#### **ORGANIC CHEMISTRY**

#### HALOGEN DERIVATIVE

1. Match the reactions in List-I with the features of their products in List-II and choose the correct option.

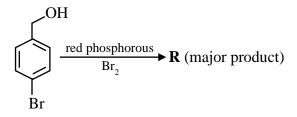
[JEE(Advanced) 2023]

List-I

List-II

- $\begin{array}{ccc} \text{(P)} & \text{(-)-1-Bromo-2-ethylpentane} & \underline{\text{aq. NaOH}} \\ & \text{(single enantiomer)} & \overline{S_N 2 \text{ reaction}} \end{array}$
- (1) Inversion of configuration
- (Q) (-)-2-Bromopentane aq. NaOH (single enantiomer)  $S_N$ 2 reaction
- (2) Retention of configuration
- (R) (-)-3-Bromo-3-methylhexane aq. NaOH (single enantiomer)  $S_{N1}$  reaction
- (3) Mixture of enantiomers
- (S) Me H Me Br  $\frac{\text{aq. NaOH}}{\text{S}_{\text{N}1} \text{ reaction}}$
- (4) Mixture of structural isomers
- (5) Mixture of diastereomers
- (A)  $P \rightarrow 1$ ;  $Q \rightarrow 2$ ;  $R \rightarrow 5$ ;  $S \rightarrow 3$
- (B)  $P \rightarrow 2$ ;  $Q \rightarrow 1$ ;  $R \rightarrow 3$ ;  $S \rightarrow 5$
- (C)  $P \rightarrow 1$ ;  $Q \rightarrow 2$ ;  $R \rightarrow 5$ ;  $S \rightarrow 4$
- (D)  $P \rightarrow 2$ ;  $Q \rightarrow 4$ ;  $R \rightarrow 3$ ;  $S \rightarrow 5$
- **2.** Consider the following reaction.

[JEE(Advanced) 2022]



On estimation of bromine in 1.00 g of **R** using Carius method, the amount of AgBr formed (in g) is \_\_\_\_\_.

[Given : Atomic mass of H = 1, C = 12, O = 16, P = 31, Br = 80, Ag = 108]

3. The weight percentage of hydrogen in  $\mathbf{Q}$ , formed in the following reaction sequence, is \_\_\_\_\_.

[JEE(Advanced) 2022]

C1
$$\frac{1. \text{ NaOH, 623 K, 300 atm}}{2. \text{ conc. H}_2\text{SO}_4 \text{ and then}} \bullet \mathbf{Q} \text{ (major product)}$$
conc. HNO<sub>3</sub>

[Given : Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35]

- 4. The correct statement(s) for the following addition reactions is(are)
- [JEE(Advanced) 2017

(i) 
$$H_3C$$
 $CH_3$ 
 $Br_2/CHCl_3$ 
 $M$  and  $N$ 

(ii) 
$$H_3C$$
  $\longrightarrow$   $CH_3$   $\xrightarrow{Br_2/CHCl_3}$   $\bullet$  O and  $\bullet$ 

- (A) (M and O) and (N and P) are two pairs of diastereomers
- (B) Bromination proceeds through trans-addition in both the reactions
- (C) O and P are identical molecules
- (D) (M and O) and (N and P) are two pairs of enantiomers
- For the following compounds, the correct statement(s) with respect of nucleophilic substitution reactions is(are):[JEE(Advanced) 2017]

(I) Br (III) 
$$H_3C - C - Br$$
 (IV)  $Br$ 

- (A) I and II follow S<sub>N</sub>2 mechanism
- (B) The order of reactivity for I, III and IV is: IV > I > III
- (C) I and III follow S<sub>N</sub>1 mechanism
- (D) Compound IV undergoes inversion of configuration
- **6.** Which of the following combination will produce  $H_2$  gas?

[JEE(Advanced) 2017]

- (A) Zn metal and NaOH(aq)
- (B) Au metal and NaCN(aq) in the presence of air
- (C) Cu metal and conc. HNO<sub>3</sub>
- (D) Fe metal and conc. HNO<sub>3</sub>
- 7. In the following reaction, the major product is -

[JEE(Advanced) 2015]

$$CH_3$$
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_3$ 

$$(A) CH_{2} CH_{3}$$

$$Br$$

$$(C)$$
 $H_2C$ 
 $CH_3$ 
 $Br$ 

$$(D)$$
 $H_3C$ 
 $Br$ 

**8.** Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) –

[JEE(Advanced) 2015]



$$(C) \begin{tabular}{c} $H_2C$ & $H_2C$ & $Br$ & $H_2C$ & $H_2C$$$

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

Mono halo substituted derivative when 
$$X_2=l_2$$

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

$$\text{tri halo substituted derivative when } X_2=Cl_2$$

The observed pattern of electrophilic substitution can be explained by -

[JEE(Advanced) 2014]

- (A) The steric effect of the halogen
- (B) The steric effect of the tert-butyl group
- (C) The eletronic effect of the phenolic group
- (D) The electronic effect of the turt-butyl group

# **SOLUTIONS**

### 1. Ans. (B)

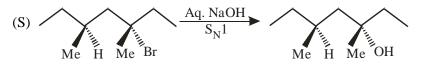
Sol. 
$$P \rightarrow 2, Q \rightarrow 1, R \rightarrow 3, S \rightarrow 5$$

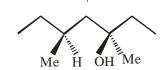
$$(P) \xrightarrow{\text{Br}} \underbrace{\begin{array}{c} \text{Aq. NaOH} \\ \text{S}_{\text{N}}^{2} \end{array}}_{\text{Retention of configuration}} \circ H$$

Inversion of configuration

(R) 
$$*$$
  $Aq. NaOH$   $*$   $OH$   $+$   $OH$   $OH$ 

Mixture of enantiomers





Diastereomeric mixture

# 2. Ans. (1.49 - 1.51)

Sol. 
$$OH$$

$$Br$$

$$Br$$

$$Br$$

$$M.W. = 250 \text{ g/mol}$$

$$Br$$

$$(R)$$

$$1g R \rightarrow \frac{1}{250} moles$$

No. of Br Atoms 
$$\rightarrow \frac{2}{250}$$
 moles

Moles of AgBr 
$$\rightarrow \frac{2}{250}$$
 moles

Mass of AgBr = 
$$\frac{2}{250} \times (108+80) = 1.504$$

## **ALLEN®**

### 3. Ans. (1.30 - 1.32)

Sol. ONa OH OH ONA OH NO2 Conc. 
$$H_2SO_4$$
 and conc.  $HNO_3$  NO2 Mass % of  $H$  Picric acid  $=\frac{3}{229} \times 100 = 1.31\%$ 

#### 4. Ans. (A, B)

(M) and (N) are identical meso compounds

(O) and (P) are enantiomers

Explanation of 4 options:

- (A) (M) and (O) are distereomers of each other.
  - (N) and (P) are distereomers of each other.
- (B) Addition of Br<sub>2</sub> on alkene follows non-classical carbocation mechanism. It is anti or trans addition.
- (C) (O) and (P) are enantiomers
- (D) (M) and (N) are identical and (O) and (P) are enantiomers.

(M and O) are distereomers and (N and P) are distereomers.

#### $5. \quad Ans. (A, B, C, D)$

Sol. 
$$CH_2$$
-Br  $CH_2$ -Br  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

- (A) I and II follow S<sub>N</sub>2 mechanism as they are primary
- (B) Reactivity order IV > I > III
- (C) I and III follows S<sub>N</sub>1 mechanism as they form stable carbocation
- (D) Compound IV undergoes inversion of configuration.

$$\begin{array}{c|c}
CH_3 & Nu^{\Theta} \\
Br & SN^2
\end{array}$$

(inverted product)

(inverted product) (retained product)

#### 6. Ans. (A)

**Sol.** (A) 
$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

(B) 
$$4Au + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

(C) 
$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
  
(conc.)

(D) Formation of passive layer of Fe<sub>2</sub>O<sub>3</sub> on the surface of Fe and NO<sub>2</sub> gas is evolved.



# 7. Ans. (D)

Machanism:

# 9. Ans. (A, B, C)

Sol.

OH
$$C(CH_3)_3$$

Orientation in electrophilic substition reaction is decided by

- (A) The steric effect of the halogen
- (B) The steric effect of the tert-butyl group
- (C) The electronic effect of the phenolic group