ORGANIC CHEMISTRY

CARBONYL COMPOUND

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

[JEE(Advanced) 2023]

$$CH_{3}CH_{2}CH(CH_{3})CH_{2}CN \xrightarrow{\text{(i) PhMgBr, then } H_{3}O^{\oplus}} P$$

$$\begin{array}{c} O \\ || \\ Ph-H + CH_3CCl \end{array} \xrightarrow[(ii) \text{ anhyd. AlCl}_3]{(ii) \text{ PhMgBr, then } H_2O} \bullet Q$$

$$CH_{3}CH_{2}CC1 \xrightarrow{(i)\frac{1}{2}(PhCH_{2})_{2}Cd} R$$

$$PhCH_{2}CHO \xrightarrow{\begin{subarray}{c} (i) PhMgBr, then $H_{2}O$\\ \hline & (ii) CrO_{3}, dil. H_{2}SO_{4}\\ \hline & (iii) HCN\\ & (iv) H_{2}SO_{4}, \Delta \end{subarray}} S$$

The correct statement(s) about **P**, **Q**, **R**, and **S** is(are)

- (A) Both \mathbf{P} and \mathbf{Q} have asymmetric carbon(s).
- (B) Both \mathbf{Q} and \mathbf{R} have asymmetric carbon(s).
- (C) Both \mathbf{P} and \mathbf{R} have asymmetric carbon(s).
- (D) **P** has asymmetric carbon(s), **S** does **not** have any asymmetric carbon.
- 2. In the reaction scheme shown below \mathbf{Q} , \mathbf{R} and \mathbf{S} are the major products.

[JEE(Advanced) 2020]

$$\begin{array}{c|c} CH_3 \\ H_3C \\ H_3C \\ \end{array} \begin{array}{c} CH_3 \\ O \\ \hline \\ AlCl_3 \\ \end{array} \begin{array}{c} O \\ \hline \\ (i) \ Zn-Hg/HCl \\ \hline \\ (ii) \ H_3O^+ \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} (i) \ CH_3MgBr \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array} \begin{array}{c} SR \\ \hline \\ (iii) \ H_2SO_4/\Delta \\ \end{array}$$

The correct structure of

(A)
$$\mathbf{S}$$
 is H_3C CH_3 H_3C CH_3 CH_3

$$H_3C$$
 CH_3
 H_3C
 CH_3
 CH_3
 CH_3
 CH_3

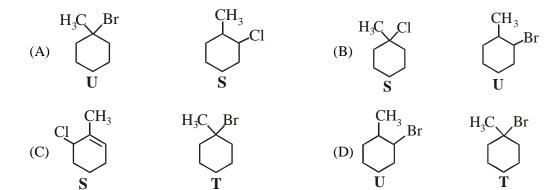
(B)
$$\mathbf{Q}$$
 is H_3C CH_3 H_3C CH_3 H_3C CH_3

$$\begin{array}{c} H_3C \\ H_3C \\ \end{array} \begin{array}{c} H_3C \\ \end{array} \begin{array}{c} CH_3 \\ \end{array} \\ (D) \ \mathbf{S} \ \mathrm{is} \ H_3C \\ \end{array}$$

3. Choose the correct option(s) for the following set of reactions

[JEE(Advanced) 2019]

$$\begin{array}{ccc} \mathbf{C_{6}H_{10}O} \xrightarrow{\text{i) MeMgBr}} & \mathbf{Q} \xrightarrow{\text{Conc. HCl}} & \mathbf{S} \\ & \downarrow^{20\% \text{ H}_{3}\text{PO}_{4}, 360 \text{ K}} & \\ & \mathbf{T} \\ \text{(major)} & \xrightarrow{\text{ii) H}_{2}, \text{Ni}} & \mathbf{R} \xrightarrow{\text{HBr, benzoyl peroxide}} & \mathbf{U} \\ \text{(major)} & & \text{(major)} & \end{array}$$



- **4.** The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)
- [JEE(Advanced) 2018]

(A)
$$Conc. H_2SO_4$$

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

(C) $Conc. H_2SO_4$

$$\Delta$$
(D) CHO
$$CHO$$

- 5. In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is
 - (Atomic weight 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]

$$\begin{array}{c|c}
\hline
 & NaOBr \\
\hline
 & H_3O^+
\end{array}
\begin{array}{c}
A \\
\hline
 & (60\%)
\end{array}
\begin{array}{c}
NH_3, \Delta \\
\hline
 & B \\
\hline
 & (50\%)
\end{array}
\begin{array}{c}
Br_2/KOH \\
\hline
 & C \\
\hline
 & (50\%)
\end{array}
\begin{array}{c}
Br_2(3 \text{ equiv}) \\
\hline
 & AcOH
\end{array}
\begin{array}{c}
D \\
\hline
 & (100\%)
\end{array}$$

6. Positive Tollen's test is observed for

[JEE(Advanced) 2016]

$$(A) \underset{H}{\overset{H}\longrightarrow O} \qquad (B) \underset{Ph}{\overset{OH}\longrightarrow Ph} \qquad (D) \underset{Ph}{\overset{O}\longrightarrow Ph}$$

7. The major product of the following reaction sequence is:

[JEE(Advanced) 2016]

8. Reagent(s) which can be used to bring about the following transformation is(are)

[JEE(Advanced) 2016]

- (A) LiAlH₄ in $(C_2H_5)_2O$
- (C) NaBH₄ in C₂H₅OH

- (B) BH₃ in THF
- (D) Raney Ni / H₂ in THF
- **9.** The major product of the following reaction is -

[JEE(Advanced) 2015]

$$CH_3$$
 I. KOH, H_2O II. H^+ , Heat

10. Among the following the number of reaction(s) that produce(s) benzaldehyde is –

[JEE(Advanced) 2015]

I.
$$CO, HCl$$

Anhydrous AlCl₃/CuCl

II. H_2O
 $100^{\circ}C$

III. H_2

Pd-BaSO₄

IV. CO_2Me

DIBAL-H

Toluene, $-78^{\circ}C$
 H_2O

Paragraph For Questions No. 11 and 12

In the following reaction

[JEE(Advanced) 2015]

$$C_{8}H_{6} \xrightarrow{\text{Pd-BaSO}_{4}} C_{8}H_{8} \xrightarrow{\text{(i) } B_{2}H_{6}} X$$

$$H_{2}O$$

$$H_{2}O$$

$$HgSO_{4}, H_{2}SO_{4}$$

$$C_{8}H_{8}O \xrightarrow{\text{(i) } EtMgBr, H_{2}O} Y$$

$$(ii) H^{+}, heat$$

11. Compound X is:

$$(A) \bigcirc CH_3$$

12. The major compound Y is:

$$CH_2$$
 CH_3

SOLUTIONS

1. Ans. (C, D)

Sol. Formation of P

$$CH_3 - CH_2 - CH - CH_2 - CN \xrightarrow{PhMgBr} H_3O^+$$

$$PhMgBr \\ then H_3O^+$$

$$Asymmetric \\ carbon \\ (P)$$

Formation of Q

Formation of R

$$C - C1 + \frac{1}{2} (Ph - CH_2)_2 Cd$$

$$Ph MgBr$$

$$then H_3 O^+$$

$$asymmetric$$

$$carbon$$

$$(R)$$

Formation of S

(S) No asymmetric carbon

2. Ans. (B, D)

3. Ans. (B, D)

Sol.

OH Conc. HCl Cl conc. HCl S

Br (i)
$$H_2$$
, Ni (ii) Br_2 , hv R

HBr, benzoyl peroxide U

4. Ans. (A, B, D)

ol. (A)
$$Conc H_2SO_4$$

$$A$$
(B) $Me = H$

$$Conc H_2SO_4$$

$$A$$
(C) $COOH$

$$COOH$$

5. Ans. (495)

Sol.
$$NaOBr$$
 NH_{3} , Δ NH_{3} , Δ NH_{3} , Δ NH_{3} , Δ NH_{2} NH_{2} NH_{2} NH_{2} NH_{2} NH_{2} NH_{3} NH_{2} NH_{3} , Δ NH_{2} NH_{2

6. Ans. (A, B, C)

Sol. Tollens's test is given by compounds having aldehyde group. Also α -hydroxy carbonyl gives positive tollen's test.

(B)
$$CH=O$$
 Tollen's CO_2^- + Ag mirror (+ve test)

Benzaldehyde

(D) PhCH=CH-C-Ph
$$\xrightarrow{\text{Tollen's}}$$
 No reaction (-ve test)

7. Ans. (A)

Sol.

$$\begin{array}{c|cccc} OH & OH & OH \\ \hline & H-C-H/NaOH \\ \hline & [Cross aldol reaction] & \hline & H-C-H/NaOH \\ \hline & [Cross cannizaro \\ & reaction] & \hline \end{array} \\ \begin{array}{c|cccccc} OH & OH & OH \\ \hline & CH_2 & OH$$

$$\begin{array}{c|c} OH & OH \\ CH_2 & O \\ \hline & H-C-H/H^{^+} \\ \hline & Acetal formation \end{array}$$

8. Ans. (C, D)

Sol.

LiAlH₄ in $(C_2H_5)_2O$; BH₃ in (THF); Raney Ni (H₂) either can reduce all functional group or can reduce some of the functional group of the compound given above in reactant side.

But NaBH₄ is example of selective reducing agent. It can not reduce $\overset{-}{\text{C}}$ -O- (ester group) $\overset{-}{\text{C}}$ -OH ,

(carboxylic acid group), (epoxide group) , but reduces –CH=O (aldehyde group)into –CH $_2$ OH

(1º alcohol)

9. Ans. (A)

Sol.

Mechanism:

$$\begin{array}{c|c} OH^{\Theta} & OH^{\Theta} \\ \hline \\ OH^{O} & OH^{O} \\ \hline \\ OH^{O} & OH^{$$

10. Ans. (4)

Sol. I.
$$\bigcirc$$
 CO , HCl \bigcirc CH=O Anhydrous AlCl $_3$ /CuCl

this reaction is called Gattermann koch synthesis

II.
$$\bigcirc$$
 CH $<$ Cl \bigcirc H₂O \bigcirc CH=O

this reaction is called Rosenmund reduction

11. Ans. (C)

Sol.
$$\begin{bmatrix} C_8H_6 \xrightarrow{Pd\text{-BaSO}_4} & C_8H_8 \end{bmatrix} \xrightarrow{(1) B_2H_6} \xrightarrow{\Theta} CH_2 \xrightarrow{C-H} H$$

$$D.U. = 6$$
Aromatic alkyne
$$H_2O \\ HgSO_4, H_2SO_4$$

$$OH$$

$$CH_2 \xrightarrow{C} H$$

$$H_2O \\ HgSO_4, H_2SO_4$$

$$OH$$

$$H_2O$$

$$HgSO_4, H_2SO_4$$

12. Ans. (D)

Sol.
$$H_2O, HgSO_4, H_2SO_4$$

$$EtMgBr, H_2O$$

$$H^+$$

$$\Delta$$

$$H^+$$