ORGANIC CHEMISTRY

AROMATIC COMPOUND

1. Consider the following reaction scheme and choose the correct option(s) for the major products \mathbf{Q} , \mathbf{R} and \mathbf{S} . [JEE(Advanced) 2023]

Styrene
$$\xrightarrow{\text{(i) B}_2\text{H}_6}$$
 $\xrightarrow{\text{(ii) CrO}_3, \text{H}_2\text{SO}_4}$ \mathbf{P} $\xrightarrow{\text{(ii) CrO}_3, \text{H}_2\text{SO}_4}$ \mathbf{Q} \mathbf{P} $\xrightarrow{\text{(ii) SOCl}_2}$ \mathbf{R} $\xrightarrow{\text{conc.H}_2\text{SO}_4}$ \mathbf{S} \mathbf{S} \mathbf{Q} \mathbf{R} $\xrightarrow{\text{COOH}}$ \mathbf{SO}_3 \mathbf{Q} \mathbf{R} \mathbf{S} \mathbf{Q} \mathbf{R} \mathbf{S} \mathbf{Q} \mathbf{R} \mathbf{S} \mathbf{S} \mathbf{Q} \mathbf{R} \mathbf{S} \mathbf{S} \mathbf{Q} \mathbf{R} \mathbf{S} \mathbf{S} \mathbf{Q} \mathbf{R} \mathbf{S} $\mathbf{S$

2. In the given reaction scheme, P is a phenyl alkyl ether, Q is an aromatic compound; R and S are the major products. [JEE(Advanced) 2023]

$$\mathbf{P} \xrightarrow{\text{HI}} \mathbf{Q} \xrightarrow{\text{(ii) NaOH} \atop \text{(iii) CO}_2} \mathbf{R} \xrightarrow{\text{(i)(CH}_3\text{CO)}_2\text{O}} \mathbf{S}$$

The correct statement about S is

- (A) It primarily inhibits noradrenaline degrading enzymes.
- (B) It inhibits the synthesis of prostaglandin.
- (C) It is a narcotic drug.
- (D) It is *ortho*-acetylbenzoic acid.
- 3. The major products obtained from the reactions in List-II are the reactants for the named reactions mentioned in List-I. Match List-I with List-II and choose the correct option. [JEE(Advanced) 2023]

	List-I		List-II
(P)	Etard reaction	(1)	Acetophenone $\xrightarrow{\text{Zn-Hg, HCl}}$
(Q)	Gattermann reaction	(2)	$\begin{array}{c} \text{Toluene} & \xrightarrow{\text{(i) KMnO}_4, \text{KOH, } \Delta} \\ \hline & \text{(ii) SOCl}_2 \end{array}$
(R)	Gattermann-Koch reaction	(3)	Benzene $\xrightarrow{\text{CH}_3\text{Cl}}$ anhyd. AlCl ₃
(S)	Rosenmund reduction	(4)	Aniline $\xrightarrow{\text{NaNO}_2/\text{HCl}}$ $\xrightarrow{\text{273-278 K}}$
		(5)	Phenol $\xrightarrow{Zn, \Delta}$
(A) $P \rightarrow 2$; $Q \rightarrow 4$; $R \rightarrow 1$; $S \rightarrow 3$			(B) $P \rightarrow 1$; $Q \rightarrow 3$; $R \rightarrow 5$; $S \rightarrow 2$
(C) $P \rightarrow 3$; $Q \rightarrow 2$; $R \rightarrow 1$; $S \rightarrow 4$			(D) $P \rightarrow 3$; $Q \rightarrow 4$; $R \rightarrow 5$; $S \rightarrow 2$

"Paragraph II" for Question No. 4

A trinitro compound, 1, 3,5 tris-(4-nitrophenyl) benzene, on complete reaction with an excess of Sn/HCl gives major product, which on treatment with an excess of NaNO₂/HCl at 0°C provides $\bf P$ as the product. $\bf P$, upon treatment with excess of H₂O at room temperature, gives the product $\bf Q$. Bromination of $\bf Q$ in aqueous medium furnishes the product $\bf R$. The compound $\bf P$ upon treatment with an excess of phenol under basic conditions gives the product $\bf S$.

The molar mass difference between compounds \mathbf{Q} and \mathbf{R} is 474 mol⁻¹ and between compounds \mathbf{P} and \mathbf{S} is 172.5 g mol⁻¹. [JEE(Advanced) 2023]

4. The number of heteroatoms present in one molecule of **R** is _____.

[Use: Molar mass (in g mol⁻¹): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5

Atoms other than C and H are considered as heteroatoms]

"Paragraph II" for Question No. 5

A trinitro compound 1, 3, 5 tris-(4-nitrophenyl) benzene, on complete reaction with an excess of Sn/HCl gives major product, which on treatment with an excess of NaNO₂/HCl at 0°C provides $\bf P$ as the product. $\bf P$, upon treatment with excess of H₂O at room temperature, gives the product $\bf Q$. Bromination of $\bf Q$ in aqueous medium furnishes the product $\bf R$. The compound $\bf P$ upon treatment with an excess of phenol under basic conditions gives the product $\bf S$.

The molar mass difference between compounds \mathbf{Q} and \mathbf{R} is 474 mol⁻¹ and between compounds \mathbf{P} and \mathbf{S} is 172.5 g mol⁻¹. [JEE(Advanced) 2023]

5. The total number of carbon atoms and heteroatoms present in one molecule of **S** is _____. [Use: Molar mass in g mol⁻¹]: H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5

Atoms other than C and H are considered as heteroatoms

6. If the reaction sequence given below is carried out with 15 moles of acetylene, the amount of the product **D** formed (in g) is _____.

HC=CH
$$\xrightarrow{\text{(red hot)}}$$
 A $\xrightarrow{\text{H}_3\text{C}}$ Cl B $\xrightarrow{\text{CH}_3\text{COCH}_3}$ C $\xrightarrow{\text{CH}_3\text{COCI}}$ D $\xrightarrow{\text{pyridine}}$ D $\xrightarrow{\text{(100 \%)}}$

The yields of **A**, **B**, **C** and **D** are given in parentheses.

[Given : Atomic mass of H = 1, C = 12, O = 16, Cl = 35]

[JEE(Advanced) 2022]

7. Considering the following reaction sequence, the correct statement(s) is(are) [JEE(Advanced) 2022]

$$\begin{array}{c}
O \longrightarrow O \\
\hline
AlCl_3
\end{array}
\xrightarrow{P} \xrightarrow{Zn/Hg, HCl} Q \xrightarrow{SOCl} R \\
\xrightarrow{AlCl_3} AlCl_3$$
a hydrocarbon $\swarrow Zn/Hg, HCl \searrow S$

- (A) Compounds **P** and **Q** are carboxylic acids.
- (B) Compound S decolorizes bromine water.
- (C) Compounds **P** and **S** react with hydroxylamine to give the corresponding oximes.
- (D) Compound **R** reacts with dialkylcadmium to give the corresponding tertiary alcohol.

8. Consider the following transformations of a compound **P**.

$$(Optically active) (ii) NaNH2 (C9H12) (P4 (ii) X(reagent) Q (C8H12O6) (C8H12O6) (Optically active acid) (Optically active acid)
$$(Pt/H2) (CH3) (CH3) (CH3) (CH3) (CH3) (Optically active acid) (Optically active acid) (Optically active acid) (Optically active acid)$$$$

Choose the correct option(s).

[JEE(Advanced) 2020]

(B) X is Pd-C/quinoline/H₂

9. Consider the reaction sequence from P to Q shown below. The overall yield of the major product Q from P is 75%. What is the amount in grams of Q obtained from 9.3 mL of P?

(Use density of $P = 1.00 \text{ g mL}^{-1}$, Molar mass of C = 12.0, H = 1.0, O = 16.0 and $N = 14.0 \text{ g mol}^{-1}$)

[JEE(Advanced) 2020]

$$P = NH_2 \xrightarrow{\text{(i) NaNO}_2 + HCl/0-5°C} Q$$

$$\xrightarrow{\text{(ii) CH}_2CO_2H/H_2O} QH$$

10. Choose the correct option(s) for the following reaction sequence

$$\underbrace{ \begin{array}{c} \text{i)} \text{Hg}^{2^{+}}, \text{ dil.} \text{H}_{2} \text{SO}_{4} \\ \text{ii)} \text{AgNO}_{3}, \text{ NH}_{4} \text{OH} \\ \text{iii)} \text{Zn-Hg, conc. HCl} \end{array}}_{\text{iii)} \text{Zn-Hg, conc. HCl}} Q \xrightarrow{\text{i)} \text{SOCl}_{2} \text{ pyridine}} R \xrightarrow{\text{Zn-Hg} \\ \text{conc. HCl}} S$$

Consider Q, R and S as major products

[JEE(Advanced) 2019]

(A)
$$MeO$$
 Q
 CO_2H
 MeO
 S

(B) MeO
 Q
 CO_2H
 MeO
 R

(C) MeO
 R
 MeO
 R

Paragraph for Question No. 11 & 12

The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives \mathbf{Q} , The compound \mathbf{Q} on treatment with H_2SO_4 at 0°C gives \mathbf{R} . The reaction of \mathbf{R} with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compounds S.

[Et it compounds **P** is ethyl group]

$$(H_3C)_3C$$
 CO_2Et
 $Q \longrightarrow R \longrightarrow S$

- 11. The reactions, \mathbf{Q} to \mathbf{R} and \mathbf{S} to \mathbf{S} , are -
 - (A) Dehydration and Friedel-Crafts acylation
 - (B) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
 - (C) Aromatic sulfonation and Friedel-Crafts acylation
 - (D) Friedel-Crafts alkylation and Fridel-Crafts acylation

12. The product S is -

[JEE(Advanced) 2017]

$$(H_{3}C)_{3}C$$

$$COCH_{3}$$

$$(H_{3}C)_{3}C$$

$$H_{3}COC$$

$$(H_{3}C)_{3}C$$

$$H_{3}C$$

$$CH_{3}$$

$$(H_{3}C)_{3}C$$

$$COCH_{3}$$

$$(H_{3}C)_{3}C$$

$$COCH_{3}$$

$$(D)$$

13. Among the following reaction(s) which gives (give) tert-butyl benzene as the major product is(are)

[JEE(Advanced) 2016]

Paragraph For Q.14 & Q.15

Treatment of compound \mathbf{O} with KMnO₄ / H⁺ gave \mathbf{P} , which on heating with ammonia gave \mathbf{Q} . The compound \mathbf{Q} on treatment with Br₂ / NaOH produced \mathbf{R} . On strong heating, \mathbf{Q} gave \mathbf{S} , which on further treatment with ethyl 2-bromopropanoate in the presence of KOH following by acidification, gave a compound \mathbf{T} . [JEE(Advanced) 2016]

14. The compound \mathbf{R} is:

15. The compound T is:

(A) Glycine (B) Alanine (C) Valine (D) Serine

16. In the following reactions, the product S is -

[JEE(Advanced) 2015]

$$H_3C$$
 $I. O_3$
 $R \longrightarrow S$

$$(A) \xrightarrow{H_3C} N$$

$$(C)$$
 H_3C

17. For the identification of β -naphthol using dye test, it is necessary to use

[JEE(Advanced) 2014]

- (A) dichloromethane solution of β -naphthol
- (B) acidic solution of β -naphthol
- (C) neutral solution of β -naphthol
- (D) alkaline solution of β -naphthol

SOLUTIONS

1. Ans. (B)

Sol.

2. Ans. (B)

Sol. P is phenyl alkyl etherQ is aromatic compoundR and S are the major producti.e.

Phenyl alkyl ether

$$(Q)$$
 $(Aspirin)$

Pain killer

Acetyl salicylic acid

 $(Non-narcotic analgesic)$

Aspirin inhibits the synthesis of chemicals known as prostaglandin's.

3. Ans. (D)

Sol. $P \rightarrow 3, Q \rightarrow 4, R \rightarrow 5, S \rightarrow 2$

(i)
$$Ph - C - CH_3$$
 $Zn-Hg/HCl$ $Ph - CH_2 - CH_3$ Acetophenone

(ii)
$$CH_3$$
 $C-Cl$ CHO CHO

(iii)
$$CH_3 - CI$$
 $CH_3 - CI$ $CH_3 - CI$

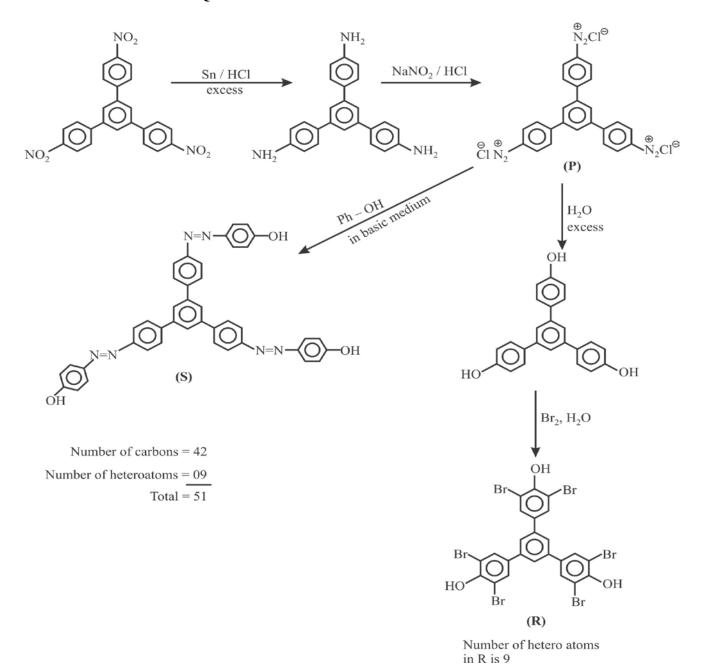
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(iv)
$$NaNO_2/HCl$$
 Cu/HCl Cu/HCl CHO Gattermann reaction (Q)

(V) Zn/Δ CO/HCl $AlCl_3$ $Cattermann Koch reaction (R)$

- 4. Ans. (9.00)
- 5. Ans. (51.00)

Sol. Common solution for Q.No. 4 and 5



6. Ans. (135.80 - 136.20)

Sol.

3HC
$$\equiv$$
CH $\xrightarrow{\text{Iron tube}}$ $\xrightarrow{\text{red hot}}$ $\xrightarrow{\text{H}_3C}$ $\xrightarrow{\text{H}_3C}$ $\xrightarrow{\text{Cl}}$ $\xrightarrow{\text{L}_1 O_2}$ $\xrightarrow{\text{L}_2 O_2}$ $\xrightarrow{\text{L}_3 O_$

7. Ans. (A, B, C or A, C)

Sol.

8. Ans. (B, C)

Sol.

9. Ans. (18.60)

Sol.

$$\begin{array}{c|c} NH_2 & & \\ \hline \\ NaNO_2 + HCl \\ \hline \\ O-5^{\circ}C \end{array} \\ \hline \\ OH \\ + NaOH \\ \hline \end{array}$$

$$\begin{array}{c} N=N-Ph \\ OH \\ \hline \\ Q \end{array} \qquad \begin{array}{c} CH_3CO_2H \\ \hline \\ H_2O \end{array} \qquad \begin{array}{c} N=N-Ph \\ \hline \\ O^- \end{array}$$

Molecular weight of

aniline =
$$M.wt.$$
 of C_6NH_7

$$=72+7+14=93$$

density of $P = 1 \text{ gm ml}^{-1}$

9.3 ml of P = 9.3 gm P

$$=\frac{9.3}{9.3}=0.1$$
 mole P

The mole ratio
$$PhNH_2: PhN_2^+:$$

= 1 : 1 : 1

so the mole of Q formed will be 0.1 mole and extent of reaction is 100% but if it is 75% yield.

OH

Then amount of Q =
$$0.1 \times \frac{75}{100} = 0.075$$
 mol

The molecular formula of $Q = C_{16}H_{12}ON_2$

so M.wt. of Q =
$$16 \times 12 + 12 \times 1 + 16 + 2 \times 14$$

$$= 192 + 12 + 16 + 28$$

= 248 gm

so amount of $Q = 248 \times 0.075$

= 18.6 gm

10. Ans. (B, D)

Sol.

$$MeO \longrightarrow C = C - CH_2 - CH = O \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CH = O \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CH_2 - CH_2 - CO_2 \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CO_2 \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CO_2 \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CO_2 \longrightarrow MeO \longrightarrow C - CH_2 - CH_2 - CH_2 - CO_2 \longrightarrow MeO \longrightarrow C - CH_2 - CO_2 - CH_2 - CH$$

11. Ans.(B) Sol.

12. Ans. (D)

13. Ans. (B, C, D)

Sol.
$$Br + NaOC_2H_5 \xrightarrow{E_2}$$

3° alkyl bromide

$$\begin{array}{c} + \bigcirc \longrightarrow \text{No reaction} \\ \\ \nearrow \\ \text{Cl} + \text{AlCl}_3 \longrightarrow \begin{array}{c} 1,2 \text{ shift} \\ \text{of } \text{H}^- \end{array} \\ \xrightarrow{+} \begin{array}{c} \bigcirc \\ \text{AlCl}_4^{\Theta} \end{array}$$
 tert-butyl benzene

tert-butyl benzene

14. Ans. (A)

15. Ans. (B)

Solution for Q.14 & 15

Q to R is Hoffmann's bromamide degradation reaction

S to T is Gabriel's phthalimide sysnthesis

16. Ans. (A)

Sol.
$$(1) O_3$$
 $(2) Zn/H_2O$ $(2) Zn/H_2O$ $(3) Zn/H_2O$ $(3) Zn/H_2O$ $(4) C=O$ $(5) Zn/H_2O$ (5)

17. Ans. (D)

Sol. In alkaline medium the activating nature of –OH group increases and the rate of electrophilic substitution (Coupling Reaction) increases on aromatic ring.

$$\begin{array}{c} OH \\ OH^{-} \\ \hline \end{array}$$

-OH group converts to −O

Electron releasing nature of $-O^{\Theta}$ is more than -OH

Nucleophilicity of β -napthol increases in basic medium

$$\begin{array}{c} \text{N-Ph} \\ \parallel \\ \text{N} \\ \text{OH} \\ \text{Ph-N}_2\text{Cl}^{\Theta} \\ \end{array} \begin{array}{c} \text{OH} \\ \text{(Coloured dye)} \end{array}$$