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CHEMISTRY ORGANIC CHEMISTRY II

Level & Board	AQA (A-LEVEL)
TOPIC:	AROMATIC CHEMISTRY
PAPER TYPE:	SOLUTION - 3
TOTAL QUESTIONS	10
TOTAL MARKS	56

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Aromatic Chemistry - 3

1.

Reagents:

The reagents used to produce the electrophile for the nitration of benzene are concentrated nitric acid (conc. HNO_3) and concentrated sulfuric acid (conc. H_2SO_4).

Equation:

 $2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$

Mechanism:





Product:



(6)

2. (a)

Reagents:

Concentrated nitric acid (conc. HNO3) and concentrated sulfuric acid (conc. H2SO4).

Equation:

 $2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$

(3)

(b)

Mechanism:



(3)

(1)

(1)

(c)

There are 2 number of peaks in the 'H n.m.r. spectrum of TNT.



 $2C_7H_5N_3O_6 \rightarrow 5H_2O + 3N_2 + 7C + 7CO$

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3.

(a) Equation:

Reaction of propanal with HCN

 $CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$

Name the product:

2-hydroxybutanenitrile

(b)

Name of the mechanism: Nucleophilic addition

Mechanism:



Product: CH₃CH₂CH(OH)CN

(5)

(2)

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Nitration of Benzene:

- **Reagents:** Concentrated HNO_3 and concentrated H_2 SO₄.
- Conditions: Heat to 50-60°C.
- **Product**: Nitrobenzene $(C_6 H_5 NO_2)$.

Reduction of Nitrobenzene:

- Reagents: Sn/HCl or Fe/HCl, or H₂ /Ni.
- Conditions: Room temperature to reflux for Sn/HCl or Fe/HCl; elevated temperature and pressure for H₂ /Ni.
- **Product:** Phenylamine (aniline, $C_6 H_5 NH_2$).

Why Phenylamine Cannot Be Prepared from Bromobenzen

- **C-Br Bond:** The C-Br bond is stronger and less polar, making it less reactive.
- Nucleophilicity:
 NH₃ is a nucleophile, but benzene is typically attacked by electrophiles, not nucleophiles.
- Br Lone Pair Delocalization: The lone pair on Br can be delocalized into the ring, reducing reactivity.

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(s)

5. The reducing agent in the following conversion is NaBH₄

 $\begin{array}{ccc} H_3C-C-CH_2CH_3 & \longrightarrow & H_3C-CH-CH_2CH_3 \\ \parallel & & \mid \\ O & & OH \end{array}$

Name of the mechanism:



(s)

6.

(a)

The enthalpy of hydrogenation of cyclohexene is typically -120 kJ/mol. Cyclohexa-1,4-diene has two isolated double bonds, each similar to cyclohexene.

Therefore, the enthalpy of hydrogenation for cyclohexa-1,4-diene is:

 $2 \times (-120 \text{ kJ/mol}) = -240 \text{ kJ/mol}$

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So, the enthalpy of hydrogenation of cyclohexa-1,4-diene is -240 kJ/mol.

(1)

(b)

The predicted enthalpy of hydrogenation for cyclohexa-1,3-diene is around -220 kJ/mol,

 (\mathbf{I})

(c)

For cyclohexa-1,3-diene, the enthalpy of hydrogenation is less negative compared to cyclohexa-1,4-diene due to the close proximity of the double bonds, which increases repulsion between electron clouds.

There is some delocalization of pi electrons in cyclohexa-1,3-diene, providing extra stability.



Compound X:

Chlorocyclohexane or Bromocyclohexane





Reagent: HBr

Name of the mechanism: Electrophilic addition

Reaction 2

Reagent: Ammonia

Condition: Excess ammonia or sealed in a tube

Name of the mechanism: Nucleophilic substitution



Step I:

Nitration of methylbenzene to form nitromethylbenzene.

- Type of Reaction: Electrophilic substitution (nitration)
- Reagent(s): HNO_3 (nitric acid) + H_2 SO₄ (sulfuric acid)

Step 2:

Reduction of Nitromethylbenzene to 2-Methylaniline

- Type of Reaction: Reduction
- Reagent(s): Hydrogen gas (H_2) with a metal catalyst such as palladium on carbon (Pd/C) or Raney nickel (Ni)

Step 3:

Sulfonation of 2-methylaniline to form 5-amino-2methylbenzenesulfonic acid.

- Type of Reaction: Electrophilic substitution (sulfonation)
- **Reagent(s)**: Concentrated sulfuric acid (H₂ SO₄)
- Nitration of methylbenzene to form nitromethylbenzene.
- Reduction of nitromethylbenzene to form 2-methylaniline.
- Sulfonation of 2-methylaniline to form 5-amino-2-methylbenzenesulfonic acid.

Following is the equation for the formation of the reactive inorganic species involved in the mechanism in Step I.

 $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

9.

Nitration of Benzene:

- **Reagents:** Concentrated HNO_3 (nitric acid) + Concentrated $H_2 SO_4$ (sulfuric acid)
- Name of Mechanism: Electrophilic substitution
- Overall Equation:

$$C_6H_6+HNO_3 \xrightarrow{\text{H2SO4}} C_6H_5NO_2+H_2O$$

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(4)

(2)

(4)

10.

Benzene's structure and bonding can be described as the π -bonding:

- *π*-Bonding:
 - p-Orbitals Overlap:

The delocalized π -bonds in benzene are formed by the overlap of p-orbitals on adjacent carbon atoms.

• Above and Below the Ring:

These p-orbitals overlap both above and below the plane of the carbon atoms, resulting in a delocalized π -electron cloud.



Delocalized π-Bonds:

The π -electrons in benzene are delocalized over the entire ring, providing stability to the molecule.

• Planar Structure:

Benzene's ring is planar, with all carbon atoms lying in the same plane.

• Equal Bond Lengths:

The carbon-carbon bonds in benzene have equal lengths, which are intermediate between a single bond and a double bond, reflecting the delocalization of π -electrons.

• Bond Angles:

The bond angles between carbon-carbon bonds in benzene are approximately 120°, consistent with a trigonal planar geometry.

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