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)
$$OH$$

$$OH$$

$$OCH_{2}$$
(i) NaOH/ Δ
(ii) NaOH/ Δ

$$OH$$

$$OH$$

(b) OMgBr
$$\xrightarrow{H_3O^+}$$
 OH $\xrightarrow{\Delta}$

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 C₆H₆O gives a characteristic colour with aqueous FeCl₃ solution. When 'A' is treated with CO₂ and NaOH at 400 K under pressure, 'B' is obtained. B on acidification gives C when C treated with CH₃COCl 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 :

(a)
$$Oldsymbol{$$

B-2. Complete the following reaction :

(a)
$$\xrightarrow{\text{Phosgene}}$$
 Product

Excess NH_2 $\xrightarrow{\text{S-CI}}$ $\xrightarrow{\text{NH}_2}$ $\xrightarrow{\text{NH}_2}$ $\xrightarrow{\text{Br}_2/\text{CS}_2}$ (c) $\xrightarrow{\text{Br}_2/\text{H}_2\text{O}}$

- B-3. Why does aniline soluble in aqueous HCl?
- **B-4.** Write following conversions :

 - (b) acetanilide $\longrightarrow p$ -nitroaniline
- **B-5.** What is the product when C₆H₅CH₂NH₂ reacts with HNO₂?
- B-6.> How will you carry out the following conversion?

$$\bigcirc \longrightarrow \bigcirc \bigvee_{NO}^{NH_2}$$

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?

$$\begin{array}{c}
NH_2 \\
NO_2
\end{array}$$

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

(a)
$$O$$
 Br O Br O

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

$$NH_{2} \longrightarrow NH_{2} \longrightarrow NCH_{3} \longrightarrow NCH_{3$$

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

In which of the following reactions phenol is not obtained:

$$(A) \bigcirc OH \longrightarrow NaOH/CaO \longrightarrow (B) \bigcirc H_3O^+ \longrightarrow (C) \bigcirc CI \longrightarrow NaOH \longrightarrow (D) \bigcirc H_2O \longrightarrow$$

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

A-3.2a
$$+ CH_3-CH=CH_2 \xrightarrow{H_3PO_4} A \xrightarrow{(1) O_2, \Delta} B + C$$

The products B & C are respectively:

- (A) Phenol & acetic acid
- (C) Benzoic acid & acetone

- (B) Phenol & acetaldehyde
- (D) Phenol & acetone
- $\xrightarrow{\mathrm{Br_2}}$ product. The major product obtained is



OCH₃

$$(D) \xrightarrow{\mathsf{Br}} \mathsf{Br}$$

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

$$(A) \begin{array}{c} OH \\ Br \\ Br \\ Br \\ Br \\ Br \\ COOH \\ (B) \\ Br \\ COOH \\ (C) \\ Br \\ COOH \\ (D) \\ Br \\ Br \\ Br \\ (D) \\ Br \\ Br \\ (D) \\ Br \\ (D) \\ COOH \\ (D) \\ COOH \\ (D) \\ (D)$$

A-6. An organic compound having the molecular formulaf C₇H₈O is insoluble in NaHCO₃ solution but dissolves in aqueous NaOH. When treated with bromine water the compound rapidly forms a precipitate having the molecular formula C₇H₅OBr₃. The organic compound is

(A) o-cresol

(B) m-cresol

(C) p-cresol

(D) anisole

A-7.28
$$CH_3$$
 CH_3 CH_4 CH_5 CH_5

A-8. Identify the product in following reaction?

$$(A) \xrightarrow{D_2SO_4 \text{ (excess)}} D$$

$$(B) \xrightarrow{D_2SO_4 \text{ (excess)}} D$$

$$(C) \xrightarrow{D_2SO_4 \text{ (excess)}} D$$

$$(D) \xrightarrow{D_2SO_4 \text{ (excess)}} D$$

$$(D) \xrightarrow{D_2SO_4 \text{ (excess)}} D$$

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

$$(A) \begin{tabular}{lll} \begin{tabular}{llll} \begin{tabular}{lll} \begin{tabular}{lll} \begin{tabular}{lll} \begin{tabular}{lll} \b$$

A-10.2
$$OH$$
 + CH_2I_2 + NaOH \rightarrow , the product is :

(A) OH (B) OH (C) OH (D) OH ONa

- **A-11.** In the reaction sequence \bigcirc SO₃Na $\xrightarrow{\text{NaOH}}$ A $\xrightarrow{\text{CH}_3\text{I}}$ B $\xrightarrow{\text{HI}}$ C + D
 - A, B, C and D are given by the set:
 - (A) Sodium phenate, anisole, C₆H₅I, CH₃OH
- (B) Sodium phenate, phenitole, C₂H₅I, C₆H₅OH
- (C) Sodium phenate, anisole, C₆H₅OH, CH₃I
- (D) Sodium phenate, phenitole, C₆H₅I, C₂H₅OH

A-12. B
$$\leftarrow$$
 NaOH \leftarrow OH \rightarrow Distillation A

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

- (A) benzene, methyl benzoate
- (B) benzene, phenyl acetate

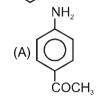
(C) phenyl acetate, benzene

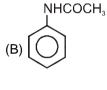
(D) benzene, phenylacetyl chloride

Section (B): Nitrogen containing compounds

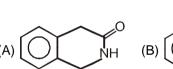
- B-1. Which of the following sequence is best suited to convert benzene to 3-chloro aniline?
 - (A) nitration, reduction, chlorination
 - (B) chlorination, nitration, reduction
 - (C) nitration, chlorination, reduction
 - (D) nitration, reduction, acetylation, chlorination, hydrolysis

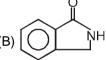
B-2.2
$$(A)$$
 $\xrightarrow{Br_2/NaOH}$ (A) $\xrightarrow{CH_3COCI/reflux}$ (B) , Identify the major product (B) .

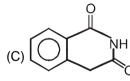






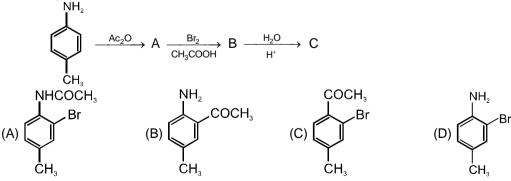






- B-4. Aniline when treated with acetyl chloride in presence of alkali, the product formed is :
 - (A) acetanilide
- (B) benzoyl chloride
- (C) acetophenone
- (D) aniline hydrochloride

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

<u>Aron</u>	natic Compounds /	
B-7.≿		lic potash and another compound (Y) then foul smelling vas formed by reacting compound (Z) with Cl_2 in the (C) CH_3OH (D) $\text{C}_6\text{H}_5\text{NH}_2$
B-8.	p-Chloro aniline and anilinium chloride can be d (A) Sandmayer reaction (C) Hinsberg's reaction	listinguished by (B) Carbyl amine reaction (D) AgNO ₃
B-9.	The best reagent for converting 2–phenylpropar (A) excess H ₂ (C) iodine in the presence of red phosphorus	(B) Br ₂ in aqueous NaOH
B-10.	Hoffmann bromamide degradation reaction is sl (A) ArNH ₂ (B) ArCONH ₂	nown by (C) ArNO ₂ (D) ArCH ₂ NH ₂
B-11.	The best reagent for converting, 2-phenylpropa (A) excess H ₂ /Pt (B) NaOH/Br ₂	namide into 1- phenylethanamine is (C) NaBH ₄ /methanol (D) LiAlH ₄ /ether
B-12.≽	In order to prepare a 1º amine from an alkyl hat carbon chain, the reagent used as source of nite (A) Sodium amide, NaNH2 (C) Potassium cyanide, KCN	alide with simultaneous addition of one CH_2 group in the rogen is (B) Sodium azide, NaN_3 (D) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$
B-13.	Best method for preparing primary amines from atoms in the chain is (A) Hoffmann Bromamide reaction (C) Sandmeyer reaction	m alkyl halides without changing the number of carbon (B) Gabriel phthalimide synthesis (D) Reaction with NH ₃
B-14.	The product formed by the reaction of acetamid (A) CH ₃ CN (B) CH ₃ CHO	e with Br ₂ in presence of NaOH is : (C) CH ₃ CH ₂ OH (D) CH ₃ NH ₂
Section C-1.	on (C): Benzene diazonium salt & its I	reactions
•	$C_6H_5NH_2 \xrightarrow{NaNO_2 + HCI} (A) \xrightarrow{CuCN} (B) \xrightarrow{H^+}$	$\frac{H_2O}{}$ (C)
	(A) C ₆ H ₅ CH ₂ NH ₂ (B) C ₆ H ₅ COOH	(C) C ₆ H ₅ OH (D) none of these
C-2.	Benzenediazonium chloride can be converted in (A) H_3PO_3 (B) H_3PO_4	nto benzene on treatement with: (C) H ₃ PO ₂ (D) HPO ₃
C-3.	$C_6H_5NH_2 \xrightarrow{NaNO_2+HCI} X \xrightarrow{H_2O} Y$, the prod	uct Y is:
	(A) Benzenediazonium chloride (C) Phenol	(B) Nitrobenzene (D) Cresol
	NH ₂ I	
C-4.2	$\frac{\text{(i) Br}_2/\text{H}_2\text{O}}{\text{(ii) HNO}_2 \text{ (0-5°C)}} \text{ (A). The major production}$ $\frac{\text{(iii) HNO}_2 \text{ (0-5°C)}}{\text{(iii) HBF}_4^2/\Delta}$	uct (A) is
	$(A) \bigcup_{Br}^{F} \qquad \qquad (B) \bigcup_{F}^{Br}$	$(C) \xrightarrow{F} F \qquad (D) \xrightarrow{Br} Br$
C-5.	Diazonium salt + Cu + HCl \rightarrow ; the reaction	on is known as
	(A) Chlorination (C) Perkin reaction	(B) Sandmeyer's 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

C-8. (major product) X will be -
$$NH_2$$

$$(A) \bigvee_{NH_{2}}^{OH} N_{2}P$$

$$(D) \begin{array}{c} PhN_2 \\ \hline \end{array}$$

C-9.2a
$$\rightarrow$$
 + Ph- $\stackrel{+}{N_2}$ $\stackrel{(pH=9-11)}{\longrightarrow}$ X (major product)

X will be:

$$(A) \bigvee_{NH_2}^{OH} N_2 Pt$$

$$(C) \bigvee_{NH_{a}}^{N_{2}Pn}$$

$$(D) \bigcup_{N_2 Ph}^{OH}$$

PART - III: MATCH THE COLUMN

1. Match the column:

	Column-I		Column-II
(A)	$RNH_2 + CHCl_3 + KOH (alc) \xrightarrow{\Delta}$	(p)	Schotten-Baumann reaction
(B)	$C_6H_5N_2CI \xrightarrow{CuBr/HBr} \Delta$	(q)	Coupling reaction
(C)	$C_6H_5NH_2 + C_6H_5COCI \xrightarrow{NaOH(aq.)}$	(r)	Carbylamine reaction
(D)	$C_6H_5N_2CI + C_6H_5OH \xrightarrow{pH9-10}$	(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		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)	$C_6H_6 + CH_3CH(CI)-CH_3 \xrightarrow{anhydrous AICI_3} \rightarrow$	(p)	Diazocoupling reaction.
(B)	$C_6H_5NH_2 + C_6H_5N_2CI \xrightarrow{\text{dil.HCl}}$	(q)	Friedel-Craft reaction
(C)	$C_6H_6 + C_6H_5COCI \xrightarrow{anhydrous AICl_3} \rightarrow$	(r)	Reimer-Tiemann reaction
(D)	$C_6H_5OH \xrightarrow{(i) CCI_4/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.

$$O_{2}N \longrightarrow \begin{array}{c} C_{6}H_{5} \\ C - O - O - H \longrightarrow \\ C_{6}H_{5} \end{array}$$

$$(A) \bigcirc \begin{array}{c} C - C_{6}H_{5} + C_{6}H_{5}OH \\ O \end{array} \qquad (B) O_{2}N \longrightarrow \begin{array}{c} C - C_{6}H_{5} + C_{6}H_{5} - C - C_{6}H_{5} \end{array}$$

$$(C) O_{2}N \longrightarrow \begin{array}{c} C - C_{6}H_{5} + C_{6}H_{5}OH \\ O \end{array} \qquad (D) \bigcirc \begin{array}{c} C - C_{6}H_{5} + C_{6}H_{6} \\ O \end{array}$$

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

3. OH
$$H_2SO_4$$
, $100^{\circ}C$ $NaOH/fusion$ X

$$H_2SO_4$$
, $15^{\circ}C$ $NaOH/fusion$ Y

$$OH$$
 OH OH SO_3H

$$SO_3H$$
 OH
 OH
 OH
 OH

(B)
$$x = \bigcirc OH$$
 OH OH OH OH OH OH SO₃H , $y = \bigcirc OH$ SO₃H

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

$$\frac{1. \text{ CCI}_4+ \text{ NaO4H/}\Delta}{2. \text{ H}^{\oplus}} \text{ x > y}$$

Option	Acid Strength	H₂O Solubility	Volatility	Melting Point y > x	
(A)	y > x	y > x	x > y		
(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 :

$$O - CH_2 - CH = \overset{*}{C}H_2$$

$$CH_3$$

$$O - CH_2 - CH = \overset{*}{C}H_2$$

$$O - CH_2 - CH = \overset{*}{C}H_2$$

$$O - CH_2 - CH = \overset{*}{C}H_2$$

$$O - CH_3 - CH = \overset{*}{C}H_3$$

$$O - CH_3 - CH = CH$$

6.2. (P)
$$\xrightarrow{Br_2}$$
 (Q) $\xrightarrow{CH_3COCl}$ (R) $\xrightarrow{(i) Br_2/CH_3COOH}$ $\xrightarrow{(ii) H_3O^+}$

The reactant (P) is:



(B)
$$\bigvee_{NH_2}^{CONH_2}$$

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

(A) R-NO₂
$$\xrightarrow{\text{RaneyNi}}$$

(B) R-NO₂
$$\xrightarrow{\text{LiAIH}_4}$$
 $\xrightarrow{\text{ether}}$

(C)
$$R-NO_2 \xrightarrow{Sn/HCI}$$

(D) R–NO₂
$$\xrightarrow{\text{Zn/NH}_4Cl}$$
 $\xrightarrow{\Delta}$

- **8.** Para toluidine is treated with HNO₂ 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:

(A)
$$(CH_3)_2N$$
 $N=N$ $N=N$ $N+CH_3$

(B)
$$(CH_3)_2N$$
 NH NH NH:

- **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 :

(A)
$$O_2N$$
 $N = N$ OCH_3

(B)
$$O_2N$$
 \longrightarrow $N = N - CH_2O$ \longrightarrow (D) O_2N \longrightarrow $O - CH_2$

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

Aniline
$$\xrightarrow{\text{(i) NaNO}_2/\text{HCl, 273 K}}$$
 (X) $\xrightarrow{\text{(i) DIBAL-H}}$ (Y)

PART - II: SINGLE OR DOUBLE INTEGER TYPE

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

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2. How many toluidines on reaction with NaNO₂/HCl followed by H₃PO₂ treatment gives Toluene.

3.2.
$$NO_2$$

$$\xrightarrow{Sn/HCl} \xrightarrow{NaNO_2} \xrightarrow{H_2O, \Delta} Product Z$$

Find the molecular weight of Z.

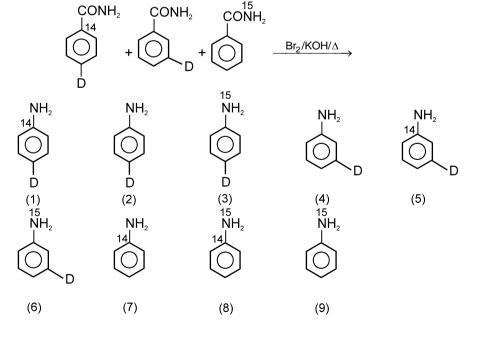
Molecular weight of T will be:

5. How many N atom are present in final product

6. Ph-NO₂
$$\xrightarrow{\text{Sn/HCl}}$$
 $\xrightarrow{\text{NaNO}_2}$ $\xrightarrow{\text{Basic medium}}$ 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.

OH OH CHO
$$CHC_3 + NaOH \xrightarrow{\Delta} CHO$$

3.2. (i) CHCl₃+NaOH, Δ (P > Q) % yield

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 :

Ph-OH
$$\xrightarrow{\text{(i) CHCl}_3 + \text{OH}^-}$$
 Products

- (B) OH (Major)
- (D) OH (Minor)
- 5.> Which of the following reaction is/are correct

$$(C) \begin{array}{c} & & CH_2=O \\ \hline & & HCI \end{array}$$

$$(B) \stackrel{\mathsf{CHFCl}_2}{\underset{\mathsf{H}}{\bigvee}} \xrightarrow{\mathsf{CHFCl}_2} \mathsf{F}$$

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

7.> The products of following sequence of reactions are

$$(A) H = (C) G = (D) F = (D) F$$

$$(B) I = (D) F = (D) F$$

$$(C) G = (D) F = (D) F$$

Which of the following statement is/are correct:

- (A) P is benzene diazonioum 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.

9.28 $(i) \ \frac{\text{NO}_2}{\text{(ii) } \ \text{NNO}_3/\text{H}_2\text{SO}_4} \rightarrow P \ \frac{\text{(i) } \ \text{HNO}_2}{\text{(ii) } \ \text{H}_2\text{O}, \ \Delta} Q \ \frac{\text{(i) } \ \text{NaOH, } \ \text{CO}_2, \ 6 \ \text{atm, } \ \Delta}{\text{(ii) } \ \text{HCI}} \rightarrow R \ \frac{\text{(i) } \ \text{Sn/HCI}}{\text{(ii) } \ \text{NaOH}}$

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

$$Q \xrightarrow{R} S$$

$$\downarrow CO_2/OH^{-}$$

$$AICI_3 \longrightarrow X \xrightarrow{O_2, hv} Z + Y$$

$$\downarrow CI_2/OH^{-}$$

$$W + CH_3COO^{-} \bigvee_{P} W/OH^{-}$$

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

(A) (B) (C) (D)
$$OH$$

2.a 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

$$\begin{array}{c}
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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 $-NO_2$ group in an aromatic ring deactivates the ortho and para positions for an electrophilic attack. When $-NO_2$ group is present at ortho or para positions of a leaving group (Nucleofuge) it activates the ring for nucleophilic attack. The reduction of $-NO_2$ group by metal in acid causes its reduction to $-NH_2$ group and then the ring becomes strongly activated for a electrophilic attack. The strong activation of $-NH_2$ group is moderated by its acylation with CH_3COCI to -NHAC group. Deacylation is carried out by hydrolysis with H_3O^+ or OH^- . The ring alkylation by using RX/AIX_3 is not possible in presence of $-NO_2$ or $-NH_2$ group but is possible in presence of -NHAC group.

(G)
$$\leftarrow$$
1. Sn/HCI
2. CH₃COCI
3. CH₃-CH=CH₂/H⁺
4. H₃O⁺ / Δ
1. KCN, Δ
2. Br₂/Fe
1. Br₂/Fe
2. KCN, Δ
(I)

7. The product (G) is:

(B)
$$CH(CH_3)_2$$
 $CH(CH_3)_2$
 $COCH_3$
 $CH(CH_3)_2$
 $CH(CH_3)_2$

8. The product (H) is:

$$(C) \bigcup_{CN}^{CI} Br \qquad (D) \bigcup_{N}^{BI}$$

9. The product (I) is:

$$(A) \begin{array}{c} CI \\ NC \\ NO_2 \end{array} \qquad (B) \begin{array}{c} Br \\ NO_2 \end{array} \qquad (C) \begin{array}{c} CN \\ NO_2 \end{array} \qquad (D) \begin{array}{c} CN \\ NO_2 \end{array}$$

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:

$$R - C - NH_2 + NaOH + Br_2 \longrightarrow R - N = C = O \xrightarrow{hydrolysis} R - NH_2$$
 isocyanate

Mechanism:

$$R - \overrightarrow{C} - NH_{2} \xrightarrow{OH^{-}} R - \overrightarrow{C} - NH \xrightarrow{Br} \overrightarrow{Br} \xrightarrow{Br} R - \overrightarrow{C} - NH - Br \xrightarrow{OH^{-}} R - \overrightarrow{C} - N$$

If the migrating group is chiral then its cofiguration 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 :

(A)
$$CH_3$$
 (B) $CH_3-CH_2-C-NH-Ph$ (C) NO_2 (D) $Ph-C-NH_2$

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

Comprehension # 5

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

ionoming table.							
Column-I, 2 and 3 contain starting materials, reaction conditions and type of reactions resp							
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 + A□	(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]

$$CH_{2}CH_{2}CH_{3} \xrightarrow{CI_{2} \text{ / FeCl}_{3}} A \xrightarrow{Na-Hg \text{ / HCl}} B \xrightarrow{HNO_{3} \text{ / }H_{2}SO_{4}} C$$

$$\mathsf{E} \xleftarrow{\mathsf{H}_2 \ / \ \mathsf{Pd} \ / \ \mathsf{C}} \mathsf{D} \xleftarrow{\mathsf{CH}_2 = \mathsf{CH} - \mathsf{CH}_2 - \overset{\ominus}{\mathsf{O}} \ \mathsf{Na}} \mathsf{Na}$$

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

(a)
$$\longrightarrow$$
 COOH

(b) \longrightarrow Aspirin

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]

$$\begin{array}{c}
NO_2 \\
\hline
\end{array}$$

$$\begin{array}{c}
NO_2 \\
\hline
\end{array}$$

$$OH$$

C \leftarrow C \leftarrow A \rightarrow A \rightarrow B (brown coloured gas with pungent odour)

(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. $\begin{array}{c} O \\ C - NH_2 \\ + \\ O \\ C - NH_2 \end{array}$ under Hofmann conditions will give : [JEE 2006, 5/184]

$$(A) \bigcirc NH_2 + \bigcirc NH_2$$

$$(B) \bigcup_{D}^{15} \underbrace{NH_2}_{15} + \bigcup_{NH_2}^{15} \underbrace{NH_2}_{15}$$

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
- [IIT-JEE 2006, 5/184]
- (D) N-Bromo succinamide

9. Which step is rate determining step

[IIT-JEE 2006, 5/184]

- (A) Formation of II
- (B) Formation of III
- (C) Formation of V
- (D) Formation of IV
- 10. $CH_3NH_2 + CHCI_3 + KOH \rightarrow Nitrogen containing compound + KCI + H_2O$.

Nitrogen containing compound is:

[IIT-JEE 2006, 3/184]

- (A) CH₃–C≡N
- (B) CH₃-NH-CH₃
- (C) $CH_3-N^-\equiv C^+$
- (D) CH₃-N+≡C-

11.
$$\bigcirc \xrightarrow{CH_3 - CH_2 - CH_2CI / AICI_3} P \xrightarrow{O_2, H_3O^{\bigoplus}} Q + Phenol$$

What are P & Q.

[IIT-JEE-2006, 5/184]

(A)
$$CH_2 - CH_2 - CH_3$$
 + $CH_3 - C - CH_3$

$$(C) \bigcirc CH_3 \qquad O \\ CH_3 + CH_3 - CH_2 - C - H_3$$

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.

$$\begin{array}{c|c} OH & & & & & & & & \\ \hline ONA & & & & & & \\ \hline ONA & & & & & \\ \hline CHO & & & & & \\ \hline CH3 & & & & & \\ \hline CH3 & & & & & \\ \hline (I) & & & & & \\ \hline (II) & & & & \\ \hline \end{array}$$

12. Which one of the following reagents is used in the above reaction? [IIT-JEE 2007, 4/162]

(A) aq. NaOH + CH₃CI

(B) aq. NaOH + CH₂Cl₂

(C) aq. NaOH + CHCl₃

(D) aq. NaOH + CCI4

13. The electrophile in this reaction is:

(A):CHCI

ONa

[IIT-JEE 2007, 4/162]

ONa

- (B) +CHCl₂
- (C) :CCl₂
- (D) °CCI₃

14. The structure of the intermediate I is:

CH₂CI CHCl₂ (B)

ONa

15. In the reaction
$$\frac{\text{NaOH(aq.)/Br}_2}{\text{NaOH(aq.)/Br}_2}$$
 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)	$\begin{array}{c c} OH \ OH \\ \hline \\ H_3C - C - C - CH_3 & \xrightarrow{H_2SO_4} & H_3C \\ \hline \\ CH_3CH_3 & & CH_3 \end{array}$	(q)	Addition reaction
(C)	$ \begin{array}{c c} & O \\ & CH_3 \\ \hline & 2. H_3O^+ \end{array} $ $ \begin{array}{c} & CH \\ & CH_3 $	(r)	Substitution reaction
(D)	$HS \longrightarrow CI \xrightarrow{Base} S$	(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 NaNO₂ in dilute HCl followed by addition to an alkaline solution of β-naphthol is : [JEE-2011, 3/160]

 $N(CH_3)_2$

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

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

OH

$$CHCI_{3}$$

$$CHCI_{3}$$

$$OH$$

$$CHO$$

$$OH$$

$$CHO$$

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

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

Comprehension #3 (Q.21 to 22)

 ${f P}$ and ${f Q}$ are isomers of dicarboxylic acid C₄H₄O₄. Both decolorize Br₂/H₂O. On heating, ${f P}$ 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 form 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 :

mono halo substituted derivative when
$$X_2 = I_2$$

$$X_2 \longrightarrow \text{di halo substituted derivative when } X_2 = Br_2$$

$$C(CH_3)_3 \longrightarrow \text{tri halo substituted derivative when } X_2 = Cl_2$$

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.	н -=- н	1.	Scheme I (i) KMnO ₄ , HO, heat (ii) H $^{\oplus}$, H ₂ O (iii) SOCI ₂ , (iv) NH ₃ ? \longrightarrow C ₇ H ₆ N ₂ O ₃
Q.	OH	2.	Scheme II (i) Sn/HCI (ii) CH ₃ COCI (iii) conc. H ₂ SO ₄ (iv) HNO ₃ (v) dil. H ₂ SO ₄ , heat (vi) HO C ₆ H ₆ N ₂ O ₂
R.	NO ₂	3.	Scheme III (i) red hot iron, 873 K (ii) fuming HNO ₃ , H ₂ SO ₄ , heat (iii) H ₂ S.NH ₃ (iv) NaNO ₂ , H ₂ SO ₄ (v) hydrolysis ? C ₆ H ₅ NO ₃
S.	NO° CH3	4.	Scheme IV (i) conc. H_2SO_4 , 60°C (ii) conc. HNO_3 , conc. H_2SO_4 (iii) dil. H_2SO_4 , heat ? $C_6H_5NO_4$

Code:

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

- S 3 2 (A) (C)
- Q R 2 (B) 3 1 4 (D) 3 2
- 26. Among the following the number of reaction(s) that produce(s) benzaldehyde is

[JEE(Advanced)-2015, 4/168]

Anhydrous AlCl₃/CuCl
$$H_2$$
 IV.

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]

→ W

$$(B) \bigvee_{N=N} OH$$

, NaOH

29.* The product(s) of the following reaction sequence is(are)

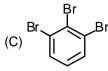
[JEE(Advanced)-2016, 4/124]



- Acetic anhydride/pyridine
- KBrO₃/HBr (ii)
- (iii)
- H₃O⁺, heat NaNO₂/HCl, 273–278K (iv)
- Cu/HBr







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

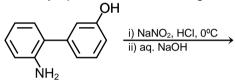
Cumene (C₉H₁₂)
$$\xrightarrow{\text{(i) O}_2}$$
 P $\xrightarrow{\text{CHCl}_3/\text{NaOH}}$ **Q** (major) + **R** (minor)

$$\mathbf{Q} \xrightarrow{\text{NaOH}} \mathbf{S}$$

- (A) R is steam volatile
- (B) Q gives dark violet coloration with 1% aqueous FeCl₃ solution
- (C) **S** gives yellow precipitate with 2, 4-dinitrophenylhydrazine
- (D) S gives dark violet coloration with 1% aqueous FeCl₃ solution

31. The major product of the following reaction is

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



$$(B) \bigvee_{N_2CI} ONa^{\dagger}$$

Comprehension #4 (Q.32 to 33)

The reaction of compound **P** with CH₃MgBr (excess) in (C₂H₅)₂O followed by addition of H₂O gives **Q**. The compound Q on treatment with H₂SO₄ at 0°C gives R. The reaction of R with CH₃COCl in the presence of anhydrous AlCl₃ in CH₂Cl₂ followed by treatment with H₂O produces compound S. [Et in compound **P** is ethyl group]

32. The product S is

$$(C)$$
 $(H_3C)_3C$ O CH_3 $COCH_3$

(B)
$$(H_3C)_3C$$
 $(H_3C)_3C$ $(H_3C)_3C$ (B)

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]

(A)
$$Conc.H_2SO_4$$
 Δ

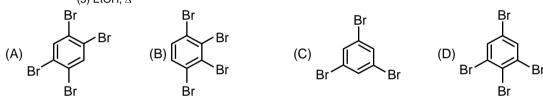
(C) $Conc.H_2SO_4$
 Δ

1) Br₂, NaOH
 $Conc.H_2SO_4$
 $Conc.H_2SO_4$
 Δ
3) sodalime, Δ

(B) Me
$$\longrightarrow$$
 H heated iron tube 873K CHO

(D) OHC CHO

35.* Aniline reacts with mixed acid (conc. HNO₃ and conc. H₂SO₄) at 288 K to give **P** (51%), **Q** (47%) and R (2%). The major product(s) of the following reaction sequence is (are)



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: H = 1, C = 12, N = 14, O = 16, 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

2. 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.

3. The reaction of chloroform with alcoholic KOH and p-toluidine forms :

[AIEEE-2003, 3/225]

(1)
$$H_3C$$
 \longrightarrow CN

(3)
$$H_3C \longrightarrow NHCHCl_2$$

4. Fluorobenzene (C₆H₅F) can be synthesized in the laboratory

[AIEEE-2006, 3/165]

- (1) from aniline by diazotisation followed by heating the diazonium salt with HBF₄.
- (2) by direct fluorination of benzene with F₂ 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 :

6.
$$OH + CHCl_3 + NaOH \longrightarrow CHC$$

The electrophile involved in the above reaction is:

[AIEEE-2006, 3/165]

- (1) Dichloromethyl cation (CHCl₂)
- (2) Dichlorocarbene (:CCl₂)
- (3) Trichloromethyl anion ($\overset{\circ}{\mathsf{C}}\mathsf{Cl}_3$)
- (4) Formyl cation (CHO)
- 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) C₂H₅NC and K₂CO₃

(2) C₂H₅NC and 3KCl

(3) C₂H₅CN and 3KCl

- (4) CH₃CH₂CONH₂ and 3KCI
- 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-rinitrobenzene
- 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:

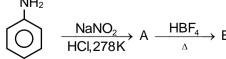
[AIEEE-2008, 3/105]

- (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

- Phenol is heated with a solution of mixture of KBr and KBrO₃. 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
- An organic compound A upon reacting with NH₃ gives B. On heating B gives C. C in presence of KOH reacts with Br₂ to given CH₃CH₂NH₂. A is : [JEE (Main) 2013, 4/120]
 - (1) CH₃COOH

(2) CH₃CH₂CH₂COOH

(3) CH₃— CH— COOH | | CH₃

- (4) CH₃CH₂COOH
- 15. Sodium phenoxide when heated with CO₂ under pressure at 125°C yields a product which on acetylation produces C. [JEE(Main)-2014, 4/120]

ONa + CO₂
$$\xrightarrow{125^{\circ}}$$
 B $\xrightarrow{H^{+}}$ C

The major product C would be:

16. In the reaction

the product E is:

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

- 17. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br₂ used per mole of amine produced are : [JEE(Main)-2016, 4/120]
 - (1) Four moles of NaOH and two moles of Br₂
 - (2) Two moles of NaOH and two moles of Br₂
 - (3) Four moles of NaOH and one mole of Br2
 - (4) One mole of NaOH and one mole of Br₂
- 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 react 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]

1)
$$CO_2H$$
 CO_2H C

JEE(MAIN) ONLINE PROBLEM

1. The following reaction

is known as:

- (1) Perkin reaction
- (3) Kolbe's reaction

[JEE(Main) 2014 Online (11-04-14), 4/120]

- (2) Gattermann-Koch formylation
- (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 [JEE(Main) 2014 Online (12-04-14), 4/120] reactions?
 - (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]

$$\begin{array}{c|c}
OH_3 \\
\hline
OH_3 \\
\hline
OH_2 \\
FeBr_3
\end{array}$$

$$B \xrightarrow{Sn/HCl} C \xrightarrow{NaNO_2} D \xrightarrow{CuBr} B$$

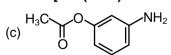
$$HCl \\
HBr \\
HBr \\
FeBr_3$$

- 5. Fluorination of an aromatic ring is easily accomplished by treating a diazonium salt with HBF₄. Which of the following conditions is correct about this reaction? [JEE(Main) 2016 Online (10-04-16), 4/120] (1) Only heat (2) NaNO₂/Cu (3) Cu₂O/H₂O (4) NaF/Cu
- The major product of the following reaction is: 6.

[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]



$$(1)$$
 $(a) < (b) < (c) < (d)$ (2) $(a) < (d) < (b) < (c)$ (3) $(a) < (d) < (c) < (b)$ (4) $(d) < (c) < (b) < (a)$

$$(2)$$
 $(a) < (d) < (b) < (c)$

$$(A)(d) = (c) = (b) = (a)$$

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]

$$(1) \begin{array}{c} (i) \text{ OHCCH}_2\text{COCI} \\ (ii) \text{ H}_2\text{SO}_4, \text{ heat} \\ (2) \\ \text{OMe} \\ \text$$

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 O₂ followed by treatment with dil. HCl are:

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

$$(1) \bigcirc O \qquad (2) \bigcirc CH_3$$

$$O \qquad (2) \bigcirc O \qquad and CH_3-OH$$

$$O \qquad O \qquad O \qquad OH$$

$$O \qquad O \qquad OH$$

$$O \qquad OH \qquad OH$$

$$O \qquad OH \qquad OH$$

$$OH \qquad$$

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

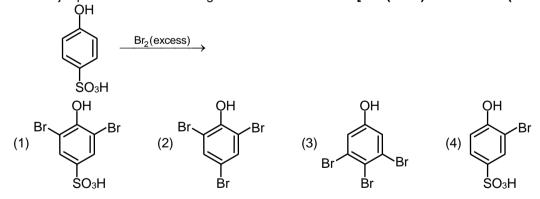
[JEE(Main) 2019 Online (10-01-19), 4/120]

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 cabylamine test. Compound 'X' is: [JEE(Main) 2019 Online (11-01-19), 4/120]
 - (1) CH3COCH2NHCH3
 - (3) CH₃CH₂COCH₂NH₂

- (2) CH₃CON(CH₃)₂
- (4) CH₃CH₂CH₂CONH₂

etion 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.

A-3. OH OH OH CH(CH₃)₂
$$+$$
 CH₃ -CH-CH₃ $\xrightarrow{\text{HF}}$ CH(CH₃)₂

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

A-4. (a)
$$OH + HNO_3(dil.) \longrightarrow OH + CHCl_3 + NaOH \xrightarrow{343K} OH + CHCl_3 + NaOH \xrightarrow{343K} OH + CHCl_3 + CHCl$$

$$\textbf{A-5.} \quad \textbf{A} \rightarrow \bigcirc, \ \textbf{B} \rightarrow \bigcirc, \ \textbf{C} \rightarrow \bigcirc, \ \textbf{D} \rightarrow \bigcirc, \ \textbf{D} \rightarrow \bigcirc$$

A-6. A \rightarrow Zn, B \rightarrow CH₃Cl / FeCl₃ and C \rightarrow Strong oxidising reagent

$$\textbf{B-1.} \hspace{0.3cm} \textbf{(a)} \hspace{0.1cm} \overbrace{\hspace{0.1cm}}^{\text{NH}_3/\text{Cu}_2\text{O}/\Delta} \hspace{0.1cm} \hspace{0.1cm} \overbrace{\hspace{0.1cm}}^{\text{NH}_2} \hspace{0.1cm} ; \hspace{0.3cm} \textbf{(b)} \hspace{0.1cm} \overbrace{\hspace{0.1cm}}^{\text{NO}_2} \hspace{0.1cm} \xrightarrow{\text{Fe/HCI}} \hspace{0.1cm} \hspace{0.1cm} \overbrace{\hspace{0.1cm}}^{\text{NH}_2} \hspace{0.1cm}$$

B-3. Aniline forms the salt anilinium chloride which is water soluble.

B-4. (a)
$$NH_2$$
 NHCOCH₃

NHCOC

B-5. $C_6H_5CH_2NH_2 \xrightarrow{HNO_2} C_6H_5CH_2OH + N_2 \uparrow$

B-6. Conc.
$$HNO_3 + H_2SO_4$$

$$(CH_3CO_2)_2O$$

$$Pyridine$$

$$NH_2$$

$$H_2O/H^+$$

$$NO_2$$

$$Conc. HNO_3 + H_2SO_4$$

$$NHCOCH_3$$

$$NHCOCH_3$$

$$NHCOCH_3$$

B-7. (i) Isocyanide test

(ii) Hinsberg test

(iii) NaNO₂ + HCl test

C-3. (a & b)
$$O$$

NHCOCH₃

NHCOCH₃

NHCOCH₃

NHCOCH₃

NH₂

Conc. HNO₃ +Conc. H₂SO₄

NO₂

Br₂/ CH₃COOH

NO₂

Br₂/ CH₃COOH

NO₂

Br₂/ CH₃COOH

NO₂

NH₂

NO₂

NO₂

C-4.
$$V = N = N$$
 CH_3
 CH_3
 CH_3
 CH_3

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.

$$O_2N$$
 \longrightarrow $N_2^+CI^ O_2N$ \longrightarrow O_2N \longrightarrow

C-6. (a)
$$Oldsymbol{CH} Oldsymbol{CH} Oldsy$$

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

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

EXERCISE - 2

PART - I

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

PART - II

- 1. 75
- 2.
- 3. 94
- 4. 78
- 5. Zero (0).

- 6. 99
- 7. 3 (1, 4, 9)

03

PART - III

- 1. (ABCD)
- 2.
- (AB)
- 3. (BC)
- 4. (AC)
- 5. (ABCD)

- 6. (ABCD)
- 7.
- (BCD)
- 8. (ACD)
- 9. (BD)
- 10. (BCD)

PART - IV

(A)

(B)

- 1. (C)
- 2.
- (B)

(B)

- 3.
- 4.
- 5. (B)

- 6. (D)
- 7.
- 8.
- 9.
- 10. (B)

- 11. (D)
- 12. (A)
- 13. (B)
- 14.
- (D)

(A)

(C)

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+

$$A = CI \qquad CH_2 - CH_2 - CH_3$$

$$C = \begin{array}{c} OH \\ I \\ CH(CH_2)_2CH_3 \end{array}$$

$$\mathsf{E} = \bigcup_{\begin{subarray}{c} \mathsf{OH} \\ \mathsf{CHCH}_2\mathsf{CH}_2\mathsf{CH}_3\\ \mathsf{O-CH}_2\mathsf{-CH}_2\mathsf{-CH}_3\\ (\mathsf{E}) \end{subarray}} \mathsf{OH}$$

$$D = \bigcup_{O-CH_2-CH=CH_2}$$

$$(D)$$

- 4. (a) (i) Conc. H_2SO_4 (ii) KHF_2/Δ
 - (i) conc. HNO₃/H₂SO₄ (ii) Sn + HCl (iii) NaNO₂ + HCl & HBF₄/ Δ or
 - (i) NaOH + CO₂ (ii) H[⊕] (iii) (CH₃CO)₂O (b)



(A) H_2SO_4 (conc.), 6.

(B) Br₂,

(C) $\mathsf{NO_2}^\oplus$,

NO₂ O₂N (D)

(T.N.T. = Trinitrotoluene)

 $\dot{N}O_2$

7. (A) 8. (B) 9. (D) 10. (D) 11. (D)

(C)

(B)

12. (C) 13.

14.

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)

(B) 33.

34.* (ABD)

35.* (D) 36. 495

PART – II

JEE(MAIN) OFFLINE PROBLEM

4.

(1)

5. (1)

1. 6.

(3) (2)

2.

(1)

3.

(4)

9.

11.

(3)

7. 12. (2) (4)

(3)

8.

(1)

(4)

10.

13. (1) 14. (4) 15. (1)

(2)

(3)

(3)

16.

(3)

17.

18. (2) 19.

20.

JEE(MAIN) ONLINE PROBLEM

1.

(4)

(1)

(Bonus)

3. (3) 4.

(2)

(2)

(1)

5. (1)

6.

(3)

2. 7.

12.

(3)

8.

(1)

(1)

9.

14.

10.

11.

16.

(3)

(1)

13.

(2)

15. (4)