

CHEMISTRY

ORGANIC CHEMISTRY & ANALYSIS

LEVEL: A LEVEL

BOARD: EDEXCEL

TOPIC: BENZENE & AROMATIC COMPOUNDS

PAPER TYPE: MARK SCHEME



CHEMISTRY ONLINE
— **TUITION** —

www.chemistryonlinetuition.com

Time Allowed: 80Min

Score: /64

Percentage: /100

Question 1a

The shape and structure of cyclohexene is:

Any **four** of the following points:

- Each carbon has 4 covalent bonds; [1 mark]
- 4 of the 6 carbons attempt to have a tetrahedral shape
AND
With a bond angle of 109.5° ; [1 mark]
- 2 of the 6 carbons form a pi bond; [1 mark]
- 2 of the 6 carbons attempt to have a trigonal planar shape
AND
With a bond angle of 120° ; [1 mark]
- There is a mixture of C-C and C=C bond lengths; [1 mark]

[Total: 4 marks]

- Although the presentation of this question is unusual, there should be little difference in how you approach your answer
- For a shape and structure question, your answer should talk about:
 - The number and type of bonds
 - The overall shape
 - The bond angles
 - What is happening with electrons (pi bond or pi cloud)
 - The length of the bonds

Question 1b

The value for the hydrogenation of the theoretical compound, cyclohexa-1,3,5-triene is:

- $(3 \times -120 =) -360 \text{ kJ mol}^{-1}$; [1 mark]
- Benzene is more stable than cyclohexa-1,3,5-triene; [1 mark]
- (Because) the electrons are delocalised across the structure; [1 mark]

[Total: 3 marks]

- Most questions about the structure of benzene relate to its stability and require you to talk about:
 - The carbon/carbon bonds being 0.140 nm which is intermediate of a C-C bond (0.154 nm) and a C=C bond (0.134 nm)
 - The stability of benzene by comparing the enthalpy of hydrogenation for benzene (-208 kJ mol^{-1}) with the theoretical molecule cyclohexatriene (-360 kJ mol^{-1})
 - The delocalisation of electron density into the pi-cloud / the overlap of p-orbitals

Question 1c

The reactivity of benzene, chlorobenzene, methylbenzene and phenol in electrophilic substitution is as follows:

- Chlorobenzene is the least reactive; [1 mark]
- (Because) the chlorine group withdraws electron density (making the ring less susceptible to electrophilic attack); [1 mark]
- Toluene / methylbenzene
AND
Phenol are the most reactive; [1 mark]
- (Because) in toluene / methylbenzene, the methyl group donates electron density to the benzene ring (making the ring more susceptible to electrophilic attack); [1 mark]
- (Because) in phenol, the hydroxyl group delocalises one of the electron pairs from an oxygen atom in to the benzene ring (making the ring more susceptible to electrophilic attack); [1 mark]

[Total: 5 marks]

- For this question:
 - Remember the exam command work “compare” means that you should talk about any similarities and differences between the compounds
 - “Compare the **relative** reactivities” is guiding you to make direct comparisons or rank the compounds so your answer should include words like more, most, less, least
 - You cannot distinguish between the reactivity of toluene and phenol because they both activate the ring, but in different ways
 - You could comment about the reactivity of benzene but it may not be a marking point as chlorobenzene is the least reactive and toluene/phenol are the most reactive - by definition benzene must be in the middle.
- The reactivity of benzene derivatives focuses on benzene’s pi-cloud of electrons:
 - Certain functional groups deactivate the ring by withdrawing electron density from benzene’s pi-cloud due to their electronegativity, e.g. chlorine
 - Certain functional groups activate the ring by increasing the electron density of benzene’s pi-cloud due to the inductive effect, e.g. alkyl groups, or due to the donation of a lone pair, e.g. hydroxyl groups

Question 1d

- Pi / π bond in hexene / C_6H_{12} contains localised electrons / area of high electron density; [1 mark]
- Pi / π bond in hexene / C_6H_{12} induces a partial / delta / δ positive / + and partial / delta / δ negative / - in the bromine / Br_2 molecule; [1 mark]
- Partial / delta / δ positive / + bromine / Br attracted to pi / π bond in hexene / C_6H_{12} leaving a carbocation intermediate; [1 mark]
- The carbocation intermediate attracts the partial / delta / δ negative / - bromine / Br atom; [1 mark]
- In benzene / C_6H_6 there are no localised electrons with areas of high electron density therefore it is unable to polarise the bromine molecule
OR
In benzene / C_6H_6 there are delocalised electrons with no areas of high electron density therefore it is unable to polarise the bromine molecule; [1 mark]

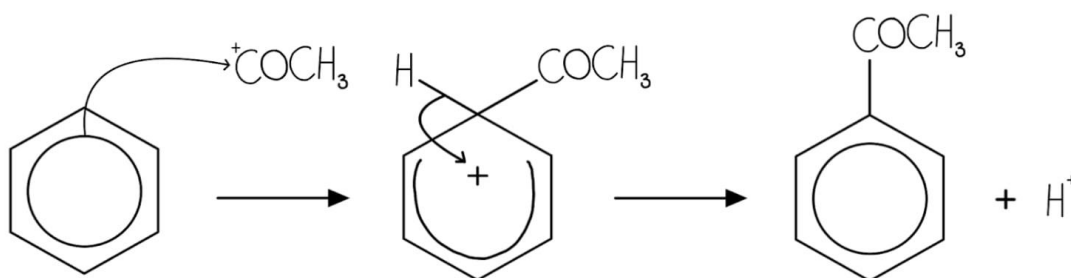
[Total: 5 marks]

- Alkenes will undergo electrophilic addition to form haloalkanes when they react with halogen molecules
- The double bond in the alkene is very reactive due to the high electron density
- In order for benzene to react with a halogen molecule, a halogen carrier such as aluminium bromide, AlBr_3 must be used
- Also, benzene will not undergo electrophilic addition with a halogen, it will undergo electrophilic substitution (an H atom will be substituted for a halogen atom)

Question 2a

The catalyst used to form the electrophile in the reaction between benzene and ethanoyl chloride is:

- Aluminium chloride / AlCl_3 ; [1 mark]
- $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}^+\text{O} + \text{AlCl}_4^-$; [1 mark]
The positive charge on the electrophile in the equation can be shown on the carbon or the oxygen



- Curly arrow from the ring within benzene to the C^+ ; [1 mark]
The + must be on the correct C of the COCH_3
- Correct intermediate structure with horseshoe covering more than half of the Ring but not extending past carbons 2 and 6; [1 mark]
- Curly arrow from the C-H bond back to the + within the ring
AND
Correct benzene product
AND
 H^+ shown; [1 mark]

[Total: 5 marks]

- Benzene mechanisms are electrophilic substitution reactions and the common mistakes are to:
 - Not draw the hydrogen that is being substituted
 - Draw the hydrogen being substituted in the wrong position
 - Forget to put the + in the correct place on the intermediate, especially using the Kekule structure for the mechanism
 - Draw the ring inside the intermediate structure incorrectly, if using the ring structure for the mechanism

Question 2b

A suitable reagent for the reduction of the organic product from part a would be:

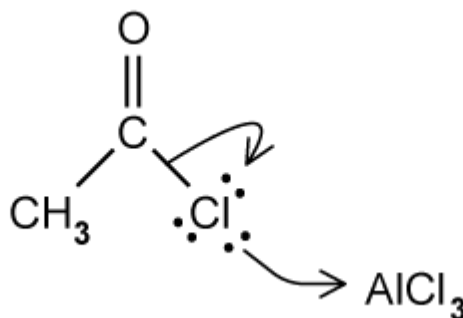
- NaBH_4 / LiAlH_4
OR
 H_2 with Ni / Pd / Pt; [1 mark]
- $\text{C}_6\text{H}_5\text{COCH}_3 + 2[\text{H}] \rightarrow \text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$; [1 mark]

[Total: 2 marks]

Due to specific detail of the electrophilic substitution mechanism (in terms of placement of arrows and +), the questions that follow often use quite standard reactions

Question 2c

The mechanism for the reaction of the ethanoyl chloride with the catalyst is:



- Curly arrow from the C-Cl bond to the Cl; [1 mark]
- Curly arrow from one of the Cl lone pairs to the AlCl_3 ; [1 mark]

[Total: 2 marks]

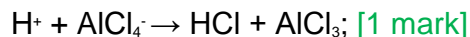
- If you were asked for the equation, instead of the mechanism, the equation is as follows:
 - $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$
- If you know the equation, then you can use this to work out the mechanism
- From this equation:
 - You know that the chlorine is leaving the ethanoyl chloride, so that bond must break
 - You know that AlCl_4^- is forming, so move the chlorine over using a curly arrow

Question 2d

The aluminium chloride catalyst reforms because:

- There is a H^+ from the electrophilic substitution of benzene; [1 mark]
- The H^+ reacts with AlCl_4^- to form HCl and AlCl_3

OR



[Total: 2 marks]

- Remember that a catalyst is a chemical that lowers the activation energy of a reaction by providing an alternative reaction pathway
- A catalyst can be directly involved in the reaction but must reform at the end of the reaction

Question 3a

The reagents and the name of the mechanism used to convert benzene into nitrobenzene are:

Reagents:

- (Concentrated) nitric acid
AND
(Concentrated) sulfuric acid; [1 mark]

Mechanism:

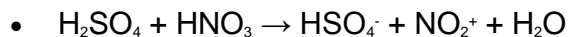
- Electrophilic substitution; [1 mark]

[Total: 2 marks]

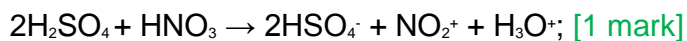
- You are expected to know the reagents and mechanism for the nitration of benzene
- **Tip:** Drawing benzene and nitrobenzene can help visualise the mechanism
- One of the hydrogens is replaced / **substituted** by the nitro group
- The benzene ring has a large area of delocalised electron making it attractive to electrophiles
- Therefore, the mechanism will be electrophilic substitution

Question 3b

The equation for the formation of the nitronium ion is:



OR

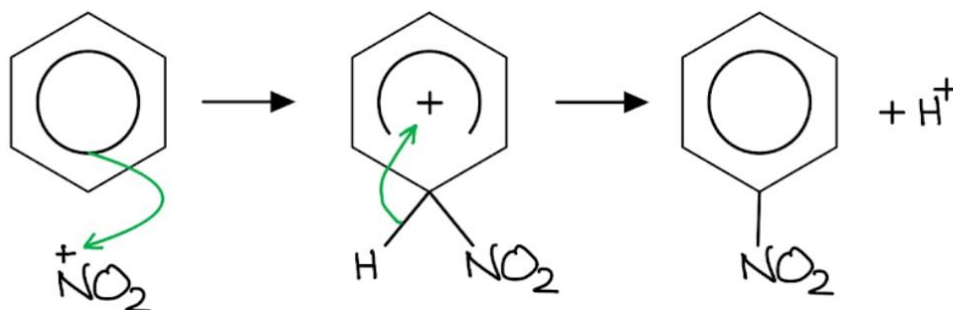


[Total: 1 mark]

- You need to be able to quote one of these two equations to form the electrophilic nitronium ion used in the nitration of benzene

Question 3c

The mechanism for the nitration of benzene is:



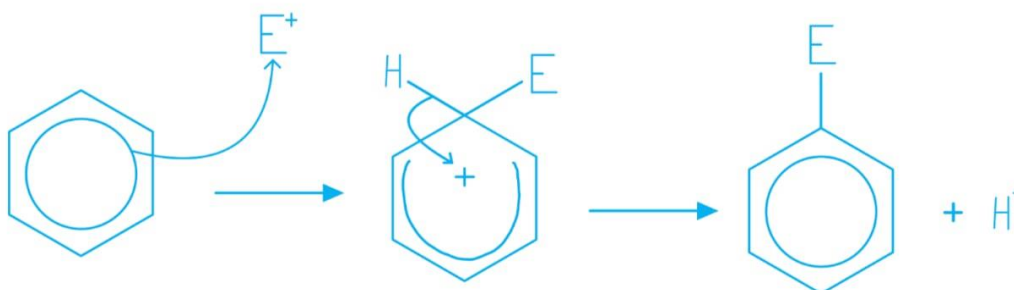
- Curly arrow going from benzene ring to the positive N of the nitronium ion / NO_2^+ ; [1 mark]
- Correct carbocation structure and positive charge in the (horseshoe) ring; [1 mark]
- Curly arrow going from the middle of the C-H bond towards the positive charge of the benzene cation; [1 mark]
- Correct structure of nitrobenzene

AND

H^+ ; [1 mark]

[Total: 4 marks]

- All electrophilic substitution mechanisms follow the same general pattern:



- The electrophile bonds to the benzene ring, forming an intermediate with a partially delocalised electron system - shown as a horseshoe with + inside
- There are only two locations that you should draw the + charge, either on the electron deficient carbon atom on the benzene ring or in the centre of the benzene ring
- The intermediate then loses a proton, restoring the delocalised electron system

Question 3d

The reagents for the conversion of nitrobenzene into aniline are:

- Step 1:

Fe / Zn / Sn

AND

HCl / H₂SO₄ / CH₃COOH; [1 mark]

- Step 2:

NaOH / KOH; [1 mark]

[Total: 2 marks]

- You are expected to know that aniline is the aminated benzene formed by the reduction of nitrobenzene
 - The IUPAC name of aniline is phenylamine but it is sometimes called aminobenzene as well

Question 4a

The synthesis of 4-aminophenol from phenol involves:

Step 1:

- Reagents = Concentrated nitric acid **AND** concentrated sulphuric acid; [1 mark]
- Condition = 50°C; [1 mark]
- Electrophile formation = $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$; [1 mark]
- Product = 4-nitrophenol

OR



- Correct structure; [1 mark]

Step 2:

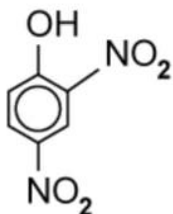
- Reagent = concentrated HCl **AND** Fe / Sn
OR
H₂ **AND** Ni / Pd / Pt catalyst; [1 mark]

[Total: 5 marks]

- Nitration is a standard reaction for benzene, you are expected to know the stepwise and overall equations for the formation of the nitronium ion:
 - Overall - $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$
- The stepwise equations are less commonly required:
 - $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightleftharpoons \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$
 - $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$
 - $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$

Question 4b

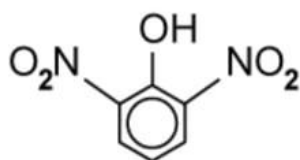
The possible dinitrophenol isomers leading to the formation of 2,4,6-trinitrophenol are:



•

OR

2,4-dinitrophenol; [1 mark]



•

OR

2,6-dinitrophenol; [1 mark]

- Position / Positional (isomerism); [1 mark]

Do not allow any other isomers

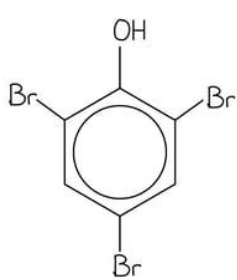
[Total: 3 marks]

- This question is specific and misleading at the same time because, theoretically, there are a number of possible dinitrophenol isomers:
 - - 2,3-dinitrophenol
 - 2,4-dinitrophenol
 - 2,5-dinitrophenol
 - 2,6-dinitrophenol
 - 3,4-dinitrophenol
 - 3,5-dinitrophenol
- However, the question does state that it must be possible to make 2,4,6-trinitrophenol, which reduces the possible isomers to only:
 - 2,4-dinitrophenol
 - 2,6-dinitrophenol

Question 4c

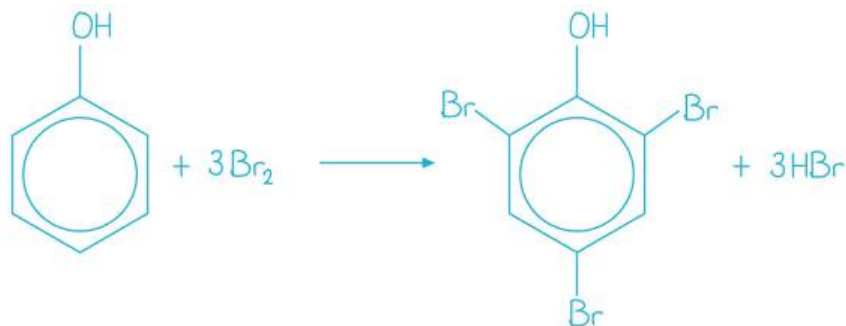
The structure and name of the organic product giving the white precipitate is:

- 2,4,6-tribromophenol; [1 mark]
- Correct structure; [1 mark]



- Phenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperature

- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol
- This is also known as the **bromination of phenol**
- The orange bromine solution is decolourised
- The overall reaction is:



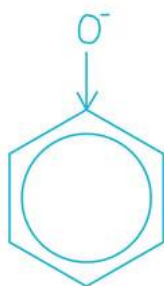
Question 4d

Phenol can act as a weak acid because:

- Phenol can donate the H in the OH group; [1 mark]
- $\text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{O}^- + \text{H}_3\text{O}^+$
OR
 $\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{O}^- + \text{H}^+$; [1 mark]
- Phenoxide ion is stable as lone pair of electrons delocalised with the electron cloud on the whole ion; [1 mark]

[Total: 3 marks]

- Remember as phenol is acting as a weak acid the dissociation is reversible so you must use a reversible reaction
- The phenoxide ion has an oxygen atom which is very electronegative, therefore this will attract hydrogen ions back towards it, therefore phenol can only be classed as a weak acid, not a strong acid
- One of the lone pairs of electrons on the oxygen is delocalised with the electron cloud of the whole phenoxide ion
- Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen

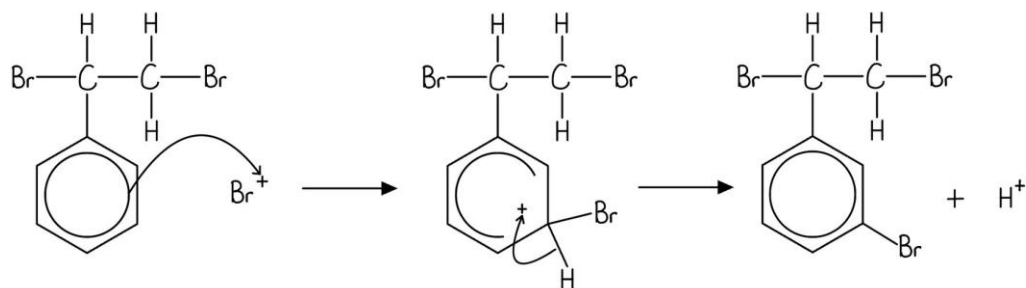


Question 5b

The name and outline of the mechanism to form Compound B from Compound A is:

- Electrophilic substitution; [1 mark]
-

The mechanism is:



- Curly arrow from the ring inside benzene to the Br^+ electrophile; [1 mark]
- Correct intermediate structure; [1 mark]

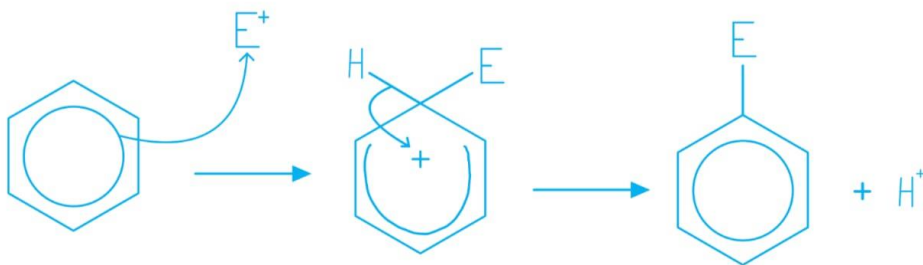
*The horseshoe must cover at least half of the ring with the 'gap' at the correct C
It must cover more than half of the benzene but must not extend past carbon 2 or 4*

- Curly arrow from the C-H bond back to the $+$ within the ring
AND

Correct products shown; [1 mark]

[Total: 4 marks]

- The general mechanism for electrophilic substitution:



Question 5c

The percentage atom economy for Step 1 is:

- $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$; [1 mark]
- Mr of $\text{C}_6\text{H}_6 = 78$ and Mr of $\text{CH}_3\text{Cl} = 50.5$
- So, total mass of reactants = $78 + 50.5 = 128.5$; [1 mark]
- Percentage atom economy = Mr of wanted product / Total Mr of reactants $\times 100 = 92 / 128.5 \times 100 = 71.6\%$; [1 mark]

[Total: 3 marks]

- Despite its simplicity, percentage atom economy is still poorly answered by students
- You are credited a mark for the reaction equation here, because you have to know the full reaction equation to be able to calculate the atom economy
 - Careful: don't forget the HCl byproduct that is made during the reaction
 - A good way to double check if you are unsure, is to calculate the total Mr of all reactants and the total Mr of all products - they should be exactly the same!

Question 5d

i. The role of the nitric acid is:

- A base; [1 mark]
- (Because) it accepts a proton
AND
From the sulphuric acid; [1 mark]

ii. The role of the sulphuric acid in the overall nitration reaction is:

- A catalyst
AND
Because it donates an electron to form the electrophile / NO_2^+ **AND** is reformed at the end of the reaction; [1 mark]

[Total: 3 marks]

- Questions about roles of chemicals are often answered poorly, with a lot of students simply guessing "catalyst"
- The main roles for any chemicals involved in a reaction are:
 - Acid
 - Base
 - Catalyst
 - Reducing agent
 - Oxidising agent