CHEMISTRY

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question, or part question.

This document consists a total of **9** printed pages.

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1 **(a)** Explain why chlorobenzene does **not** undergo nucleophilic substitution with a nucleophilic reagent like sodium hydroxide, **nor** addition reactions with an electrophilic reagent like bromine. [4]

B2 – For nucleophilic substitution (Award 1 pt for 1 correct reason)

- Steric hindrance from the bulky benzene ring / phenyl group prevents attack of a nucleophile / repels nucleophile.
- Lone pairs in chlorine delocalise into the benzene ring (or overlap with pi electrons of the benzene ring), so the carbon—chlorine bond has partial double bond character and is stronger and harder to break.

B2 – For addition (Award 1 pt for 1 correct reason)

- Addition reactions will destroy the aromaticity of the benzene ring
- which requires a huge activation energy due to the stability owing to the aromaticity of the benzene ring, hence making the reaction extremely unfeasible.

(b) To replace the chloro- group in chlorobenzene, chlorobenzene first undergoes a nitration reaction.

(i) Describe the mechanism of this nitration reaction where 4-nitrochlorobenzene is formed. State the reagents and conditions of this reaction. [4]

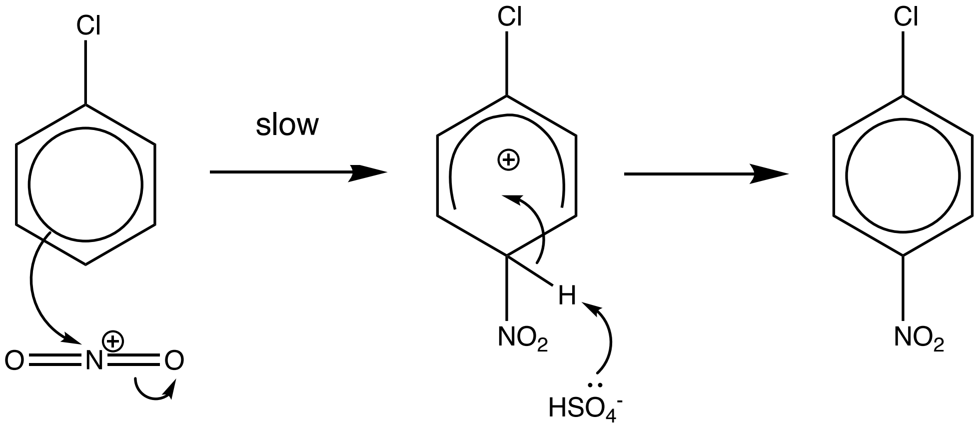
B1 – Correct reagents and conditions
Concentrated HNO_3 and concentrated H_2SO_4, heat at 55 degrees Celsius

B1 – Correct name of mechanism: Electrophilic aromatic substitution

B2 – Correct mechanism

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

Electrophilic aromatic substitution reaction



Deduct 0.5 pts per mistake (up to 2 marks)

- Slow step indicated
- Generation of electrophile shown (mechanism not required)
- Correct curly arrows
- Correct intermediate drawn (positive "horseshoe")

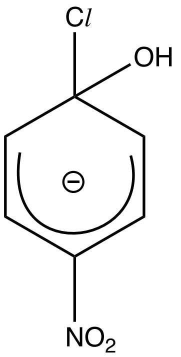
(ii) Compare the rate of the nitration reaction if methylbenzene was used instead. Explain your answer. [2]

B1 – Rate is higher because methylbenzene is electron-donating (by induction) henceforth activating the benzene ring, making it more susceptible to the attack of an electrophile.

B1 – Chlorobenzene is electron-withdrawing (by induction) which deactivates the benzene ring.

(iii) When 4-nitrochlorobenzene is reacted with aqueous sodium hydroxide at high temperatures, 4-nitrophenol is formed.

The intermediate below is formed in this reaction.



Distinguish between the 6 carbon atoms in terms of their hybridisation and the number of pi electron(s) they carry. [3]

The candidate must label the carbon atoms / refer to them unambiguously, or this question will be marked as zero. The benefit of doubt cannot be given.

Let carbon A be the carbon that has a covalent bond with chlorine.

B1 – Correct hybridisation
A: sp^3, the rest: sp^2

B2 – Correct number of pi electrons (Award 1 pt for 1 correct)

- A: 0
- The rest: 6 pi electrons that are **delocalised** amongst the carbon atoms
  - Reject: 1 particular carbon atom has 2 pi electrons, while the rest have 1 each
  - The word delocalised must be present to show that the 6 pi electrons do not particularly belong to 1 carbon atom. They are "shared".

(c) It is known that benzene has 6 *delocalised* electrons in its 6-membered ring.

(i) Explain the meaning of the word *delocalisation* or *delocalised* in the context of the structure and bonding in

- benzene; and
- graphite. [2]

B1 each:
Benzene: 6 pi electrons that are shared amongst the 6 unhybridised p-orbitals of the carbon atoms

Graphite: On average each carbon atom contributes 1 pi electron to the delocalised electrons of graphite that reside in the conjugated system of unhybridised p-orbitals of sp^2 carbon atoms in a plane.

(ii) With reference to your answer in **(i)**, explain why benzene is a **non**-conductor of electricity, but graphite is a conductor of electricity. [2]

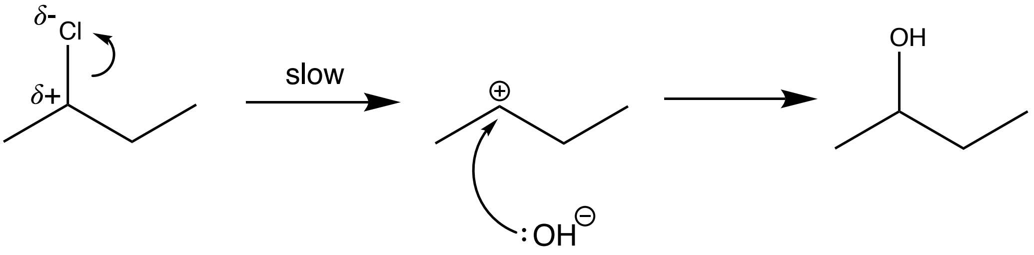
B1 each:
Benzene: The electrons are delocalised within the molecule only, but not between molecules, so these electrons cannot act as mobile charge carriers.

Graphite: Electrons are delocalised throughout the plane. As long as the potential difference is applied along the plane (formed by the carbon atoms), these electrons can act as mobile charge carriers as they can travel from 1 end to another unrestricted within the plane.

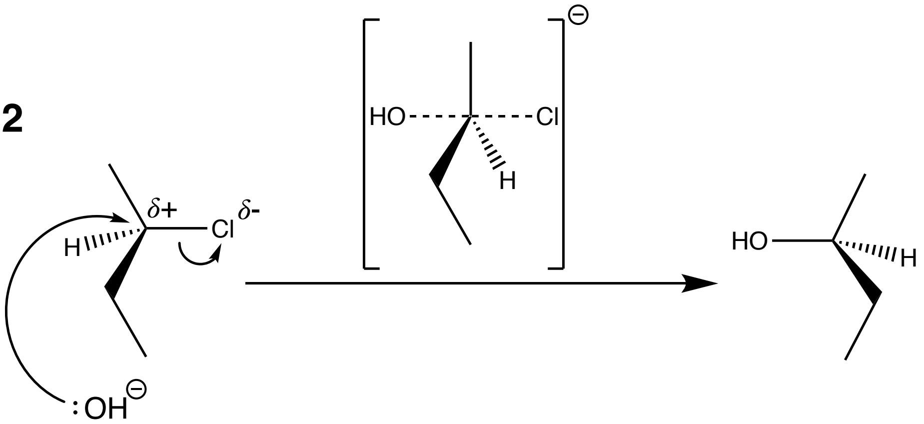
2 **(a)** Describe the mechanisms where butan-2-ol is formed from 2-chlorobutane via the S_N1 and S_N2 mechanism. [6]

B3 each

S_N1



S_N2



Penalise 0.5 pts per mistake up to 3 pts per mechanism pathway

For S_N1:

- Slow step identified
- Partial charges identified
- Correct intermediate and reactant and product
- Identifies the S_N1 mechanism
- Arrows drawn correctly
  - Arrow points to an atom, not a positive charge!

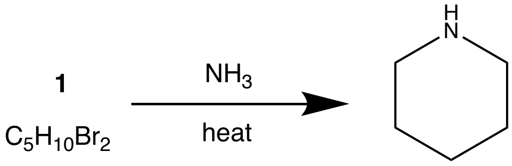
For S_N2:

- Shows stereospecificity of this reaction (penalise 1 pt for not doing so)
  - 3D structures drawn
  - For wrong stereochemistry (of the product), penalise 0.5 pts
- Partial charges identified
- Arrows drawn correctly
- Intermediate drawn correctly
  - Overall negative charge indicated on the intermediate
  - Correct disjoint lines used for C—Cl bond and C—O bond to indicate the transition state
- Identified the S_N2 mechanism

(b) Draw the structures of the unknowns, **1** to **8**, of the following reactions. [8]

B1 each

(i)



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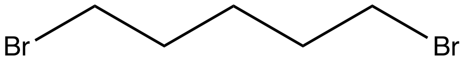
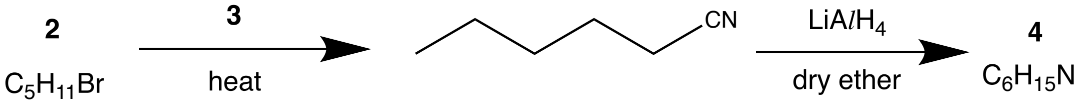


(ii)



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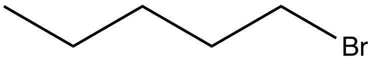
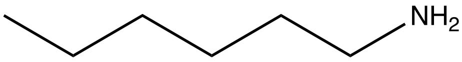
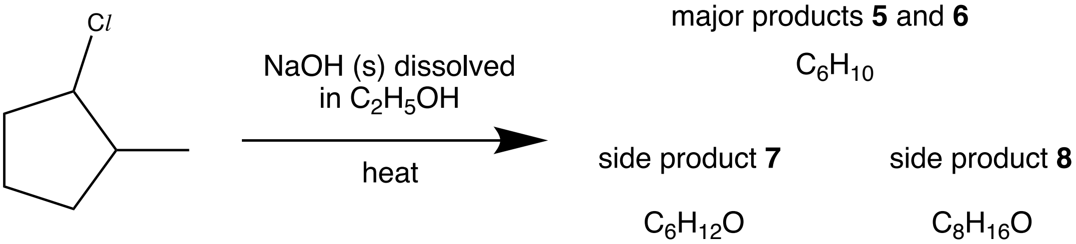


3 – KCN or NaCN

4



(iii)



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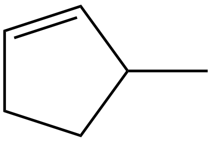

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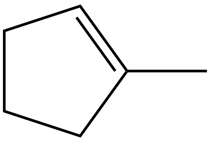

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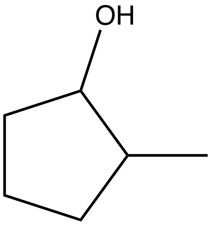

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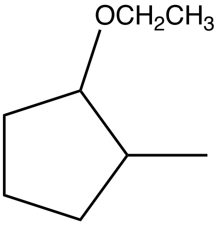

(c) Explain how, with a simple chemical test, you would distinguish between 1-chlorobutane and 1-bromobutane. [3]

B1 – To the separate samples in a test tube, add NaOH (aq) and **heat**.

- Note: This step extracts the halogen atoms in their halide ion form.

B1 – Add these reagents in the following order: excess HNO_3 (aq), $AgNO_3$ (aq) and NH_3 (aq) until no further change.

B1 – The test tube whose white precipitate dissolves when NH_3 is added contains chlorobutane, and the test tube whose cream precipitate does not dissolve when NH_3 is added contains 1-bromobutane. (Both correct observations must be stated for the mark)

Do not accept:

- Shake/heat in ethanolic $AgNO_3$ (immediate zero)
- Note that each B1 mark can only be credited only if the previous B1 mark is awarded. Your proposed test must make sense!

Simple test means that you should use test-tube tests. It is an overkill to use distillation apparatus for example to determine the boiling point of a sample in the context of a "simple" chemical test.

Furthermore, a "chemical" test will mean that you ought to test the chemical properties of the sample, not a physical property like boiling point or degree of optical rotation (in the context of tests regarding enantiomers)

Nitric acid is added to neutralise any excess NaOH (aq), which is vital because the addition of silver nitrate to an alkaline medium yields a grey precipitate of silver oxide.

(d) Neopentyl chloride, $(CH_3)_3CCH_2Cl$, is a primary alkyl halide that does **not** undergo nucleophilic substitution.

(i) Explain why neopentyl chloride cannot undergo the S_N1 mechanism. [1]

B1 – Hypothetical carbocation formed is primary which is unstable due to the lack of electron-donating alkyl groups attached to the carbon centre.

(ii) Suggest why neopentyl chloride cannot undergo the S_N2 mechanism, with reference to steric factors. [1]

B1 – The $–C(CH_3)_3$ group is a bulky group which poses significant steric hindrance for a nucleophile to approach the carbon centre.