11 Arenes

Methylbenzene is a useful starting material for the synthesis of many intermediates used to make pharmaceuticals, dyes and agrochemicals. It can also be used as an additive in unleaded petrol.

(a) Suggest the reagents and conditions needed for each of the reactions I, II and III in the following scheme. State the type of reaction undergone in each case.

(b) (i) Suggest the mechanism, including curly arrows showing the movement of electrons, for reaction II.

(ii) How many positional isomers (structural isomers) could be formed in reaction II? Draw their structural formulae.

(c) Write a balanced equation for the oxidation of 1,4-dimethylbenzene to form benzene-1,4-dicarboxylic acid.

1 (a) I: limited amount of Cl₂ or use excess methylbenzene, UV light or heat

Free-radical substitution

II: Cl₂(g), AlCl₃

Electrophilic substitution

III: KMnO₄, dilute H₂SO₄, heat

Side-chain oxidation
(b) (i) Name of mechanism: **Electrophilic substitution**

\[ \text{Cl—Cl} + \text{AlCl}_3 \rightarrow \text{Cl}^+ + \text{AlCl}_4^- \]

\[ \begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{E} \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{H} \\
\text{Cl} \\
\text{CH}_3 \\
\text{Cl} \\
\end{array} \quad \text{slow} \quad \begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{E} \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{H} \\
\text{Cl} \\
\text{CH}_3 \\
\text{Cl} \\
\end{array} \]

\[ \text{Cl}^+ + \text{AlCl}_3 \rightarrow \text{Cl}^- + \text{AlCl}_4^- \]

Substitution allow the aromatic character of benzene to be restored

(ii) ( position 4 isomer is given in question)

(c)

\[ \begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{E} \\
\text{C} \\
\text{H}_3 \\
\text{COOH} \\
\text{H}_2\text{O} \\
\end{array} \quad \begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{H}_3 \\
\text{Cl} \\
\text{E} \\
\text{C} \\
\text{H}_3 \\
\text{COOH} \\
\text{H}_2\text{O} \\
\end{array} \]

2. Predict the major organic products of the following reactions:

(a) \[ \begin{array}{c}
\text{CHO} \\
\text{CH}_3 \\
\text{NO}_2 \\
\text{CHO} \\
\end{array} \quad \text{conc. HNO}_3, \text{conc. H}_2\text{SO}_4 \rightarrow 55^\circ\text{C} \rightarrow \begin{array}{c}
\text{CHO} \\
\text{CH}_3 \\
\text{NO}_2 \\
\text{CHO} \\
\end{array} \]

(b) \[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{NO}_2 \\
\text{Br} \\
\text{Br} \\
\end{array} \quad \text{Br}_2, \text{FeBr}_3 \quad \text{warm} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{Br} \\
\text{Br} \\
\text{NO}_2 \\
\end{array} \]

(c) \[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{NO}_2 \\
\text{C} \\
\text{CO}_2^- \\
\text{C} \\
\text{CO}_2^- \\
\end{array} \quad \text{KMnO}_4/\text{OH}^- \quad \text{heat} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{NO}_2 \\
\text{C} \\
\text{CO}_2^- \\
\text{C} \\
\text{CO}_2^- \\
\end{array} \]

(d) \[ \begin{array}{c}
\text{I} \\
\text{AlCl}_3 \rightarrow \begin{array}{c}
\text{I} \\
\text{HCl} \\
\end{array} \]
3 State the reagents and conditions required to perform each of the following conversions in the laboratory. Draw the structural formulae of the intermediates, P, Q, R and S.

(a) benzene \( \xrightarrow{(i)} \) P \( \xrightarrow{(ii)} \) 4-chloronitrobenzene

(b) methylbenzene \( \xrightarrow{(iii)} \) Q \( \xrightarrow{(iv)} \) 3-nitrobenzoic acid

(c) methylbenzene \( \xrightarrow{(v)} \) R \( \xrightarrow{(vi)} \) S \( \xrightarrow{(vii)} \) 2-bromo-4-nitrobenzoic acid

3 (a) (i) \( \text{Cl}_2, \text{FeCl}_3, \text{warm} \)
    (ii) concentrated HNO\(_3\), concentrated H\(_2\)SO\(_4\), heat

(b) (iii) KMnO\(_4\), dilute H\(_2\)SO\(_4\), heat
    (iv) concentrated HNO\(_3\), concentrated H\(_2\)SO\(_4\), heat

(c) methylbenzene \( \xrightarrow{(v)} \) R \( \xrightarrow{(vi)} \) S \( \xrightarrow{(vii)} \) 2-bromo-4-nitrobenzoic acid
    (v) concentrated HNO\(_3\), concentrated H\(_2\)SO\(_4\), 30°C
    (vi) Br\(_2\), FeBr\(_3\)
    (vii) KMnO\(_4\), dilute H\(_2\)SO\(_4\), heat
4 Suggest a simple chemical test to distinguish between each of the following pairs of compounds. State the reagents and conditions required, expected observations for each compound and the type of reaction undergone (if any), writing relevant equations where appropriate.

(a) hexene and benzene

(b) benzene, methylbenzene and ethylbenzene

(a) Reagents & Conditions:
Br$_2$(aq) or Br$_2$ in CC$_4$

Observations:
For hexene: yellow Br$_2$(aq) or reddish-brown Br$_2$ in CC$_4$ is decolourised.
For benzene: yellow Br$_2$(aq) is reddish-brown Br$_2$ in CC$_4$ is not decolourised.

Equation:
CH$_3$CH$_2$CH$_2$CH$_2$CH=CH$_2$ + Br$_2$(aq) → CH$_3$CH$_2$CH$_2$CH$_2$CHOHCH$_2$Br
Electrophilic addition

(b) Reagents & Conditions:
KMnO$_4$, dilute H$_2$SO$_4$, heat

Observations:
For benzene: purple KMnO$_4$ solution is not decolourised.
For methylbenzene: purple KMnO$_4$ solution is decolourised and white precipitate of benzoic acid is formed.
For ethylbenzene: purple KMnO$_4$ solution is decolourised, white precipitate of benzoic acid is formed (when cooled) and effervescence of CO$_2$ is observed.

\[
\text{CH}_3 + 3[\text{O}] \rightarrow \text{CO}_2\text{H} + \text{H}_2\text{O} \\
\text{CH}_2\text{CH}_3 + 6[\text{O}] \rightarrow \text{CO}_2\text{H} + 2\text{H}_2\text{O} + \text{CO}_2
\]
Side-chain oxidation
Compound A has molecular formula C₈H₈. When a solution of bromine in CCl₄ is added to A, it decolorises immediately. On heating A under reflux with alkaline KMnO₄, with subsequent cooling and acidification, a white crystalline solid, B, C₇H₆O₂, is obtained.

One mole of A reacts with one mole of hydrogen in the presence of platinum to form C, C₈H₁₀. C shows no apparent change when bromine is added in the dark but gives dense white fumes when bromine is added in the presence of a little iron powder.

Identify (structure) compounds A to C. Explain the chemistry of the reactions, giving equations where appropriate. i.e.
1. Type of reaction
2. Identify functional groups reacted or formed
3. What give rise to observations?

<table>
<thead>
<tr>
<th>Ratio of C:H ≈ 1:1 in A.</th>
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<tbody>
<tr>
<td>✓ A contains a benzene ring.</td>
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Bromine is decolourised when added to A. **Electrophilic addition** has occurred. ✓ A contains alkene group(s).

![Structure of A](image)

A is

\[
\text{H} \quad \text{H} \quad \text{C=C-H} \\
\text{H} \quad \text{H} \\
\]

\[\text{H} \quad \text{C=C-H} + \text{Br}_2 \rightarrow \text{H} \quad \text{CH-CH}_2 \quad \text{Br} \quad \text{Br} \]

C=C in A undergoes **oxidative cleavage** with hot alkaline KMnO₄ to give B.

![Structure of B](image)

B is

\[
\text{COOH} \\
\]

A undergoes **catalytic hydrogenation** (reduction) with H₂ in a 1:1 mole ratio to give C. ✓ A contains one alkene group.

![Structure of C](image)

C is

\[
\text{CH}_2\text{CH}_3 \\
\]

C does not react with Br₂ in the dark. ✓ C contains no alkene group.

C undergoes **electrophilic substitution** with Br₂ and Fe and white fumes of HBr produced.
Br₂ reacts with Fe to form FeBr₃ to act as a catalyst for the electrophilic substitution.

\[
\text{C}_6\text{H}_5\text{C}_2\text{H}_3 + \text{Br}_2 \xrightarrow{\text{FeBr}_3} \text{C}_6\text{H}_5\text{C}_2\text{H}_3 + \text{HBr} + \text{Br}_2 \text{C}_6\text{H}_5\text{C}_2\text{H}_3
\]

6 Compounds L and M, both C₉H₁₀, are all oxidized by hot concentrated alkaline KMnO₄, followed by acidification, to give benzene-1,2-dicarboxylic acid, N.

Compound L reacts with Br₂(aq), but compound M does not. Suggest structures for compounds L and M.

Self-practice Questions

GCE A-level Chemistry Paper

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