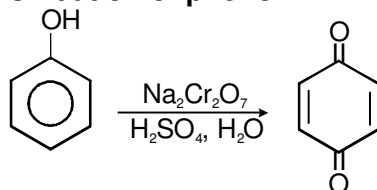
(6) Reimer-Tiemann formylation reaction :



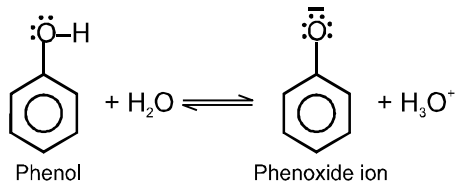
Mechanism :



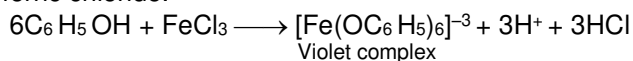
(7) **Reimer-Tiemann carboxylation reaction :**(8) **Kolbe carboxylation reaction :****Preparation of aspirin :**(13) **Williamson ether synthesis**(14) **Protection of -OH and -NH₂ group.**

**(15) Fries rearrangement :****(16) Oxidation of phenol :****(d) Test of phenol :**

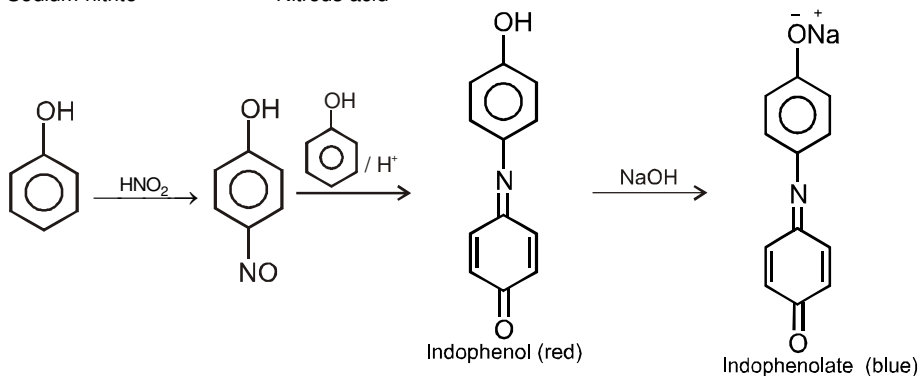
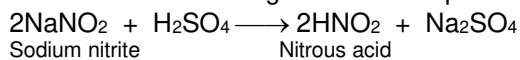
(1) Phenols turn blue litmus red. Phenols behave as acid and ionise in aqueous solution to give H^+ ions.



(2) **Reaction with ferric chloride** : Phenol gives a violet-coloured water soluble complex with neutral ferric chloride.



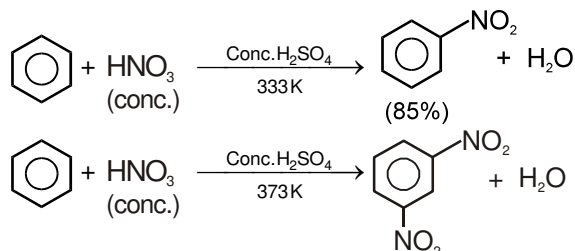
(3) **Libermann's test** : When a sodium nitrite ($NaNO_2$) is added to a phenol dissolved in conc. sulphuric acid, red or brown colour is produced and changes to blue by the addition of a strong alkali. This test can be used to distinguish between phenols from alcohols.



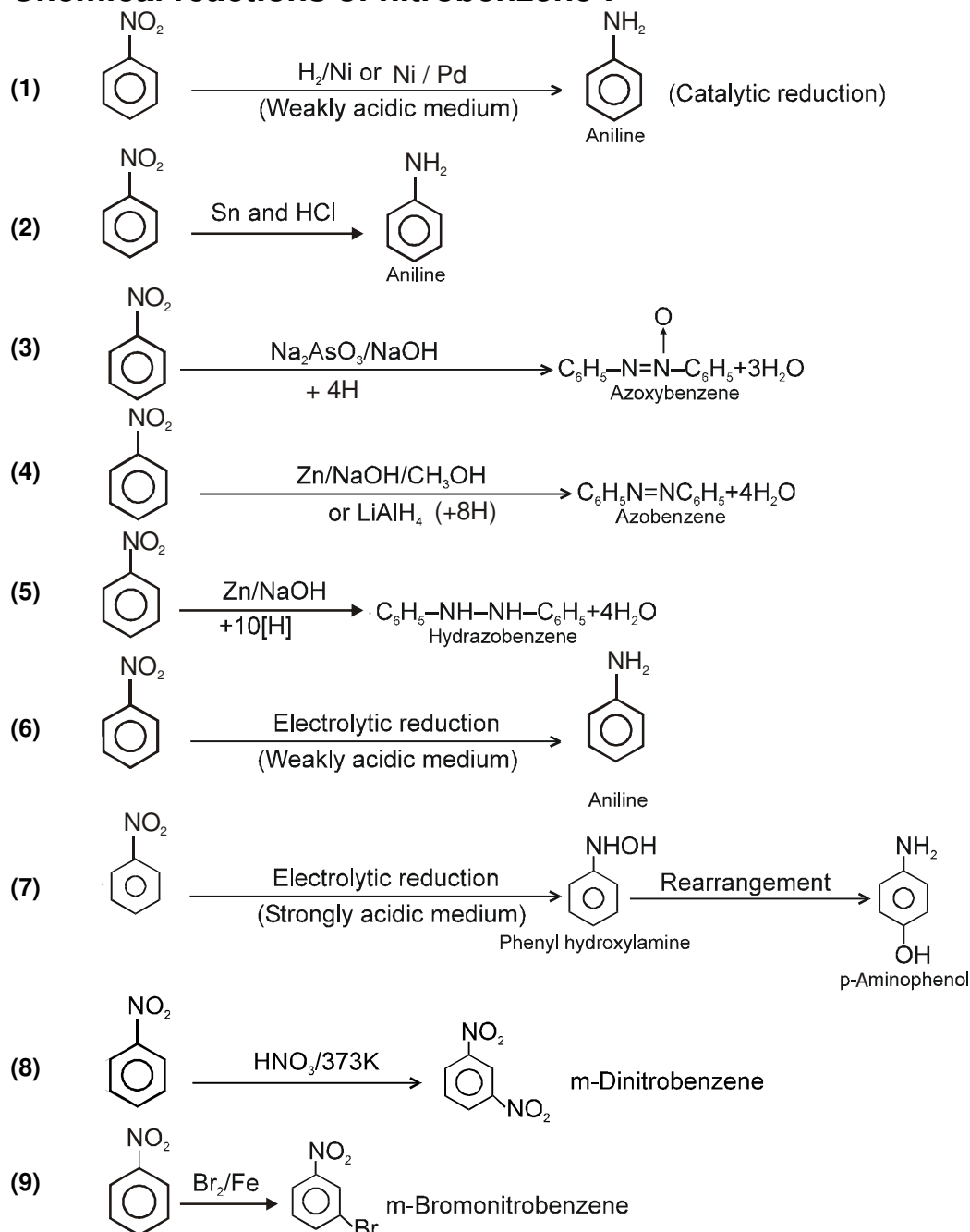


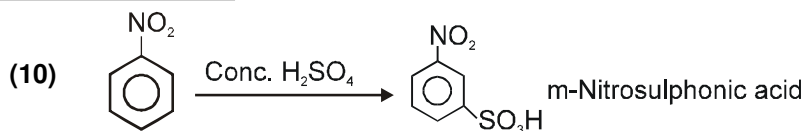
Section (B) : Nitrogen containing compounds (Nitrobenzene & Aniline)

(a) Preparation of nitrobenzene :

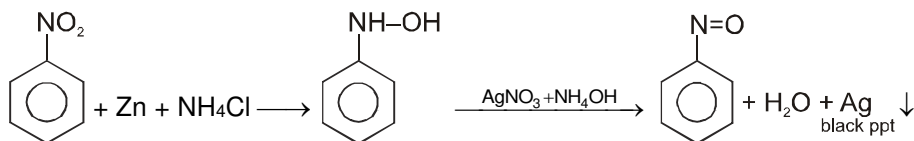


(b) Chemical reactions of nitrobenzene :

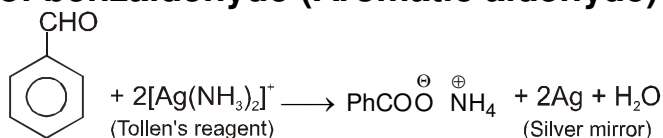




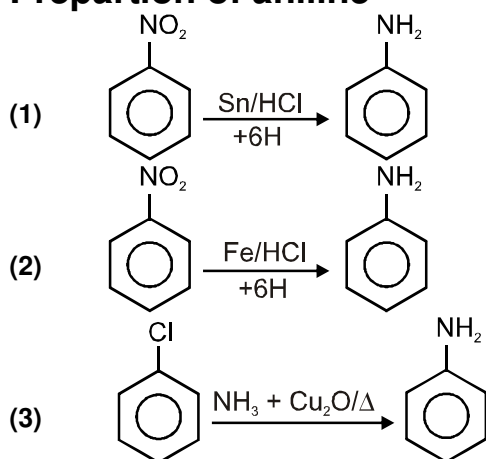
(c) **Test of nitrobenzene : (Mulliken- Barker's test)**



(d) **Test of benzaldehyde (Aromatic aldehyde)**

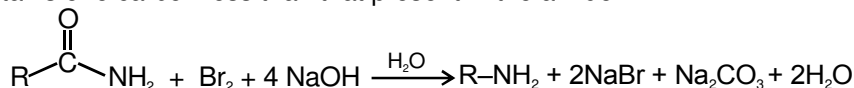


(e) **Preparation of aniline**

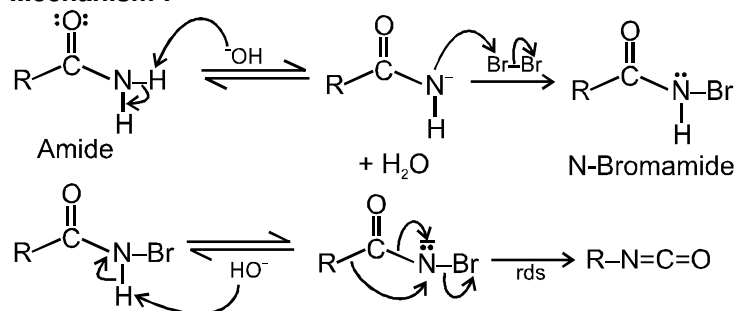


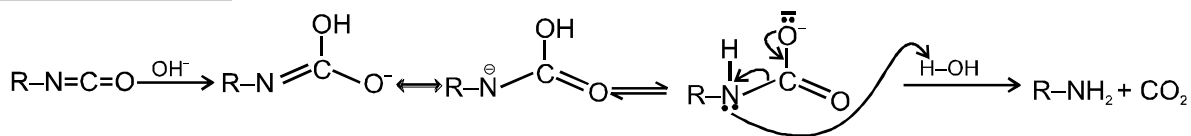
(4) **Hofmann bromamide degradation reaction :**

Hofmann developed a method for preparation of **primary amines** by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.



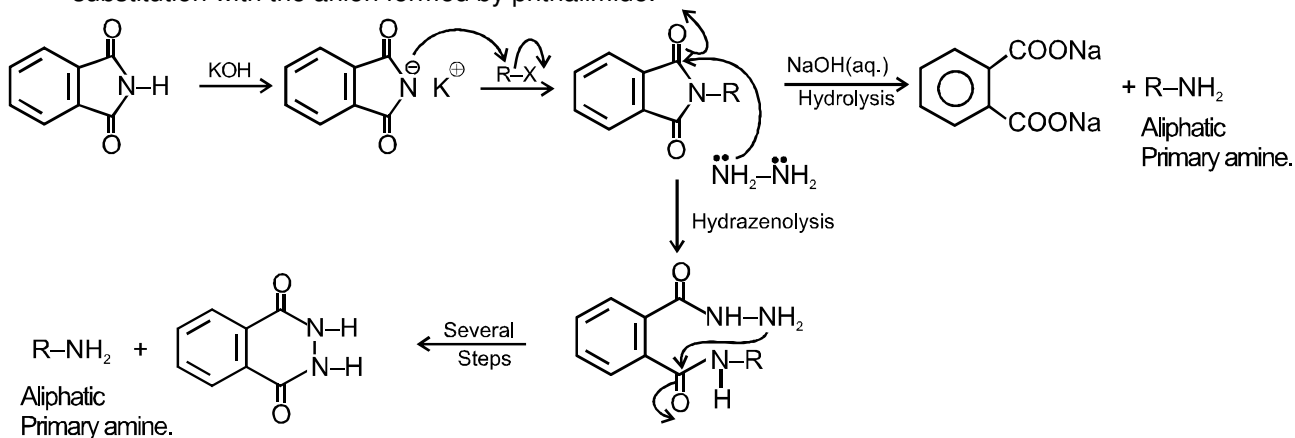
Mechanism :



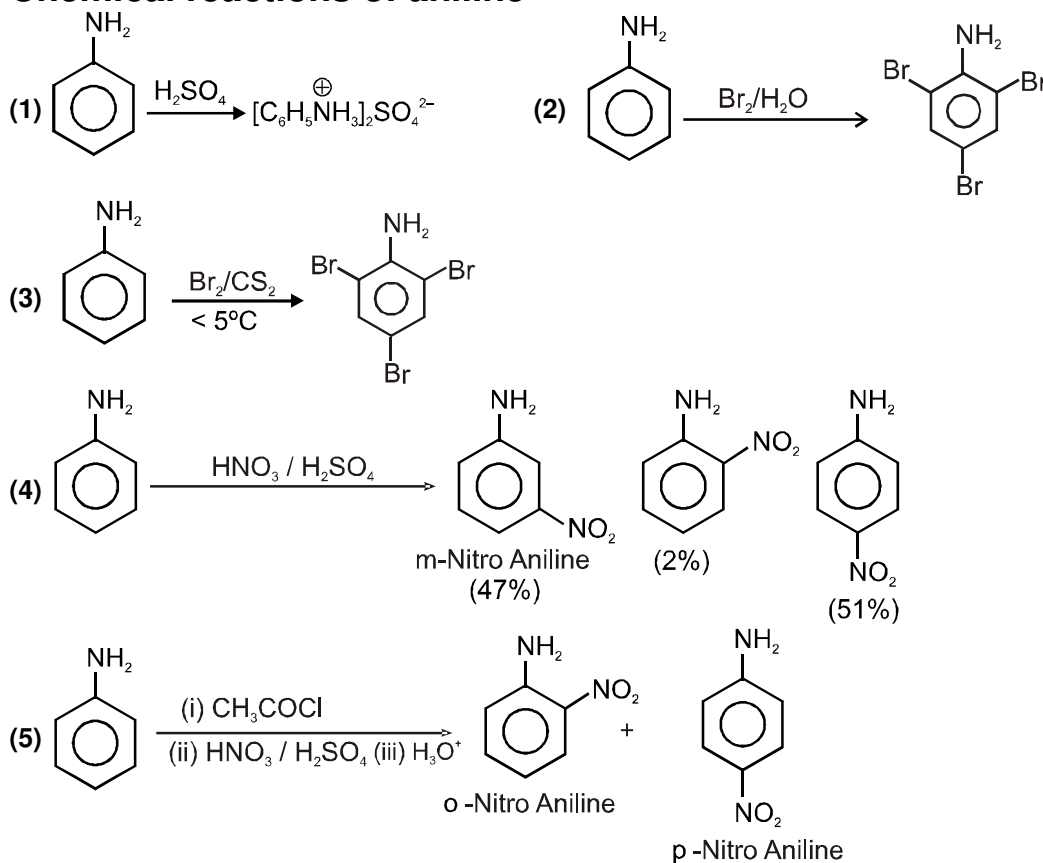


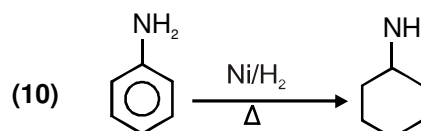
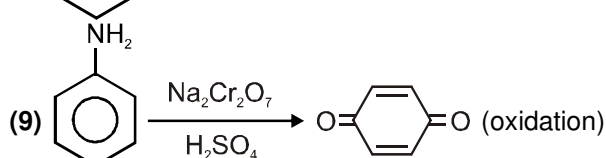
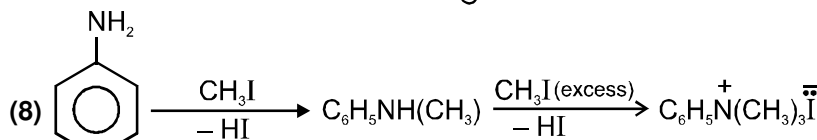
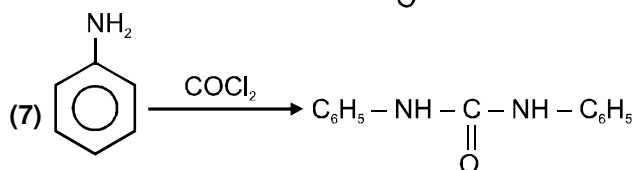
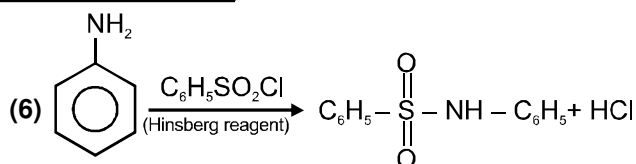
(5) Gabriel phthalimide synthesis :

Gabriel synthesis is used for the preparation of **aliphatic primary amines**. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. **Aromatic primary amines** cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

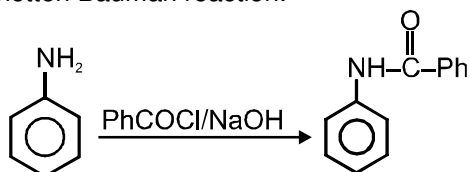


(f) Chemical reactions of aniline





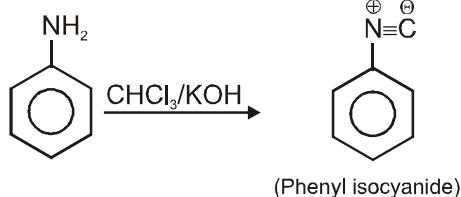
(11) Schotten Bauman reaction.



(g) Test of aniline :

(1) Carbylamine reaction

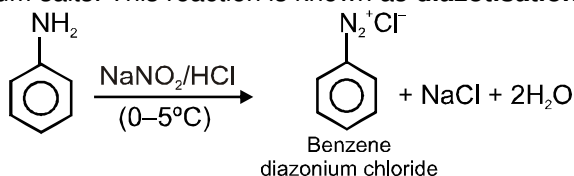
Primary amines (aliphatic as well as aromatic) react with chloroform (CHCl_3) on heating in the presence of ethanolic solution of KOH to form isocyanides (also called carbylamines) which are foul smelling substances. Secondary and tertiary amines do not undergo this reaction, therefore this reaction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



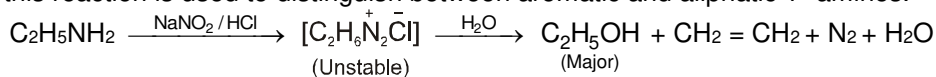
(2) Reaction with nitrous acid

Amines of different classes react with nitrous acid (unstable acid). HNO_2 is prepared by the reaction of sodium nitrite (NaNO_2) and dilute hydrochloric acid.

Primary aromatic amines react with nitrous acid at low temperature (273-278 K) to give aromatic diazonium salts. This reaction is known as **diazotisation**.

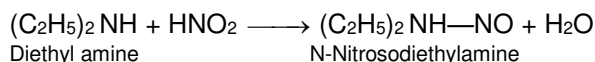
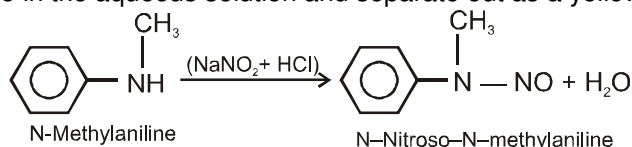


Primary aliphatic amines also react with nitrous acid to form diazonium salt, however, the aliphatic diazonium salts being unstable, decompose to yield mixture of alcohols, alkenes along with nitrogen gas. So this reaction is used to distinguish between aromatic and aliphatic 1^o amines.

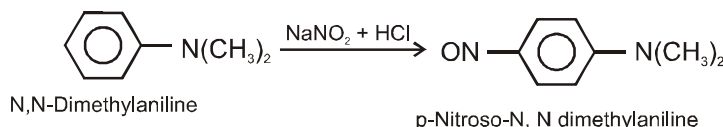
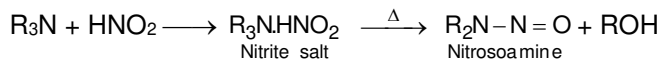




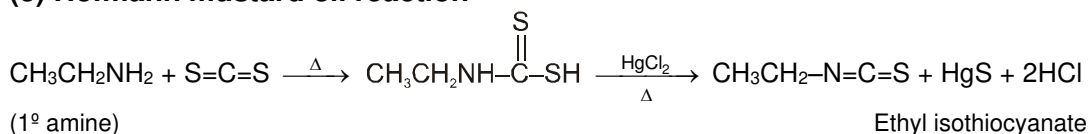
Secondary aliphatic and aromatic amines react with nitrous acid to produce nitroso-amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.



Tertiary aliphatic amines react with nitrous acid to form salts, which decompose on warming to nitrosoamine and alcohol while **tertiary aromatic amines** undergo electrophilic substitution at the ring.



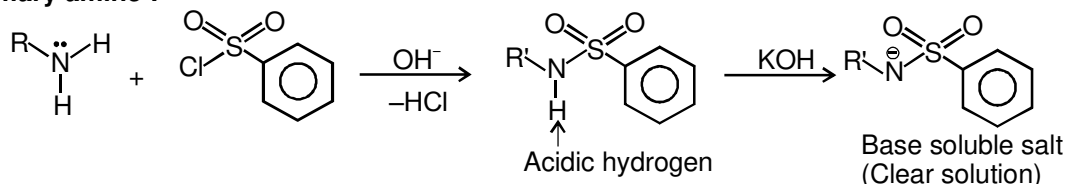
(3) Hofmann mustard oil reaction



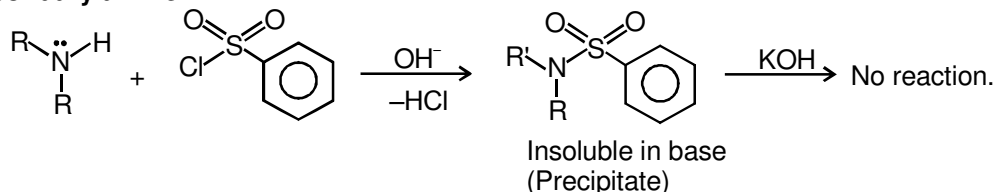
(4) The Hinsberg test :

The hinsberg test can be used to demonstrate whether an amine is primary, secondary or tertiary

Primary amine :



Secondary amine :

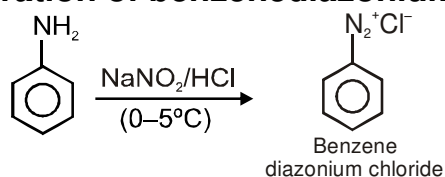


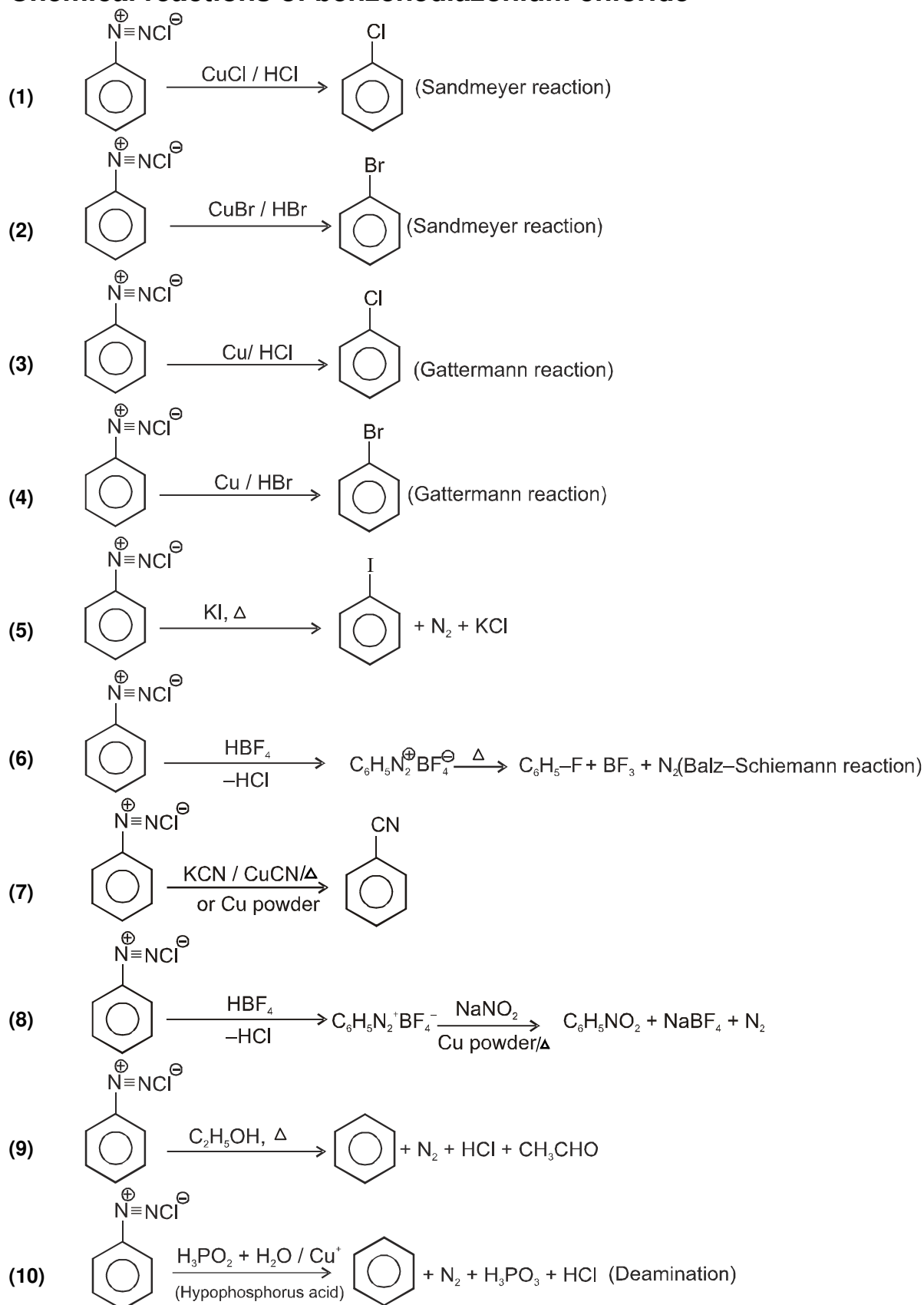
Tertiary amine :

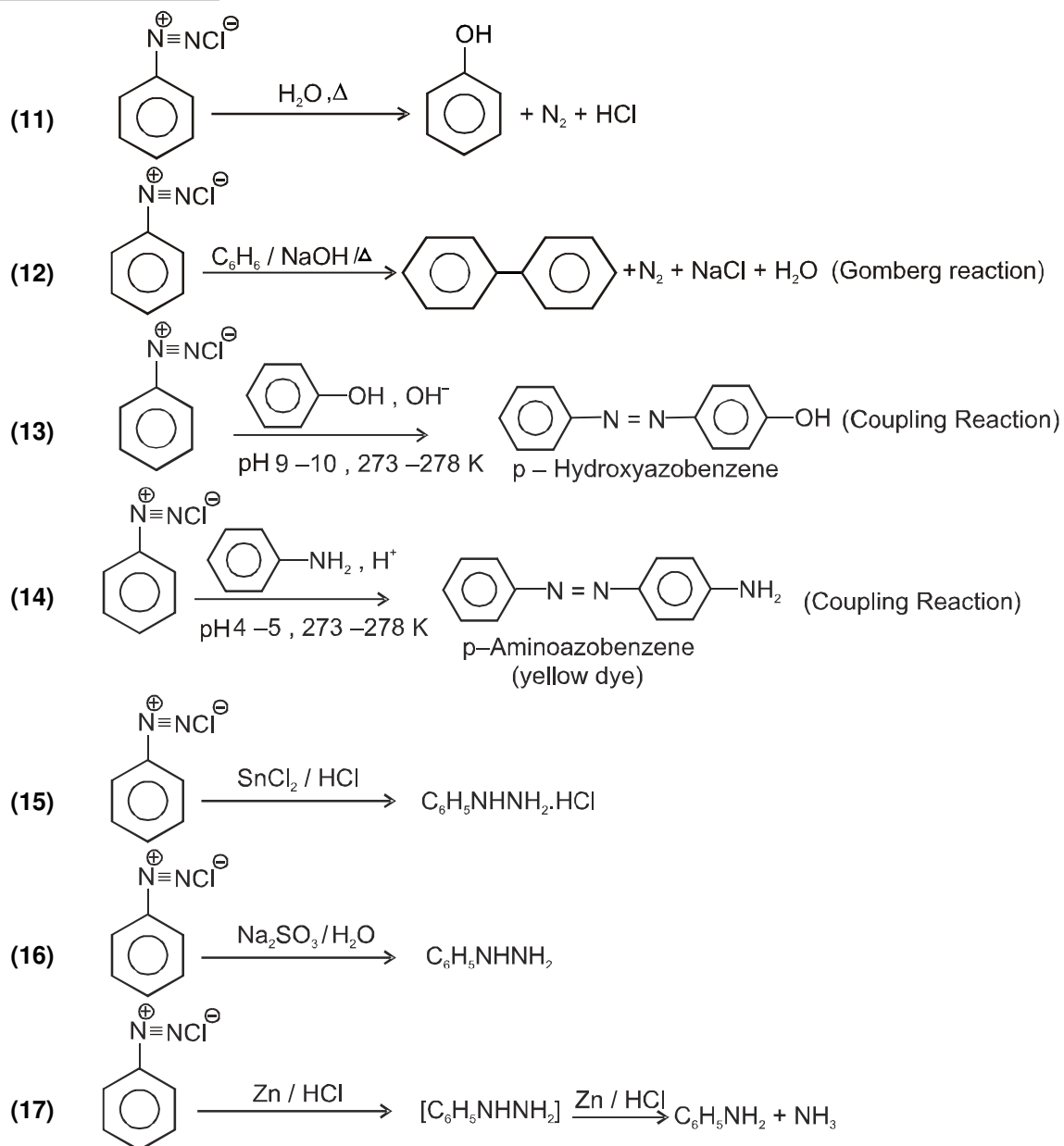
If the amine is tertiary amine and it is water insoluble no apparent change will take place in the mixture as we shake it with benzene sulfonyl chloride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

Section (C) : Benzenediazonium salt and its reaction

(a) Preparation of benzenediazonium salt




(b) Chemical reactions of benzenediazonium chloride






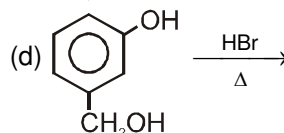
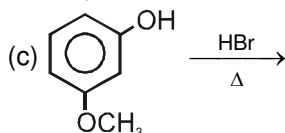
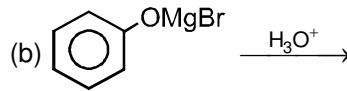
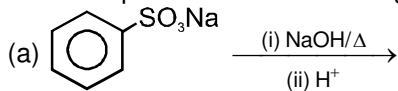
Exercise-1

Marked questions are recommended for Revision.

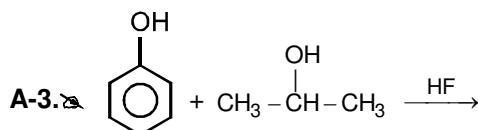
PART - I : SUBJECTIVE QUESTIONS

Section (A) : Phenol

A-1. Write the products of the following reactions :

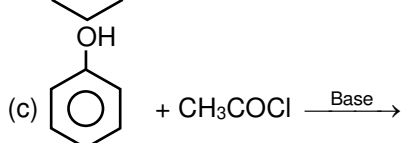
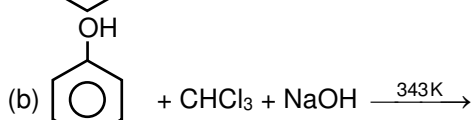
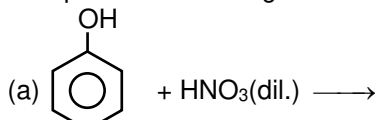


A-2. Explain why nucleophilic substitution reactions are not very common in phenols.

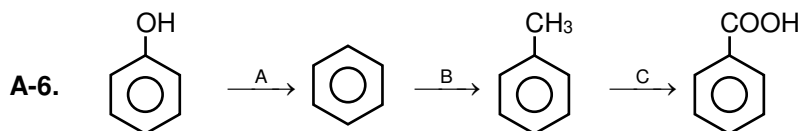


Give the products of the above reactions.

A-4. Complete the following :



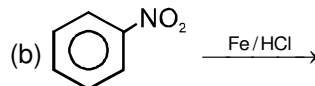
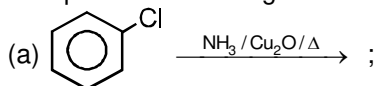
A-5. An organic compound 'A' having molecular formula $\text{C}_6\text{H}_6\text{O}$ gives a characteristic colour with aqueous FeCl_3 solution. When 'A' is treated with CO_2 and NaOH at 400 K under pressure, 'B' is obtained. B on acidification gives C when C treated with CH_3COCl gives a popular pain killer D. Deduce the structures of A, B, C and D.



Identify A, B and C in above reaction ?

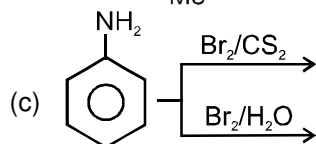
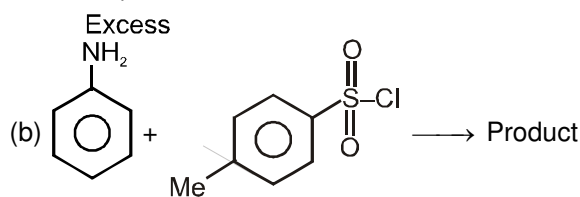
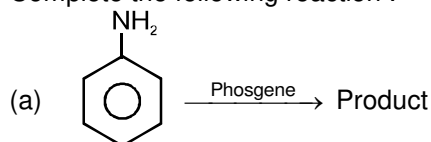
Section (B) : Nitrogen containing compounds

B-1. Complete the following reactions :





B-2. Complete the following reaction :



B-3. Why does aniline soluble in aqueous HCl ?

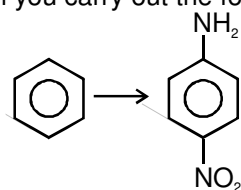
B-4. Write following conversions :

(a) nitrobenzene \longrightarrow acetanilide

(b) acetanilide \longrightarrow *p*-nitroaniline

B-5. What is the product when $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ reacts with HNO_2 ?

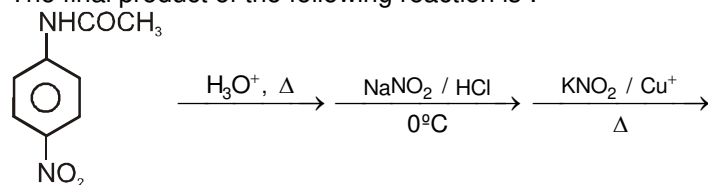
B-6. How will you carry out the following conversion ?



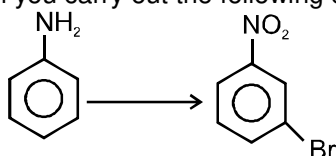
B-7. Give 3 methods to distinguish primary amine from secondary and tertiary.

Section (C) : Benzene diazonium salt & its reaction

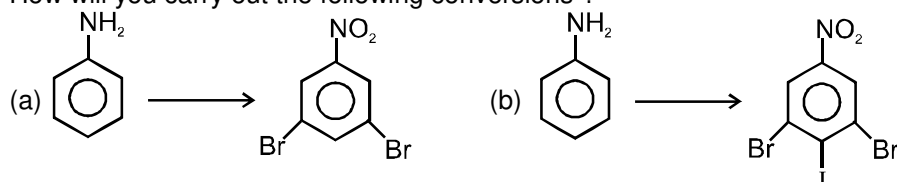
C-1. The final product of the following reaction is :



C-2. How will you carry out the following conversion ?

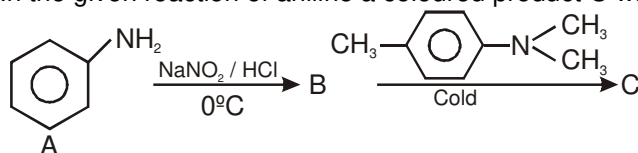


C-3. How will you carry out the following conversions ?





C-4. In the given reaction of aniline a coloured product C was obtained. The structure of C would be :



C-5. A solution contains 1 g mol. each of *p*-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

C-6. How will you carry out the following conversions ?

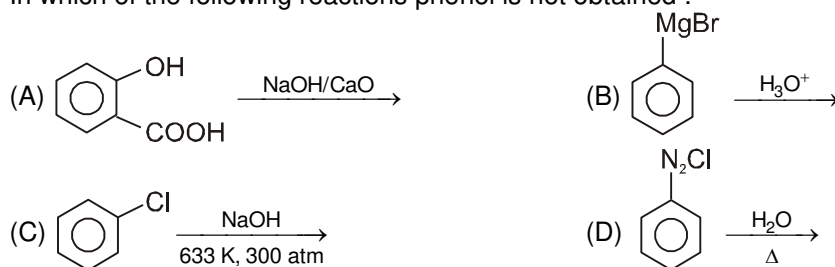
(a) toluene \longrightarrow *p*-toluidine

(b) *p*-toluene diazonium chloride \longrightarrow *p*-toluic acid

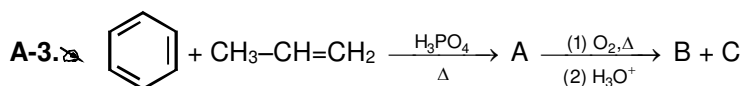
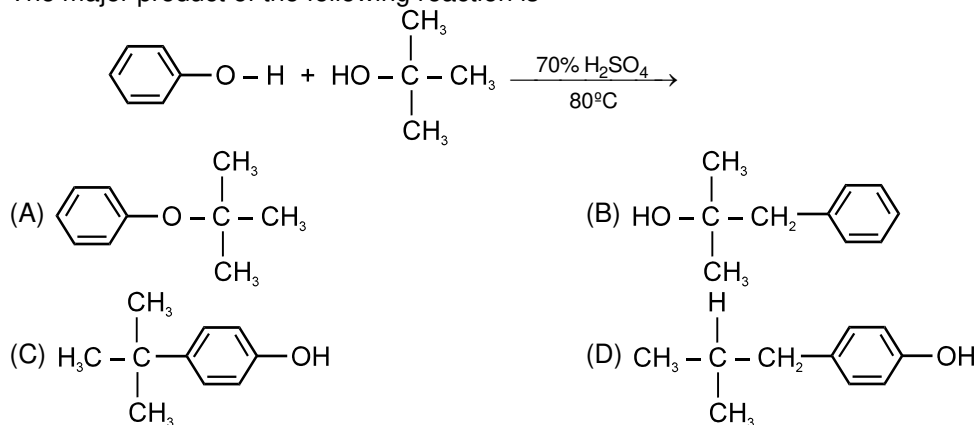
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Phenol

A-1. In which of the following reactions phenol is not obtained :



A-2. The major product of the following reaction is



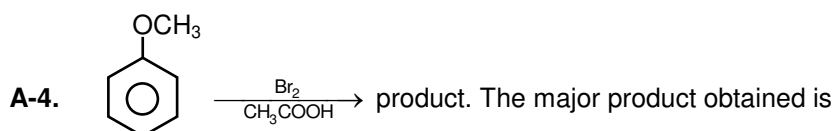
The products B & C are respectively :

(A) Phenol & acetic acid

(B) Phenol & acetaldehyde

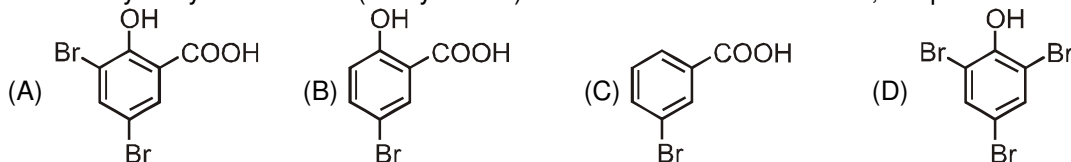
(C) Benzoic acid & acetone

(D) Phenol & acetone

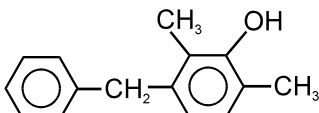


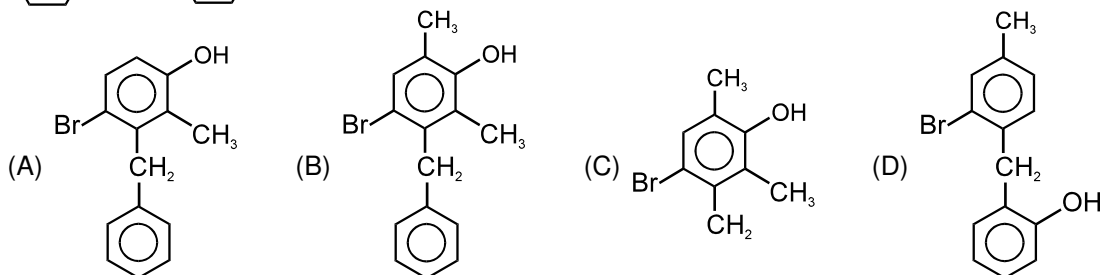


A-5. When 2-hydroxybenzoic acid (salicylic acid) is treated with bromine water, the product formed is

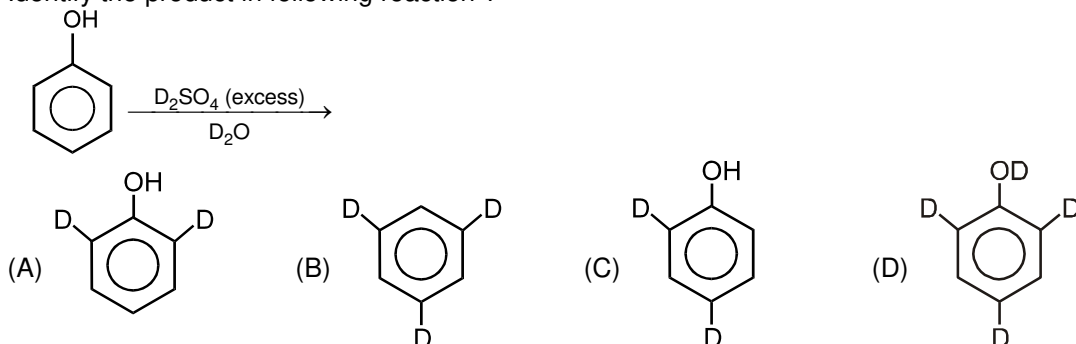


A-6. An organic compound having the molecular formula C_7H_8O is insoluble in $NaHCO_3$ solution but dissolves in aqueous $NaOH$. When treated with bromine water the compound rapidly forms a precipitate having the molecular formula $C_7H_5OBr_3$. The organic compound is
(A) o-cresol (B) m-cresol (C) p-cresol (D) anisole

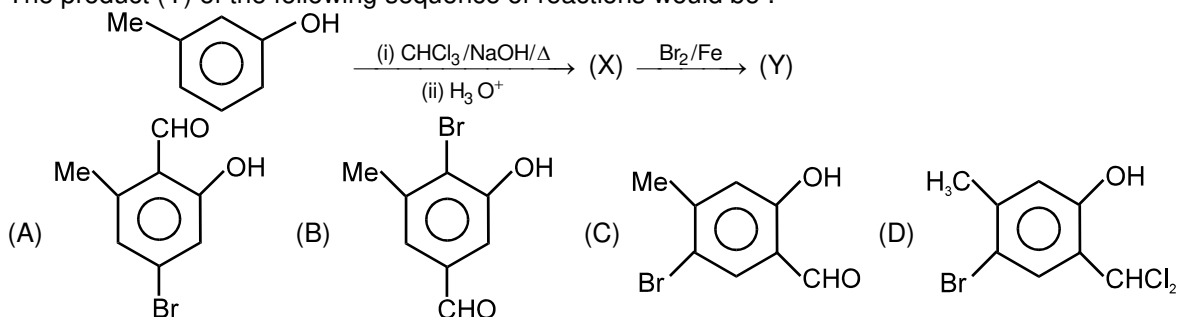
A-7.  The product is :




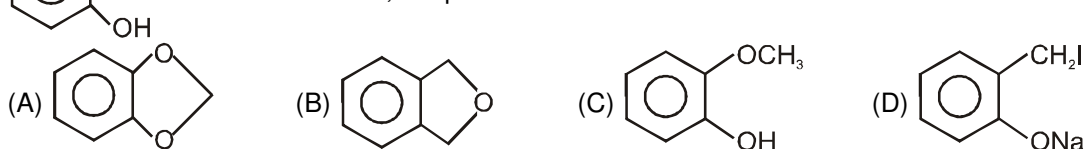
A-8. Identify the product in following reaction ?



A-9. The product (Y) of the following sequence of reactions would be :



A-10.  the product is :





A-11. In the reaction sequence c1ccccc1S(=O)(=O)[Na] >>[NaOH, 350^\circ] A >>[CH_3I] B >>[HI] C + D

A, B, C and D are given by the set :

- (A) Sodium phenate, anisole, C_6H_5I, CH_3OH (B) Sodium phenate, phenitole, C_2H_5I, C_6H_5OH
 (C) Sodium phenate, anisole, C_6H_5OH, CH_3I (D) Sodium phenate, phenitole, C_6H_5I, C_2H_5OH

A-12. c1ccccc1O >>[NaOH, CH_3COCl] B >>[Zn, Distillation] A

The compounds A and B in the above reaction sequence are :

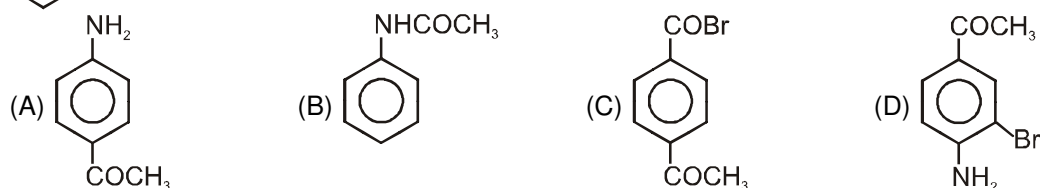
- (A) benzene, methyl benzoate (B) benzene, phenyl acetate
 (C) phenyl acetate, benzene (D) benzene, phenylacetyl chloride

Section (B) : Nitrogen containing compounds

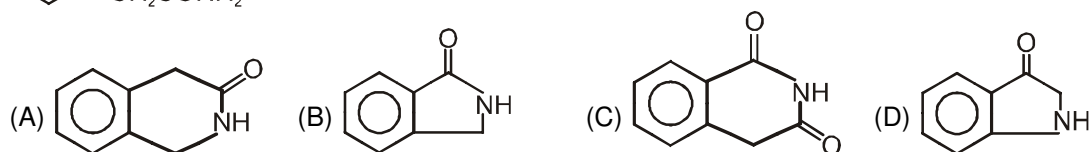
B-1. Which of the following sequence is best suited to convert benzene to 3-chloro aniline ?

- (A) nitration, reduction, chlorination
 (B) chlorination, nitration, reduction
 (C) nitration, chlorination, reduction
 (D) nitration, reduction, acetylation, chlorination, hydrolysis

B-2. c1ccccc1C(=O)N >>[Br_2/NaOH] (A) >>[CH_3COCl/reflux] (B), Identify the major product (B).



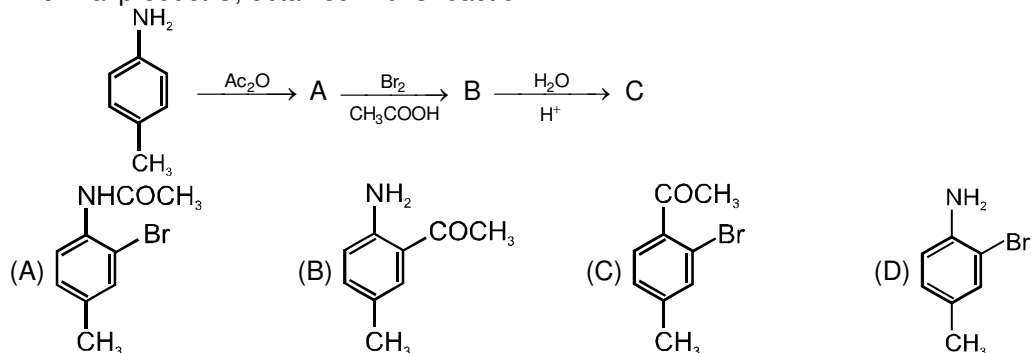
B-3. c1ccccc1C(=O)OC >>[(i) Br_2/NaOH, (ii) H_3O^+ / \Delta] Product. The major product obtained is



B-4. Aniline when treated with acetyl chloride in presence of alkali, the product formed is :

- (A) acetanilide (B) benzoyl chloride (C) acetophenone (D) aniline hydrochloride

B-5. The final product C, obtained in this reaction



B-6. Chloroform when treated with aniline and alcoholic KOH, the product formed is ?

- (A) Phenyl cyanide (B) Phenyl isocyanide
 (C) Chlorobenzene (D) Phenol



- B-7.** An aromatic amine (X) was treated with alcoholic potash and another compound (Y) then foul smelling gas C_6H_5NC is formed. The compound (Y) was formed by reacting compound (Z) with Cl_2 in the presence of slaked lime. The compound (Z) is :
 (A) $CHCl_3$ (B) CH_3COCH_3 (C) CH_3OH (D) $C_6H_5NH_2$
- B-8.** p-Chloro aniline and anilinium chloride can be distinguished by
 (A) Sandmeyer reaction (B) Carbyl amine reaction
 (C) Hinsberg's reaction (D) $AgNO_3$
- B-9.** The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is _____.
 (A) excess H_2 (B) Br_2 in aqueous $NaOH$
 (C) iodine in the presence of red phosphorus (D) $LiAlH_4$ in ether
- B-10.** Hoffmann bromamide degradation reaction is shown by _____.
 (A) $ArNH_2$ (B) $ArCONH_2$ (C) $ArNO_2$ (D) $ArCH_2NH_2$
- B-11.** The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is _____.
 (A) excess H_2/Pt (B) $NaOH/Br_2$ (C) $NaBH_4$ /methanol (D) $LiAlH_4$ /ether
- B-12.** In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____.
 (A) Sodium amide, $NaNH_2$ (B) Sodium azide, NaN_3
 (C) Potassium cyanide, KCN (D) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$
- B-13.** Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is
 (A) Hoffmann Bromamide reaction (B) Gabriel phthalimide synthesis
 (C) Sandmeyer reaction (D) Reaction with NH_3
- B-14.** The product formed by the reaction of acetamide with Br_2 in presence of $NaOH$ is :
 (A) CH_3CN (B) CH_3CHO (C) CH_3CH_2OH (D) CH_3NH_2

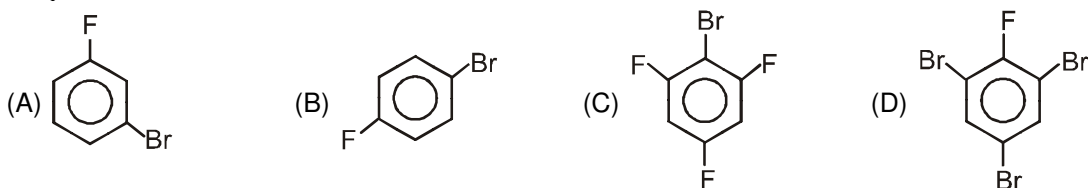
Section (C) : Benzene diazonium salt & its reactions

- C-1.** In the reaction, the product (C) is :

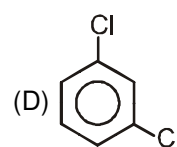
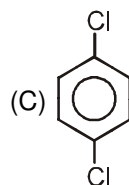
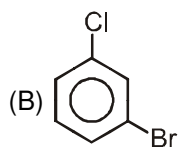
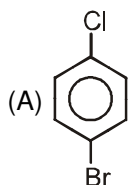
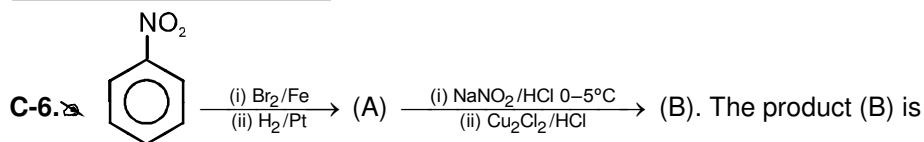
$$C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2 + HCl} (A) \xrightarrow[KCN]{CuCN} (B) \xrightarrow{H^+/H_2O} (C)$$

 (A) $C_6H_5CH_2NH_2$ (B) C_6H_5COOH (C) C_6H_5OH (D) none of these
- C-2.** Benzenediazonium chloride can be converted into benzene on treatment with:
 (A) H_3PO_3 (B) H_3PO_4 (C) H_3PO_2 (D) HPO_3
- C-3.** $C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2 + HCl} X \xrightarrow[\Delta]{H_2O} Y$, the product Y is :
 (A) Benzenediazonium chloride (B) Nitrobenzene
 (C) Phenol (D) Cresol

- C-4.** (A). The major product (A) is



- C-5.** Diazonium salt + $Cu + HCl \rightarrow$; the reaction is known as
 (A) Chlorination (B) Sandmeyer's reaction
 (C) Perkin reaction (D) Gattermann reaction



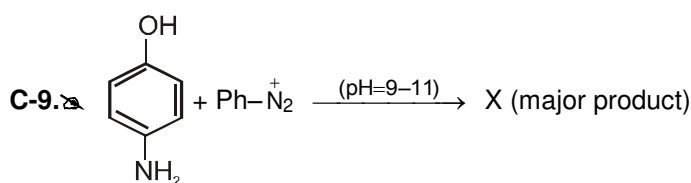
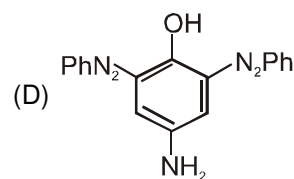
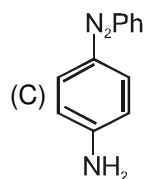
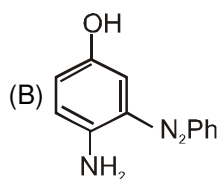
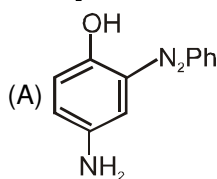
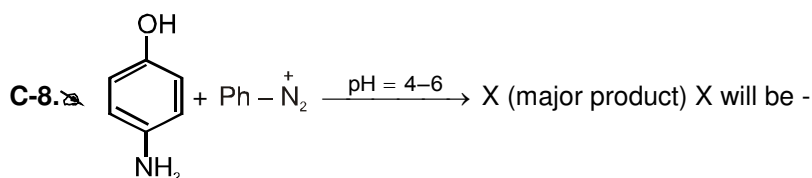
C-7. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride.

(A) Aniline

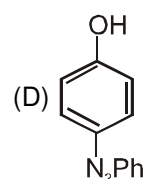
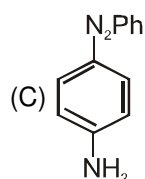
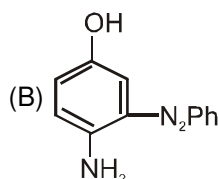
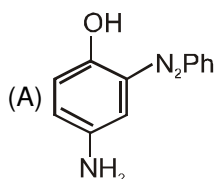
(B) Phenol

(C) Anisole

(D) Nitrobenzene



X will be :



PART - III : MATCH THE COLUMN

1. Match the column:

	Column-I		Column-II
(A)	$\text{RNH}_2 + \text{CHCl}_3 + \text{KOH (alc)} \xrightarrow{\Delta}$	(p)	Schotten-Baumann reaction
(B)	$\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow[\Delta]{\text{CuBr/HBr}}$	(q)	Coupling reaction
(C)	$\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{NaOH(aq.)}}$	(r)	Carbylamine reaction
(D)	$\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{pH } 9-10}$	(s)	Sandmeyer reaction



2. Match the reactions given in Column I with the statements given in Column II.

	Column-I		Column-II
(A)	Ammonolysis	(p)	Amine with lesser number of carbon atoms
(B)	Gabriel phthalimide synthesis	(q)	Detection test for primary amines.
(C)	Hoffmann Bromamide reaction	(r)	Reaction of phthalimide with KOH and R—X
(D)	Carbylamine reaction	(s)	Reaction of alkylhalides with NH ₃

3. Match the compounds given in Column-I with the items given in Column-II.

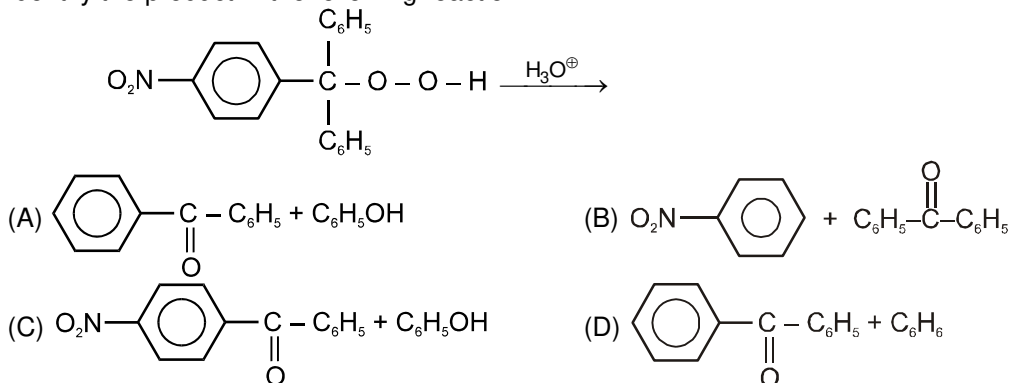
	Column-I		Column-II
(A)	$\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}(\text{Cl})-\text{CH}_3 \xrightarrow{\text{anhydrous AlCl}_3}$	(p)	Diazocoupling reaction.
(B)	$\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow{\text{dil. HCl}}$	(q)	Friedel-Craft reaction
(C)	$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{anhydrous AlCl}_3}$	(r)	Reimer-Tiemann reaction
(D)	$\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CCl}_4 / \text{NaOH}}$	(s)	Product is Isopropyl benzene
		(t)	Electrophilic substitution reaction

Exercise-2

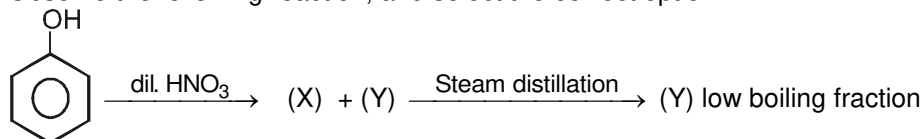
Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

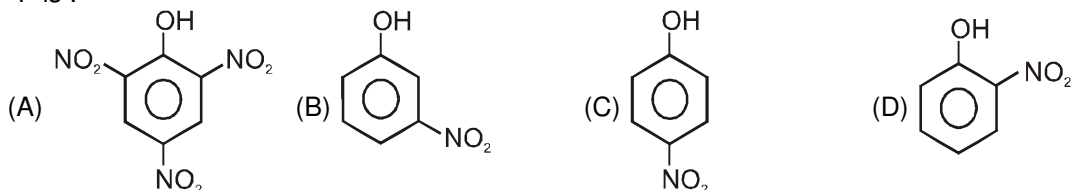
1. Identify the product in the following reaction.



2. Observe the following reaction, and select the correct option

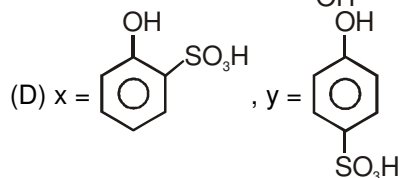
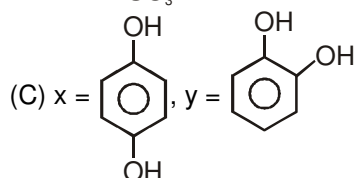
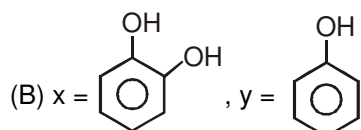
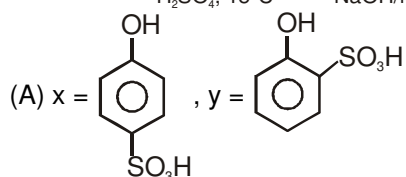
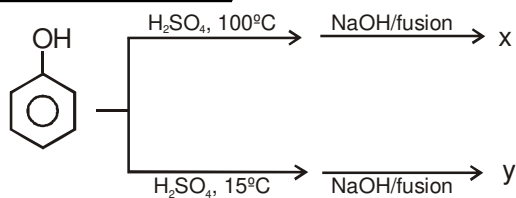


'Y' is :



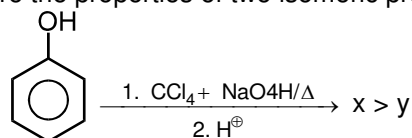


3.



4.

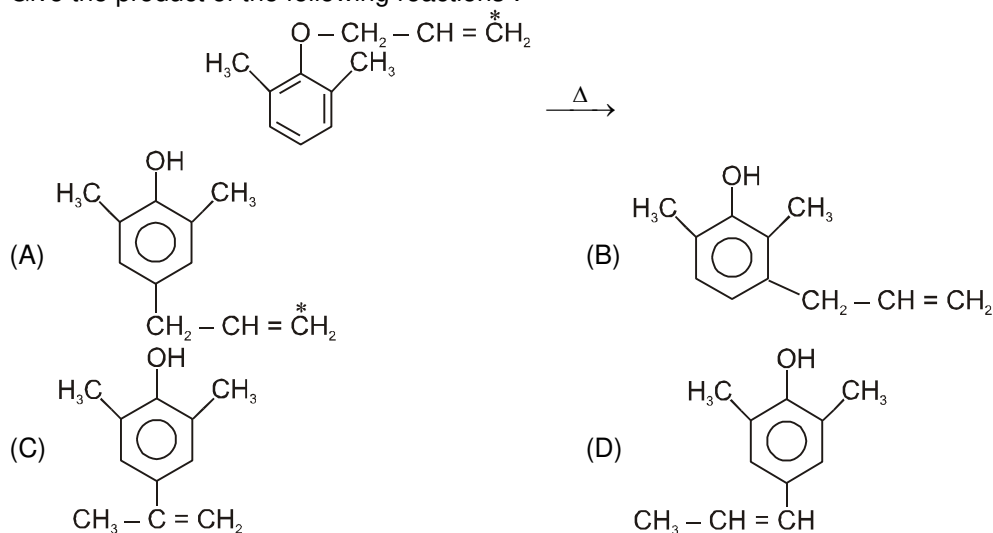
Compare the properties of two isomeric products x and y formed in the following reaction.

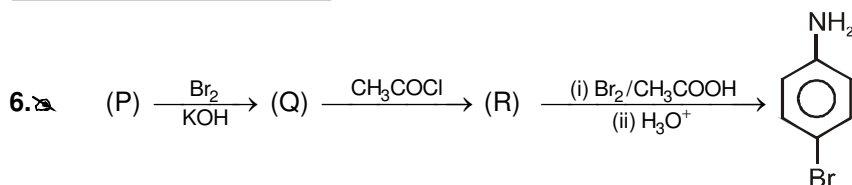


Option	Acid Strength	H ₂ O Solubility	Volatility	Melting Point
(A)	y > x	y > x	x > y	y > x
(B)	x > y	x > y	y > x	x > y
(C)	y > x	x > y	y > x	y > x
(D)	x > y	y > x	x > y	y > x

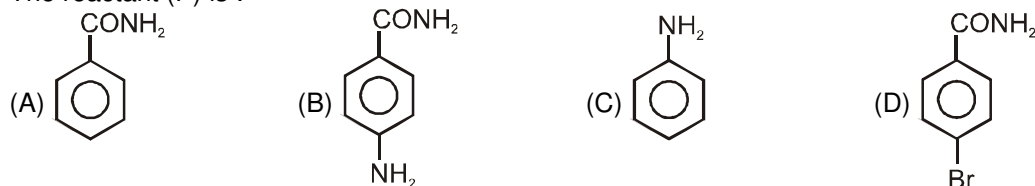
5.

Give the product of the following reactions :

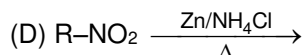
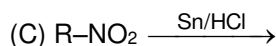
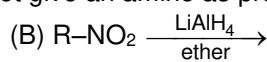
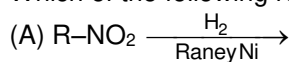




The reactant (P) is :



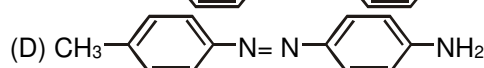
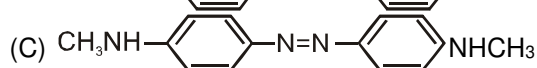
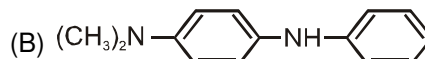
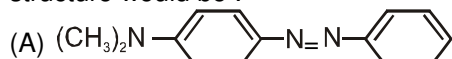
7. Which of the following reduction reaction does not give an amine as product ?



8. Para toluidine is treated with HNO_2 at ice cold conditions and then boiled with water. The final product obtained is :

(A) anthranilic acid (B) p-cresol (C) toluic acid (D) phenol

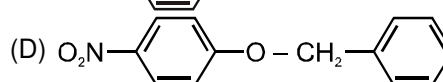
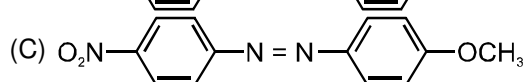
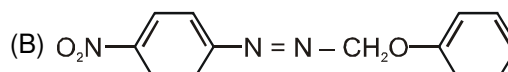
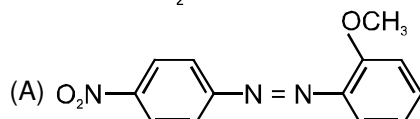
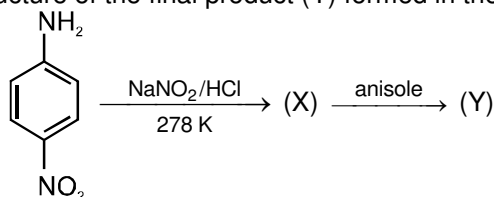
9. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be :



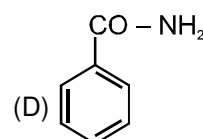
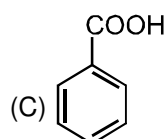
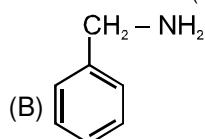
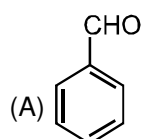
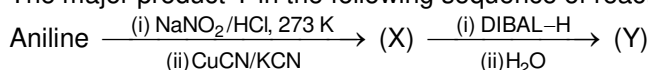
10. In the diazotisation of aniline with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to :

- (A) suppress the concentration of free aniline available for coupling
(B) suppress hydrolysis of phenol
(C) insure a stoichiometric amount of nitrous acid
(D) neutralize the base liberated

11. The structure of the final product (Y) formed in the following reaction sequence is :



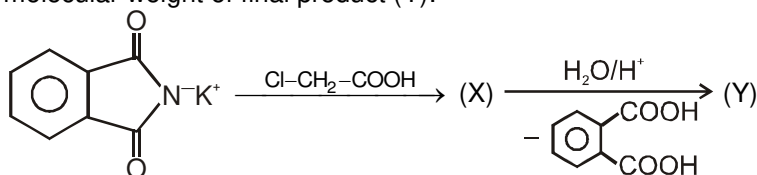
12. The major product Y in the following sequence of reaction is :



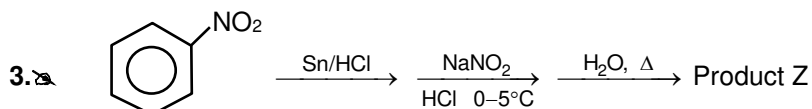


PART - II : SINGLE OR DOUBLE INTEGER TYPE

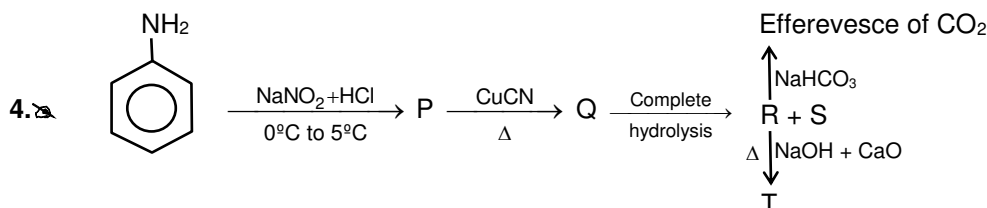
1. Identify molecular weight of final product (Y).



2. How many toluidines on reaction with NaNO_2/HCl followed by H_3PO_2 treatment gives Toluene.

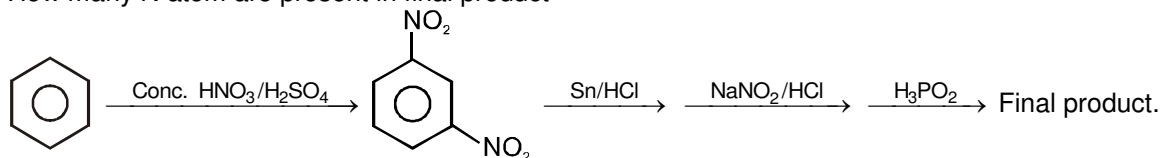


Find the molecular weight of Z.



Molecular weight of T will be :

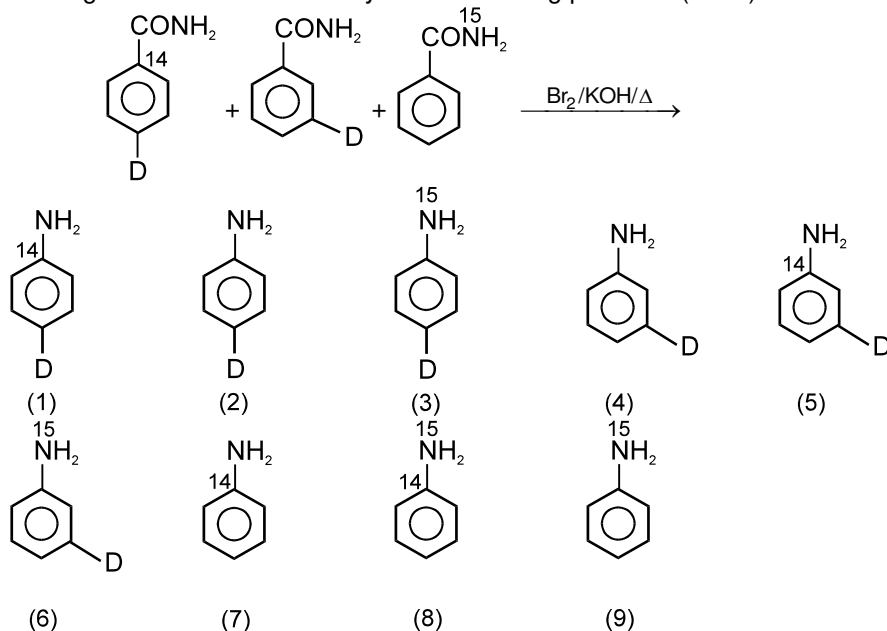
5. How many N atom are present in final product



6. $\text{Ph-NO}_2 \xrightarrow{\text{Sn/HCl}} \xrightarrow[\text{HCl, } 0^\circ\text{C}-5^\circ\text{C}]{\text{NaNO}_2} \xrightarrow[\text{Ph-OH}]{\text{Basic medium}} \text{Product Y}$

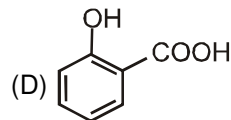
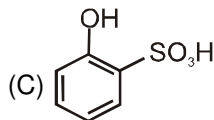
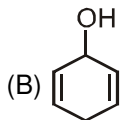
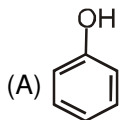
Find the molecular weight of Y report your answer as $\frac{\text{Molecular weight}}{2}$.

7. In the given reaction how many of the following products (1 – 9) can be formed.

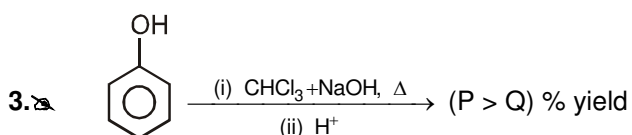
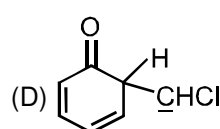
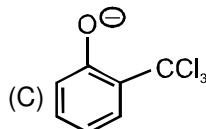
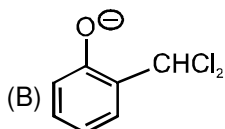
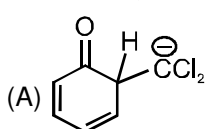
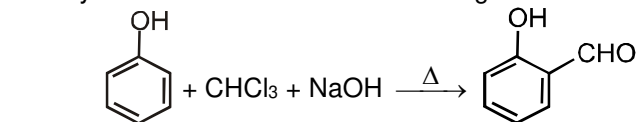



PART - III : ONE OR MORE THAN ONE OPTION CORRECT TYPE

1. Which of the following can decolourise bromine water solution?



2. Identify the intermediates of the following reaction.

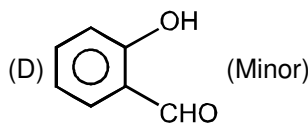
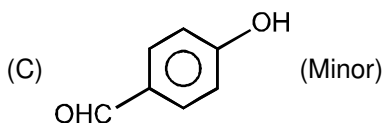
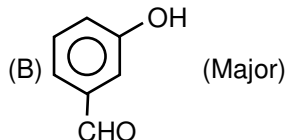
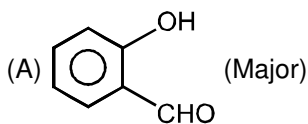
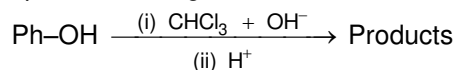


Select the correct options :

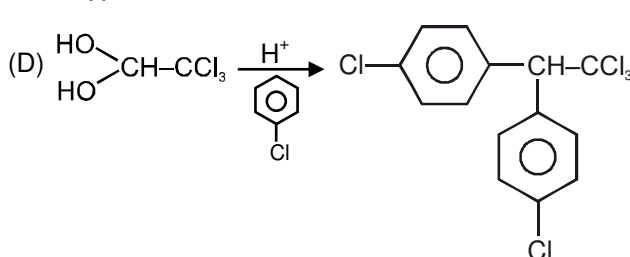
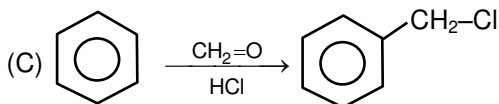
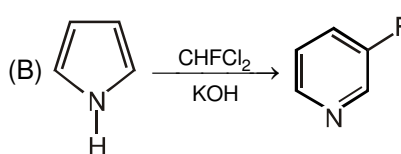
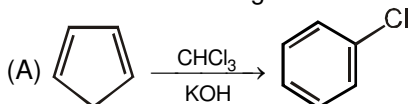
- (A) Boiling point, (P > Q)
(C) Water solubility, (P < Q)

- (B) Melting point, (Q > P)
(D) Acid Strength, (Q < P)

4. Correct options for the given below reaction :

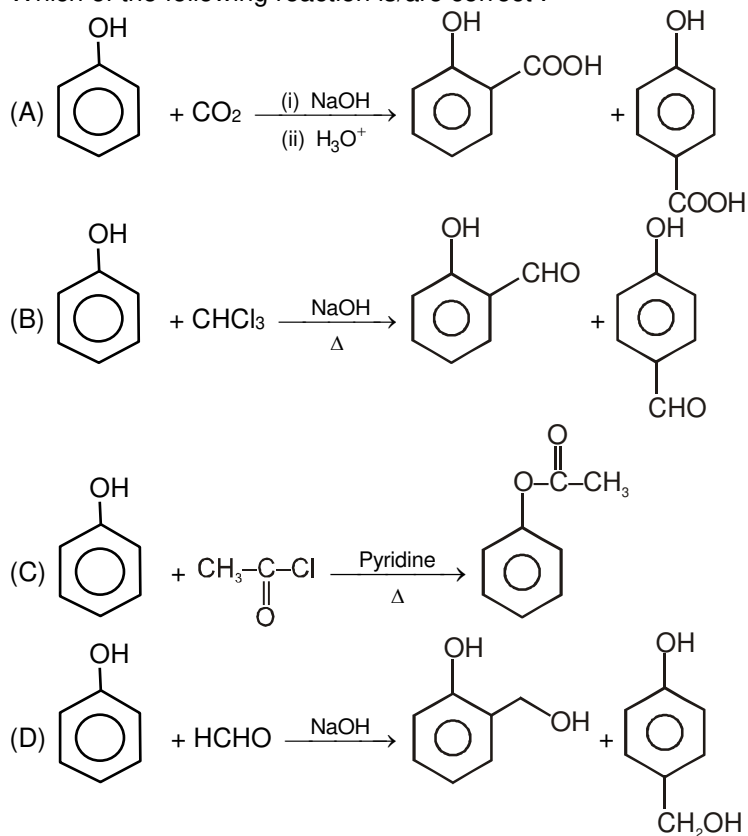


5. Which of the following reaction is/are correct

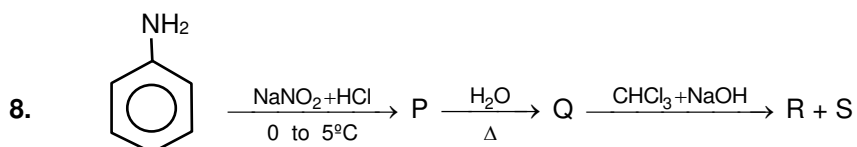
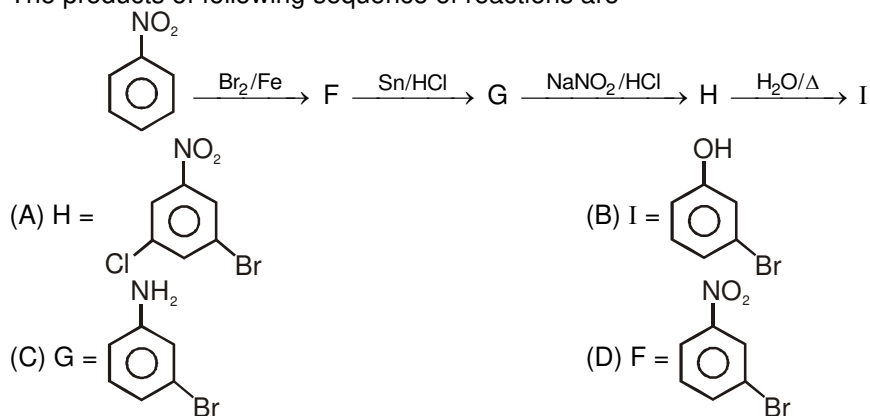




6. Which of the following reaction is/are correct :

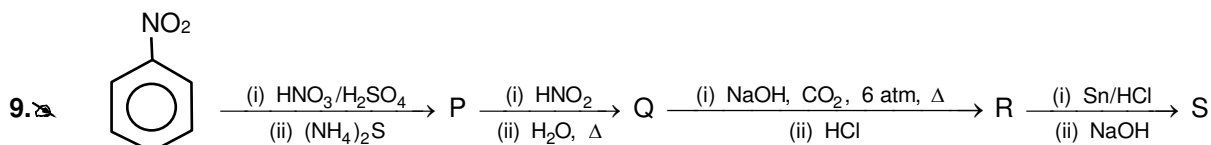


7. The products of following sequence of reactions are

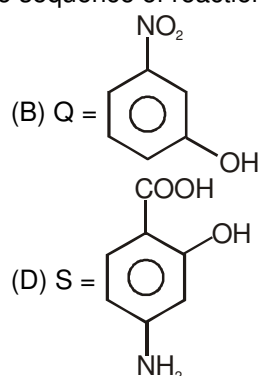
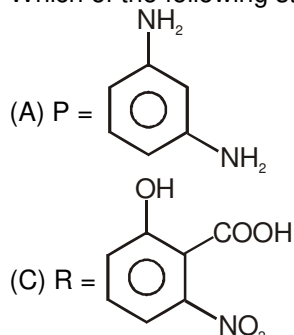


Which of the following statement is/are correct :

- (A) P is benzene diazonium chloride
- (B) Q can not give bromine water test
- (C) R and S are position isomers
- (D) During the formation of R and S from Q, formation of a new C–C bond will takes place.



Which of the following statement(s) for the above sequence of reactions is/are correct

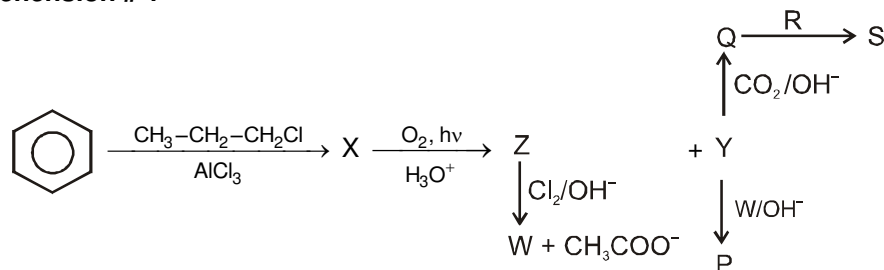


10. Coupling reaction takes place when benzene diazonium chloride is treated with :
 (A) Benzaldehyde (B) α -naphthol
 (C) N,N-dimethyl aniline (D) Phenol

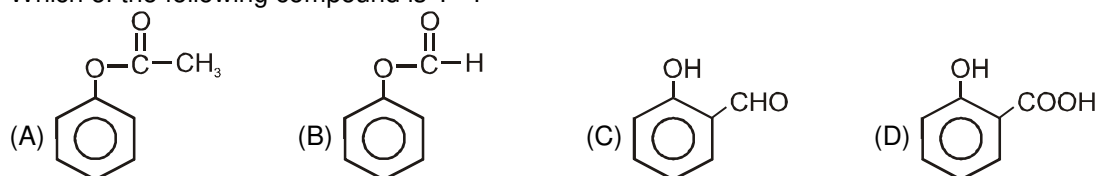
PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

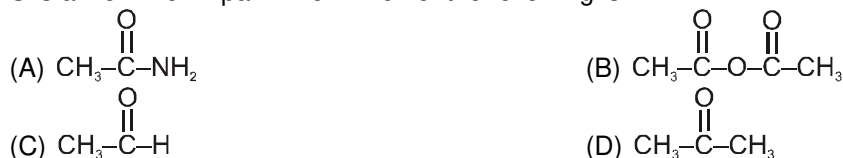
Comprehension # 1



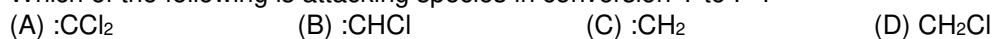
1. Which of the following compound is 'P' ?



2. S is a well known pain killer which of the following is 'R' ?

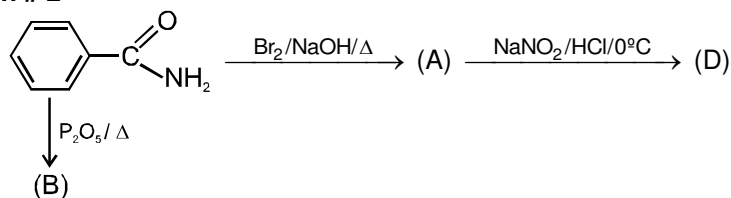


3. Which of the following is attacking species in conversion Y to P ?





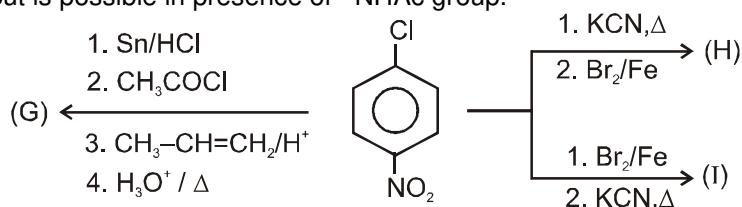
Comprehension # 2



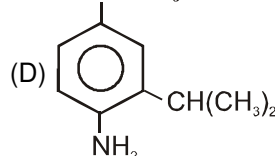
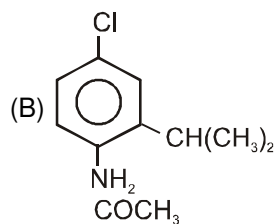
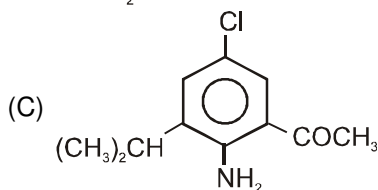
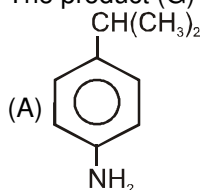
4. The intermediates which are involved in the conversion from benzamide to (A) are :
 (A) N-bromamide (B) carbocation (C) carbene (D) isocyanide
5. (B) on treatment with Zn/HCl gives :
 (A) aniline (B) benzylamine
 (C) phenylisocyanide (D) N-methylaniline
6. (D) on reaction with phenol under alkaline conditions gives :
 (A) diazobenzene (B) hydrazobenzene
 (C) benzidine (D) para hydroxy azobenzene

Comprehension # 3

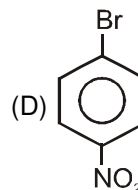
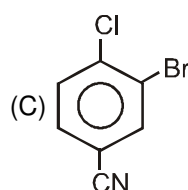
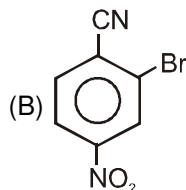
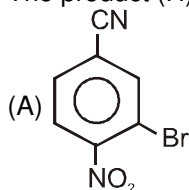
The $-\text{NO}_2$ group in an aromatic ring deactivates the ortho and para positions for an electrophilic attack. When $-\text{NO}_2$ group is present at ortho or para positions of a leaving group (Nucleofuge) it activates the ring for nucleophilic attack. The reduction of $-\text{NO}_2$ group by metal in acid causes its reduction to $-\text{NH}_2$ group and then the ring becomes strongly activated for a electrophilic attack. The strong activation of $-\text{NH}_2$ group is moderated by its acylation with CH_3COCl to $-\text{NHAc}$ group. Deacylation is carried out by hydrolysis with H_3O^+ or OH^- . The ring alkylation by using RX/AlX_3 is not possible in presence of $-\text{NO}_2$ or $-\text{NH}_2$ group but is possible in presence of $-\text{NHAc}$ group.



7. The product (G) is :

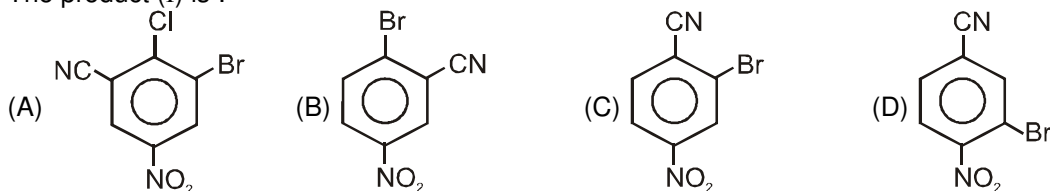


8. The product (H) is :





9. The product (I) is :

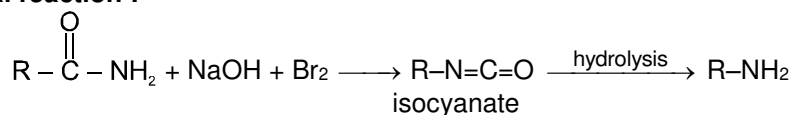


Comprehension # 4

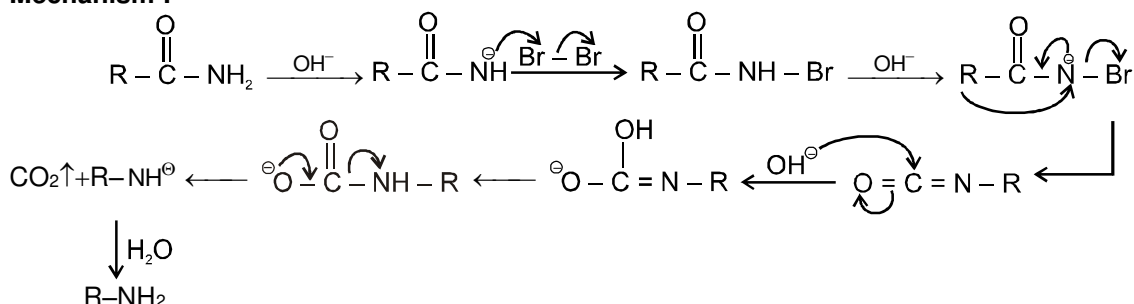
Hofmann rearrangement

In the Hofmann rearrangement an unsubstituted amide is treated with sodium hydroxide and bromine to give a primary amine that has one carbon lesser than starting amide.

General reaction :

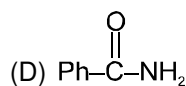
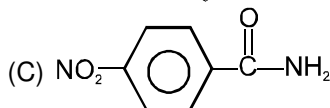
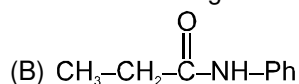
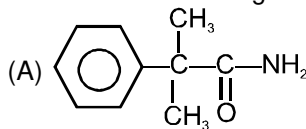


Mechanism :

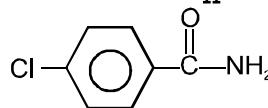
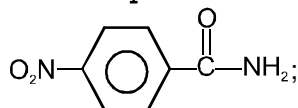
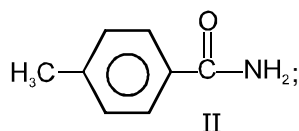
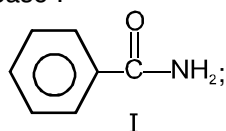


If the migrating group is chiral then its configuration is retained. Electron releasing effects in the migrating group increases reactivity of Hofmann rearrangement.

10. Which of the following compound(s) cannot give Hofmann rearrangement :



11. Arrange the following amides according to their relative reactivity when reacted with Br_2 in excess of strong base :



(A) $\text{IV} > \text{I} > \text{II} > \text{III}$

(B) $\text{II} > \text{I} > \text{III} > \text{IV}$

(C) $\text{II} > \text{IV} > \text{III} > \text{I}$

(D) $\text{II} > \text{I} > \text{IV} > \text{III}$



Comprehension # 5

Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Column-I, 2 and 3 contain starting materials, reaction conditions and type of reactions respectively.		
Column 1	Column 2	Column 3
(I) p-Fluoro nitrobenzene	(i) NaOH + heat	(P) Nucleophilic substitution
(II) Ethyl benzene carboxylate	(ii) Br ₂ + U.V	(Q) Free radical substitution
(III) 1-Bromo-1-phenyl ethane	(iii) Br ₂ + Aℓ	(R) Electrophilic substitution
(IV) Ethyl benzene	(iv) Conc. HNO ₃ + conc. H ₂ SO ₄	(S) Hydrolysis

12. Match the correct combination?
 (A) (IV) (iii) (R) (B) (I) (i) (R) (C) (III) (iv) (P) (D) (II) (ii) (R)
13. In which amongs the following product is formed by free radical mechanism?
 (A) (I) (ii) (P) (B) (IV) (ii) (Q) (C) (II) (iii) (Q) (D) (III) (iii) (P)
14. In which amongs the following more than one products are not formed?
 (A) (IV) (iv) (R) (B) (III) (ii) (Q) (C) (II) (iii) (R) (D) (I) (i) (P)

Exercise-3

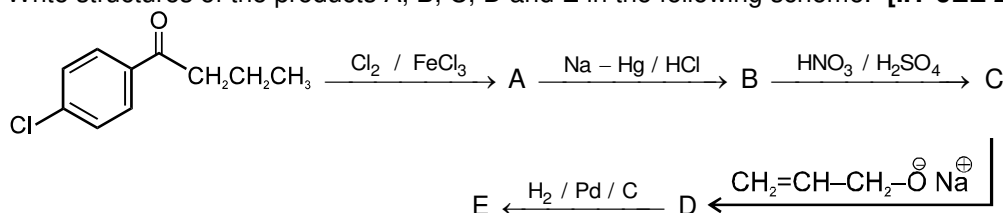
* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

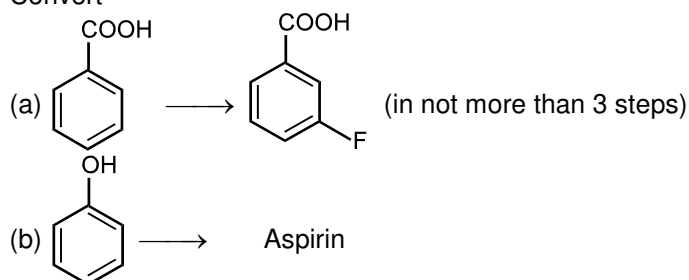
1. **Assertion** : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. [IIT-JEE 2001(S), 1/35]
 (A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
 (B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion.
 (C) Assertion is true but Reason is false.
 (D) Assertion is false but Reason is true.

2. How would you synthesised 4-methoxyphenol from bromobenzene in NOT more than five steps ? State clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme. [IIT-JEE 2001(M), 5/100]

3. Write structures of the products A, B, C, D and E in the following scheme. [IIT-JEE 2002(M), 5/60]

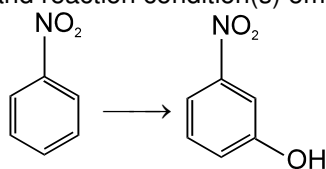


4. Convert [IIT-JEE 2003(M), 4/60]

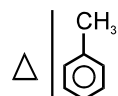




5. How would you carry out the following conversion efficiently using NOT more than four steps? Give the appropriate reagent(s) and reaction condition(s) employed in each step. [IIT-JEE 2004(M), 4/60]



6.
$$\text{C (intermediate)} \xleftarrow{\text{conc. HNO}_3} \text{A} \xrightarrow{\text{NaBr} + \text{MnO}_2} \text{B (brown coloured gas with pungent odour)}$$



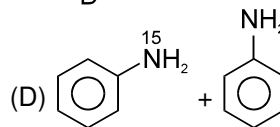
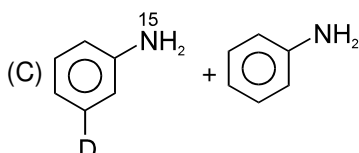
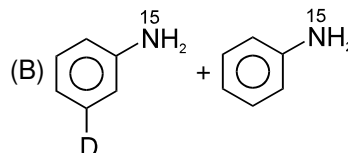
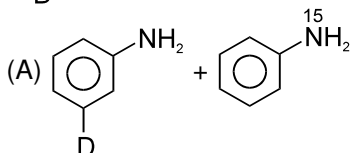
D (explosive)

Identify A, B, C, D and write the balanced chemical equation of formation of A to B and A to C.

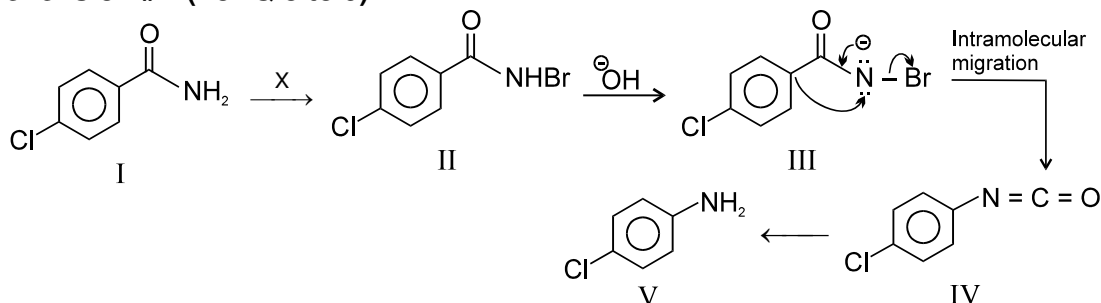
[IIT-JEE-2005(M), 4/60]

7. under Hofmann conditions will give :

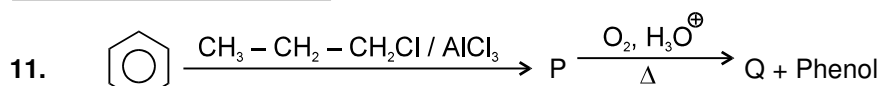
[JEE 2006, 5/184]



Comprehension # 1 (For Q.8 to 9)



8. Which reagent (X) is used to convert I to II
 (A) KBr / NaOH (B) Br₂ / NaOH (C) NaHCO₃ (D) N-Bromo succinamide [IIT-JEE 2006, 5/184]
9. Which step is rate determining step
 (A) Formation of II (B) Formation of III (C) Formation of V (D) Formation of IV [IIT-JEE 2006, 5/184]
10. $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow \text{Nitrogen containing compound} + \text{KCl} + \text{H}_2\text{O}$.
 Nitrogen containing compound is :
 (A) $\text{CH}_3\text{-C}\equiv\text{N}$ (B) $\text{CH}_3\text{-NH-CH}_3$ (C) $\text{CH}_3\text{-N}^-\equiv\text{C}^+$ (D) $\text{CH}_3\text{-N}^+\equiv\text{C}^-$ [IIT-JEE 2006, 3/184]



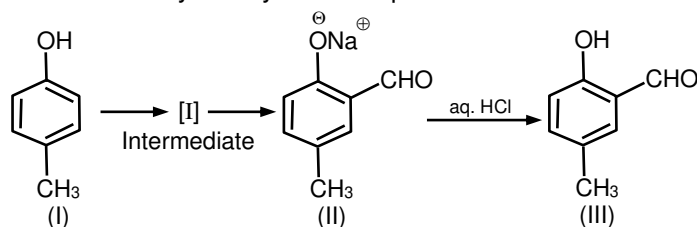
What are P & Q.

[IIT-JEE-2006, 5/184]

- (A) CCCC1=CC=CC=C1 + CC(=O)C
 (B) CCCC1=CC=CC=C1 + CCC=O
 (C) CC(C)C1=CC=CC=C1 + CCC=O
 (D) CC(C)C1=CC=CC=C1 + CC(=O)C

Comprehension # 2 (For Q.12 to 14)

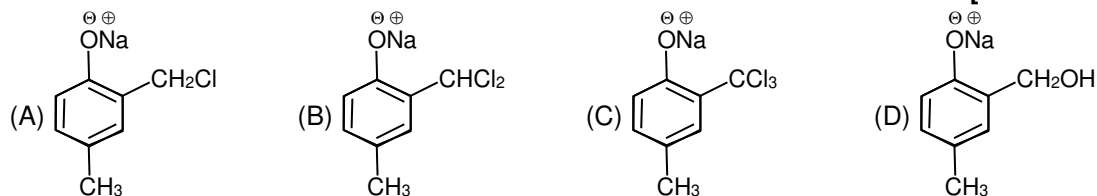
Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



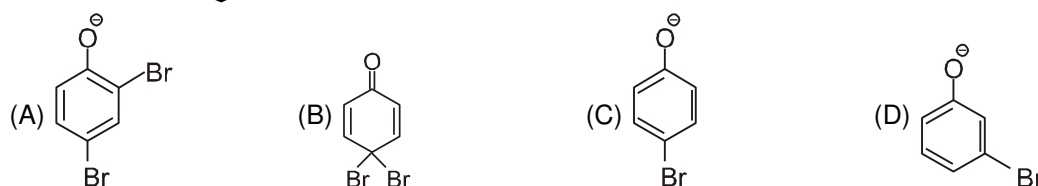
12. Which one of the following reagents is used in the above reaction ? [IIT-JEE 2007, 4/162]
 (A) aq. NaOH + CH3Cl (B) aq. NaOH + CH2Cl2
 (C) aq. NaOH + CHCl3 (D) aq. NaOH + CCl4

13. The electrophile in this reaction is : [IIT-JEE 2007, 4/162]
 (A) :CHCl (B) +CHCl2 (C) :CCl2 (D) +CCl3

14. The structure of the intermediate I is : [IIT-JEE 2007, 4/162]



15. In the reaction c1ccccc1O $\xrightarrow{\text{NaOH(aq.)}/\text{Br}_2}$ the intermediate (s) is (are) : [IIT-JEE-2010, 3/163]



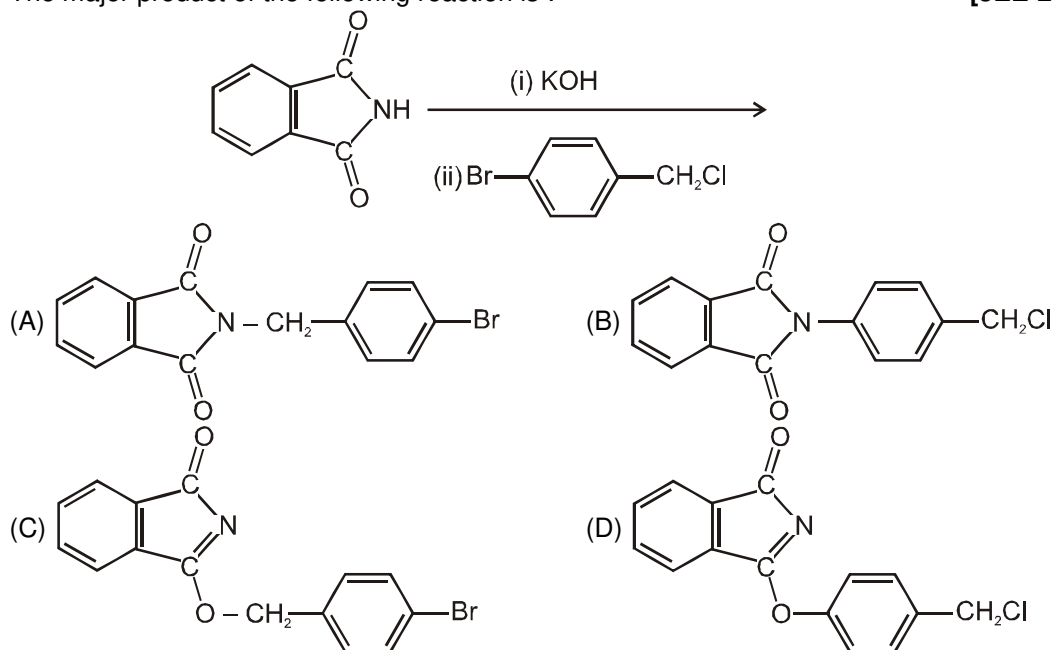


16. Match the reactions in **Column I** with appropriate options in **Column II**. [IIT-JEE 2010, 8/163]

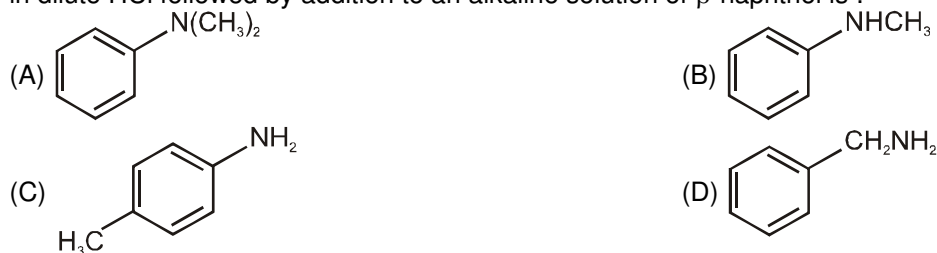
	Column-I		Column-II
(A)		(p)	Racemic mixture
(B)		(q)	Addition reaction
(C)		(r)	Substitution reaction
(D)		(s)	Coupling reaction
		(t)	Carbocation intermediate

17. The major product of the following reaction is :

[JEE-2011, 3/160]



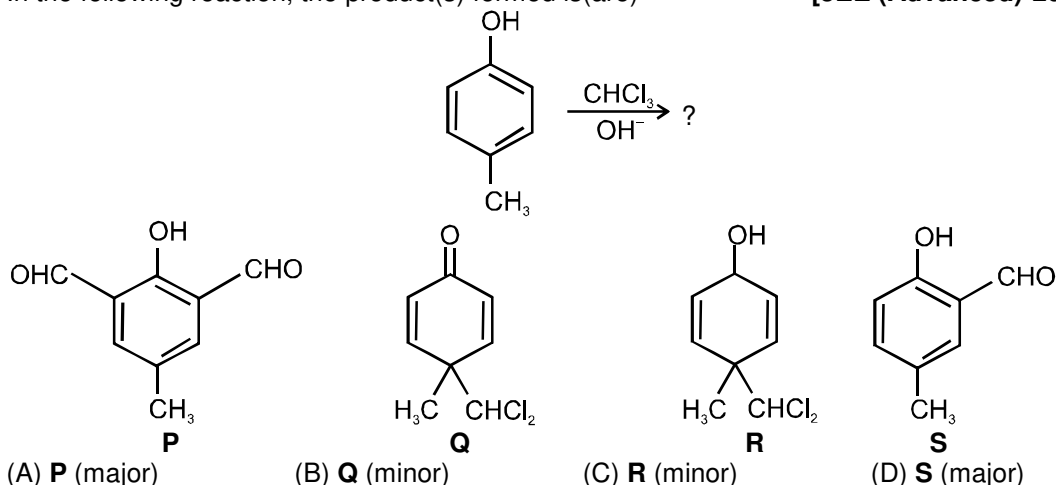
18. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with NaNO_2 in dilute HCl followed by addition to an alkaline solution of β -naphthol is : [JEE-2011, 3/160]





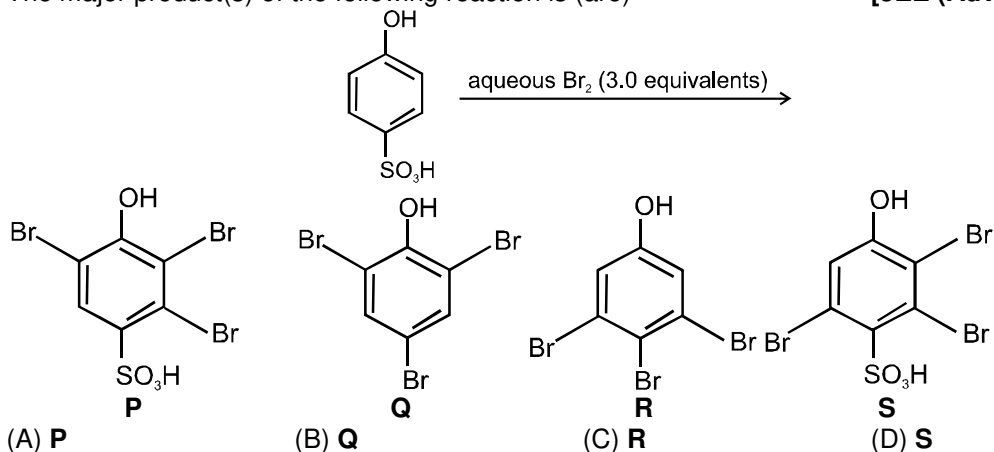
19.* In the following reaction, the product(s) formed is(are)

[JEE (Advanced)-2013, 3/120]



20. The major product(s) of the following reaction is (are)

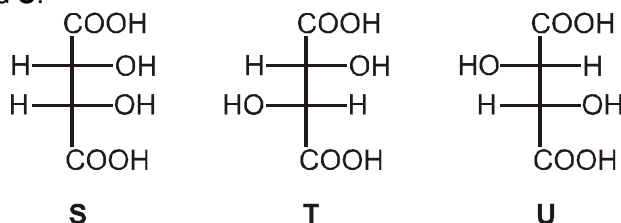
[JEE (Advance)-2013, 3/120]



Comprehension # 3 (Q.21 to 22)

P and **Q** are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O . On heating, **P** forms the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$, **P** as well as **Q** could produce one or more than one from **S**, **T** and **U**.

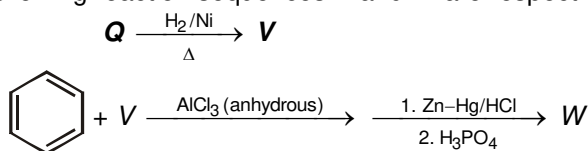


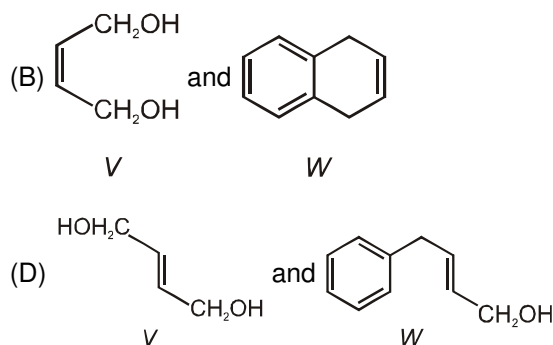
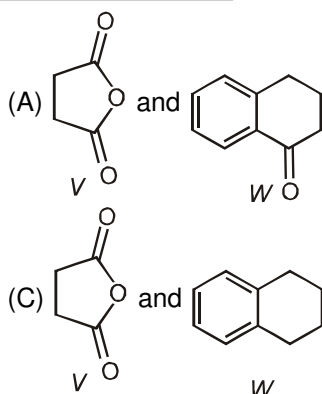
21. Compounds formed from **P** and **Q** are, respectively :

[JEE (Advance)-2013, 3/120]

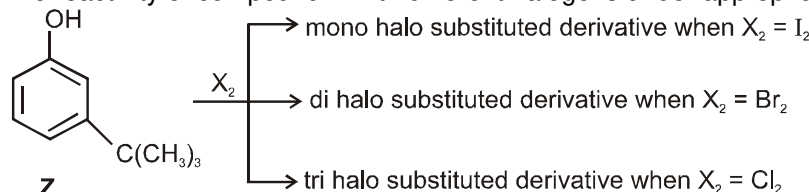
- (A) Optically active **S** and optically active pair (**T**, **U**)
 (B) Optically inactive **S** and optically inactive pair (**T**, **U**)
 (C) Optically active pair (**T**, **U**) and optically active **S**
 (D) Optically inactive pair (**T**, **U**) and optically inactive **S**

22. In the following reaction sequences **V** and **W** are respectively :




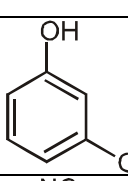
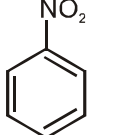
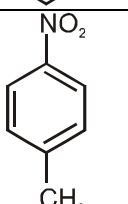


- 23.* The reactivity of compound **Z** with different halogens under appropriate conditions is given below :



The observed pattern of electrophilic substitution can be explained by [JEE(Advanced)-2014, 3/120]

- (A) the steric effect of 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. For the identification of β -naphthol using dye test, it is necessary to use : [JEE(Advanced)-2014, 3/120]
 (A) dichloromethane solution of β -naphthol. (B) acidic solution of β -naphthol.
 (C) neutral solution of β -naphthol. (D) alkaline solution of β -naphthol.
25. Match the four starting materials (**P, Q, R, S**) given in List-I with the corresponding reaction schemes (**I, II, III, IV**) provided in List II and select the correct answer using the code given below the lists.

List-I		List-II	
P.		1.	Scheme I (i) $KMnO_4$, HO^- , heat (ii) H^+ , H_2O (iii) $SOCl_2$, (iv) NH_3 ? \longrightarrow $C_7H_6N_2O_3$
Q.		2.	Scheme II (i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4 , heat (vi) HO^- ? \longrightarrow $C_6H_6N_2O_2$
R.		3.	Scheme III (i) red hot iron, 873 K (ii) fuming HNO_3 , H_2SO_4 , heat (iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis ? \longrightarrow $C_6H_5NO_3$
S.		4.	Scheme IV (i) conc. H_2SO_4 , $60^\circ C$ (ii) conc. HNO_3 , conc. H_2SO_4 (iii) dil. H_2SO_4 , heat ? \longrightarrow $C_6H_5NO_4$

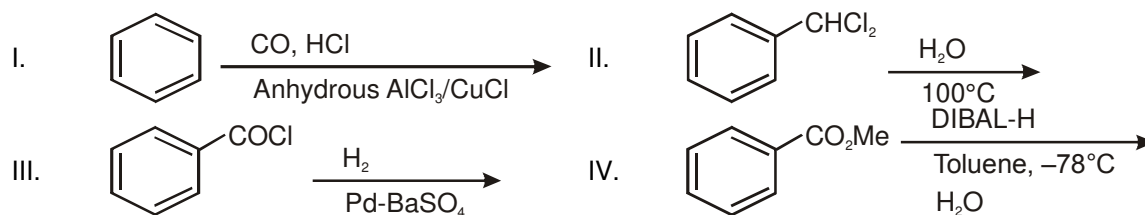
Code :

[JEE(Advanced)-2014, 3/120]

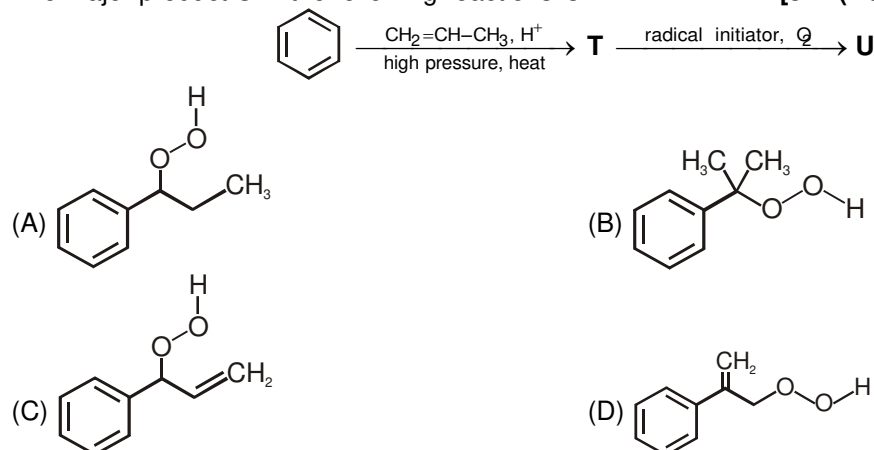
	P	Q	R	S		P	Q	R	S
(A)	1	4	2	3	(B)	3	1	4	2
(C)	3	4	2	1	(D)	4	1	3	2



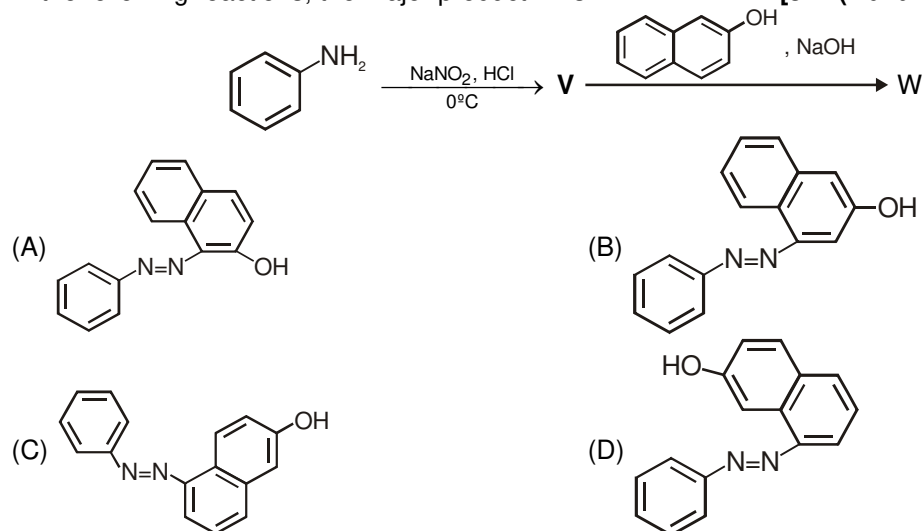
26. Among the following the number of reaction(s) that produce(s) benzaldehyde is
[JEE(Advanced)-2015, 4/168]



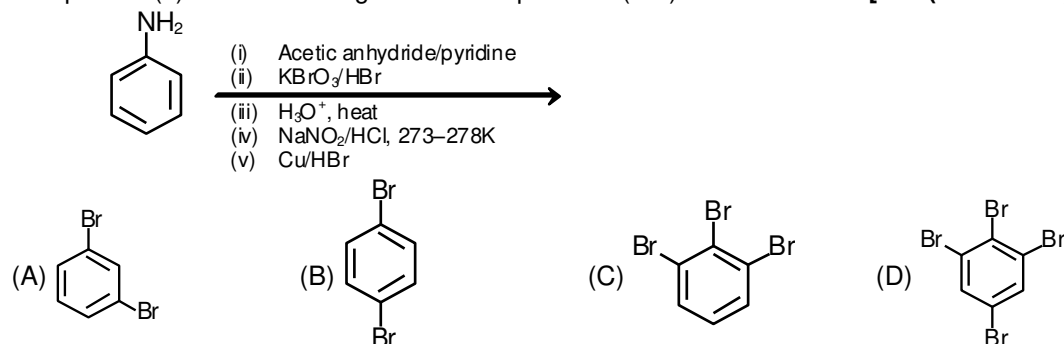
- 27.* The major product **U** in the following reactions is [JEE(Advanced)-2015, 4/168]



28. In the following reactions, the major product **W** is [JEE(Advanced)-2015, 4/168]

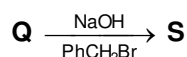
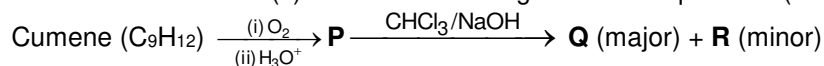


- 29.* The product(s) of the following reaction sequence is(are) [JEE(Advanced)-2016, 4/124]





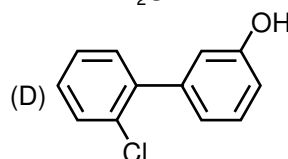
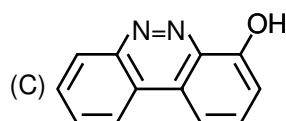
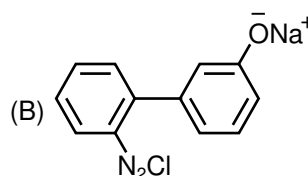
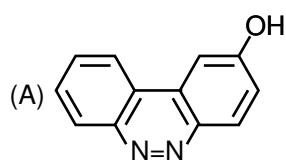
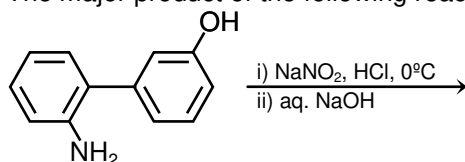
30.* The correct statement(s) about the following reaction sequence is(are) [JEE(Advanced)-2016, 4/124]



- (A) **R** is steam volatile
 (B) **Q** gives dark violet coloration with 1% aqueous $FeCl_3$ solution
 (C) **S** gives yellow precipitate with 2, 4-dinitrophenylhydrazine
 (D) **S** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

31. The major product of the following reaction is

[JEE(Advanced)-2017, 3/122]

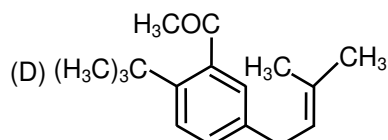
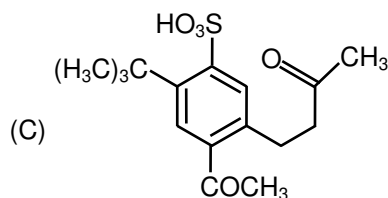
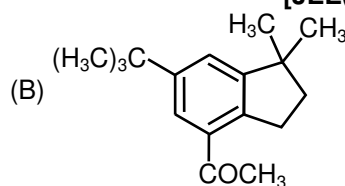
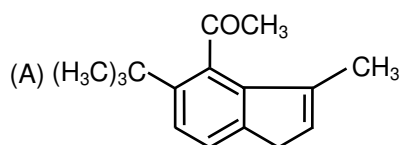


Comprehension # 4 (Q.32 to 33)

The reaction of compound **P** with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives **Q**. The compound **Q** on treatment with H_2SO_4 at $0^\circ C$ gives **R**. The reaction of **R** with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound **S**. [Et in compound **P** is ethyl group]

32. The product **S** is

[JEE(Advanced)-2017, 3/122]



33. The reactions, **Q** to **R** and **R** to **S**, are

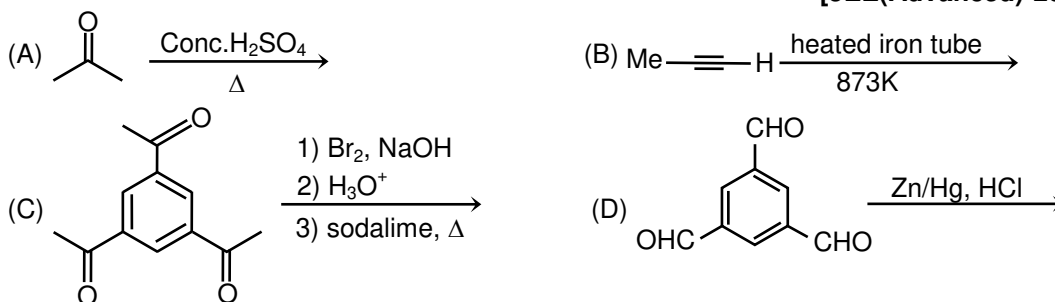
[JEE(Advanced)-2017, 3/122]

- (A) Aromatic sulfonation and Friedel-Crafts acylation
 (B) Friedel-Crafts alkylation and Friedel-Crafts acylation
 (C) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
 (D) Dehydration and Friedel-Crafts acylation



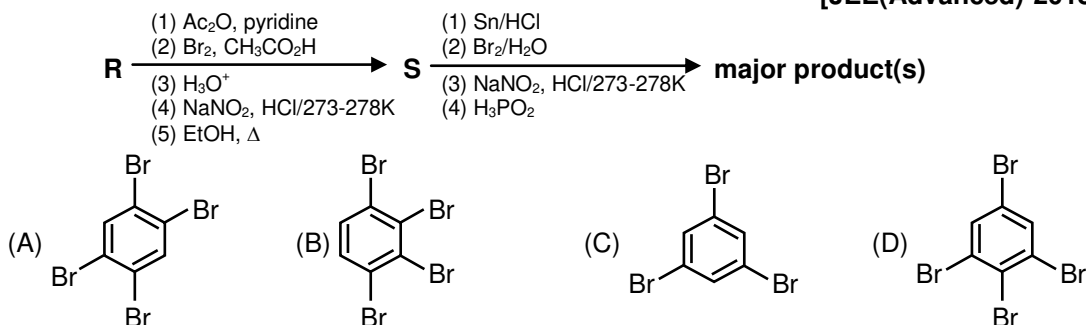
34.* The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

[JEE(Advanced)-2018, 4/120]



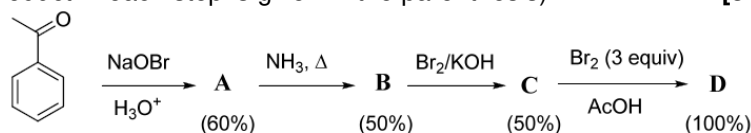
35.* Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give **P** (51%), **Q** (47%) and **R** (2%). The major product(s) of the following reaction sequence is (are)

[JEE(Advanced)-2018, 4/120]



36. In the following reaction sequence, the amount of **D** (in g) formed from 10 moles of acetophenone is..... (Atomic weights in g mol^{-1} : $\text{H} = 1$, $\text{C} = 12$, $\text{N} = 14$, $\text{O} = 16$, $\text{Br} = 80$. The yield (%) corresponding to the product in each step is given in the parenthesis)

[JEE(Advanced)-2018, 3/120]



PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEM

- Picric acid is [AIEEE-2002, 3/225]

(1) (2) (3) (4)
- When primary amine reacts with chloroform in ethanolic KOH then the product is: [AIEEE-2002, 3/225]

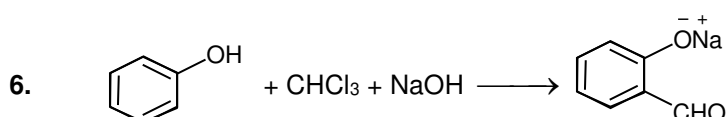
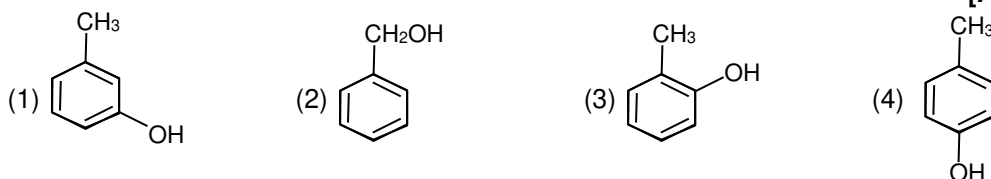
(1) an isocyanide. (2) an aldehyde. (3) a cyanide. (4) an alcohol.
- The reaction of chloroform with alcoholic KOH and p-toluidine forms : [AIEEE-2003, 3/225]

(1) (2) (3) (4)



4. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory [AIEEE-2006, 3/165]
 (1) from aniline by diazotisation followed by heating the diazonium salt with HF_4 .
 (2) by direct fluorination of benzene with F_2 gas.
 (3) by reacting bromobenzene with NaF solution.
 (4) by heating phenol with HF and KF .

5. The structure of the compound that gives a tribromo derivative on treatment with bromine water is : [AIEEE-2006, 3/165]



The electrophile involved in the above reaction is :

[AIEEE-2006, 3/165]

- (1) Dichloromethyl cation ($\overset{\oplus}{CH}Cl_2$) (2) Dichlorocarbene ($:CCl_2$)
 (3) Trichloromethyl anion ($\overset{\ominus}{CCl}_3$) (4) Formyl cation ($\overset{\oplus}{C}HO$)
7. In the chemical reaction, $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow (A) + (B) + 3H_2O$, the compounds (A) and (B) are respectively, [AIEEE-2007, 3/120]
 (1) C_2H_5NC and K_2CO_3 (2) C_2H_5NC and $3KCl$
 (3) C_2H_5CN and $3KCl$ (4) $CH_3CH_2CONH_2$ and $3KCl$

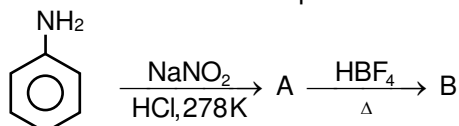
8. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives [AIEEE-2008, 3/105]
 (1) o-nitrophenol (2) p-nitrophenol (3) nitrobenzene (4) 2,4,6-trinitrobenzene

9. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains : [AIEEE-2008, 3/105]

- (1) mixture of o- and p-dibromobenzenes (2) mixture of o- and p-bromoanilines
 (3) mixture of o- and m-bromotoluenes (4) mixture of o- and p-bromotoluenes

10. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is : [AIEEE-2009, 4/144]
 (1) salicylaldehyde (2) salicylic acid (3) phthalic acid (4) benzoic acid

11. In the chemical reactions the compounds 'A' and 'B' respectively are : [AIEEE-2010, 4/144]

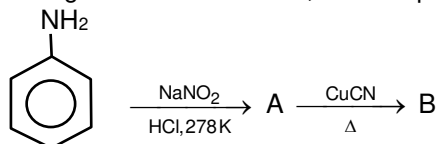


- (1) nitrobenzene and fluorobenzene
 (2) phenol and benzene
 (3) benzene diazonium chloride and fluorobenzene
 (4) nitrobenzene and chlorobenzene

12. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is : [AIEEE-2011, 4/144]
 (1) 2-Bromophenol (2) 3-Bromophenol
 (3) 4-Bromophenol (4) 2,4,6-Tribromophenol



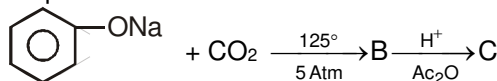
13. In the following chemical reactions, the compounds A and B are respectively : [AIEEE-2011, 4/144]



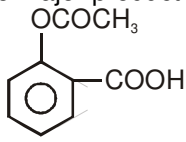
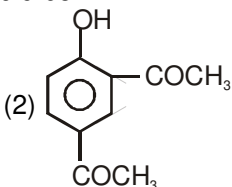
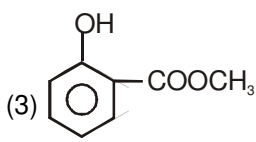
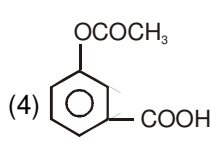
- (1) Benzene diazonium chloride and benzonitrile
 (2) Nitrobenzene and chlorobenzene
 (3) Phenol and bromobenzene
 (4) Fluorobenzene and phenol
14. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to give $\text{CH}_3\text{CH}_2\text{NH}_2$. A is : [JEE (Main) 2013, 4/120]

- (1) CH_3COOH (2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 (3) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$ (4) $\text{CH}_3\text{CH}_2\text{COOH}$

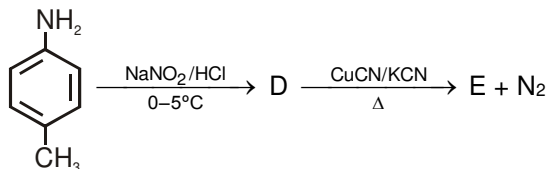
15. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C. [JEE(Main)-2014, 4/120]



The major product C would be :

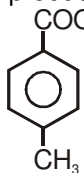
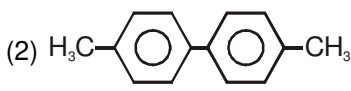
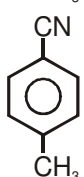
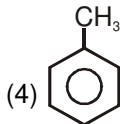
- (1)  (2)  (3)  (4) 

16. In the reaction



the product E is :

[JEE(Main)-2015, 4/120]

- (1)  (2) 
 (3)  (4) 

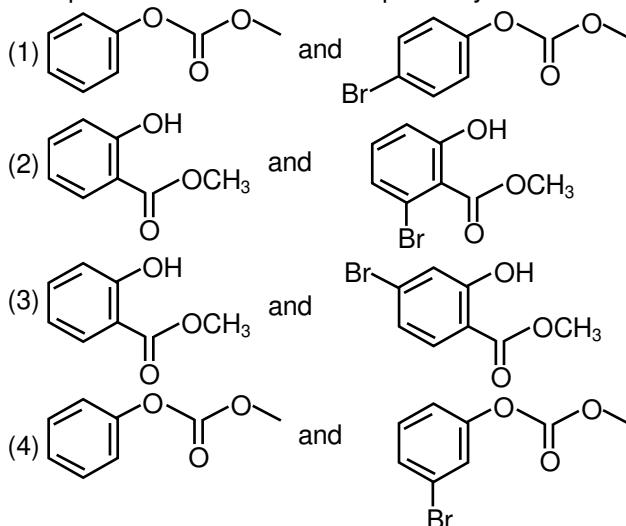
17. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : [JEE(Main)-2016, 4/120]
- (1) Four moles of NaOH and two moles of Br_2
 (2) Two moles of NaOH and two moles of Br_2
 (3) Four moles of NaOH and one mole of Br_2
 (4) One mole of NaOH and one mole of Br_2



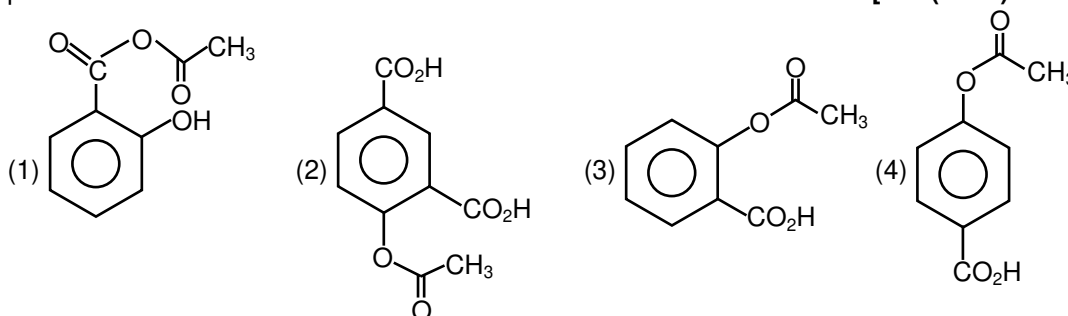
18. Which of the following compounds will form significant amount of *meta* product during mono-nitration reaction ? [JEE(Main)-2017, 4/120]



19. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br₂ to form product B. A and B are respectively : [JEE(Main)-2018, 4/120]

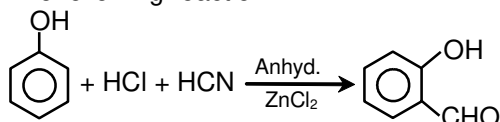


20. Phenol on treatment with CO₂ in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with (CH₃CO)₂O in the presence of catalytic amount of H₂SO₄ produces : [JEE(Main)-2018, 4/120]



JEE(MAIN) ONLINE PROBLEM

1. The following reaction



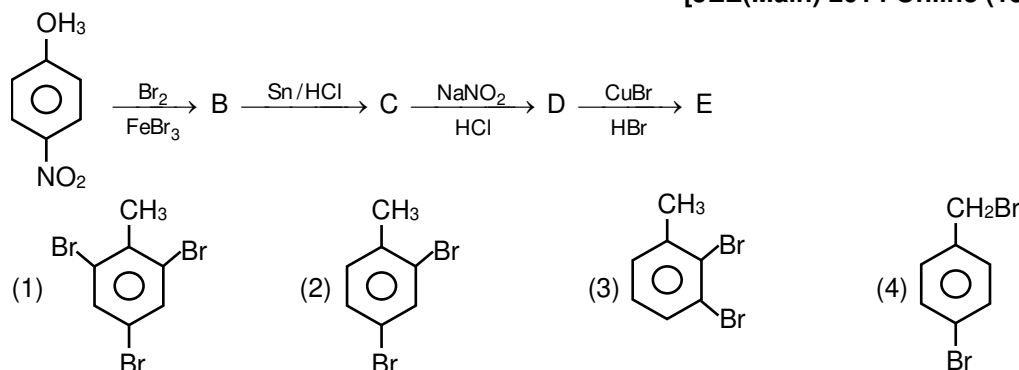
is known as :

- (1) Perkin reaction (2) Gattermann-Koch formylation
 (3) Kolbe's reaction (4) Gattermann reaction
2. Complete reduction of benzene-diazonium chloride with Zn/HCl gives : [JEE(Main) 2014 Online (11-04-14), 4/120]
- (1) Aniline (2) Phenylhydrazine
 (3) Azobenzene (4) Hydrazobenzene



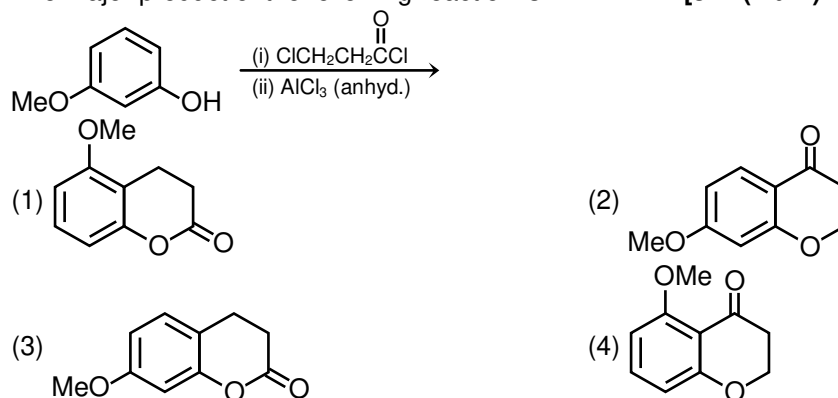
3. Conversion of benzene diazonium chloride to chloro benzene is an example of which of the following reactions? **[JEE(Main) 2014 Online (12-04-14), 4/120]**
 (1) Claisen (2) Friedel-craft (3) Sandmeyer (4) Wurtz

4. In a set of reactions p-nitrotoluene yielded a product E. The product E would be : **[JEE(Main) 2014 Online (19-04-14), 4/120]**

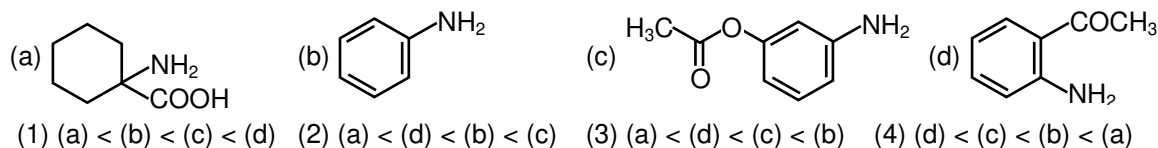


5. Fluorination of an aromatic ring is easily accomplished by treating a diazonium salt with HBF_4 . Which of the following conditions is correct about this reaction? **[JEE(Main) 2016 Online (10-04-16), 4/120]**
 (1) Only heat (2) NaNO_2/Cu (3) $\text{Cu}_2\text{O}/\text{H}_2\text{O}$ (4) NaF/Cu

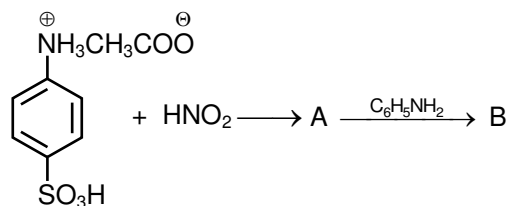
6. The major product of the following reaction is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

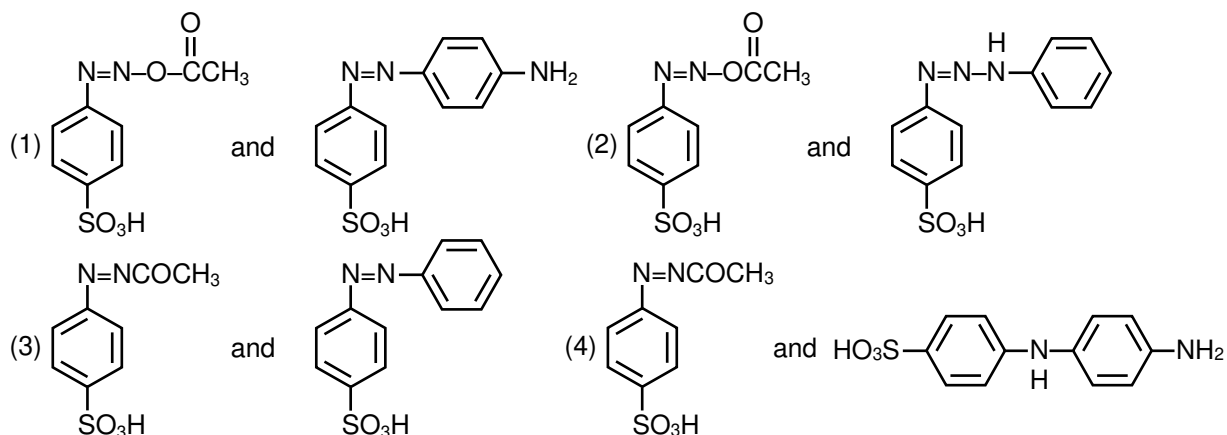


7. The increasing order of diazotization of the following compound is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**



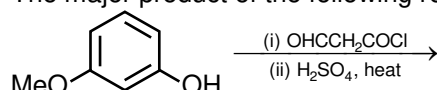
8. Products A and B formed in the following reactions are respectively : **[JEE(Main) 2018 Online (16-04-18), 4/120]**





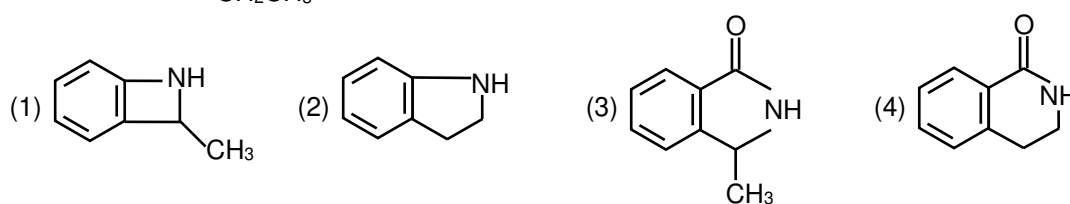
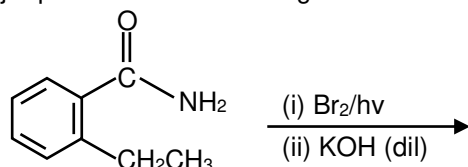
9. The major product of the following reaction is :

[JEE(Main) 2018 Online (16-04-18), 4/120]



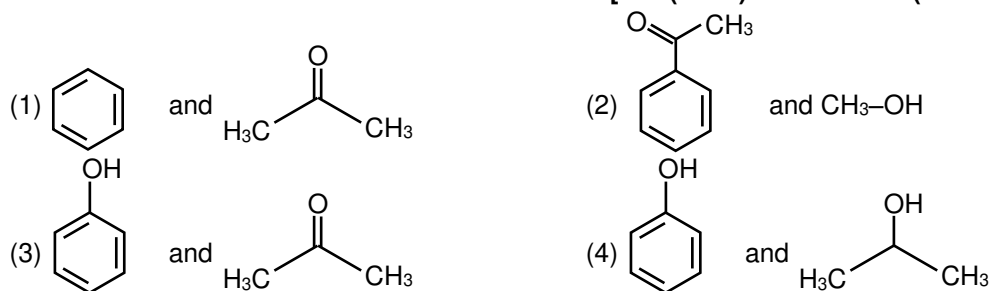
10. The major product of the following reaction is :

[JEE(Main) 2019 Online (09-01-19), 4/120]



11. The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are:

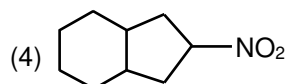
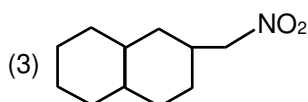
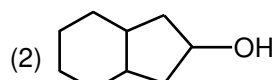
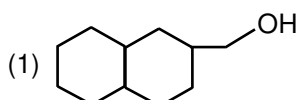
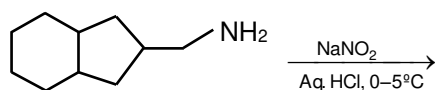
[JEE(Main) 2019 Online (09-01-19), 4/120]





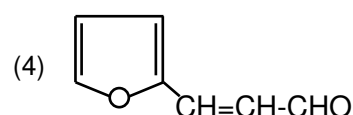
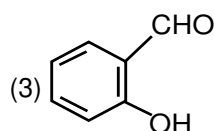
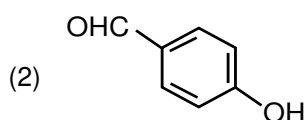
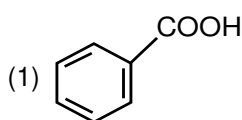
12. The major product formed in the reaction given below will be :

[JEE(Main) 2019 Online (10-01-19), 4/120]



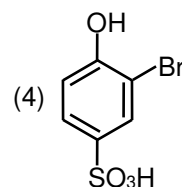
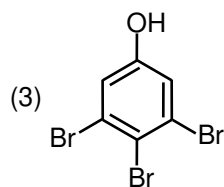
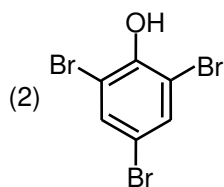
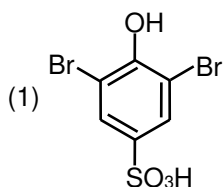
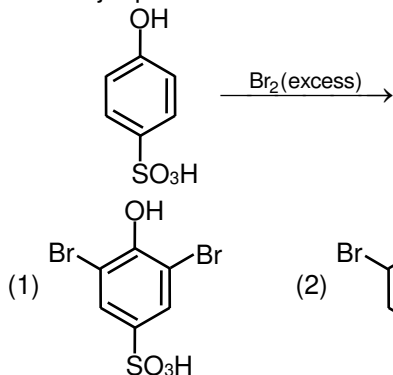
13. An aromatic compound 'A' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compounds 'B'. The compound B on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C_6H_7N . The structure of 'A' is:

[JEE(Main) 2019 Online (10-01-19), 4/120]



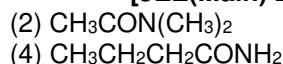
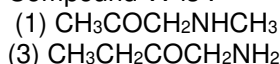
14. The major product of the following reaction is:

[JEE(Main) 2019 Online (11-01-19), 4/120]



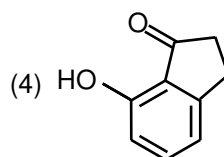
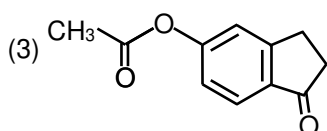
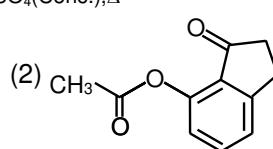
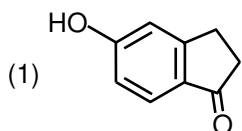
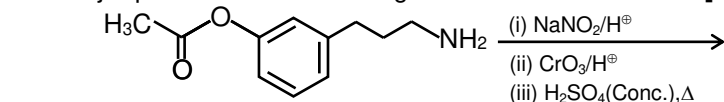
15. A compound 'X' on treatment with $Br_2/NaOH$, provided C_3H_9N , which gives positive carbylamine test. Compound 'X' is :

[JEE(Main) 2019 Online (11-01-19), 4/120]



16. The major product of the following reaction is:

[JEE(Main) 2019 Online (12-01-19), 4/120]

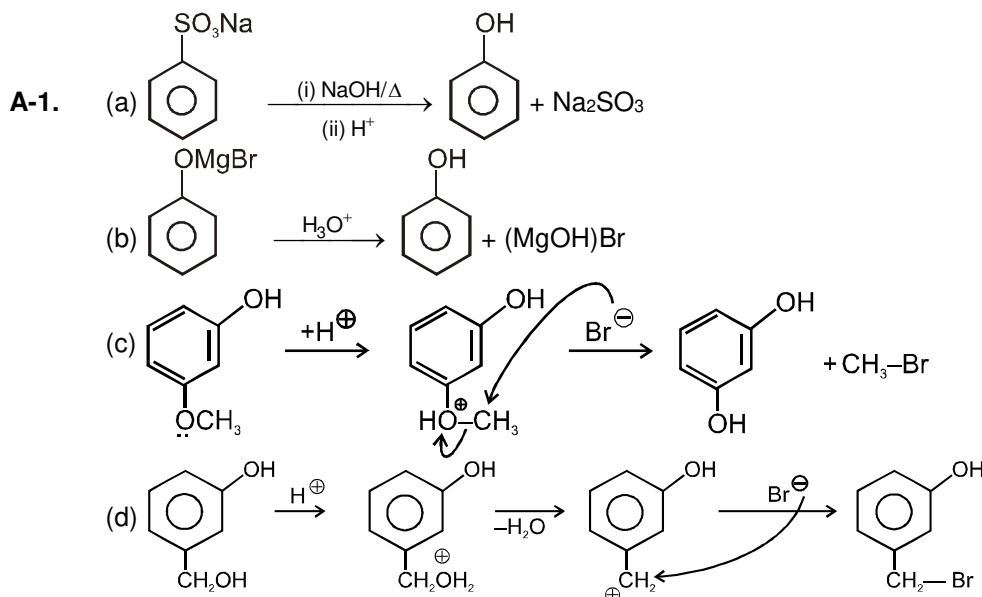




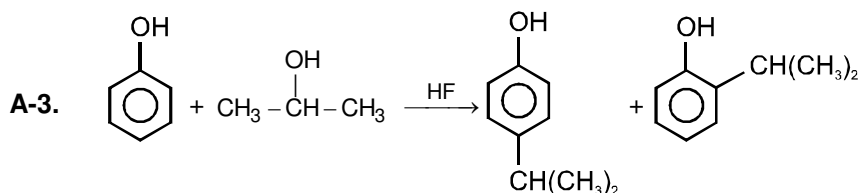
Answers

EXERCISE - 1

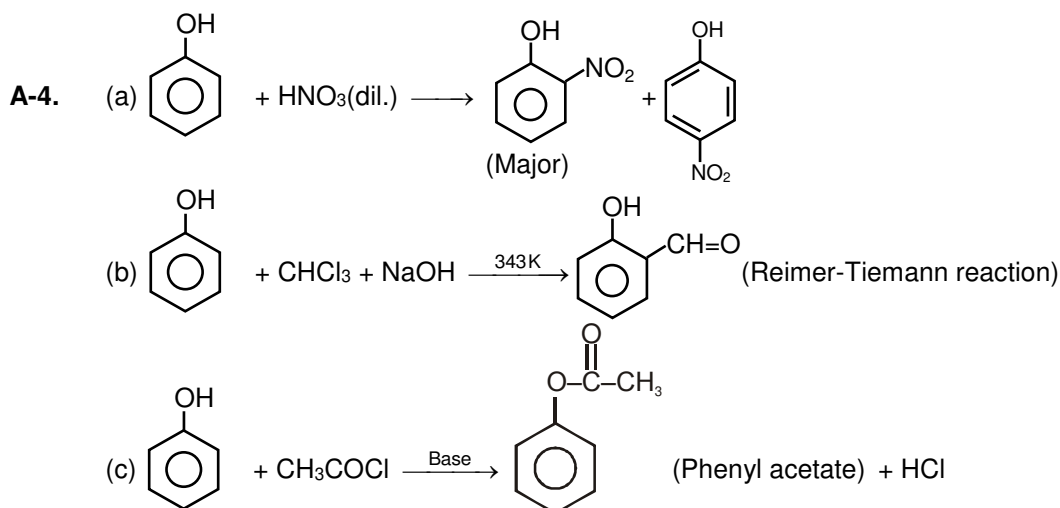
PART - I

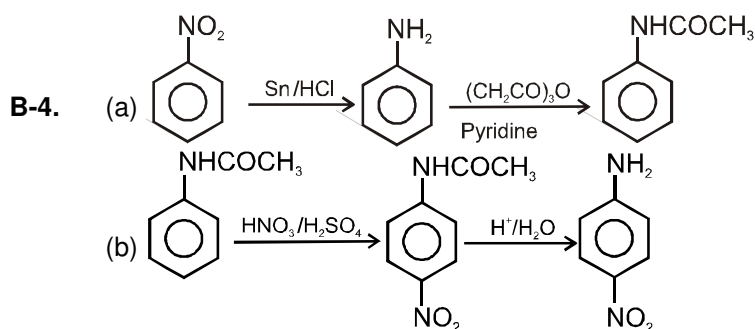
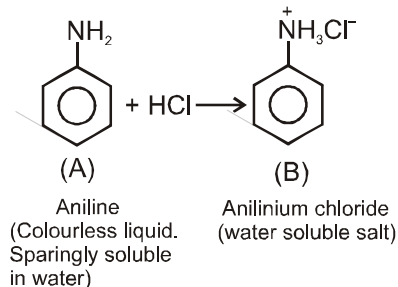
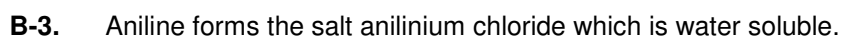
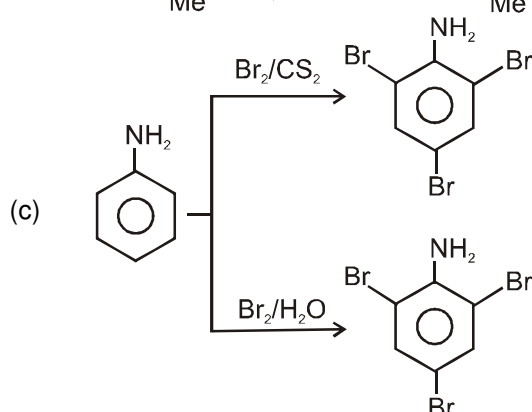
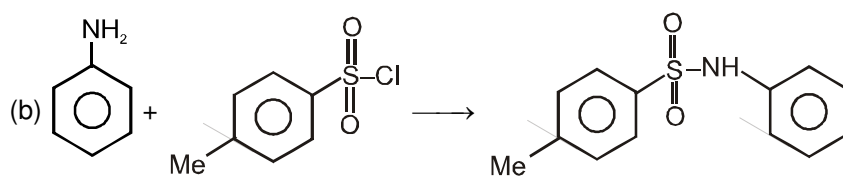
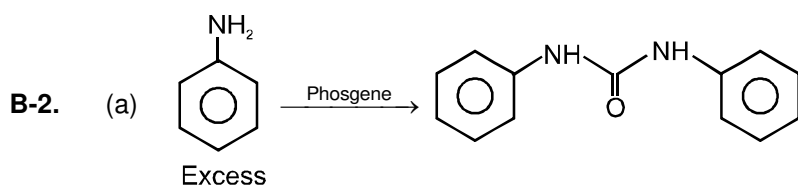
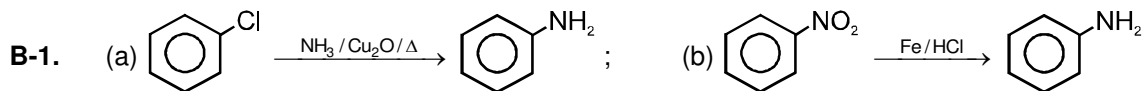
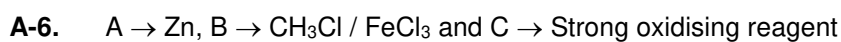
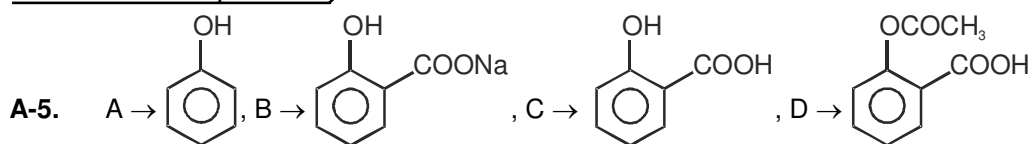


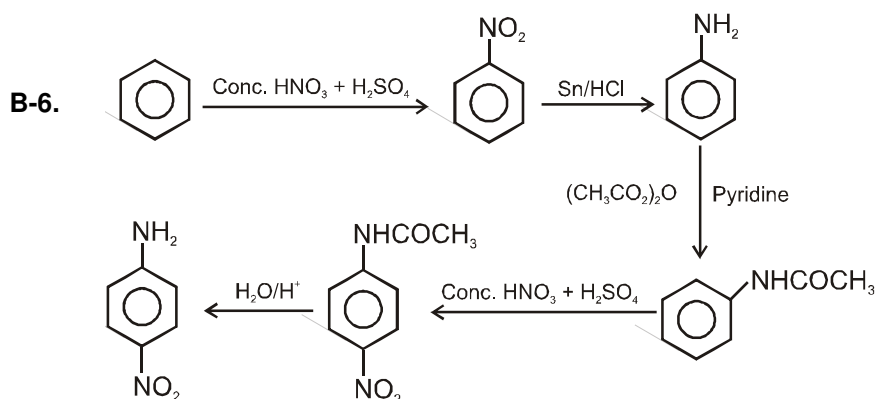
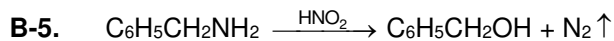
A-2. In phenol, aromatic ring is highly electron rich due to +M of -OH group. So nucleophile does not easily attack on the ring.



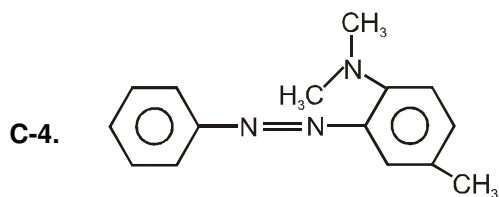
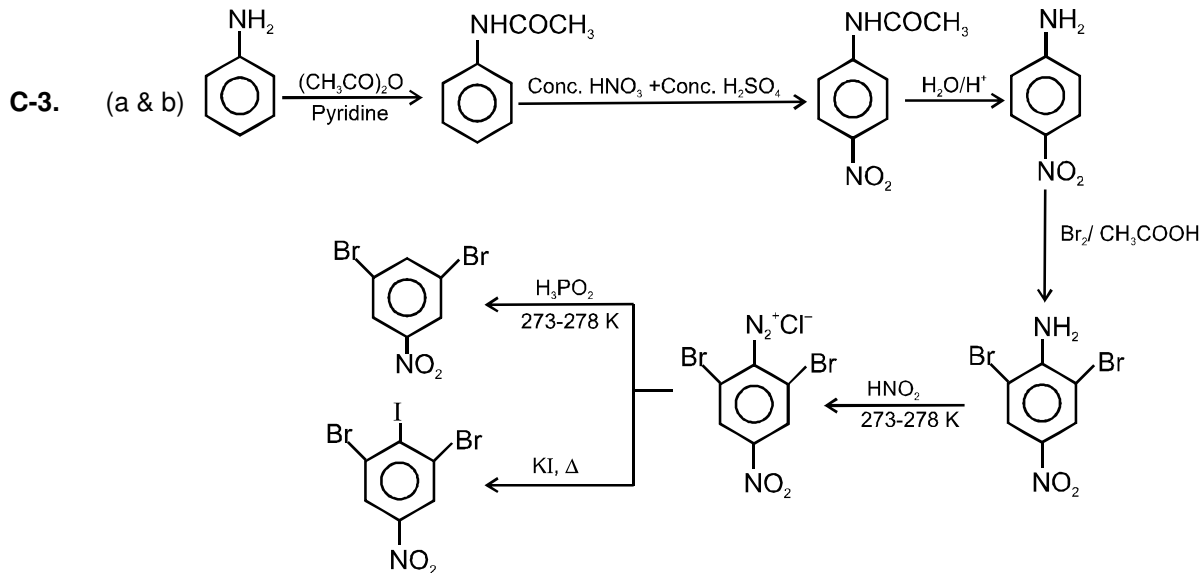
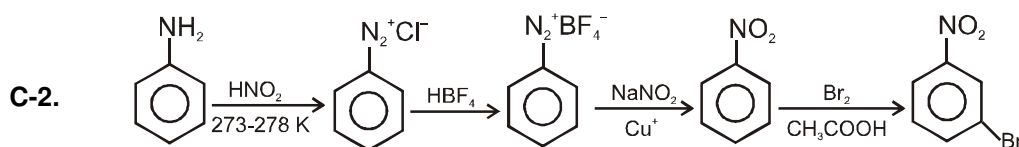
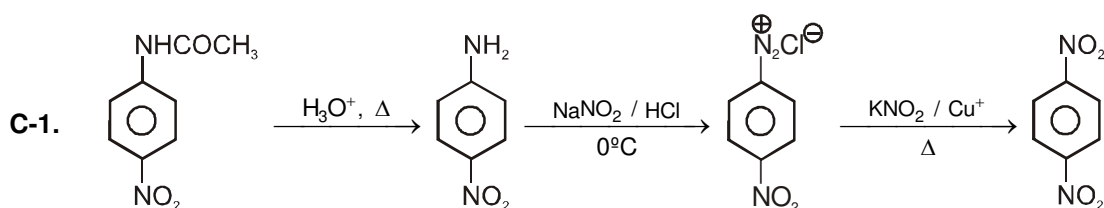
Phenols are highly reactive. Phenols are usually alkylated or acylated using relatively weak Friedel Crafts catalysts (such as HF) to avoid overalkylation.





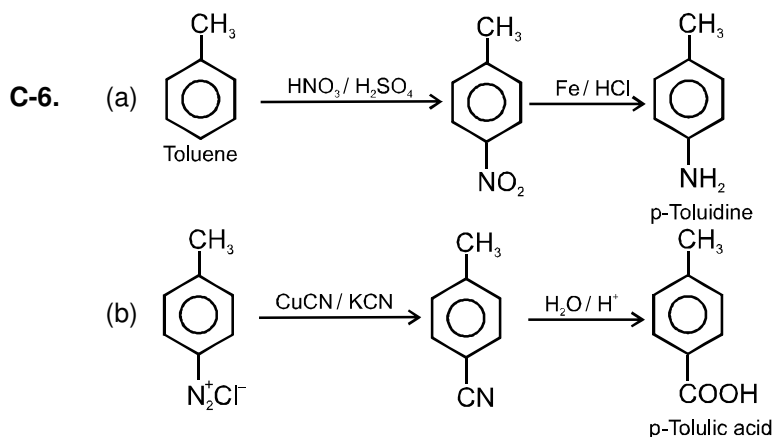
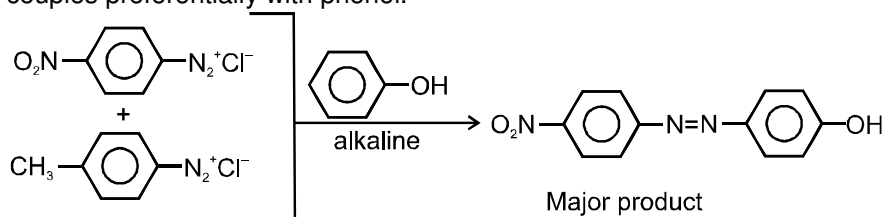


B-7. (i) Isocyanide test (ii) Hinsberg test (iii) $\text{NaNO}_2 + \text{HCl}$ test





- C-5.** This reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol generates phenoxide ion which is more electron rich than phenol and hence more reactive for electrophilic attack. The electrophile in this reaction is aryldiazonium cation. Stronger the electrophile faster is the reaction. *p*-Nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation. Therefore, it couples preferentially with phenol.



PART – II

- | | | | | |
|------------------|------------------|------------------|------------------|------------------|
| A-1. (B) | A-2. (C) | A-3. (D) | A-4. (B) | A-5. (D) |
| A-6. (B) | A-7. (B) | A-8. (D) | A-9. (C) | A-10. (A) |
| A-11. (C) | A-12. (B) | B-1. (C) | B-2. (B) | B-3. (B) |
| B-4. (A) | B-5. (D) | B-6. (B) | B-7. (B) | B-8. (D) |
| B-9. (D) | B-10. (B) | B-11. (B) | B-12. (C) | B-13. (B) |
| B-14. (D) | C-1. (B) | C-2. (C) | C-3. (C) | C-4. (D) |
| C-5. (D) | C-6. (B) | C-7. (D) | C-8. (B) | C-9. (A) |

PART – III

1. (A - r) ; (B - s) ; (C - p) ; (D - q) 2. (A - s) ; (B - r) ; (C - p) ; (D - q)
3. (A - q,s,t) ; (B - p, t) ; (C - q,t) ; (D - r,t)

EXERCISE – 2

PART – I

- | | | | | |
|---------|---------|--------|--------|---------|
| 1. (C) | 2. (D) | 3. (C) | 4. (D) | 5. (A) |
| 6. (A) | 7. (D) | 8. (B) | 9. (A) | 10. (A) |
| 11. (C) | 12. (A) | | | |



PART – II

- | | | | | |
|-------|----------------|-------|-------|--------------|
| 1. 75 | 2. 03 | 3. 94 | 4. 78 | 5. Zero (0). |
| 6. 99 | 7. 3 (1, 4, 9) | | | |

PART – III

- | | | | | |
|-----------|----------|----------|---------|-----------|
| 1. (ABCD) | 2. (AB) | 3. (BC) | 4. (AC) | 5. (ABCD) |
| 6. (ABCD) | 7. (BCD) | 8. (ACD) | 9. (BD) | 10. (BCD) |

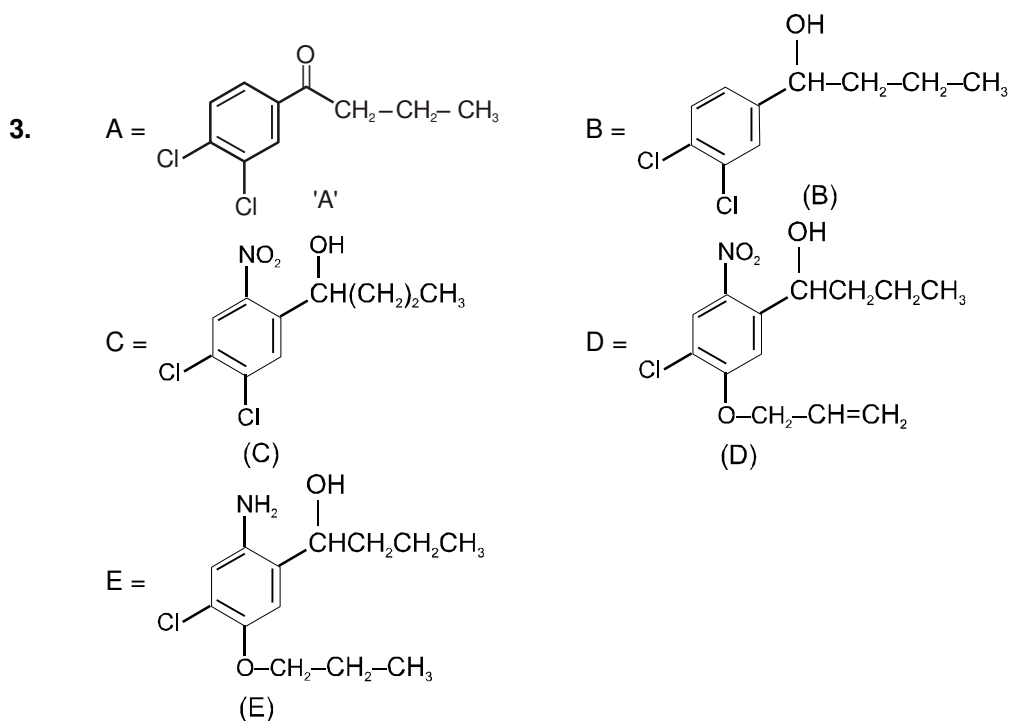
PART – IV

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (C) | 2. (B) | 3. (A) | 4. (A) | 5. (B) |
| 6. (D) | 7. (B) | 8. (B) | 9. (C) | 10. (B) |
| 11. (D) | 12. (A) | 13. (B) | 14. (D) | |

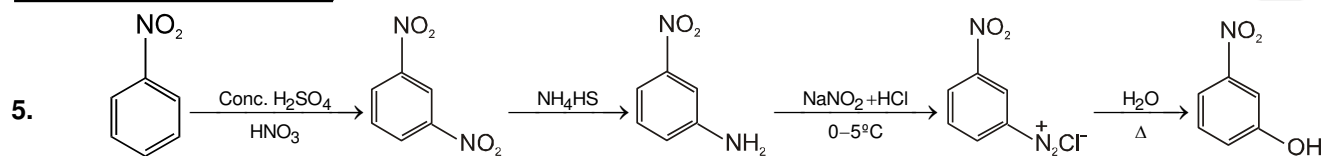
EXERCISE – 3

PART – I

1. (D)
2. Reagents are (1) NaOH / high temperature and pressure (2) Me₂SO₄ (3) conc. H₂SO₄ (4) Fusion with NaOH (5) H₃O⁺



4. (a) (i) Conc. H₂SO₄ (ii) KHF₂/Δ
 or (i) conc. HNO₃/H₂SO₄ (ii) Sn + HCl (iii) NaNO₂ + HCl & HBF₄/Δ
 (b) (i) NaOH + CO₂ (ii) H⁺ (iii) (CH₃CO)₂O



6. (A) H_2SO_4 (conc.), (B) Br_2 , (C) NO_2^\oplus , (D) Cc1c([N+](=O)[O-])cc([N+](=O)[O-])cc1[N+](=O)[O-] (T.N.T. = Trinitrotoluene)

7. (A) 8. (B) 9. (D) 10. (D) 11. (D)
 12. (C) 13. (C) 14. (B) 15. (AC)
 16. (A) - r, s ; (B) - t ; (C) - p, q ; (D) - r 17. (A) 18. (C) 19. (BD)
 20. (B) 21. (B) 22. (A) 23. (ABC) 24. (D)
 25. (C) 26. 4 27. (B) 28. (A) 29. (B)
 30. (BC) 31. (A) 32. (B) 33. (B) 34.* (ABD)
 35.* (D) 36. 495

PART – II

JEE(MAIN) OFFLINE PROBLEM

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (1) | 3. (4) | 4. (1) | 5. (1) |
| 6. (2) | 7. (2) | 8. (1) | 9. (4) | 10. (2) |
| 11. (3) | 12. (4) | 13. (1) | 14. (4) | 15. (1) |
| 16. (3) | 17. (3) | 18. (2) | 19. (1) | 20. (3) |

JEE(MAIN) ONLINE PROBLEM

- | | | | | |
|---------|-------------|---------|---------|---------|
| 1. (4) | 2. (1) | 3. (3) | 4. (2) | 5. (1) |
| 6. (3) | 7. (3) | 8. (1) | 9. (2) | 10. (3) |
| 11. (3) | 12. (Bonus) | 13. (1) | 14. (2) | 15. (4) |
| 16. (1) | | | | |



Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

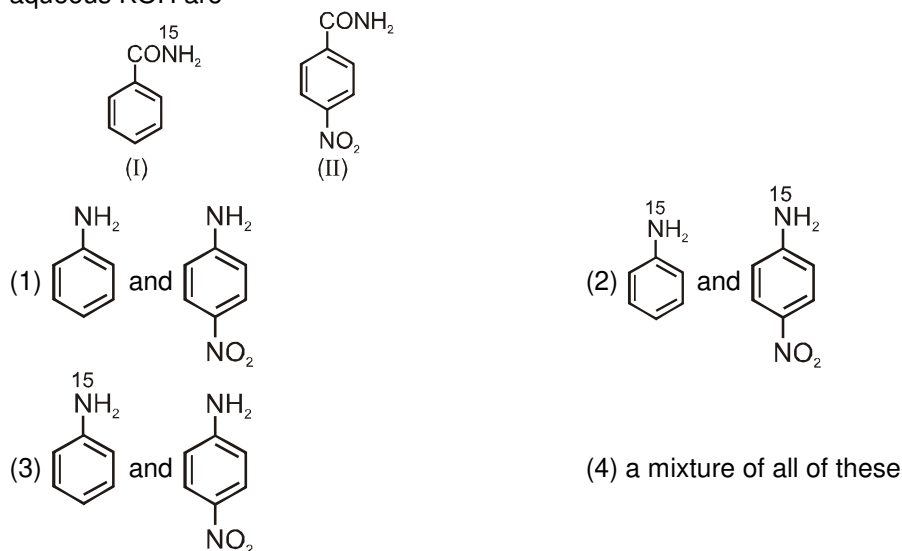
Max. Time : 1 Hr.

Max. Marks : 120

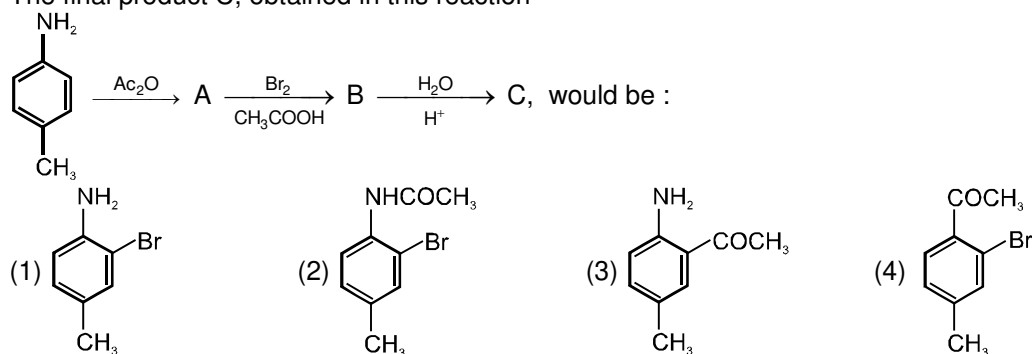
Important Instructions :

1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120**.
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **¼ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

1. The products formed when a mixture of the following two amides (I and II) are treated with bromine and aqueous KOH are

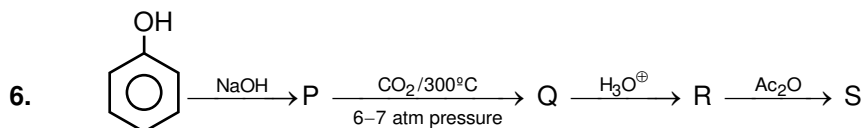
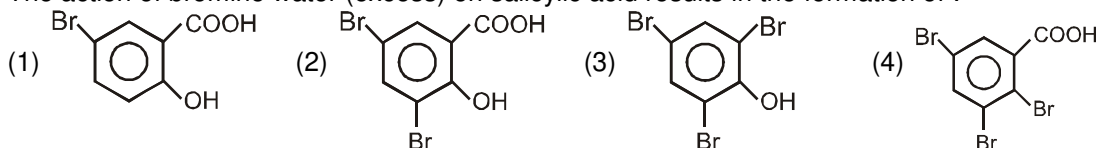


2. Which of the following does not give effervescence with NaHCO_3 ?
 (1) Phenol (2) p-Nitrophenol (3) 2, 4-dinitrophenol (4) 2, 4,6-trinitrophenol
3. The compound which does not give foul smell when heated with CHCl_3 & KOH is
 (1) m-Toluidine (2) $\text{CH}_3\text{-NH}_2$ (3) N-Methylaniline (4) $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
4. The final product C, obtained in this reaction



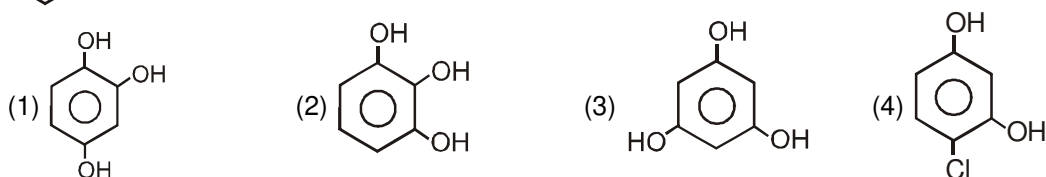
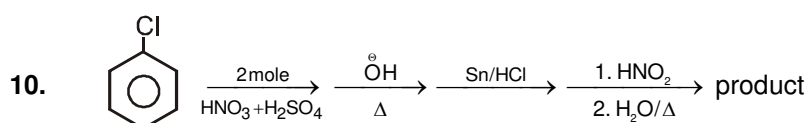
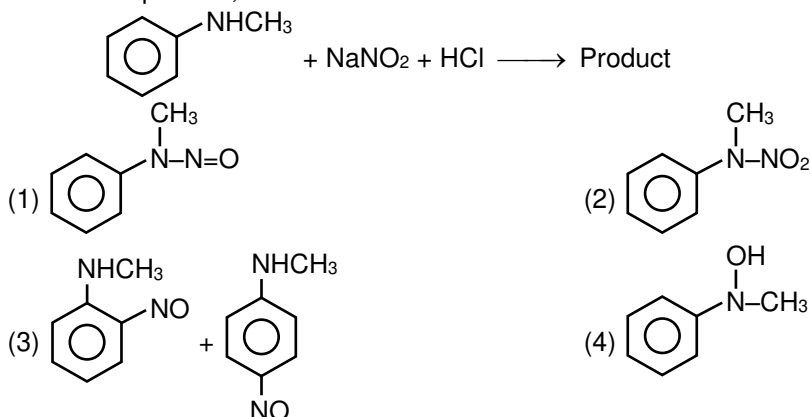


5. The action of bromine water (excess) on salicylic acid results in the formation of :

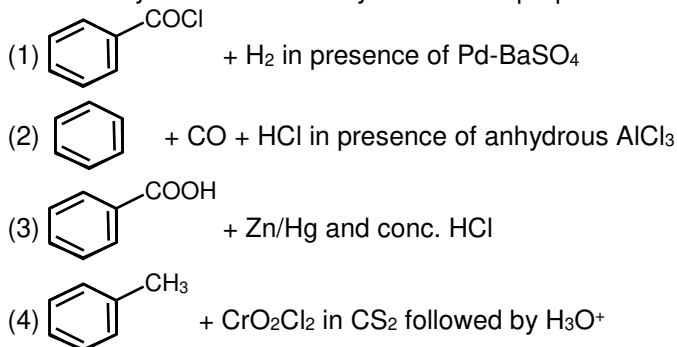


'S' is :

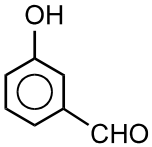
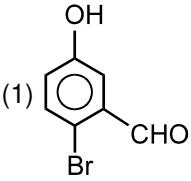
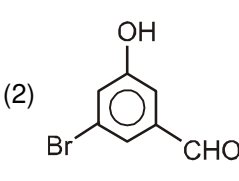
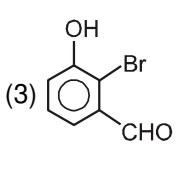
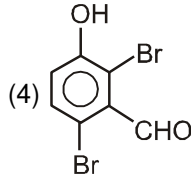
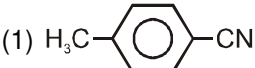
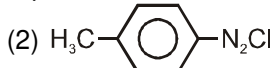
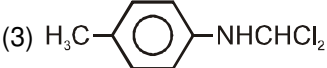

- (1) Aspirin (2) Valine (3) Cumene (4) Salicylic acid
7. Electrolytic reduction of nitrobenzene in weakly acidic medium gives.
 (1) aniline (2) nitrosobenzene
 (3) N-phenyl hydroxylamine (4) p-hydroxyaniline
8. In the following reaction, X $\xrightarrow{\text{Bromination}}$ Y $\xrightarrow[\text{HCl}]{\text{NaNO}_2}$ Z $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Boiling}}$ Tribromobenzene, X is
 (1) benzoic acid (2) salicylic acid (3) phenol (4) aniline
9. Predict the product,



11. Reaction by which Benzaldehyde cannot be prepared :

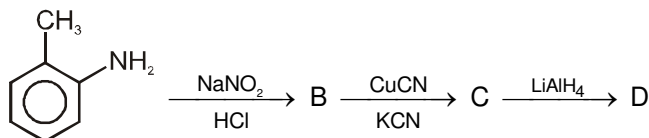




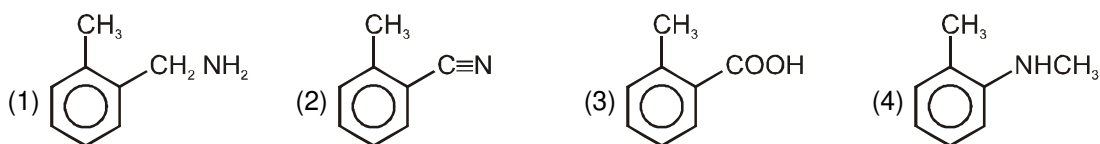
12.  $\xrightarrow{\text{Br}_2, \text{Fe}}$ P (Major)
- (1)  (2)  (3)  (4) 
13. The reaction of chloroform with alcoholic KOH and p-toluidine form :
- (1)  (2) 
 (3)  (4) 
14. An organic compound P on reduction gives compound Q which on reaction with chloroform and potassium hydroxide forms R. The compound R on catalytic reduction gives N-methylaniline. The compound P is
 (1) nitrobenzene (2) nitromethane (3) methylamine (4) aniline
15. Primary amine reacts with carbon disulphide and HgCl_2 to produce alkyl isothiocyanate. This reaction is:
 (1) Carbylamine reaction (2) Hofmann bromide reaction
 (3) Perkin reaction (4) Hofmann mustard oil reaction
16. When aniline reacts with HNO_2 ($\text{NaNO}_2 + \text{HCl}$) diazonium chloride is formed which on reaction with H_3PO_2 gives :
 (1) $\text{CH} \equiv \text{CH}$ (2) C_6H_6 (3) $\text{CH}_2 = \text{CH}_2$ (4) $\text{CH}_3 - \text{CH}_3$
17. Aniline reacts with to yield as the final product
 (1) Aqueous bromine, 2-bromoaniline (2) Aqueous bromine, 2, 4, 6-tribromoaniline
 (3) chloroform/KOH, phenyl cyanide (4) acetyl chloride, benzanilide
18. Which of following statements is/are correct ?
 (1) 1° , 2° & 3° amines can be distinguished by Hinsberg reagent.
 (2) Phenol does not give Lucas test.
 (3) Phenol & alcohols can be distinguished by neutral FeCl_3
 (4) All of these
19. Which of following statements is/are correct ?
 (1) In Reimer-Tiemann reaction, dichlorocarbene intermediate is produced.
 (2) Reimer-Tiemann reaction is example of electrophilic substitution reaction.
 (3) Highly reactive ring like aniline & highly deactivated ring like nitrobenzene, cyanobenzene do not give Friedel Craft reaction.
 (4) All of these
20. Aniline can be obtained by reduction of nitrobenzene with
 (1) Fe / HCl (2) Sn / NaOH
 (3) Electrolytic reduction under strong acidic conditions (4) All.
21. Which of the following undergoes mustard oil reaction ?
 (1) Primary amines (2) Secondary amines
 (3) Tertiary amines (4) All the above
22. $\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{AgCN}} \text{P} \xrightarrow{\text{H}_3\text{O}^+} \text{HCOOH} + \text{Q}$;
 Q is :
 (1) $\text{CH}_3 - \text{CH}_2\text{CONH}_2$ (2) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{N}$ (3) $\text{CH}_3 - \text{CH}_2 - \text{NH}_2$ (4) $\text{CH}_3 - \text{COOH}$



23. In this reaction



D would be



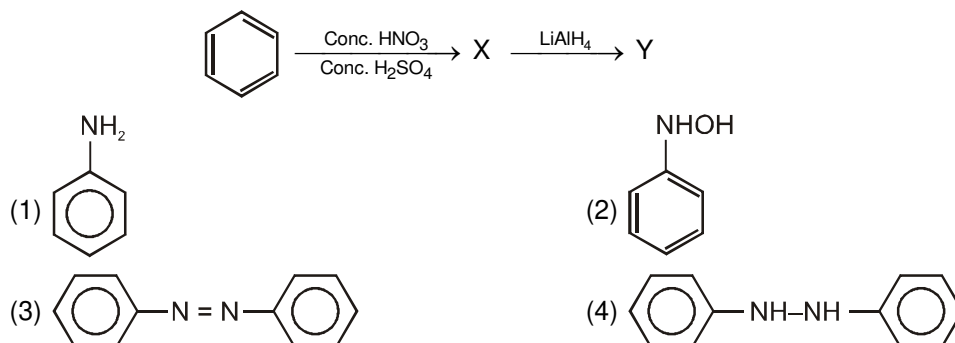
24. $\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \longrightarrow \text{C}_6\text{H}_5\text{NHCOC}_6\text{H}_5 + \text{HCl}$. This reaction is called

- (1) Schotten Baumann reaction (2) Perkin reaction
(3) Schmidt reaction (4) Claisen reaction

25. A positive carbylamine test is not given by :

- (1) N, N-dimethylaniline (2) 2, 4-Dimethylaniline
(3) 2-Methyl-4-ethylaniline (4) p-Methylbenzyl amine

26. The product 'Y' in the following reaction sequence is :

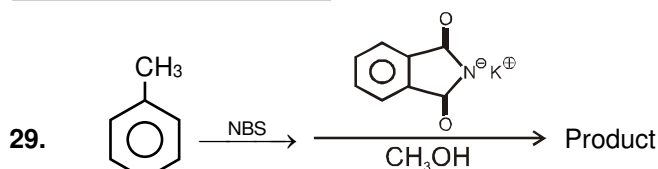


27. $\text{Ph-NH}_2 \xrightarrow[0^\circ\text{C}]{\text{HNO}_2} \text{A} \xrightarrow[\text{BF}_3]{\text{HF}} \text{B} \xrightarrow{\Delta} \text{C}$, C is :

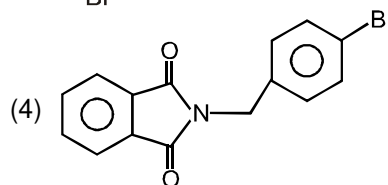
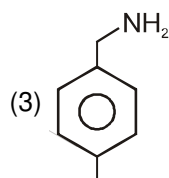
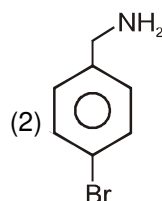
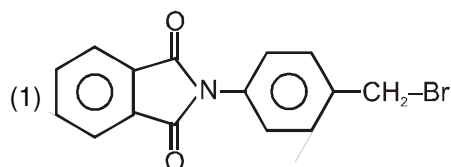
- (1) $\text{Ph-N} \equiv \text{N}^+ \text{BF}_4^-$ (2)
(3) (4) Ph-F

28. $\xrightarrow{\text{CH}_3\text{I, NaOH}}$ product

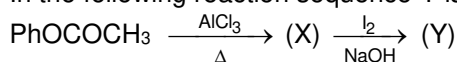
- (1) (2)
(3) (4)



Structure of product is

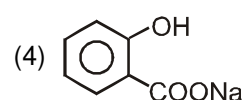
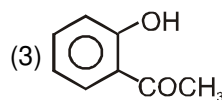


30. In the following reaction sequence Y is :



(1) PhCOONa

(2) PhCOOH



Practice Test-1 (IIT-JEE (Main Pattern))

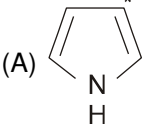
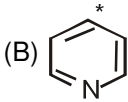
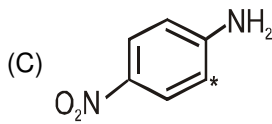
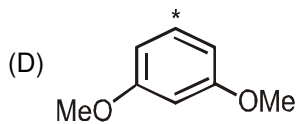
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

- Compound A is chiral and has the molecular formula $\text{C}_8\text{H}_{11}\text{N}$. When A reacts with nitrous acid then occurs a brisk evolution of N_2 gas. A dissolves in aqueous HCl . What is the identity of A ? [NSEC-2000]
 (A) 2-phenylethanamine (B) 1-phenylethanamine
 (C) 1-cyclohexylethanamine (D) N-ethylaniline
- What single isomer would be found in greatest yield when isopropyl chloride undergoes a Friedel-Crafts alkylation with t-butylbenzene ? [NSEC-2000]
 (A) p-isopropyl-t-butylbenzene (B) m-isopropyl-t-butylbenzene
 (C) o-isopropyl-t-butylbenzene (D) none of these
- The number of π molecular orbitals completely filled in the ground state of benzene is : [NSEC-2000]
 (A) three (B) one (C) six (D) none



4. An organic compound 'A' having molecular formula C_2H_3N on reduction gave another compound 'B'. Upon treatment with nitrous acid, 'B' gave ethyl alcohol on warming with chloroform and alcoholic KOH, it formed an offensive smelling compound 'C'. The compound 'C' is : **[NSEC-2001]**
 (A) $CH_3C\equiv N$ (B) $CH_3CH_2N\equiv C$ (C) $CH_3CH_2NH_2$ (D) CH_3CH_2OH
5. The compound which reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine **[NSEC-2002]**
 (A) ammonia (B) methylamine (C) dimethylamine (D) trimethylamine
6. p-Chlorobenzoic acid can be prepared by reacting p-aminobenzoic acid with **[NSEC-2002]**
 (A) HCl (B) Cu_2Cl_2
 (C) Cl_2 in presence of $AlCl_3$ (D) HNO_2 , followed by hot solution of Cu_2Cl_2 .
7. n-propylamine containing no secondary and tertiary amines as impurities is prepared by **[NSEC-2002]**
 (A) Hoffmann synthesis (B) Gabriel synthesis
 (C) reacting n-propylchloride with ammonia (D) none of these
8. The most favourable position (indicated by) for an electrophilic attack is **[NSEC-2003]**
 (A)  (B)  (C)  (D) 
9. The compound that on treatment with benzene sulphonyl chloride, forms a precipitate soluble in alkali, is **[NSEC-2003]**
 (A) $(C_2H_5)_2NH$ (B) $C_6H_5NHCOCH_2CH_3$
 (C) $C_6H_5-CH_2-NH_2$ (D) CH_3-CONH_2 .
10. The substance that gives a primary amine on hydrolysis is **[NSEC-2004]**
 (A) nitroparaffin (B) alkyl cyanide (C) oxime (D) alkyl isocyanide.
11. Toluene o/p orienting with respect to an electrophilic substitution reaction due to **[NSEC-2004]**
 (A) +I effect of the methyl group
 (B) +I as well as +M effect of the methyl group
 (C) hyperconjugation between the methyl group and the phenyl ring
 (D) +M effect to the methyl group.
12. The product obtained when 4-hydroxybenzene sulphonic acid is treated with an excess of bromine water is **[NSEC-2004]**
 (A) 2-bromo-4-hydroxybenzene sulphonic acid
 (B) 2,3-dibromo-4-hydroxybenzene sulphonic acid
 (C) 2,6-dibromo-4-hydroxybenzene sulphonic acid
 (D) 2,4,6-tribromophenol.
13. The most appropriate reaction for the conversion of bromobenzene to benzoic acid is **[NSEC-2005]**
 (A) Reimer-Tiemann reaction (B) Grignard reagent
 (C) Claisen rearrangement (D) Friedel-Crafts reaction.
14. p-bromoaniline is prepared from aniline via **[NSEC-2005]**
 (A) direct bromination of aniline in presence of Lewis acid
 (B) bromination of acetanilide followed by hydrolysis
 (C) direct bromination of aniline in presence of light
 (D) amination of bromine.
15. Which one of the following has the highest melting point ? **[NSEC-2005]**
 (A) Phenol (B) para - Nitrophenol
 (C) meta - Nitrophenol (D) ortho - Nitrophenol.
16. On bromination, the electron rich phenoxide ion will be attacked most readily **[NSEC-2006]**
 (A) on the negatively charged oxygen atom (B) on the ortho and para carbon atoms
 (C) on the meta carbon atom (D) on the ortho carbon atom.



17. thiophene I, furan II, pyrrole III
The sequence of decreasing aromaticity in the above compounds is
(A) I > II > III (B) I > III > II (C) II > III > I (D) III > II > I. [NSEC-2006]
18. Can the amino group, in the aniline molecule, become meta-directing in an electrophilic substitution reaction?
(A) No, it never shows meta directing properties.
(B) Yes, in a strongly acidic medium.
(C) Yes, in a strongly alkaline medium.
(D) Yes, in a non-polar solvent. [NSEC-2006]
19. Consider the following reactions

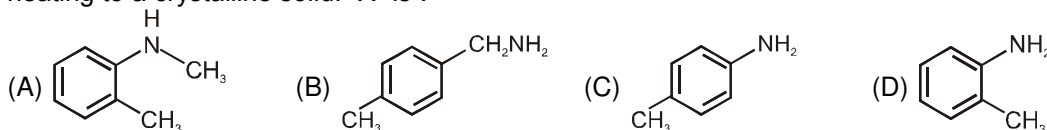
$$\text{C}_6\text{H}_6 + \text{CH}_2=\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \xrightarrow[\text{heat}]{\text{H}^+} \text{X} \xrightarrow{\text{NaOH(aq)}} \text{Y}$$
 the major product (Y) of the reaction is : [NSEC-2007]
- (A)
 (B)
 (C)
 (D)
20. The product of Reimer-Tiemann reaction is a
(A) phenolic aldehyde (B) hydroxyamine (C) nitroaldehyde (D) nitroalcohol [NSEC-2008]
21. The nitrogen atom in the following cyclic compounds can be removed as trimethylamine by successive Hoffmann eliminations (involving exhaustive methylation followed by heating with AgOH). The amine which will require a greater number of Hoffmann eliminations is : [NSEC-2009]
- (A)
 (B)
 (C)
 (D)
22. $\text{X} \xrightarrow[\text{ether}]{\text{Mg}} \text{Y} \xrightarrow[\text{H}^+]{\text{Dry CO}_2} \text{Z} \xrightarrow{\text{hot KMnO}_4} \text{P}$ [NSEC-2009]
 The two isomeric compounds which will give the same tricarboxylic acid after the above sequence of reactions, are :
- I, II, III, IV
 (A) I and II (B) III and IV (C) I and IV (D) II and III
23. Salicylic acid on treatment with bromine water will give [NSEC-2013]
 (A) 2-bromo-6-hydroxybenzoic acid (B) 2,4,6-tribromophenol
 (C) 2,6-dibromobenzoic acid (D) 1,3-dibromo-6-hydroxybenzoic acid
24. The product P obtained through the following sequence of reactions is [NSEC-2014]

$$\text{C}_6\text{H}_6 \xrightarrow[\text{conc. H}_2\text{SO}_4, \text{ warm}]{\text{conc. HNO}_3} \text{L} \xrightarrow[\text{heat}]{\text{Br}_2, \text{Fe}} \text{M} \xrightarrow{\text{Sn/HCl}} \text{N} \xrightarrow[\text{ii) Cu}_2\text{Cl}_2]{\text{i) NaNO}_2, \text{HCl}} \text{P}$$
- (A) 3-chloroaniline (B) 4-bromochlorobenzene
 (C) 3-bromochlorobenzene (D) 3-bromoaniline

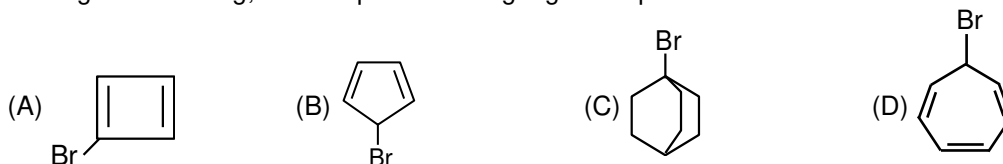


25. Triethylamine is reacted with a peracid to obtain X. The nitrogen atom in X has formal charge
 (A) 0 (B) +1 (C) -1 (D) +2 [NSEC-2014]

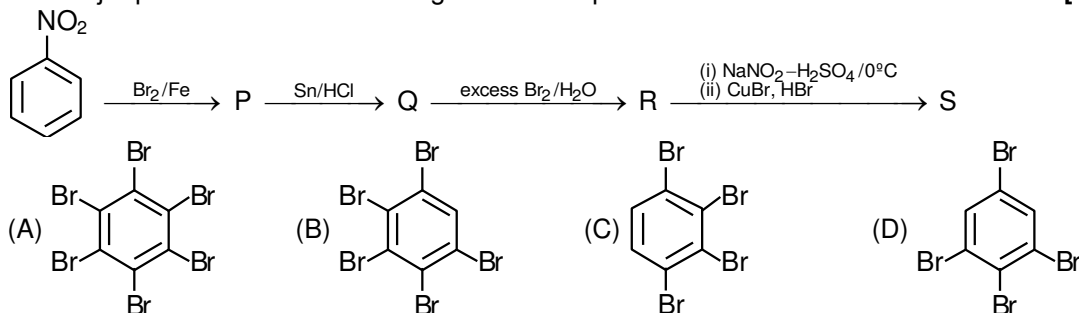
26. An organic base (X) reacts with nitrous acid at 0°C to give a clear solution. Heating the solution with KCN and cuprous cyanide followed by continued heating with conc. HCl gives a crystalline solid. Heating this solid with alkaline potassium permanganate gives a compound which dehydrates on heating to a crystalline solid. "X" is : [NSEC-2015]



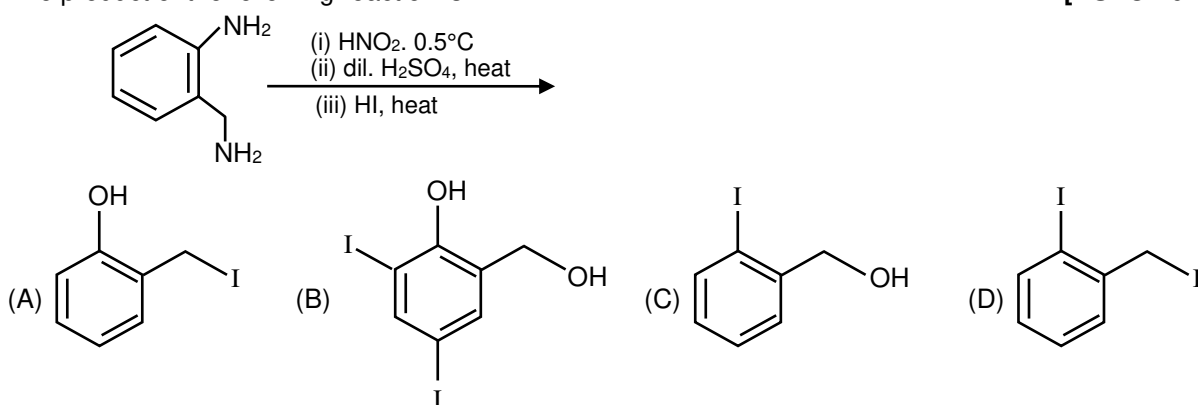
27. Organic compounds sometimes adjust their electronic as well as steric structures to attain stability. Among the following, the compound having highest dipole moment is : [NSEC-2016]



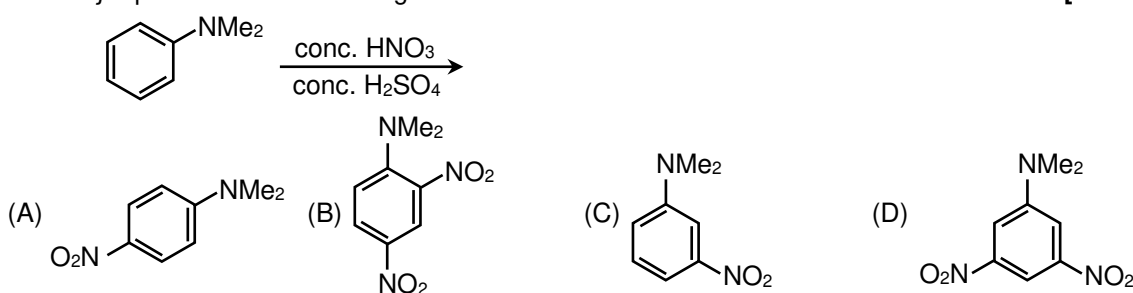
28. The major product 'S' of the following reaction sequence is : [NSEC-2016]



29. The product of the following reaction is [NSEC-2017]

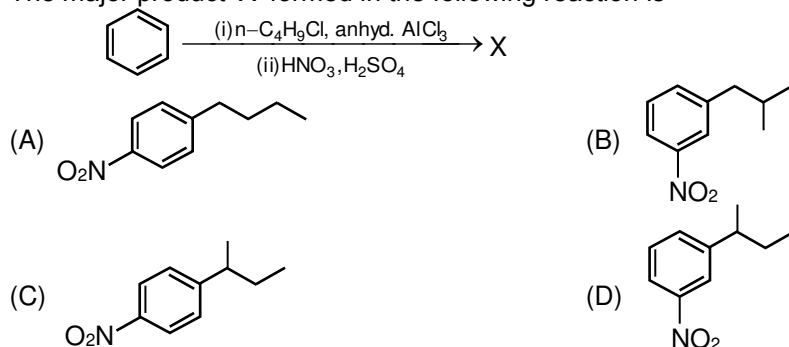


30. The major product of the following reaction is [NSEC-2018]





31. The major product 'X' formed in the following reaction is



PART - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 60

Important Instructions

A. General

1. The test is of 1 hour duration.
2. The Test Booklet consists of 21 questions. The maximum marks are 63.

B. Question Paper Format

3. Each part consists of five sections.
4. Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 3 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section-4 contains 2 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).

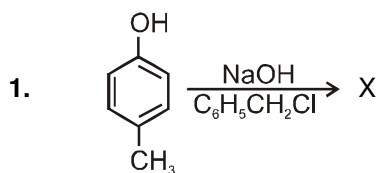
C. Marking Scheme

8. For each question in Section 1 and 4 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
9. For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
10. For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

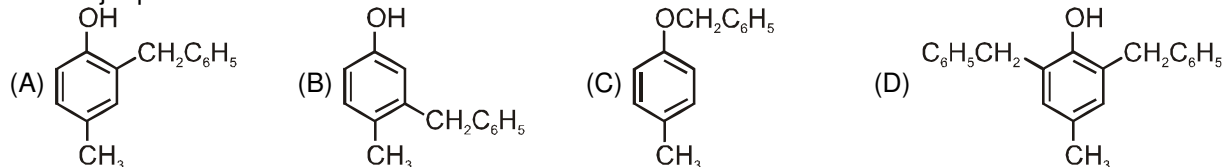


SECTION-1 : (Only One option correct Type)

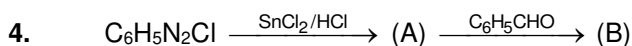
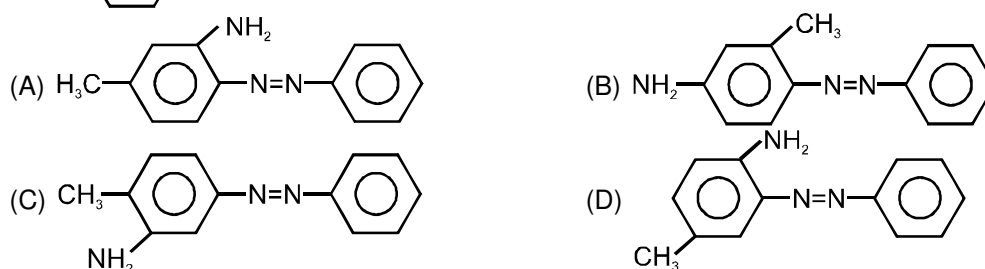
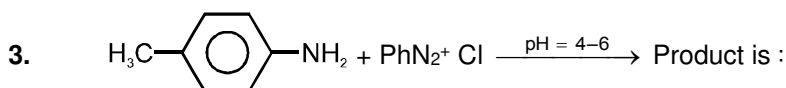
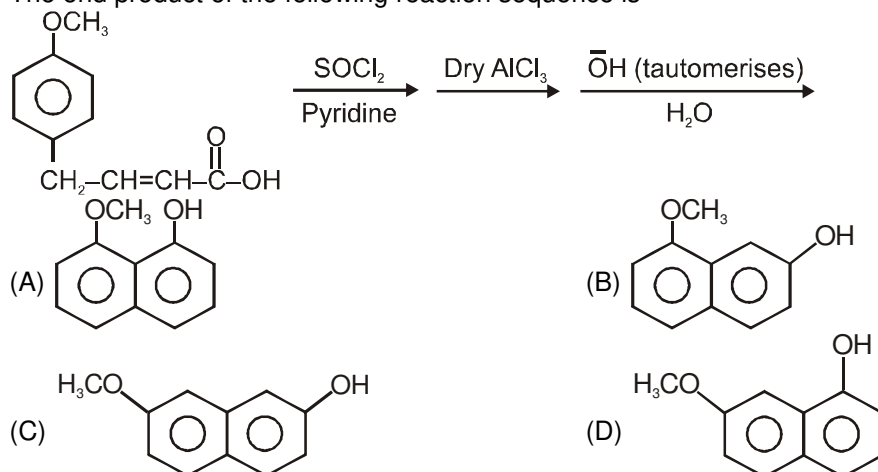
This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.



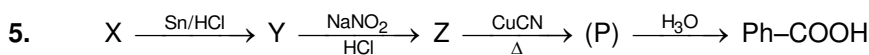
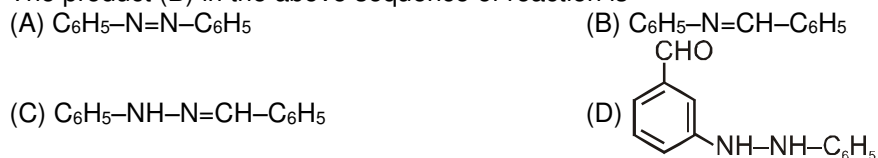
The major product X in the above reaction is



2. The end product of the following reaction sequence is



The product (B) in the above sequence of reaction is



correct options is/are :

- (A) X is Ph-NH_2 (B) Y is Ph-NO_2 (C) Z is Ph-NH_2 (D) P is Ph-CN



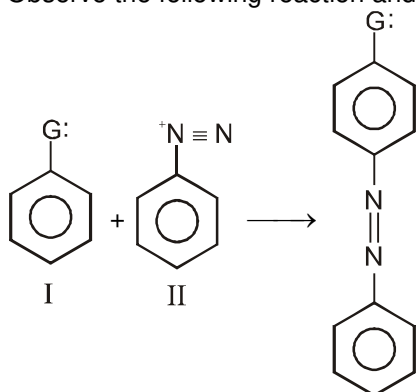
6. Product is
- (A) (B) (C) (D)
7. Which of the following is **incorrect** :
- (A) (B) (C) (D)

Section-2 : (One or More than one options correct Type)

This section contains 7 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

- 8.
- (A) Compound S = (B) Compound W = (C) Compound T = (D) Compound Q =

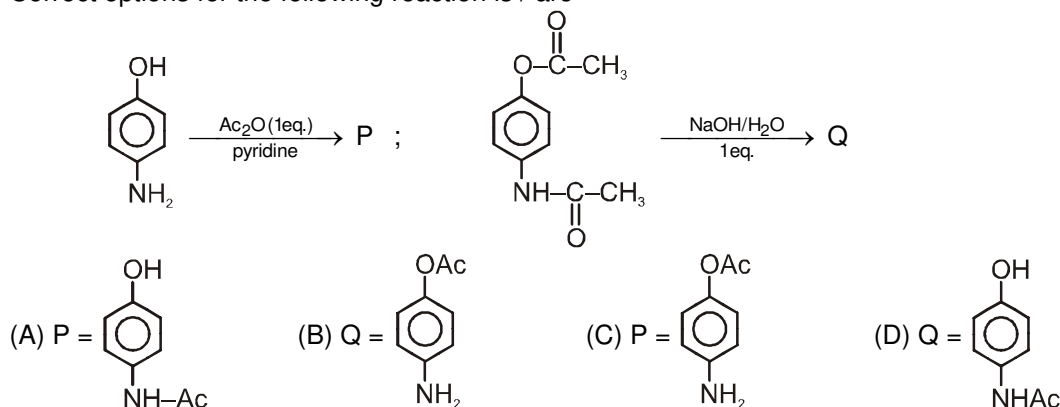
9. Observe the following reaction and determine True statement



- (A) If aromatic ring I have $-\text{NO}_2$ group then rate of reaction will decrease.
 (B) If aromatic ring II have $-\text{NO}_2$ group then rate of reaction will increase.
 (C) In this reaction Wheland intermediate will form.
 (D) In this reaction Meisenheimer intermediate is formed.



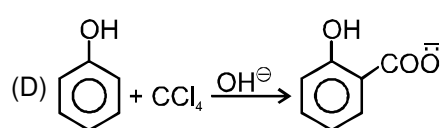
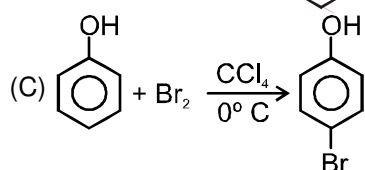
10. Correct options for the following reaction is / are



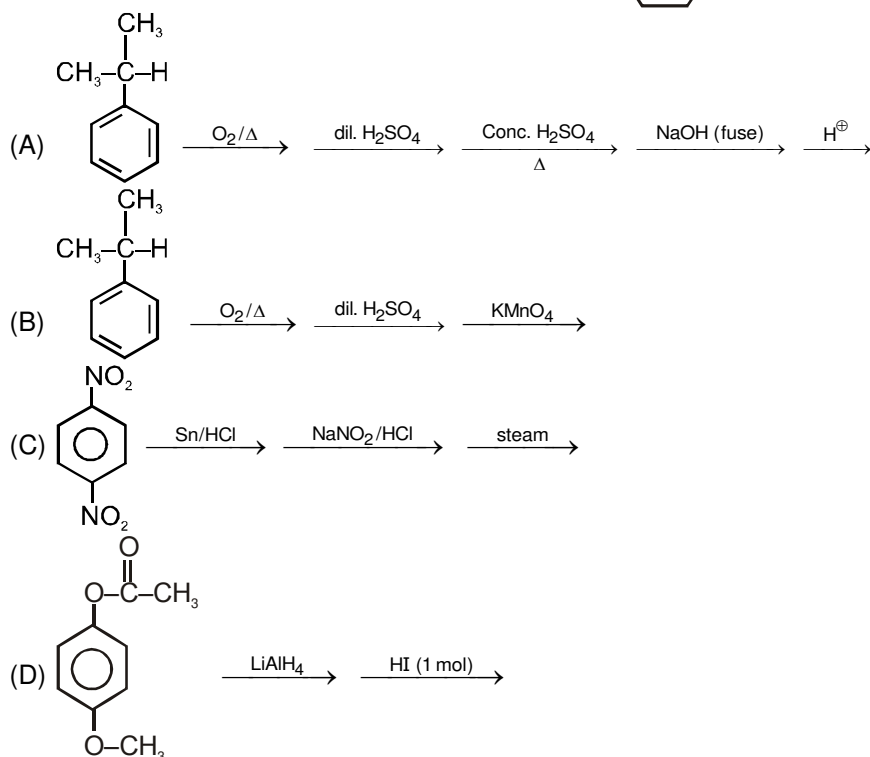
11. Which of the following is correct :

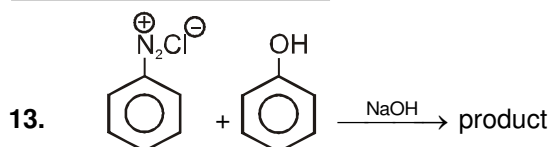
(A) Due to formation of c1ccccc1O[Al](Cl)Cl, Ph-OH does not give Friedel Craft acylation reaction (at normal temperature).

(B) Due to formation of [NH3+]c1ccccc1, Ph-NH₂ give m-nitro-aniline, in sufficient amount during nitration.



12. Which are the routes that can prepare quinol (HO-C₆H₄-OH) :

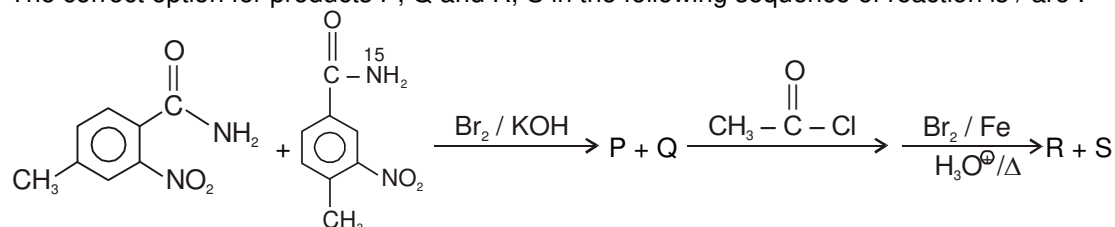




Which of the following statement is **CORRECT** about product ?

- (A) Product shows geometrical isomerism.
 (B) Product shows colour due to extended conjugation.
 (C) Electrophile attacks at para position due to its large size.
 (D) Reaction is electrophilic substitution.

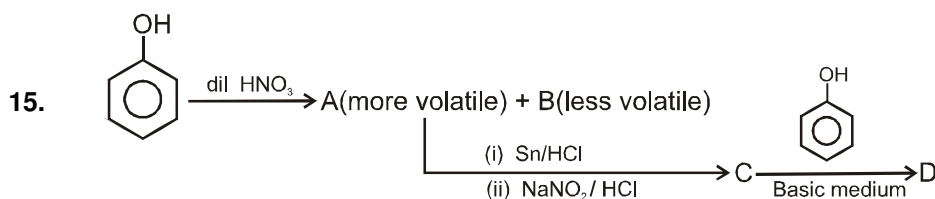
14. The correct option for products P, Q and R, S in the following sequence of reaction is / are :



- (A) P & Q are
- (B) P & Q are
- (C) R & S are
- (D) R & S are

Section-3 : (One Integer Value Correct Type.)

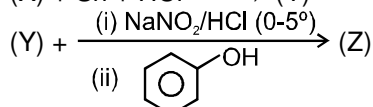
This section contains 3 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)



Double bond equivalent of D is :



16. Consider the following reaction sequence
 $p\text{-nitrophenol} + \text{C}_2\text{H}_5\text{Br} + \text{NaOH}_{\text{aq}} \longrightarrow (\text{X})$



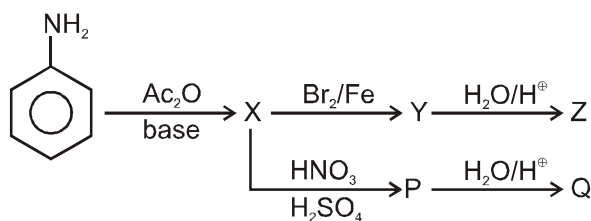
How many carbon atoms are present in Z.

17. A mixture of 1° amides (benzenoid) having molecular formula ($\text{C}_8\text{H}_9\text{NO}$) reacted with Br_2/NaOH . The number of 1° amines products formed will be :

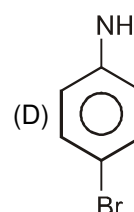
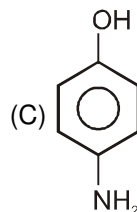
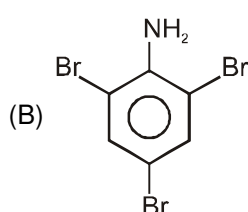
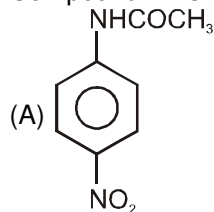
SECTION-4 : Comprehension Type (Only One options correct)

This section contains 2 paragraphs, each describing theory, experiments, data etc. 2 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

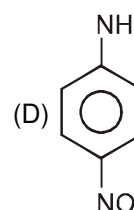
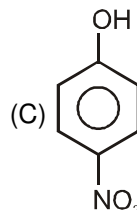
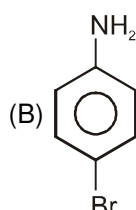
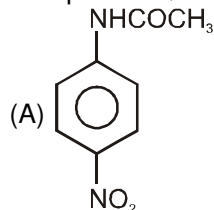
Paragraph for Questions 18 to 19



18. Compound 'Z' is :

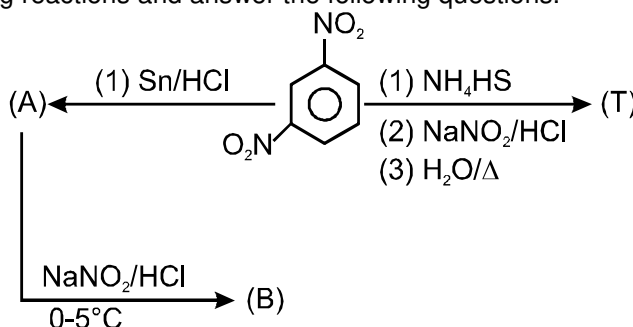


19. Compound 'Q' is :



Paragraph for Question Nos. 20 to 21

Observe the following reactions and answer the following questions.





20. For Product (T), The correct statement is :
 (A) Turns Red litmus blue
 (B) Turns FeCl_3 (Neutral) into coloured solution
 (C) Gives Friedel-Craft-Alkylations reaction
 (D) Contains two 'N' atoms
21. The product B on heating with H_2O produces :
 (A) m-cresol (B) Resorcinol (C) Salicylic acid (D) Salicylaldehyde

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21									
Ans.										



APSP Answers

PART - I

1.	(3)	2.	(1)	3.	(3)	4.	(1)	5.	(3)
6.	(1)	7.	(1)	8.	(4)	9.	(1)	10.	(1)
11.	(3)	12.	(1)	13.	(4)	14.	(1)	15.	(4)
16.	(2)	17.	(2)	18.	(4)	19.	(4)	20.	(1)
21.	(1)	22.	(3)	23.	(1)	24.	(1)	25.	(1)
26.	(3)	27.	(4)	28.	(3)	29.	(4)	30.	(4)

PART - II

1.	(B)	2.	(A)	3.	(A)	4.	(B)	5.	(C)
6.	(D)	7.	(B)	8.	(C)	9.	(C)	10.	(D)
11.	(C)	12.	(D)	13.	(B)	14.	(B)	15.	(B)
16.	(B)	17.	(B)	18.	(B)	19.	(C)	20.	(A)
21.	(B)	22.	(C)	23.	(B)	24.	(C)	25.	(B)
26.	(D)	27.	(D)	28.	(B)	29.	(A)	30.	(C)
31.	(C)								

PART - III

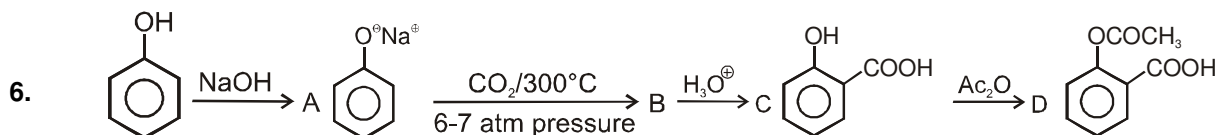
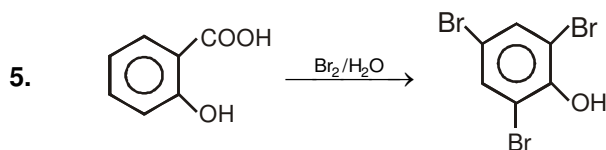
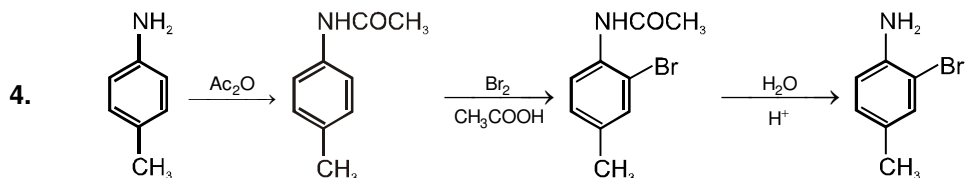
1.	(C)	2.	(D)	3.	(D)	4.	(C)	5.	(D)
6.	(C)	7.	(C)	8.	(ABC)	9.	(ABC)	10.	(AD)
11.	(ABCD)	12.	(ACD)	13.	(ABCD)	14.	(BC)	15.	D.U. = 9
16.	14	17.	04	18.	(D)	19.	(D)	20.	(B)
21.	(B)								



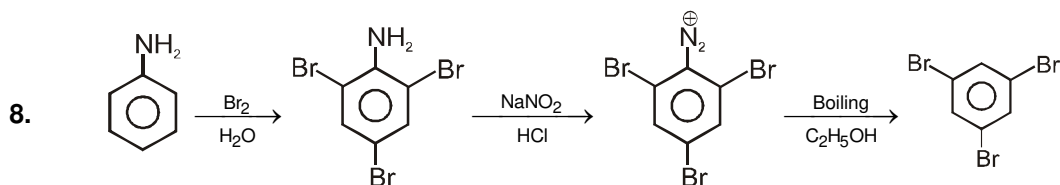
APSP Solutions

PART - I

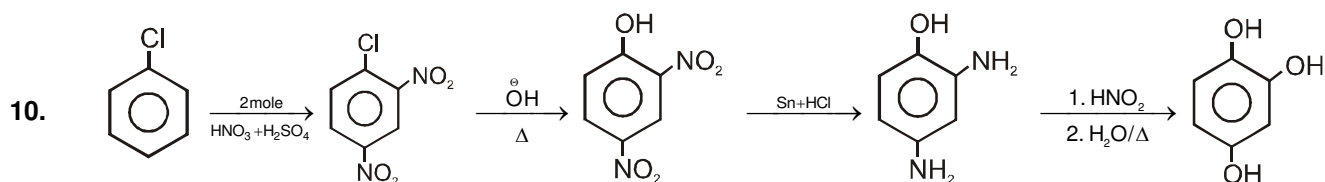
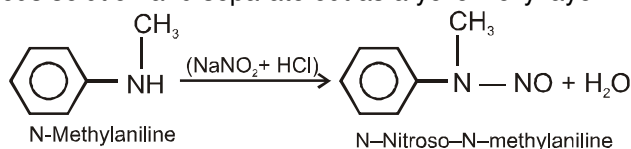
1. It is Hofmann bromamide reaction. Hofmann bromamide reaction involves an intramolecular rearrangement. So no cross products are formed even if we mix together two different amides in the reaction.
2. NaHCO_3 does not give effervescence with phenol. But ortho-para nitro phenols give effervescence with NaHCO_3 .
3. Only 1° amine give carbyl amine test.



7. It is fact.



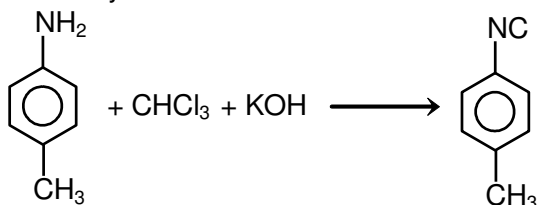
9. **Secondary aliphatic and aromatic amines** react with nitrous acid to produce nitroso-amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.



11. In (3) option the given reaction will not yield benzaldehyde.
12. Orientation decided by more activating $-\text{OH}$ group [$+\text{M}$ effect].



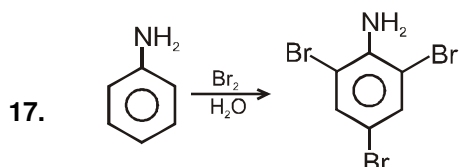
13. It is carbylamine reaction.



14. $\text{Ph-NO}_2 \xrightarrow{\text{Reduction}} \text{Ph-NH}_2 \xrightarrow{\text{CHCl}_3 + \text{KOH}} \text{Ph-NC} \xrightarrow{\text{Reduction}} \text{Ph-NH-CH}_3$
(P) (Q) (R)

15. It is fact.

16. $\text{PhN}^{\oplus}_2\text{Cl} \xrightarrow{\text{H}_3\text{PO}_2, \Delta} \text{C}_6\text{H}_6$

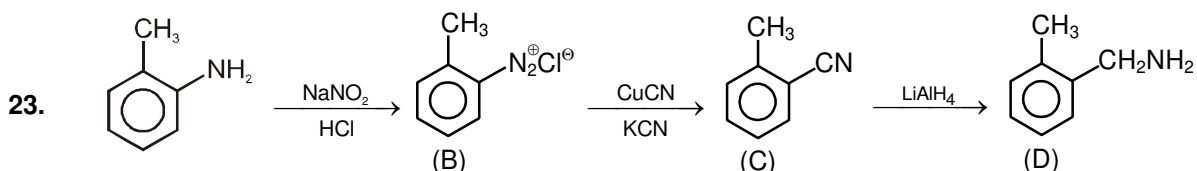


18. Lucas test is given by alcohols. Neutral FeCl_3 test is given by phenols.

20. Nitrobenzene reduced into aniline by metal/acid and electrolytic reduction in weakly acidic medium.

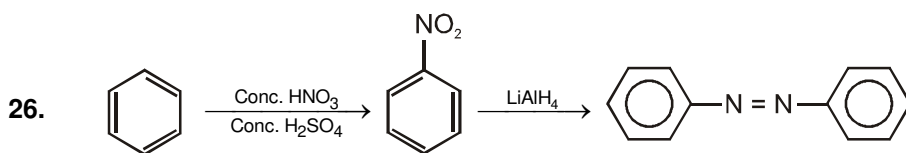
21. Mustard oil reaction given by 1° amines because it has 2 active -H atoms.

22. $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{AgCN}} \text{CH}_3\text{-CH}_2\text{-NC} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{-CH}_2\text{-NH}_2$
(P) (Q)

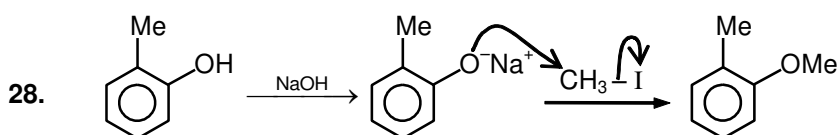


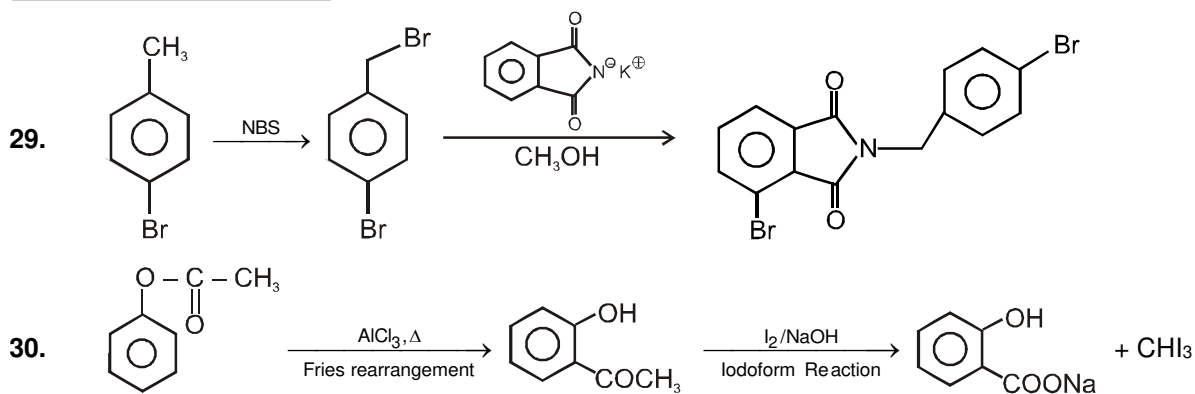
24. This reaction is known as Schotten Baumann reaction.

25. 2° & 3° amine does not give carbyl amine test.

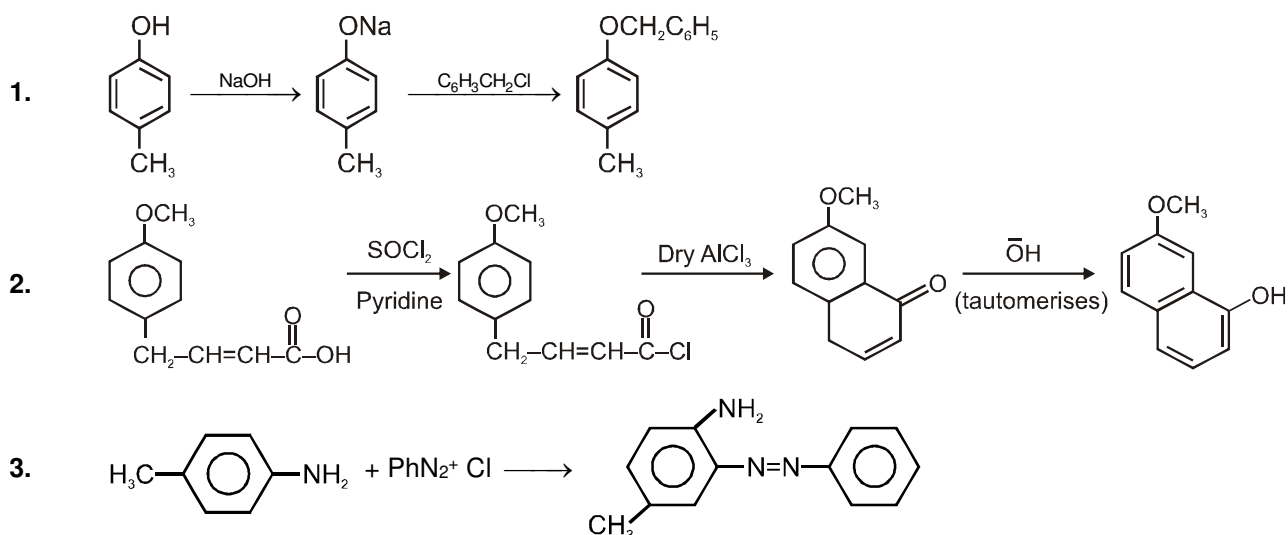


27. $\text{Ph-NH}_2 \xrightarrow[0^\circ\text{C}]{\text{HNO}_2} \text{PhN}_2\text{Cl} \xrightarrow[\text{BF}_3/\Delta]{\text{HF}} \text{Ph-F}$

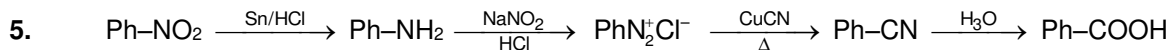
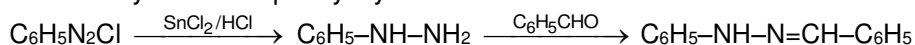




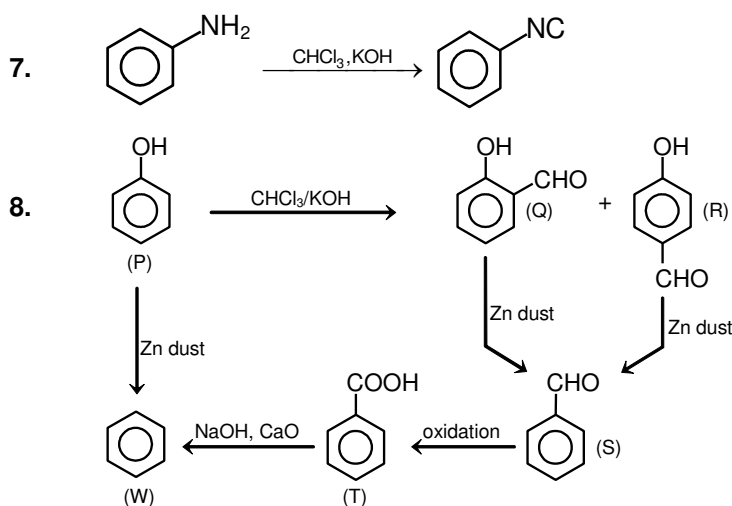
PART - III



4. Reduction of benzene diazonium chloride with SnCl_2 and HCl gives phenyl hydrazine which reacts with benzaldehyde to form phenyl hydrazone.

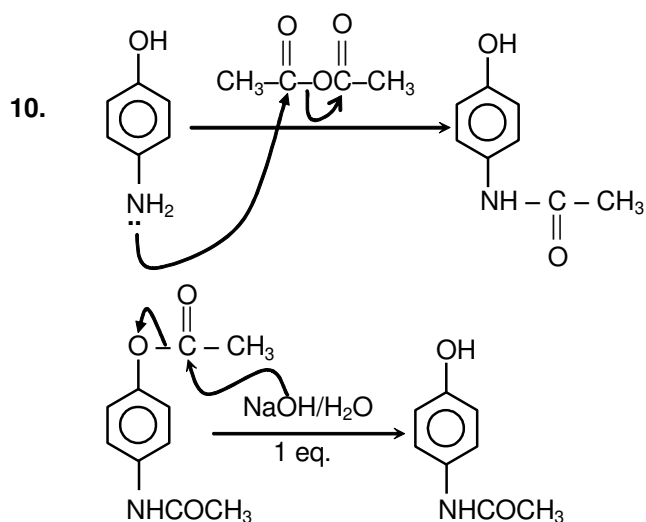


6. R-NO_2 is reduced by $\text{SnCl}_2 + \text{HCl}$ to R-NH_2 .

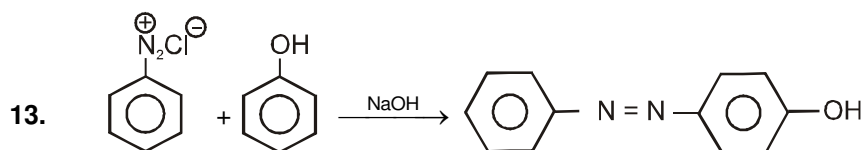
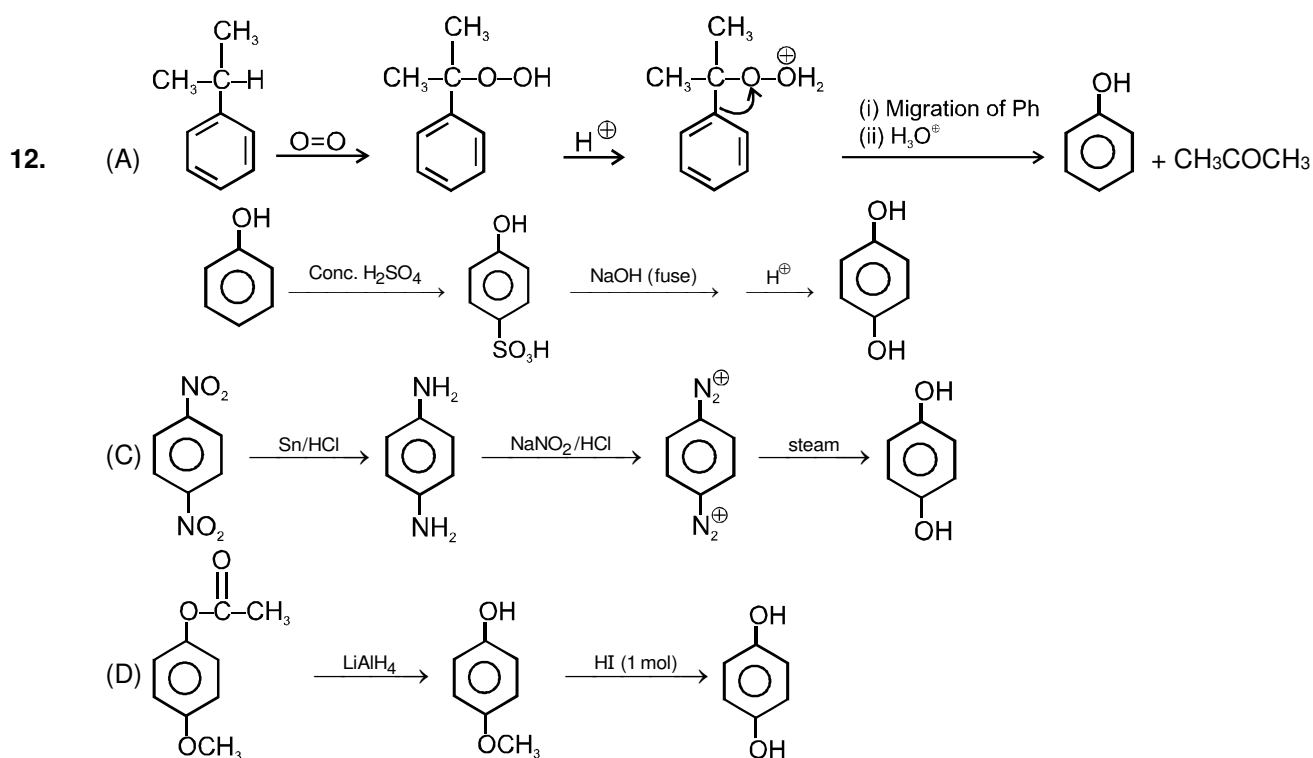


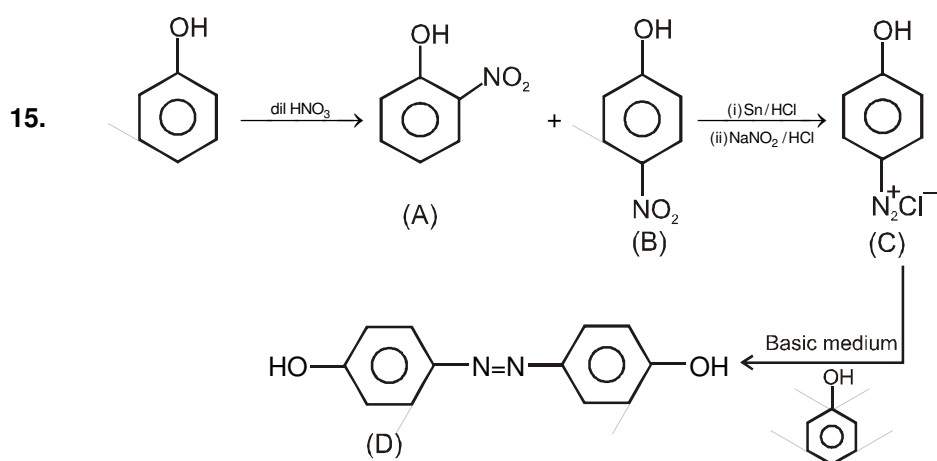
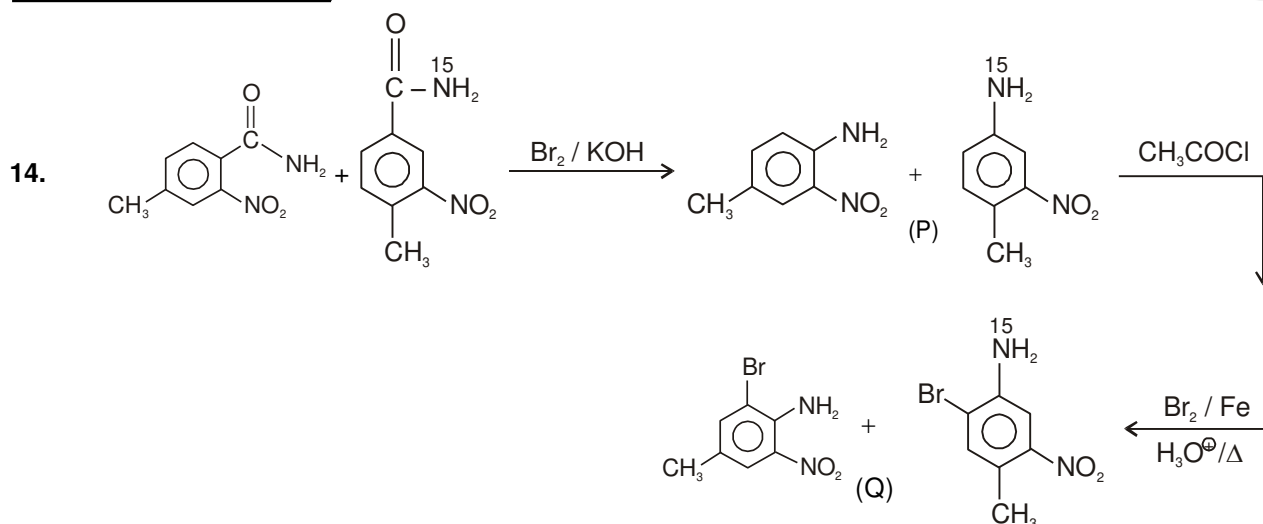


9. It is coupling reaction.



11. (D) is Reimer Tiemann carboxylation reaction.





Double bond equivalent of D is 9.

