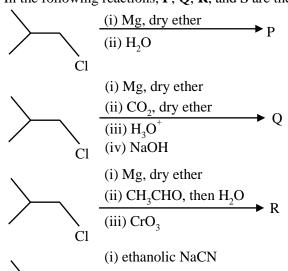
ORGANIC CHEMISTRY

AMINE DERIVATIVE

1. In the following reactions, **P**, **Q**, **R**, and **S** are the major products.

[JEE(Advanced) 2023]



The correct statement about P, Q, R, and S is

- (A) **P** is a primary alcohol with four carbons.
- (B) ${\bf Q}$ undergoes Kolbe's electrolysis to give an eight-carbon product.
- (C) **R** has six carbons and it undergoes Cannizzaro reaction.
- (D) **S** is a primary amine with six carbons.
- 2. Consider the following reaction sequence,

$$H_{3}C \xrightarrow{P} Q \xrightarrow{R} S \xrightarrow{H_{2}O} T$$

$$\downarrow U$$

$$\downarrow U$$

$$\downarrow COOH$$

the correct option(s) is(are)

[JEE(Advanced) 2022]

(A)
$$\mathbf{P} = H_2/Pd$$
, ethanol

$$\mathbf{R} = \text{NaNO}_2/\text{HCl}$$

$$U = 1. H_3 PO_2$$

2. KMnO₄ - KOH, heat

(B)
$$\mathbf{P} = \text{Sn/HCl}$$

$$\mathbf{R} = HNO_2$$

$$\mathbf{S} = \bigcup_{\mathbf{H}_{3}\mathbf{C}} \overset{\oplus}{\bigvee_{\mathbf{N}_{2}}} \mathbf{Cl}^{\ominus}$$

(C)
$$\mathbf{S} = \mathbf{H}_{3}\mathbf{C}$$

$$T = H_3C$$

$$\mathbf{U} = 1. \text{ CH}_3\text{CH}_2\text{OH}$$

2. KMnO₄ - KOH, heat

(D)
$$\mathbf{Q} = \frac{NO_2}{NO_2}$$

$$\mathbf{R} = H_2/Pd$$
, ethanol

$$T = \bigcup_{H_3C} OH$$

JEE Advanced Chemistry 10 Years Topicwise Questions with Solutions

3. The reaction of \mathbf{Q} with PhSNa yields an organic compound (major product) that gives positive Carius test on treatment with Na₂O₂ followed by addition of BaCl₂. The correct option(s) for \mathbf{Q} is (are).

[JEE(Advanced) 2021]

$$(A) \stackrel{O_2N}{\longleftarrow} F \qquad (B) \stackrel{O_2N}{\longleftarrow} -I \qquad (C) \stackrel{MeS}{\longleftarrow} -Br \qquad (D) \stackrel{O_2N}{\longleftarrow} Cl$$

4. Scheme 1 and 2 describe the conversion of **P** to **Q** and **R** to **S**, respectively. Scheme 3 describes the synthesis of **T** from **Q** and **S**. The total number of Br atoms in a molecule of **T** is ______.

[JEE(Advanced) 2019]

Scheme 1:

(i)
$$Br_2$$
 (excess), H_2O
(ii) $NaNO_2$, HCl , 273 K
(iii) $CuCN/KCN$ \longrightarrow Q
(iv) H_3O^+ , Δ (major)
(v) $SOCl_2$, pyridine

Scheme 2:

(i) Oleum
(ii) NaOH,
$$\Delta$$

(iii) H⁺
(iv) Br₂, CS₂ 273 K

Scheme 3:

$$S \xrightarrow{(i) \text{ NaOH}} T$$

$$\xrightarrow{(ii) \mathbf{Q}} \text{ (major)}$$

5. 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) the following reaction sequence is (are): [JEE(Advanced) 2018]

R
$$\xrightarrow{1) \text{Ac}_2\text{O}, \text{ pyridine}}$$
 $\xrightarrow{2) \text{Br}_2, \text{ CH}_3\text{CO}_2\text{H}}$ S $\xrightarrow{2) \text{Br}_2/\text{H}_2\text{O} \text{ (excess)}}$ $\xrightarrow{3) \text{H}_3\text{O}^+}$ S $\xrightarrow{3) \text{NaNO}_2, \text{HCl}/273-278K}$ major product(s) $\xrightarrow{4) \text{NaNO}_2, \text{HCl}/273-278K}$ $\xrightarrow{4) \text{H}_3\text{PO}_2}$

6. The major product of the following reaction is

[JEE(Advanced) 2017]

ii) aq. NaOH
$$NH_{2}$$

$$OH$$

$$N=N$$

$$N$$

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

[JEE(Advanced) 2016]

8. The major product of the reaction is:

[JEE(Advanced) 2015]

9. In the following reactions, the major product W is:

[JEE(Advanced) 2015]

10. In the reaction shown below, the major product(s) formed is / are :

[JEE(Advanced) 2014]

$$\begin{array}{c|c} NH_2 & \xrightarrow{acetic \ anhydride} \\ NH_2 & \xrightarrow{CH_2Cl_2} \end{array} product(s)$$

$$(A) \underbrace{ \begin{array}{c} H \\ N \\ O \\ NH_2 \end{array}}_{H_2} + CH_3COOH$$

$$(B) \underbrace{ \begin{array}{c} H \\ \\ \\ O \\ \\ \end{array}}_{O} + CH_{3}COOH$$

$$(C) \begin{array}{c} H \\ N \\ O \\ O \\ O \end{array} \begin{array}{c} CH_3 \\ CH_3 \end{array} + H_2O$$

$$(D) \begin{picture}(60,0)(0,0) \put(0,0){\ovalphi{15mu}} \put(0,0){\oval$$

SOLUTIONS

Sol.
$$CH_{2}MgCl \xrightarrow{(ii) Mg} CH_{2}MgCl \xrightarrow{(ii) H-O-H} CH_{3} CH_{3}(P) + Mg OH$$

$$CH_{2}MgCl \xrightarrow{O=C=O} CH_{2}MgCl \xrightarrow{O=C=O} CH_{2}-C-OMgCl$$

$$H_{3}O^{\oplus}$$

$$CH_{2}-CH_{2} \xrightarrow{C-OMgCl} CH_{2}-C-OMgCl$$

$$H_{3}O^{\oplus}$$

$$CH_{2}-CH_{2}-C-OMgCl$$

$$CH_{3}-C-OMgCl \xrightarrow{C-OMgCl} CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{3}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{3}-C-OHgCl$$

$$CH_{2}-C-OHgCl$$

$$CH_{3}-C-OHgCl$$

$$CH_{3$$

It does not give Cannizaro reaction

$$CH_{2}-CN \xrightarrow{(ii) H_{2}, Ni} CH_{2}-CH_{2}-NH_{2}$$

$$CH_{2}-CH_{2}-NH_{2}$$

$$CH_{2}-CH_{2}-NC$$

$$LiAlH_{4}, HOH$$

$$CH_{2}-CH_{2}-NH-CH_{3}$$

$$(S)$$

It's secondary amine

2. Ans. (A, B, C)

Sol.

3. Ans. (A, D)

Sol. (A)
$$O_2N - \bigcirc F \xrightarrow{PhS^{(\cdot)}Na^+} O_2N - \bigcirc PhS^{(\cdot)}Na^+ \bigcirc O_2N - \bigcirc PhS^{(\cdot)}NO_2 - \bigcirc PhS^{(\cdot)}NO$$

(D)
$$O_2N \longrightarrow Cl \xrightarrow{PhSNa} O_2N \longrightarrow SPh \xrightarrow{Na_2O_2 + BaCl_2} Sph \xrightarrow{SMe} Carius test$$

4. Ans. (4.00)

Sol. Scheme 1:

$$\begin{array}{c}
NH_{2} \\
NH_{2} \\
NH_{2} \\
Br
\\
Br
\\
Br
\\
SOCl_{2}, pyridine
\end{array}$$

$$\begin{array}{c}
NH_{2} \\
Br
\\
Br
\\
SOCl_{2}, pyridine
\end{array}$$

$$\begin{array}{c}
NH_{2} \\
Br
\\
SOCH
\\
Br
\\
SOCH
\\
Br
\\
SOCH
\\
S$$

Scheme 2:

$$\begin{array}{c}
(i) \text{ Oleum} \\
\hline
H_2SO_4 + SO_3
\end{array}$$

$$\begin{array}{c}
(ii) \text{ NaOH, } \Delta \\
\hline
(III) \text{ H}^{\oplus}
\end{array}$$

$$\begin{array}{c}
(vi) \text{ Br}_2, \text{CS}_2, 273K \\
\hline
OH \\
OH \\
Br \\
(Major)
\end{array}$$

$$\begin{array}{c}
OH \\
OH \\
OH \\
OH \\
OH
\end{array}$$

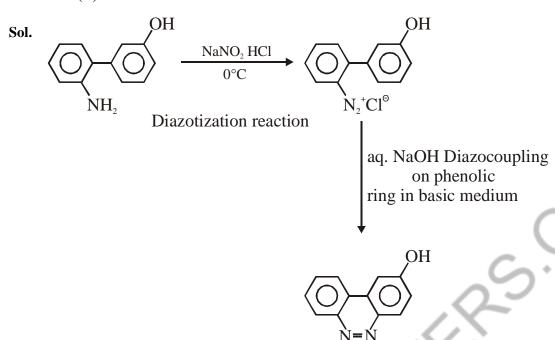
Scheme 3:

5. Ans. (D)

Sol.

$$NH_{2} \longrightarrow NO_{2} \longrightarrow NH_{2}SO_{4} \longrightarrow NO_{2}SO_{4} \longrightarrow NO_{2}SO_{5}SO_{6} \longrightarrow NO_{2}SO_{5}SO_{6} \longrightarrow NO_{2}SO_{5}SO_{6} \longrightarrow NH_{2}SO_{5}SO_{6} \longrightarrow NH_{2}SO_{6} \longrightarrow NH_{$$

6. Ans. (C)



Para is less hindered

7. Ans. (B)

Sol.

Sol.
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

 $HNO_2 + HCl \rightleftharpoons H_2 \stackrel{\oplus}{O} NO + Cl^-$
 $H_2 \stackrel{\oplus}{O} NO \rightarrow H_2O + NO^+$

$$\begin{array}{c} \text{C-OH} \\ \text{NH}_2 \\ \text{(S-Leucine)} \end{array} + \text{H}_2\text{O} \\ \begin{array}{c} \text{NH}_2 \\ \text{NH}_2 \\ \text{(S-Leucine)} \end{array} + \text{H}_3\text{O}^+ \\ \begin{array}{c} \text{NH}_2 \\ \text{NO} \\ \text{C=O} \\ \text{C=O} \\ \text{H}_2\text{O} \end{array}$$

9. Ans. (A)

Sol.
$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

 $HNO_2 + HCl \Longrightarrow H_2NO_2^+ + Cl^-$
 $H_2NO_2^+ \longrightarrow H_2O + N$
 $NH_2 \longrightarrow NO^+$
 $NH_2 \longrightarrow NO^+$

Benzenediazonium ion

The formation of V is example of diazotisation reaction.

for
$$\beta$$
-napthol, α , position is attacking site for electrophile
$$\begin{array}{c} OH \\ +NaOH \\ \beta -napthol \\ \end{array}$$
 (Azodye red colored)

The formation of W from V is example of diazocoupling reaction.

10. Ans. (A)

Sol.
$$CH_2$$
-NH $_2$ CH_3 -C $_1$ CH_2 -NH $_2$ CH_2 -NH $_$