SOLOMONS/FRYHLE/SNYDER ORGANIC CHEMISTRY FOR JEE MAIN & ADVANCED

JEE Advanced / Multidisciplinary PYQs with Answers and Solutions

ANSWERS WITH EXPLANATION

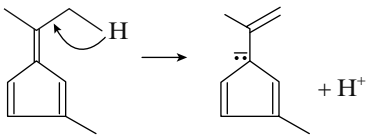
Chapter 2 Families of Carbon Compounds: Functional Groups and Intermolecular Forces

1. (B) Bond enthalpy

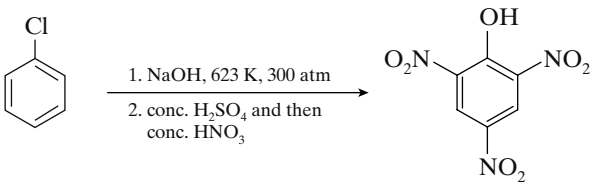
$$C-F > C-Br > C-I \Rightarrow R > P > Q$$

CHAPTER 3 An Introduction to Organic Reactions and Their Mechanisms: Acids and Bases

1.



2. The reaction gives 2, 4, 6–trinitrophenol, also known as Picric Acid, as shown below:



Calculation of the Weight Percentage of Hydrogen.

Now, let's determine the molecular weight of Picric Acid ($C_6H_3N_3O_7$):

$$M = (6 \times 12) + (3 \times 1) + (3 \times 14) + (7 \times 16)$$
$$= 72 + 3 + 42 + 112 = 229 \text{ g/mol}$$

The weight percentage of hydrogen is:

(Mass of Hydrogen)/(Molecular Mass) × 100 = (3/229) × 100 = 1.31%

The weight percentage of hydrogen is 1.31%.

CHAPTER 4 Stereochemistry: Chiral Molecules

1. In neutral aqueous medium, permanganate ion is reduced as

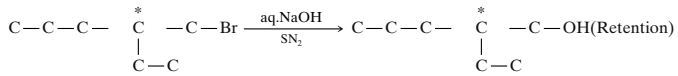
$$M_nO_4^- \rightarrow M_nO_2$$

Under these conditions, iodide ion is oxidized beyond iodine to iodate

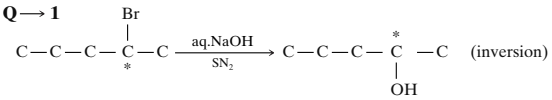
$$I^- \rightarrow IO_3^-$$

Product formed 'iodate ion'.

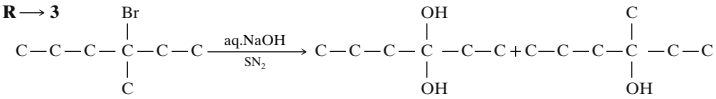
2. **P ⟶ 2**



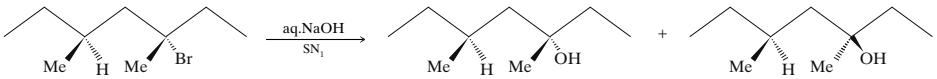
Q ⟶ 1



R ⟶ 3



S ⟶ 5



3. Let's start by negating option. (C) and (D) are not meso-isomers.

Out of the remaining, Option B (gauche from) is more stable due to intramolecular hydrogen bonding.

4. Step 1: The given compound is norbornene fused with benzene. It contains:

- A benzene ring (6 sp^2 carbon atoms).
- A double bond in the norbornene part.

Step 2: Ozonolysis Reaction (O_3, Zn/H_2O):

- Ozonlysis cleaves the C=C bond in the norbornene system and converts it into two carbonyl (–C=O) group.
- The benzene ring remains unchanged.

Thus, the intermediate after ozonolysis contains:

- A benzene ring (6 sp^2 carbons).
- Two carbonyl (–C=O) group (each carbon is sp^2 hybridized).
- Total at this stage = 6 (benzene) + 2 (carbonyls) = 8 sp^2 atoms.

Step 3: Reaction with NH_2OH (Hydroxylamine Reaction):

- NH_2OH converts the two C=O group into oximes (–C=NOH).

- In an oxime, both the carbon (C=NOH) and nitrogen (N in C=NOH) are sp^2 hybridized due to the lone pair delocalization on nitrogen.

Thus, in the final product:

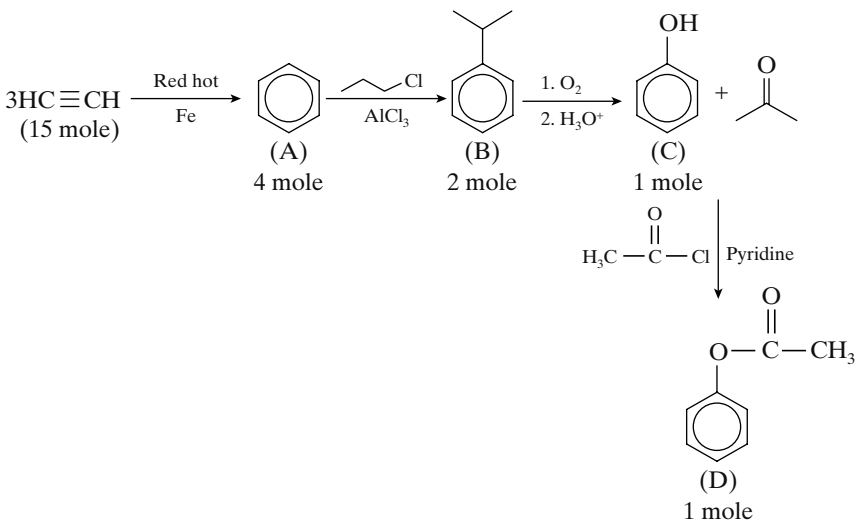
- The benzene ring still contributes 6 sp^2 carbons.
- The two oxime carbon contributes 2 more sp^2 nitrogens.

So, the total number of sp^2 hybridized atoms in the final product is:

6 (benzene) + 2 (oxime carbons) + 2 (oxime nitrogens) + 2 (additional ketone-derived sp^2 carbons) = 12

CHAPTER 7 Alkenes and Alkynes I: Properties and Synthesis. Elimination Reactions of Alkyl Halides

1.



Molecular weight = $C_8H_8O_2$

$$= 12 \times 8 + 1 \times 8 + 16 \times 2 = 96 + 8 + 32 = 136$$

Moles of product (D) formed = $\frac{15}{3} \times 0.8 \times 0.5 \times 0.5 = \frac{3}{3} = 1$

$\therefore$ Weight of product (D) = $1 \times 136 = 136$ g

2. Na in liquid NH_3 selectively reduces only the internal alkyne to a trans-alkene. Hence the correct option is (B).

CHAPTER 9 Radical Reactions

1. The given titration involves **Fe^{2+} reacting with $KMnO_4$ in acidic medium:**

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

This shows that **1 mole of $KMnO_4$ reacts with 5 moles of Fe^{2+}.**

Moles of **$KMnO_4$** used:

Given:

- Volume of **$KMnO_4$ solution** used = **12.5 mL = 0.0125 L.**
- Molarity of **$KMnO_4$ solution = 0.03 M.**

Moles of **$KMnO_4$** used:

Moles of $KMnO_4$ = Molarity × Volume

$= 0.03 \times 0.0125$

$= 3.75 \times 10^{-4}$ moles

Moles of Fe^{2+} in 25 mL Solution.

From the reaction equation:

1 mole of $KMnO_4$ reacts with 5 moles of Fe^{2+}

Moles of Fe^{2+} = 5 × Moles of $KMnO_4$

$= 5 \times 3.75 \times 10^{-4}$

$= 1.875 \times 10^{-3}$ moles in 25 mL solution

Moles of Fe^{2+} in 250 mL Solution.

Since 25 mL is a part of the total 250 mL solution:

Total moles of $Fe^{2+} = \frac{250}{25} \times 1.875 \times 10^{-3}$

$= 10 \times 1.875 \times 10^{-3}$

$= 1.875 \times 10^{-2}$ moles

Thus x = 1.875.

Mass and % of Iron in Sample.

Mass of **Fe in sample:**

Mass of Fe = Moles of Fe^{2+} × Molar mass of Fe

$= (1.875 \times 10^{-2}) \times 56$

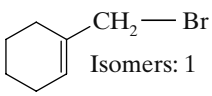
$= 1.05$ g

Percentage of **iron in sample:** $y = \left(\frac{1.05}{5.6}\right) \times 100$

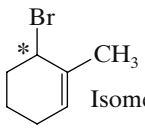
$= 18.75\%$

Thus y = 18.75%.

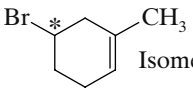
2.

1 

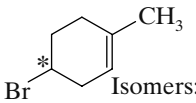
Isomers: 1

2 

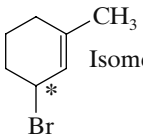
Isomers: 2

3 

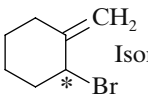
Isomers: 2

4 

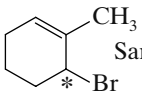
Isomers: 2

5 

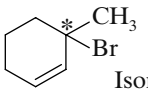
Isomers: 2

6 

Isomers: 2

7 

Same as S. No. 2

8 

Isomers: 2

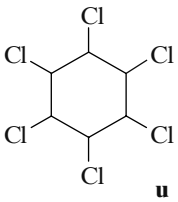
Hence maximum number of possible isomers = 13.

CHAPTER 10 Alcohols and Ethers: Synthesis and Reactions

1. **L – Glucose** $\xrightarrow[\text{2. } Cr_2O_3\text{, 775 K, 10–20 atm}]{\text{1. HI, }\Delta}$

(P)

$\xrightarrow[\text{UV}]{Cl_2\text{(excess)}}$



u

Hence solution is option (D).

CHAPTER 11 Alcohols from Carbonyl Compounds

1. **Identifying Q**

Reaction sequence:

1. **Mg, dry ether** – Forms the Grignard reagent **tert-butyl magnesium chloride**.
2. **CO_2,** dry ether – CO_2 reacts with the Grignard reagent to form a carboxylate anion.
3. **H_3O^+** – Protonation lead to **2, 2-dimethylpropanoic acid/Pivalic Acid.**
4. **NaOH** – Ensures the carboxylate form is stable.

Thus, Q = Pivalic Acid ($C_5H_{10}O_2$).

- **Kolbe's electrolysis** involves the electrolysis of carboxylates, leading to the formation of an **eight–carbon hydrocarbon**.
- Since **pivalic acid ($C_5H_{10}O_2$)** forms a carboxylate ion in NaOH, it can undergo Kolbe's electrolysis to give an **eight–carbon product**.

Thus, **statement (B) is correct**.

2. **Step 1: Determine the zero oxidation state atoms for each molecule.**

We will analyze each molecule carefully and count the atoms in the **zero oxidation state**.

1. *Br_3O_8 (Tribromooctaoxide)*
   - Oxygen is **–2**.
   - Let the oxidation state of Br be **x**:

     $3x + (8 \times -2) = 0$

     $3x - 16 = 0$

     $3x = 16 \Rightarrow x = +\frac{16}{3}$
   - Since this is a mixed oxidation state compound, there is **no Br in the zero oxidation state**.
   - **Zero oxidation state atoms: 0**.
2. *F_2O (Difluorine monoxide)*
   - Oxygen is usually **–2**, and fluorine is **+1** here.
   - No atom has an oxidation state of zero.
   - **Zero oxidation state atoms: 0**.
3. *$H_2S_4O_6$ (Tetrathionic acid)*
   - Sulfur exists in oxidation states **0, +2, +5** based on the structure of tetrathionic acid.
   - **Two sulfur atoms** are in the **zero oxidation state**.
   - **Zero oxidation state atoms: 2**.
4. *$H_2S_5O_6$ (Pentathionic acid)*
   - Similar to tetrathionic acid, sulfur atoms have oxidation states **0, +2, +4, +6**.
   - **Two sulfur atoms** are in the **zero oxidation state**.
   - **Zero oxidation state atoms: 2**.
5. *C_3O_2 (Carbon suboxide, O=C=C=C=O)*
   - This molecule contains **three carbon atoms**.
   - The oxidation states of the carbon atoms are **–2, 0, +2**.
   - **One carbon atom** is in the **zero oxidation state**.
   - **Zero oxidation state atoms:** 1.

Step 2: Sum up the zero oxidation state atoms.

$0 + 0 + 2 + 2 + 2 = 6$

3. **Step 1: Understanding the Reaction Pathway.**

We start with **styrene (C_6H_5–CH=CH_2)**, and follow the given reaction sequence:

Formation of P: Hydroboration-Oxidation.

1. **(i) B_2H_6**
2. **(ii) NaOH, H_2O_2, H_2O**
   - This is **hydroboration-oxidation**, which converts the alkene into an **alcohol**, giving **1-phenylethanol (C_6H_5–CH(OH)–CH_3)**.

Formation of Q: Oxidation and Chlorination.

1. **(i) CrO_3, H_2SO_4**
   - **1-Phenylethanol** undergoes oxidation to form **phenylacetic acid (C_6H_5–CH_2–COOH)**.
2. **(ii) Cl_2, Red phosphorus**
   - This introduces a chlorine atom at the **benzyl position** (due to the reactivity of benzylic hydrogens), forming **p-chlorophenylacetic acid**.
   - **So, Q = p-Chlorophenylacetic acid**.

Formation of R: Conversion to Amine.

1. **(i) $SOCl_2$**
   - Converts **phenylacetic acid (–COOH)** to **phenylacetyl chloride (–COCl)**.
2. **(ii) NaCN**
   - Cyanide replaces **Cl**, forming **phenylacetonitrile (–CH_2–CN)**.
3. **(iii) H_3O^+, Δ**
   - Acidic hydrolysis converts **nitrile (–CN)** to **amide (–$CONH_2$)**.
   - **So, R= Phenylacetamide (C_6H_5–CH_2–$CONH_2$)**.

Formation of S: Sulfonation

- **Concentrated H_2SO_4** introduces a –SO_3H group into the **benzene ring**.
- In electrophilic substitution, the **para position** is most favorable.
- **So, S = p-Sulfophenylacetamide (C_6H_5–SO_3H–CH_2–$CONH_2$)**.

Step 2: Matching with Given Options.

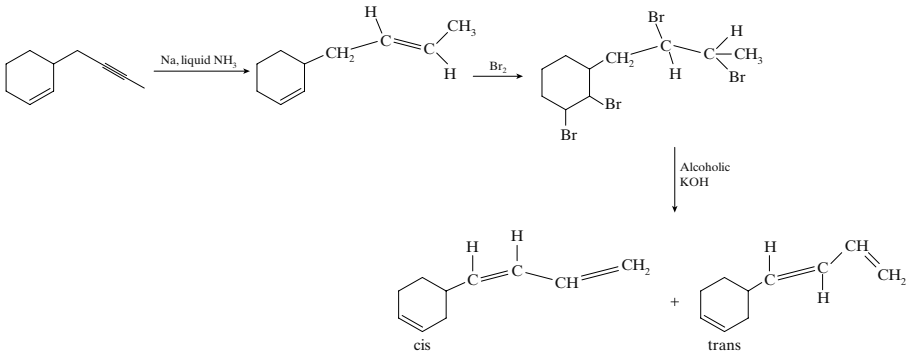
Looking at the structures in the options:

- **Q should be p-chlorophenylacetic acid.**
- **R should be phenylacetamide.**
- **S should be p-sulfophenylacetamide.**

By comparing the structures, **option (B) is correct**.

CHAPTER 12 Conjugated Unsaturated Systems

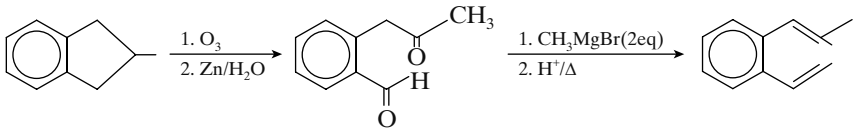
1.



Hence the answer is 2 (cis- and trans-).

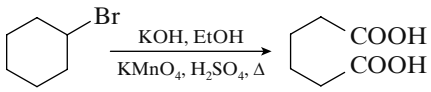
CHAPTER 13 Aromatic Compounds

1.

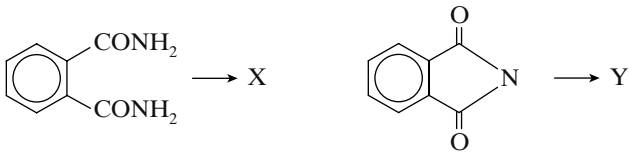


(S)

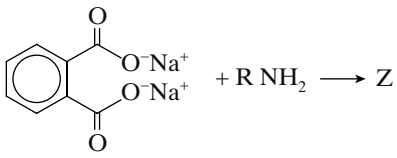
2. (C)



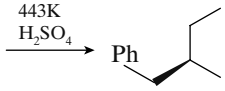
3. Both X and Y are oxygen containing compound



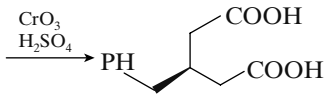
Z reacts with Hinsberg's reagent.



4. S gives Bayer's test

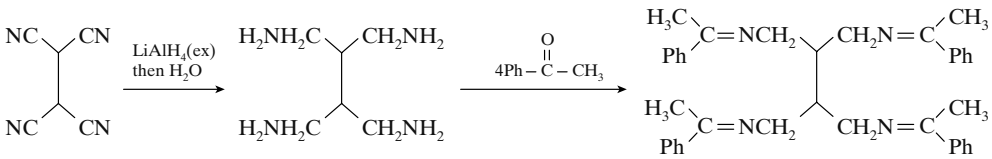


Q gives effervescence with aq · $NaHCO_3$



5. *(i) $LiAlH_4$ (excess), then H_2O*

- **$LiAlH_4$** reduces **nitriles (–CN) to primary amines (–CH_2–NH_2)**.
- As there are **four cyano groups**, they all get converted into –**CH_2–NH_2** groups.
- **Acetophenone** contains a carbonyl group **(C=O)**, which can undergo **Schiff base formation** with amines.
- Each –**CH_2NH_2** group reacts with acetophenone, forming **four imine (–CH=N) bonds**.



Counting sp^2 Hybridized Carbons:

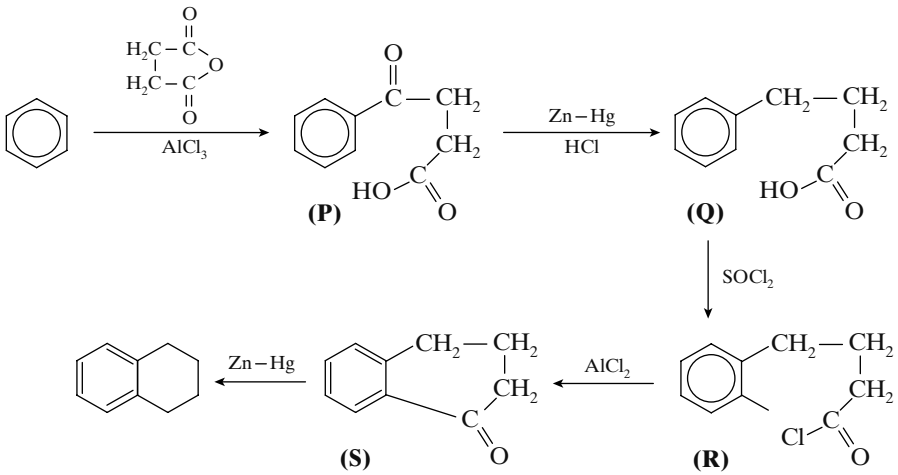
1. **Each benzene ring (C_6H_5) has 6 sp^2 carbons.** Since there are **4 benzene rings**, they contribute **$4 \times 6 = 24$ sp^2 carbons**.
2. **Each imine (–CH=N–) has a doubly bonded carbon** (C=N), which is **sp^2 hybridized.** Since there are **4 imine groups**, they contribute **4 sp^2 carbons**.

Thus, the **total number of sp^2 hybridized carbons** in **P** is: $24 + 4 = 28$.

CHAPTER 14 Reactions of Aromatic Compounds

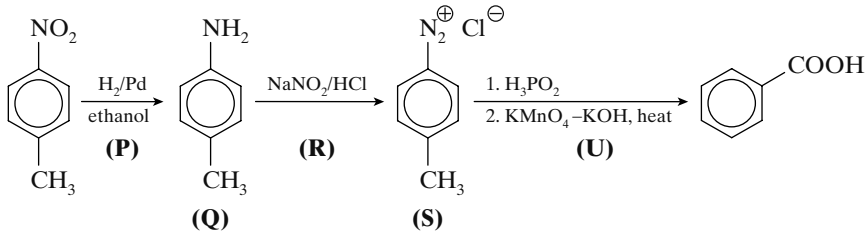
1. Fluorination of phosphorus pentachloride in a polar organic solvent, results in the formation of ionic isomers, hence option (B).

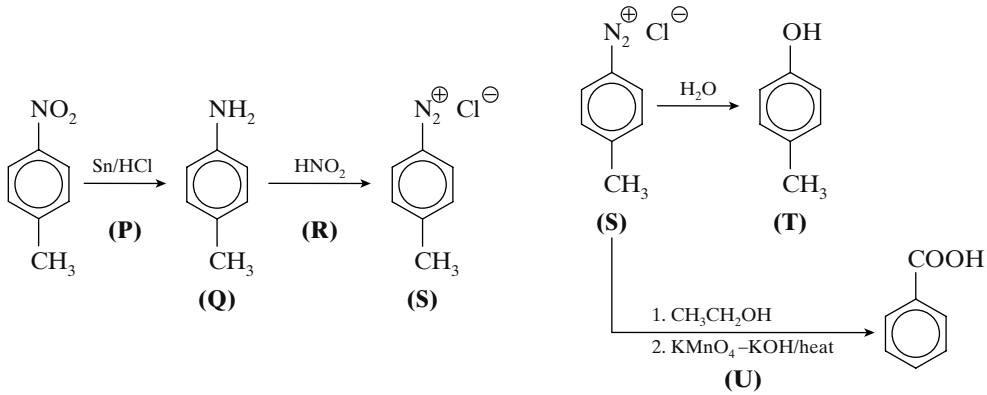
2.



From the above reaction, the answer is (A) and (C).

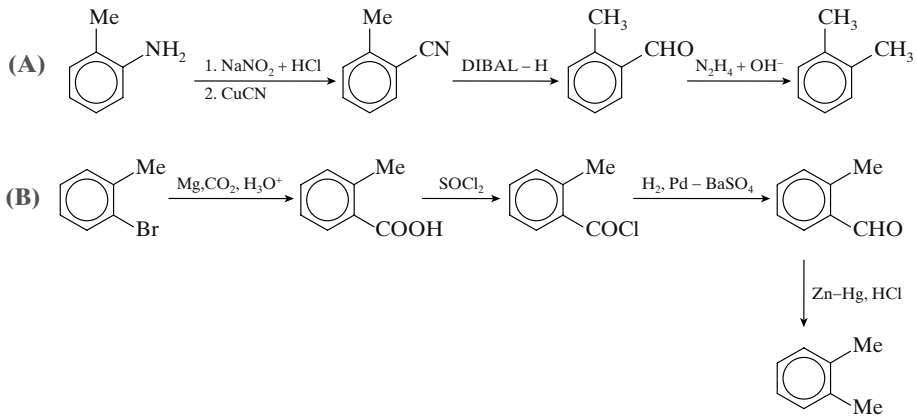
3.





Hence the right answer are (A) (B) and (C).

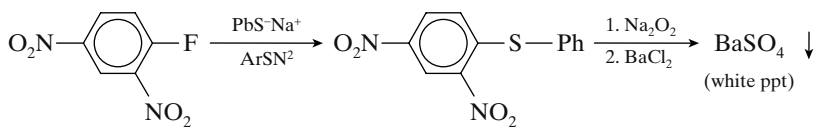
4.

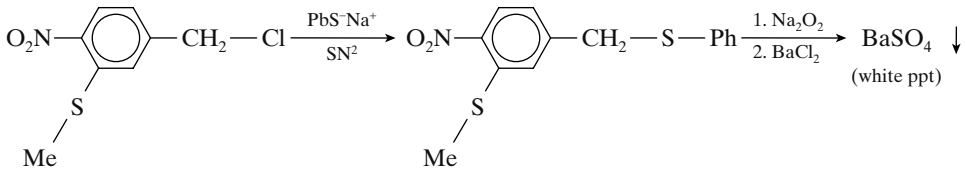


Options (C) and (D) will not give o-xylene.

Hence the correct answer is (A) and (B).

5.

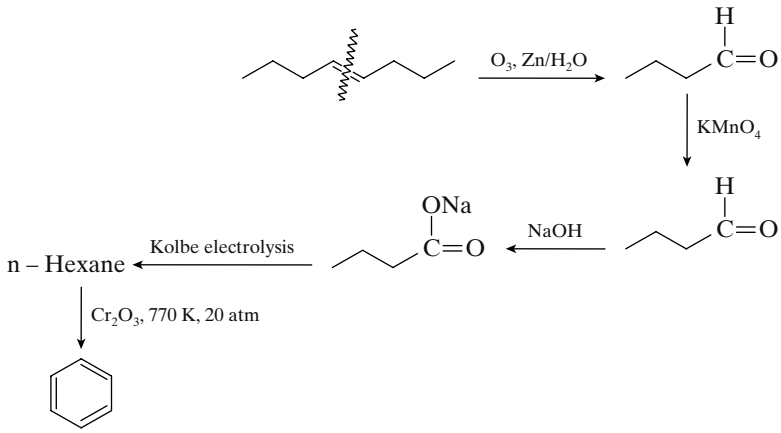




In options (B) and (C), NO_2 group, which is an electron withdrawing group, is not present at the ortho or para position with respect to the leaving group. Hence Aromatic Substitution Reaction will not be possible. Hence the right options are (A) and (D).

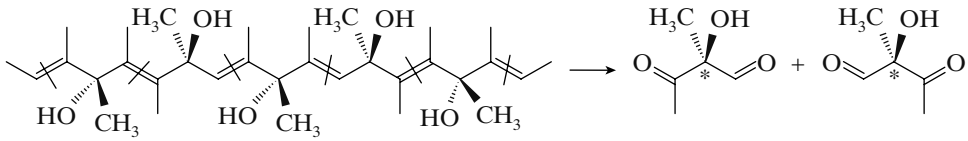
CHAPTER 15 Aldehydes and Ketones I. Nucleophilic Addition to the Carbonyl Group

1. The above reaction will give 0 methylene groups in the product as only benzene will be formed.



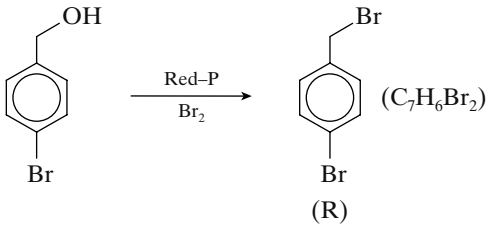
Hence the right answer is 0.

2.



2 chiral molecules are formed, hence the right answer is 2.

3.



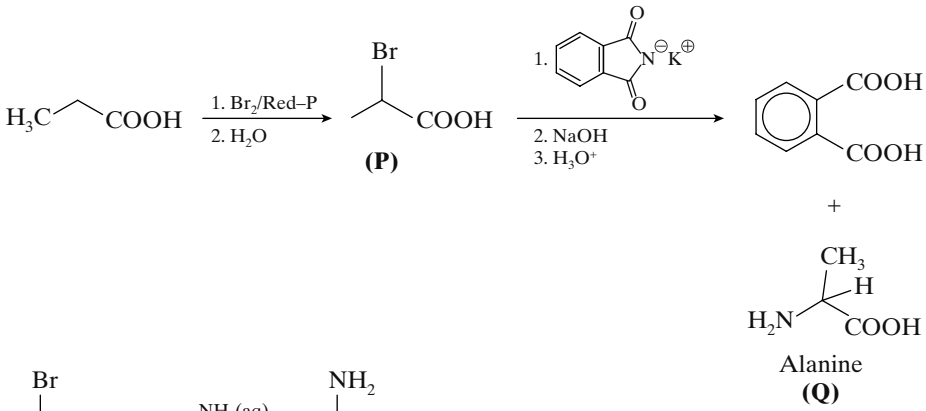
Molecular weight of (R) = $7 \times 12 + 1 \times 6 + 80 \times 2 = 250$g/mol

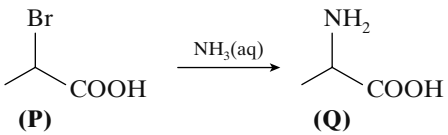
Mole of AgBr formed = $2 \times$ mole of (R)

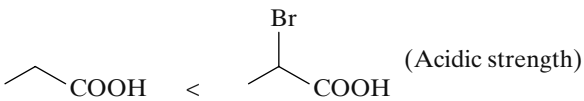
$= 2 \times \frac{1}{250} \times 188 = 8 \times 10^{-3} \times 188 =$ **1.504g**

CHAPTER 16 Aldehydes and Ketones II. Aldol Reactions

1.



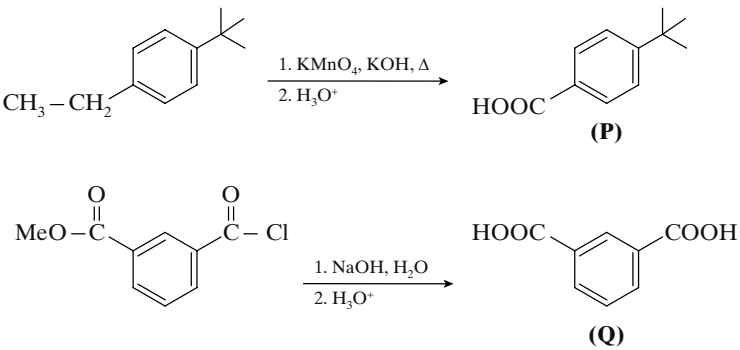


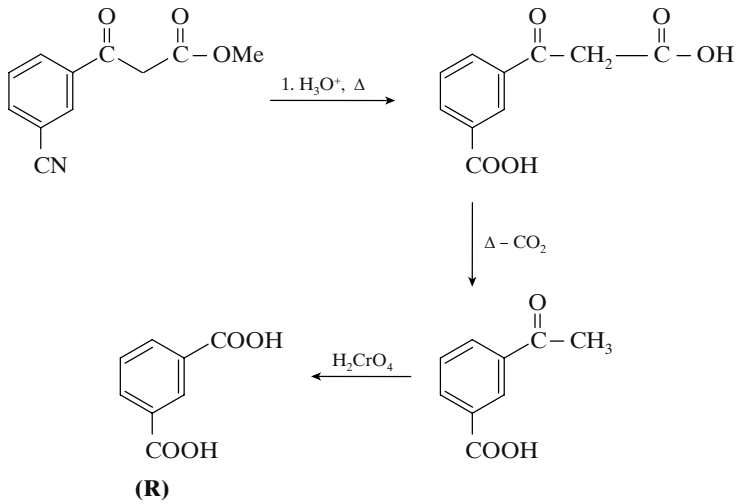


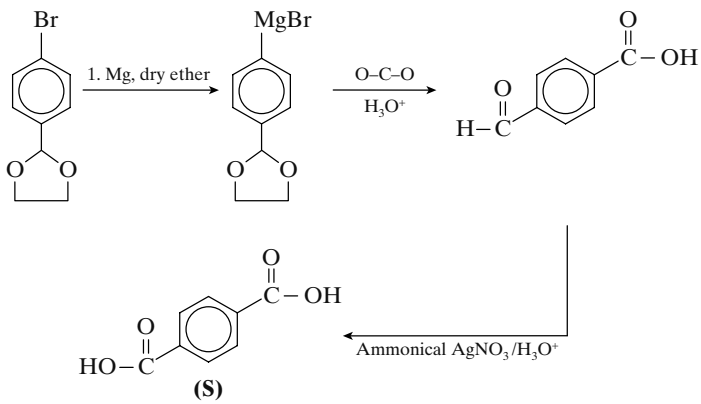
Hence solution is (B), (C) and (D).

Chapter 17 Carboxylic Acids and Their Derivatives

1.

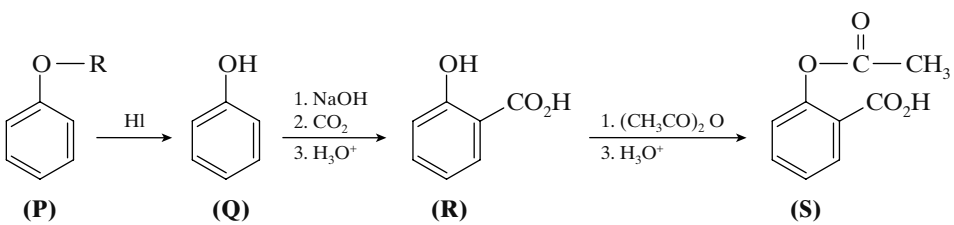






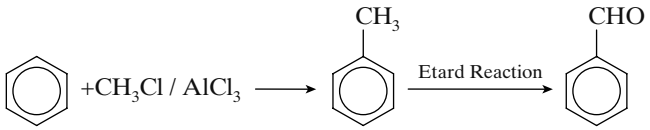
Hence the correct options are (C) and (D).

2.

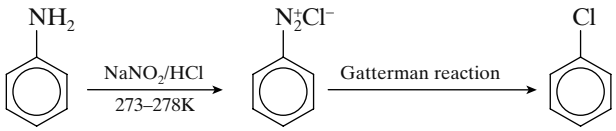


(S) is Aspirin which inhibits the synthesis of prostaglandin. Hence right option is (B).

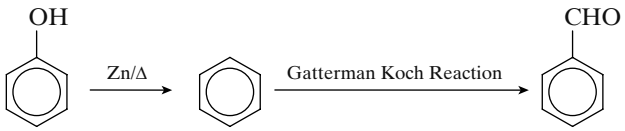
3. **P → 3**



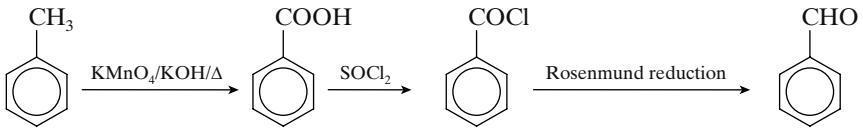
P → 4



P → 5



S → 2



Option is (D).

Chapter 18 Amines

1. Nylon - 6, 6 monomer giving positive carbylamine test → primary amine

X = hexamethylenediamine

$$(H_2N - (CH_2)_6 - NH_2)$$

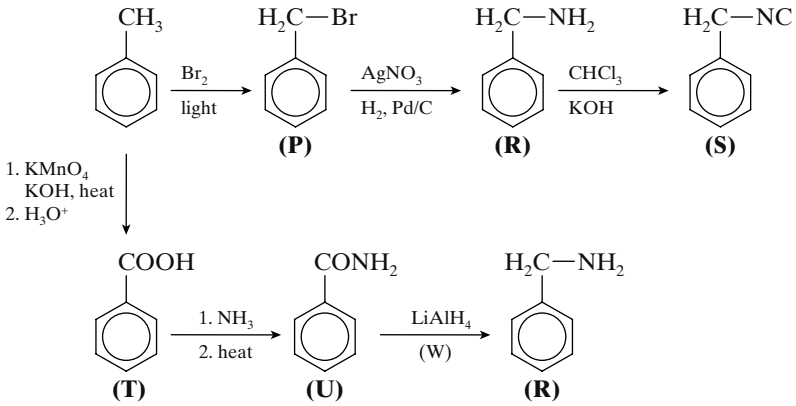
1 mol of X → 1 mol of N_2

10 mol of X → 10 mol of N_2

Mass of nitrogen gas

$$10 \times 28 = 280g$$

2.



Chapter 19 Phenols and Aryl Halides

1. Given

$C_1 = 10, x_1 = 4$

$C_2 = 16, x_2 = 10$

Take ratio

$$\log\left(\frac{x_2}{x_1}\right) = \frac{1}{n}\log\left(\frac{C_2}{C_1}\right)$$

$$\log\left(\frac{10}{4}\right) = \frac{1}{n}\log\left(\frac{16}{10}\right)$$

$$\log(2.5) = \frac{1}{n}\log(1.6)$$

Using

$$\log 2 = 0.3 \rightarrow \log 2.5 = \log\left(\frac{5}{2}\right)$$

$$= \log 5 - \log 2$$

$$= (1 - 0.3) = 0.4$$

So $\frac{1}{n} = \frac{0.4}{0.2} = 2$

Find adsorption al C = 20

$$\log x = \log 4 + 2\log\left(\frac{20}{10}\right)$$

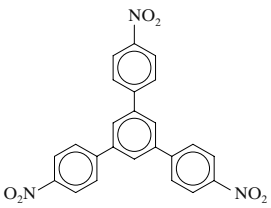
$\log x = \log 4 + 2\log 2$

$\log 4 = 2\log 2 = 0.6$

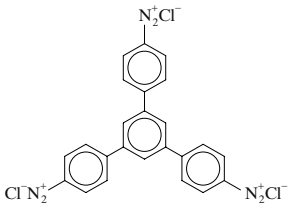
$\log x = 0.6 + 0.6 = 1.2$

$x = 10^{1.2} \approx 16$

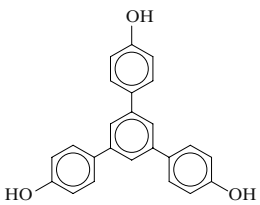
2.



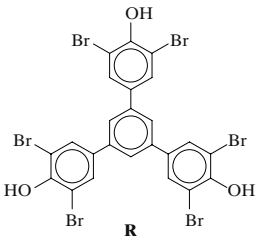
1,3,5-tris-(4-nitrophenyl)benzene



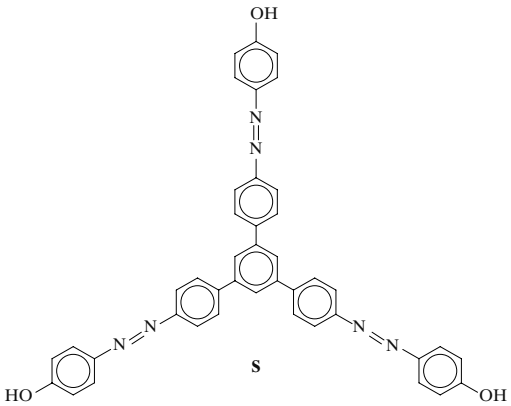
P



Q



R



S

3.
- Because Aniline contains Carbon and Nitrogen, its sodium extract gives Prussian Blue colour with $FeSO_4$/Conc. H_2SO_4.
- *o*-Cresol produces violet colour with neutral $FeCl_3$.
- Cystein contains carboxylic group, because of which it gives effervescence with $NaHCO_3$.
- Furthermore, it has C, N, S, hence its sodium extract will give red colour with $FeCl_3/H_2SO_4$.
- Caprolectum contains C and N, hence its Na extract will give Prussian blue colour.

Chapter 20 Carbohydrates

1. P-2: Contains – NH_2 (amino) and phenolic (–OH) gives purple with ninhydrin and violet with $FeCl_3$

Q-5: On complete hydrolysis gives amino acids ninhydrin positive, no phthalein dye.

R-1: Aromatic amine salt couples with phenyl diazonium salt → yellow azo dye.

S-3: Hydrazine ($NHNH_2$) reacts with glucose hydrazone

2. Let numbers of unit be

r (ribose), d(deoxyribose), g (glucose)

$$r + d + g = 8$$

Given mass % of deoxyribose

$$\frac{134d}{150r + 134d + 180g} = 0.5826$$

Put $g = 8 - r - d$

$$\frac{134d}{1440 - 30r - 46d} = 0.5826$$

$d = 5, r = 2, g = 1$

3. 1. "X cannot be oxidized by bromine water"

- Bromine water is used to oxidize reducing sugars (i.e., sugars that have a free anomeric carbon, capable of forming an open-chain structure).
- Sucrose is a non-reducing sugar because the anomeric carbons of both glucose and fructose are involved in the glycosidic bond, preventing the ring from opening.
- This means sucrose does not react with bromine water.

2. "Acid hydrolysis of X leads to a laevorotatory solution"

- Sucrose is dextrorotatory (+66.5°), but upon hydrolysis, it yields glucose (+52.5°) and fructose (–92°).
- Since fructose has a more negative rotation than glucose's positive rotation, the resulting solution is net laevorotatory.

Verifying the Structure:

- Looking at option (A), it represents sucrose, which consists of α-D-glucose and β-D-fructose linked via a 1→2 glycosidic bond, hence (A) is the correct answer.

4. 1. Oxidation of D-Glucose with HNO_3:

- D-Glucose is oxidized by nitric acid (HNO_3) to yield D-Glucaric acid, where both the aldehyde (–CHO) and primary alcohol ($-CH_2OH$) groups are oxidized to carboxylic acids (–COOH).
- The specific rotation of D-Glucaric acid is +52.7°.

2. To get the enantiomer with (α)_D = –52.7°:

- The enantiomer of D-Glucaric acid must have the opposite stereochemistry at all chiral centers.
- This enantiomer must originate from the enantiomer of D-Glucose, which is L-Glucose.
- L-Glucose also undergoes oxidation with HNO_3, yielding L-Glucaric acid, which has (α)_D = –52.7°.
- (C) and (D) both represent enantiomers of D-Glucose (i.e., L-Glucose forms), which upon oxidation give L-Glucaric acid.
- The final product is the enantiomer of D-Glucaric acid, confirming the given explanation.

Hence, the enantiomeric product is obtained from (C) and (D).

Chapter 23 Reactions of Nitrene and Electron Deficient Oxygen

1. P→2 (Stephen reaction)

It requires a nitrile as the reactant, which is formed in sequence (2)

Q→3 (Sandmeyer reaction)

It needs an aryl diazonium salt obtained from nitrobenzene → aniline → diazotisation in (3)

R→4 (Hoffmann bromamide degradation)

Hoffmann reaction requires an amide produced in sequence (4)

S→1 (Cannizzaro reaction)

It requires an aldehyde without α–H, obtained from toluene → benzaldehyde in (1)

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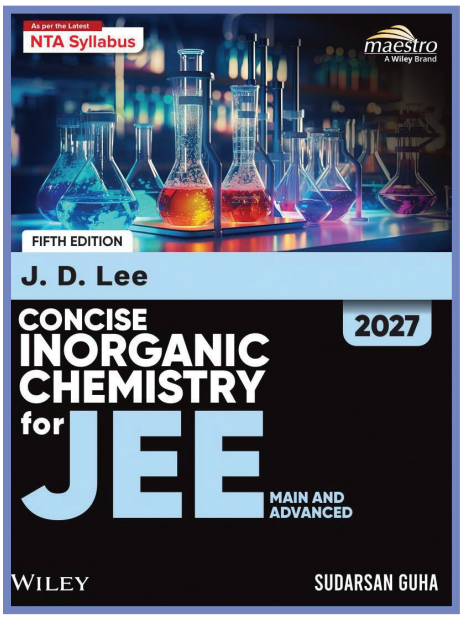

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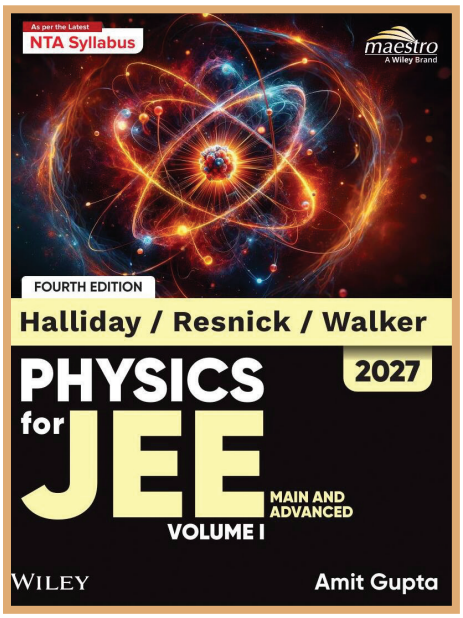

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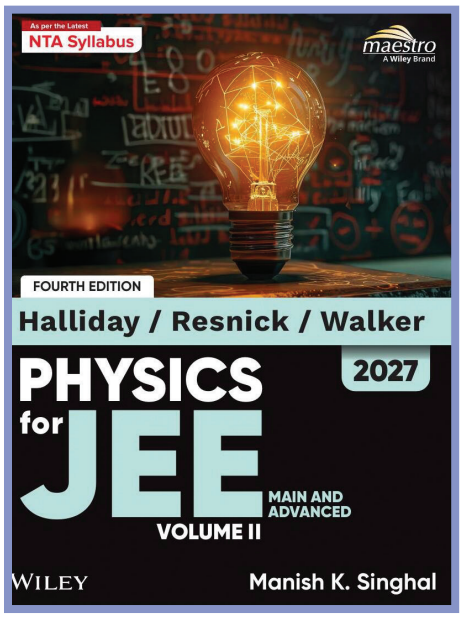

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