EXAM PAPERS PRACTICE

Level: CIE AS and A Level (9701)
Subject: Chemistry
Topic: CIE Chemistry
Type: Mark Scheme

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+

CHEMISTRY AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful

Mark Scheme

Answer 1.

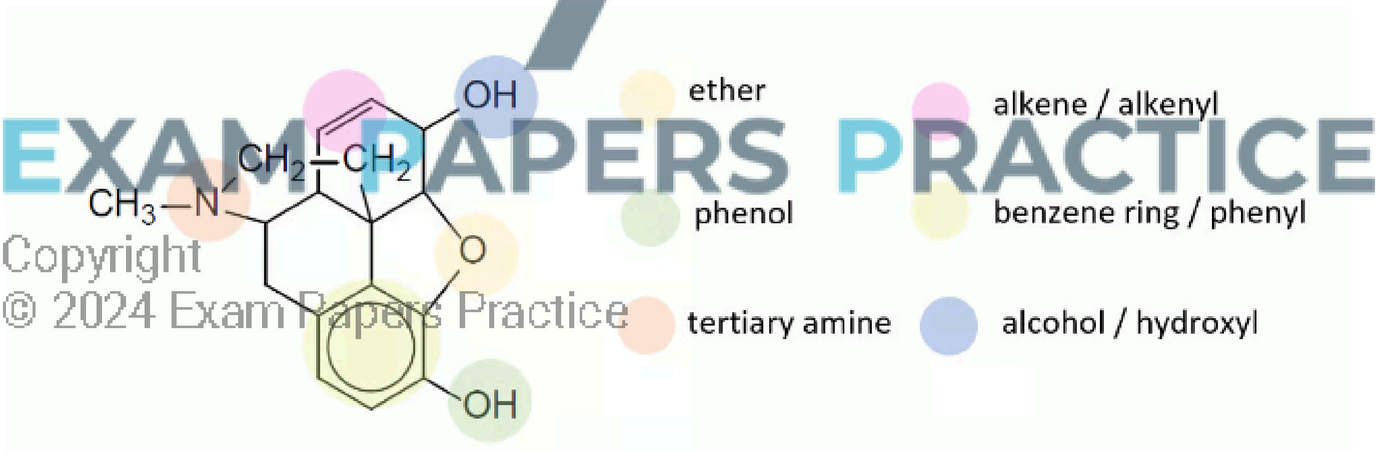
a) The functional groups found in morphine are:

TWO from: [2 marks]

- alcohol / hydroxyl;
- alkene / alkenyl;
- phenol;
- (tertiary) amine;
- ether;

[Total: 2 marks]

- You are not expected to know the ether functional group, but you may have come across it so it would be an acceptable answer
- The location of the functional groups are:

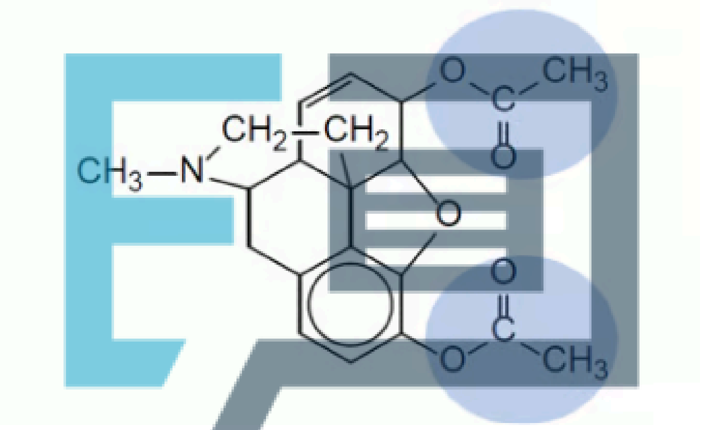


b) The functional group(s) present in heroin, but not in morphine:

- Ester / ethanoate; [1 mark]

[Total: 1 mark]

- An ester group is RCOOR, in this case, ethanoate, CH_3COO^- (rest of molecule)
- Here they are on the molecule:



c) The reagents and conditions needed to turn morphine into heroin are:

Reagent:

- Ethanoic acid / CH_3COOH / Ethanoic Anhydride / $(CH_3CO)_2O$; [1 mark]

Conditions:

- Concentrated sulfuric acid / H_2SO_4 / concentrated hydrochloric acid/ HCl / heating; [1 mark]

[Total: 2 marks]

- You may not have come across the synthesis of heroin, but you would be expected to use your knowledge and understanding of synthetic routes to deduce the reagents and conditions needed to convert one functional group into another
- You should recognise that this reaction is an esterification
- The inorganic acid is a catalyst in this reaction and it does not matter whether you use sulfuric or hydrochloric as long as it is concentrated
- Reaction conditions can include solvents, catalysts or particular temperatures and pressures

d) How morphine and heroin would react with warm acidified potassium dichromate solution:

- Morphine would turn the potassium dichromate solution from orange to green; [1 mark]
- Heroin would not react / no change / stay orange with potassium dichromate; [1 mark]
- Morphine contains a (secondary) alcohol group; [1 mark]

[Total: 3 marks]

- Primary and secondary alcohols will react with potassium dichromate solution as they can be oxidised
- Don't forget to give the before and after colours when describing test results

Answer 2.

a) Two functional groups found in farnesol are:
  - alkene/alkenyl (highlighted in blue); [1 mark]
  - (primary) alcohol/hydroxyl (highlighted in green); [1 mark]

[Total: 2 marks]

- You should be able to identify individual functional groups in structural and skeletal formulae diagrams
- Strictly speaking, the functional groups are called alkenyl and hydroxyl, respectively, and the families are called alkene and alcohol, but you wouldn't be marked down in an exam for this

b) How you would expect farnesol to react with bromine water:

- The bromine water would decolourise; [1mark]

[Total: 1 mark]

- This is a test for unsaturated compounds containing the alkene functional group
- All alkenes will decolourise bromine water, though its important to use only a few drops of bromine water as the colour may fade by not disappear completely if you use too much
- Sometimes the bromine is dissolved in cyclohexane rather than water as it can be difficult for insoluble organic compounds to react sufficiently with the aqueous bromine water, but the result is the same

c) A functional group present in the product of the first step is:

- Carboxylic acid; [1 mark]

[Total: 1 mark]

- The reagent in the first step is acidified potassium dichromate solution which is an oxidising agent
- Primary alcohols react with this oxidising agent to form aldehydes and carboxylic acids
- The intermediate has one more oxygen and two fewer hydrogens than farnesol, which is consistent with it being a carboxylic acid;
    - e.g. $CH_3CH_2OH + [O] \rightarrow CH_3COOH + H_2O$

d) A functional group present in the final product, but not in farnesol, is:

- Ester; [1 mark]

[Total: 1 mark]

- The reagent is a mixture of sulfuric acid and methanol which can be used in esterification reactions
- The product contains one more carbon and two more hydrogens, which is consistent with a (methyl) ester being formed
    - e.g. $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$

Answer 3.

a)

i) The halogenoalkane, **D**, that undergoes nucleophilic substitution in step 4 to form propan-1-ol is:

- 1-chloropropane
  OR
  1-bromopropane; [1 mark]

ii) The reagents and conditions for step 4 are:

- Aqueous sodium hydroxide / NaOH (aq)
  OR
  Aqueous potassium hydroxide / KOH (aq); [1 mark]
- Heat under reflux; [1 mark]

[Total: 3 marks]

- You are told that the reaction to form propan-1-ol is nucleophilic substitution
    - This means that in order to form propan-1-ol, an OH group **must** have substituted a halogen on carbon-1
    - This also suggests that the reagent is sodium hydroxide
- For nucleophilic substitution to occur, the reaction must be completed with aqueous sodium hydroxide
    - Otherwise, elimination would have occurred if alcoholic / ethanolic sodium hydroxide was used
- The conditions are a fact that you simply need to know - heat under reflux

b) The identity of the alkene, **C**, in Fig. 3.1 is:

- Propene; [1 mark]

[Total: 1 mark]

- This can be deduced from a correct answer to part (a) (i) or from the final product name, propan-1-ol
- Both of these suggest that the carbon chain involved has 3 carbons
- There is only one alkene with 3 carbons, propene

c) The electrophilic addition reaction in step 3 might not be favourable in an industrial multistep reaction because:

- The reaction produces more than one product / a major and minor product
  OR
  The products will need to be purified
  OR
  The reaction has low atom economy (as a second / unwanted product is formed); [1 mark]

[Total: 1 mark]

- This question tests that you know
  - Reduce the amount of steps (not applicable to this question)
  - Have a high atom economy wherever possible, which links to producing as little waste / byproducts as possible
  - Electrophilic addition to unsymmetrical alkenes can form major and minor products

Answer 4.

a) The systematic names of compounds **A**, **B** and **C** are:

- Compound **A** = benzoic acid; [1 mark]
- Compound **B** = phenylamine
  OR
  Aminobenzene; [1 mark]
- Compound **C** = 1,3-dimethylbenzene; [1 mark]

[Total: 3 marks]

- Compound **A**
  - The functional groups of this molecule are the benzene ring and the carboxylic acid
  - The carboxylic acid always provides an -oic acid suffix to the name
  - Therefore, compound **A** is benzoic acid
- Compound **B**
  - The functional groups of this molecule are the benzene ring and the amine / amino group
  - The amine / amino group can provide:
    - An amino- prefix
      - This means that one possible name for compound **B** is aminobenzene
    - Or an -amine suffix to the name
      - This means that the benzene ring should be called phenyl
      - Therefore, another possible name for compound **B** is phenylamine
  - Compound **B** is often called by its common name aniline but this will not gain the mark because it is not a systematic name
- Compound **C**
  - The functional groups of this molecule are the benzene ring and the two methyl groups
  - The two methyl groups mean that the name is prefixed with dimethyl-
  - **Remember:** You must give numbers to show the positions of the methyl groups
    - If the top methyl group is carbon-1, then the second methyl group is on carbon-3 because the functional groups are numbered to give the lowest possible numbers
  - Therefore, compound **C** is 1,3-dimethylbenzene

b) The positions that are activated for the following compounds in part **(a)** are:

- Compound **A** = 3 / three
  AND
  5 / five; [1 mark]
- Compound **B** = 2 / two
  AND
  4 / four
  AND
  6 / six; [1 mark]

[Total: 2 marks]

- You need to know the positions that are activated by electron-withdrawing groups such as COOH and electron-donating groups such as NH_2

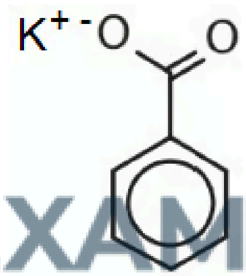
c)

i) The reagents for steps **1** - **4** are:

- Step **1** = (hot alkaline) potassium manganate(VI) / $KMnO_4$; [1 mark]
- Step **2** = (dilute) hydrochloric acid / HCl; [1 mark]
- Step **3** = (concentrated) sulfuric acid
  AND
  (Concentrated) nitric acid; [1 mark]
- Step **4** = tin / Sn
  AND
  Hydrochloric acid / HCl; [1 mark]

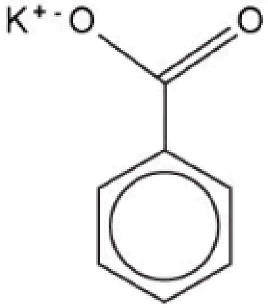
ii) The structures of compounds **D** and **E** are:

Compound **D**:

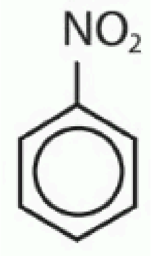
- 

; [1 mark]

Compound **D**



Compound **E**:

- 

; [1 mark]

Compound **E**

[Total: 6 marks]

- The conversion of benzene to benzoic acid / compound **A** is an oxidation reaction
  - Benzene is heated under reflux with hot alkaline potassium manganate(VI) to form compound potassium benzoate / compound **D**
  - Treating potassium benzoate / compound **D** with hydrochloric acid then forms benzoic acid / compound **A**
- The conversion of benzene to aminobenzene / phenylamine / compound **B** is a nitration reaction followed by reduction
  - Concentrated sulfuric acid and concentrated nitric acid are used to form the nitronium NO_2^+ ion
  - Benzene undergoes electrophilic substitution with the nitronium NO_2^+ ion to form nitrobenzene / compound **E**
  - Treating nitrobenzene / compound **E** with tin / Sn and hydrochloric acid / HCl then reduces the nitrobenzene / compound **E** to form aminobenzene / phenylamine / compound **B**
- You can also be expected to:
  - Give any necessary conditions, e.g. step **1** is heat / reflux
  - Name compounds **D** and **E**
  - State the types of reactions occurring at different steps, e.g. oxidation, reduction, nitration, electrophilic substitution
  - State / draw the mechanism for appropriate reaction steps

d)

i) **One** set of reagents and conditions that could be used for both steps is:

- Reagents = Chloromethane / CH_3Cl; [1 mark]
- Conditions = Aluminium trichloride / $AlCl_3$ catalyst; [1 mark]

ii) Step **2** is unlikely to occur because:

- The methyl group (on methylbenzene) activates positions 2, 4 and 6
  OR
  The methyl group (on methylbenzene) does not activate positions 3; [1 mark]

[Total: 3 marks]

- Both steps that are proposed in Fig. 4.3 are Friedel-Crafts alkylation reactions
  - These require an appropriate chloroalkane in the presence of an $AlCl_3$ catalyst
  - The $AlCl_3$ catalyst helps form the CH_3^+ electrophile by removing the chlorine from the chloroalkane
- Step **1** is likely to happen as the benzene has no attached functional groups that may affect the reaction
- Step **2** is less likely to occur because there is now a methyl group attached to the benzene ring
  - Methyl groups are electron-donating which means that they activate positions 2, 4 and 6 on the ring
  - Therefore, the formation of 1,3-dimethylbenzene / compound **C** is unlikely

Answer 5.

a)

i) The name of compound **A** and the reaction conditions for step 1 are:

- Compound **A** = nitrobenzene; [1 mark]
- Reaction conditions = reflux / heat
  AND
  Any temperature between 25 and 60 °C; [1 mark]

ii) The mechanism for the conversion of benzene into compound **A** and the reactive species are:

- Mechanism = electrophilic substitution; [1 mark]
- Species = NO_2^+ / nitronium ion; [1 mark]

[Total: 4 marks]

- The reaction of benzene with concentrated nitric acid and concentrated sulfuric acid is nitration
  - This is completed under reflux at 25 - 60 °C
  - You need to know the reagents and conditions for many organic reactions, so take the time to learn them
- Concentrated nitric acid and concentrated sulfuric acid react together to form the nitronium ion
  - The nitronium ion is an electrophile
- The nitronium ion replaces a hydrogen on the benzene ring
  - Therefore, this reaction is electrophilic substitution
- You could be asked to draw the mechanism for this reaction

b) The catalyst required for this reaction and the equation for the formation of the electrophile are:

- Aluminium trichloride / $AlCl_3$
  AND
  $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$; [1 mark]

[Total: 1 mark]

- This is another example of an electrophilic substitution reaction, that you could be asked to draw a mechanism for
- You need to know the reagents and conditions for Friedel-Crafts alkylation and acylation
  - Both reactions require an appropriate halogenoalkane and a halogen carrier catalyst such as $AlCl_3$
  - **Careful:** The catalyst that you choose must contain the same halogen as the reacting molecule
- You should also be able to explain how the catalyst forms the electrophile

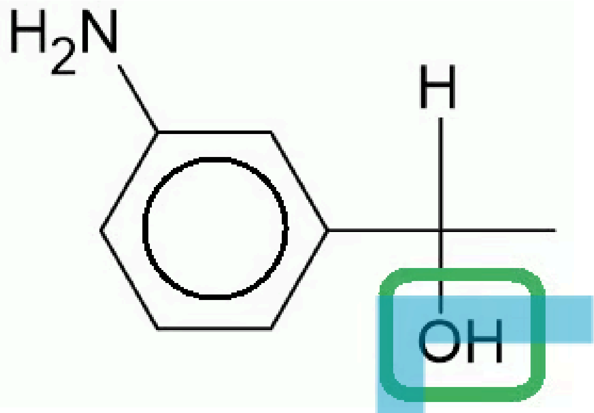
c) **Two** changes that occur to compound **B** during this reaction to show that reduction has taken place are:

- Oxygen is lost
  AND
  Hydrogen is gained; [1 mark]

[Total: 1 mark]

- You do not need to know the structure of compound **B** to answer this question
  - The key piece of information is that a nitro group / NO_2 is being converted into an amine group, NH_2
  - Therefore, oxygen is being lost and hydrogen is being gained
- **Remember:** There is more than one way to describe reduction:
  - Loss of oxygen
  - Gain of hydrogen
  - Loss of electrons

d) The aliphatic functional group that is formed **after** the reaction of compound **C** with $NaBH_4$ is:



- OH functional group correctly identified; [1 mark]

ii) The structure of compound **C** is:

- ; [1 mark]

[Total: 2 marks]

- NaBH4 is a reducing agent that is used to reduce:
    - Aldehydes ⟶ primary alcohols
    - Ketones ⟶ secondary alcohols
- This means that compound **C** was originally a ketone
    - To reverse this:
        - Remove the H opposite the OH group
        - Remove the H of the OH group
        - Replace the single C-O bond with a double C=O bond

Answer 6.

a) The other functional groups present in each molecule are:

- Ibuprofen: carboxylic acid; [1 mark]
- Paracetamol: phenol
  AND
  Amide; [1 mark]

[Total: 2 marks]

- An OH group attached to an arene ring changes its chemistry completely
  - This is why it is termed phenol rather than alcohol
- The paracetamol contains a secondary amide, although you don't need to classification to score the mark
  - A primary amide would have two hydrogens on the N

b)

i) One similarity and one difference in the physical or chemical properties between the two enantiomers are:

- Similarity: Enantiomers have identical physical and chemical properties
  AND
  Difference: The ability to rotate plane polarised light / potential biological activity; [1 mark]

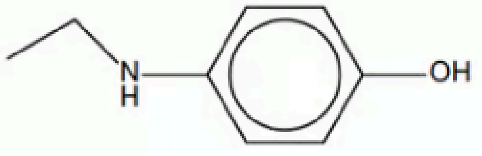
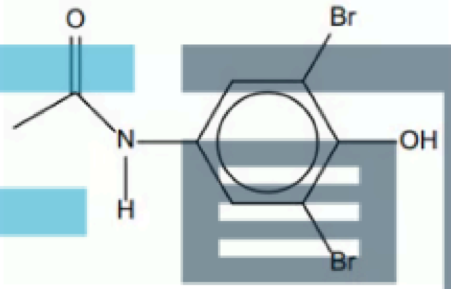
ii) The meaning of racemic mixture:

- A mixture containing equal amounts of each enantiomer; [1 mark]

[Total: 2 marks]

- Enantiomers are mirror-image molecules containing a chiral carbon, that is, a carbon with four different groups attached
- Another term for racemic mixture is a racemate

c) The completed table is:

reagent	organic product structure	type of reaction
$LiAlH_4$	 [1 mark]	**reduction**
an excess of $Br_2(aq)$	 [1 mark]	**electrophilic substitution**

- Both correct reaction types; [1 mark]

[Total: 3 marks]

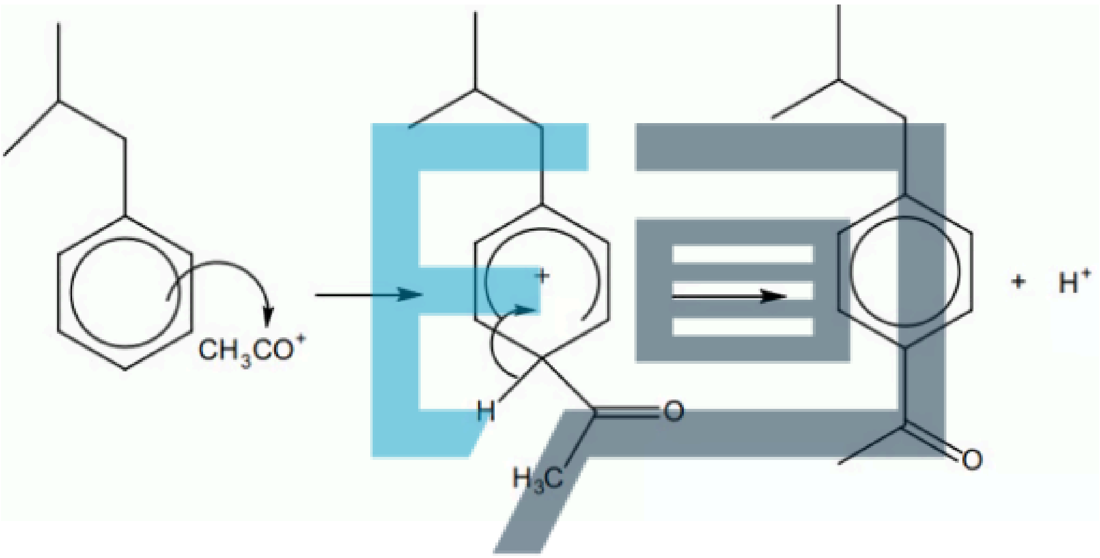
- You should know that lithium aluminium hydride is a reducing agent, so look for functional groups that can be reduced.
  - Amides can be reduced to amines
  - The products of a non-substituted amide are: a primary amine and water
  - The products of a substituted amide are: a secondary amine and water
  - Paracetamol contains a secondary amide, so a secondary amine and water are formed
- Due to the phenolic OH group, bromination would be directed to the 2, 4 and 6 positions
  - There is already a functional group attached in the 6 position so bromine will add to the 2 and 4 positions

d)

i) An equation to show how $AlCl_3$ generates the electrophile for the conversion of **X** into **Y** is:

- $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$; [1 mark]

ii) The mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows and charges:



- Curly arrow from the ring system to the CH_3CO^+ (arrow to the positively charged carbon atom); [1 mark]
- Correct intermediate structure; [1 mark]
- The curly arrow from the C–H bond into the ring
  AND
  Loss of H^+; [1 mark]

iii) An equation to show how the $AlCl_3$ is regenerated is:

- $H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$; [1 mark]

[Total: 5 marks]

- You need to know how $AlCl_3$ acts as a catalyst to form the positive ion required for the reaction, including the equations to form the ion and reform the $AlCl_3$ catalyst
- In part ii)
  - The arrows must start from inside the circle and form the middle of the C-H bond
  - The intermediate needs to have the positive charge to be correct
  - The bond is formed between the carbon of the ring and the carbonyl carbon of the CH_3CO^+ so you must show the arrow pointing to the carbon, not the oxygen
  - Mechanisms are a good way to pick up quite a few marks so it is worth practising them
  - The origin and destination of curly arrows must be clear and unambiguous or you may lose the marks

Answer 7.

a) The reagents for each step are:

- Step 1: heat with $AlCl_3$ + $(CH_3)_2CHCl$ or $CH_3CH=CH_2$; [1 mark]
- Step 2: heat with $AlCl_3$ + CH_3COCl; [1 mark]
- Step 3: NaOH + I_2 (or Cl_2) (then H^+); [1 mark]
- Step 4: $LiAlH_4$ (in dry ether); [1 mark]

[Total: 4 marks]

- Step 1 involves electrophilic substitution of a benzene ring
  - In order to form the electrophile a halogen carrier which can be $AlCl_3$ if the halogenoalkane contains a chlorine atom
  - $FeBr_3$ is also acceptable if the halogenoalkane contains a Br atom
  - $AlCl_3 + (CH_3)_2CHCl \rightarrow AlCl_4^- + (CH_3)_2CH^+$
- Step 2 involves the same type of mechanism, though a CH_3CO group is being added to the benzene ring this time
  - Therefore an acyl chloride and a halogen carrier is required
  - $AlCl_3 + CH_3COCl \rightarrow AlCl_4^- + CH_3CO^+$
- Step 3 involves the formation of a carboxylic acid from a carbonyl group (a ketone in this case)
  - Therefore the iodoform reaction is required
  - $R\text{-}CO\text{-}CH_3 + 3I_2 + 4OH^- \rightarrow CH_3I + RCOO^- + 3I^- + 3H_2O$
  - The $RCOO^-$ reacts with H^+ to form the RCOOH
- Step 4
  - The final step involves a reaction with $LiAlH_4$ to form a primary alcohol from a carboxylic acid

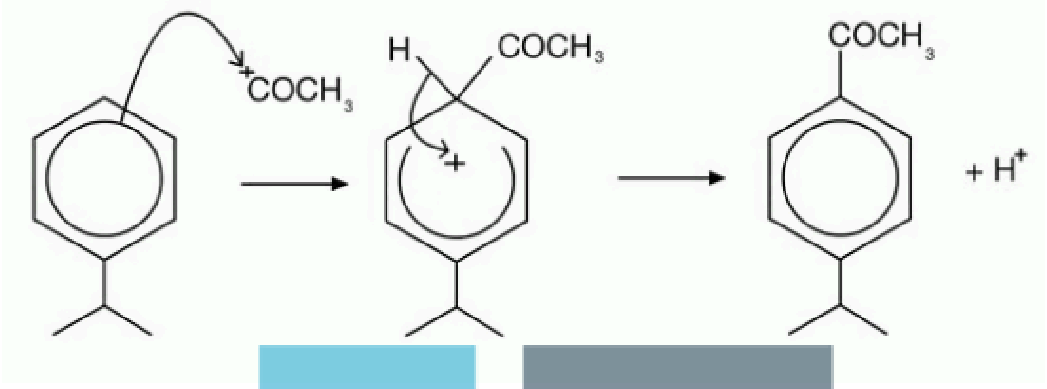
b) The mechanism for step 2 and type of reaction for step 4 are:

- Mechanism of step 2: Electrophilic (aromatic) substitution; [1 mark]
- Type of reaction in step 4: Reduction; [1 mark]

[Total: 2 marks]

- Arenes will undergo electrophilic substitution, whereby a hydrogen atom in the benzene ring is substituted for an attacking electrophile
    - Make sure you know the mechanism for this reaction
- The formation of a primary alcohol from a carboxylic acid involves reduction

c) The reaction mechanism is:



- Curly arrow from the ring within benzene to the $^+COCH_3$; [1 mark]
- 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

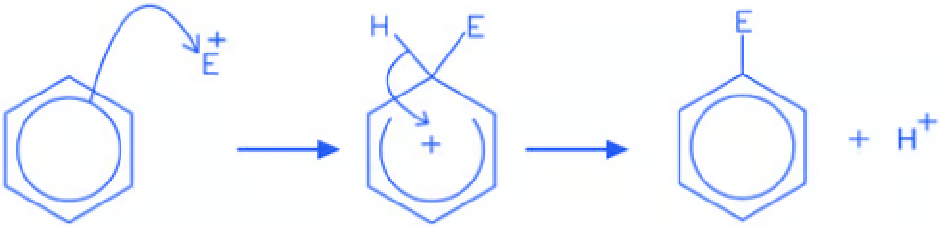
  Correct benzene product

  AND

  H^+ shown; [1 mark]

[Total: 3 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
- The general mechanism for electrophilic substitution is as follows:

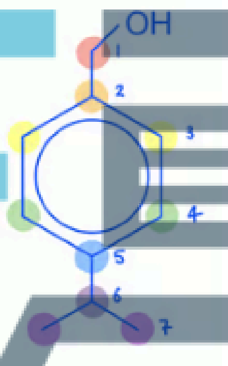


d) The number of ^{13}C peaks are:

- 7 peaks; [1 mark]

[Total: 1 mark]

- **Tip:** It helps to look for symmetry within the molecule when identifying ^{13}C peaks as this identifies equivalent carbon environments quicker
- The 7 peaks in the ^{13}C spectrum for cuminyl alcohol are:



Answer 8.

a) The synthesis of ethanal from ethane is:

i) Step 1: Ethane to chloroethane

- Reagent: chlorine / Cl_2; [1 mark]
- Conditions: UV light / high temps; [1 mark]
- Reaction type: (free radical) substitution / halogenation ; [1 mark]

ii) Step 2: Chloroethane to ethanol

- Reagent: aqueous sodium hydroxide / NaOH (aq)
  OR
  Aqueous potassium hydroxide / KOH (aq); [1 mark]
- Conditions: hot / heat under reflux; [1 mark]
- Reaction type: (nucleophilic) substitution / hydrolysis ; [1 mark]

iii) Step 3: Ethanol to ethanal

- Reagent: acidified potassium dichromate(VI)
  OR
  Acidified potassium dichromate(VI)
  OR
  Acidified potassium manganate(VII)); [1 mark]
- Conditions: distil / distillation; [1 mark]
- Reaction type: oxidation; [1 mark]

[Total: 9 marks]

- The conversion of an alkane to a haloalkane would be very impractical industrially
  - This is because it is hard to control the extent of halogenation and to prevent multiple products from forming
  - However, it is included to test the application of your knowledge of organic reactions to solve synthesis problems
- The type of mechanisms are shown in brackets, but they are not essential for the mark
- The dichromate ion, $Cr_2O_7^{2-}$, is the key oxidising agent, so it is possible to gain the mark from sodium dichromate as well as potassium dichromate

b) Suitable reagents for the synthesis of compound **A** via step 1:

- $K_2Cr_2O_7$ / potassium dichromate(VI)
  OR
  $KMnO_4$ / potassium permanganate(VII); [1 mark]
- H_2SO_4 / acidified / with acid; [1 mark]
- Oxidation; [1 mark]

[Total: 3 marks]

- An ester is commonly made from a carboxylic acid and alcohol
- A carboxylic acid cannot be produced from the second molecule which is a ketone, so the first step producing **A**, must be the oxidation of an aldehyde to carboxylic acid
- **Careful:** The question asks for names of reagents
  - You could lose marks for writing ions, e.g. $Cr_2O_7^{2-}$, as these are not reagents - a reagent is something that you can find on a laboratory shelf! Sodium dichromate(VI) is, however, an acceptable alternative

c)

i) The name of the molecule that is produced from step 2 is:

- Butan-2-ol; [1 mark]

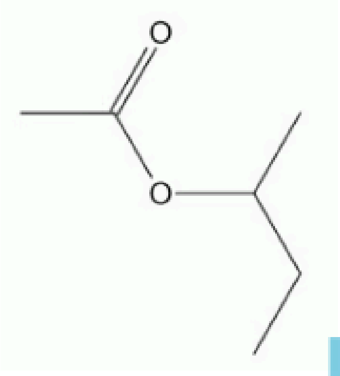
ii) Give the name of the type of reaction that is involved in step 2 and suggest a suitable reagent for the process.

- Reduction; [1 mark]
- $LiAlH_4$ / lithium aluminium hydride / lithium tetrahydridoaluminate
  OR
  $NaBH_4$ / sodium borohydride / sodium tetrahydridoborate; [1 mark]

[Total: 3 marks]

- The reduction of a ketone produces a secondary alcohol
  - This secondary alcohol is required to produce the branched chain ester
- Lithium tetrahydridoaluminate, $LiAlH_4$, is much more reactive than sodium tetrahydridoborate, $NaBH_4$, so is more dangerous to use in the laboratory
- For the purposes of this question, both reagents are suitable answers

d) The skeletal formula of the ester formed from the reaction scheme is:

-  ; [1 mark]

[Total: 1 mark]

- **Remember:** When drawing esters, the acid provides the COO portion of the ester link while the alcohol attaches to the single bonded oxygen with the elimination of a molecule of water

Answer 9.

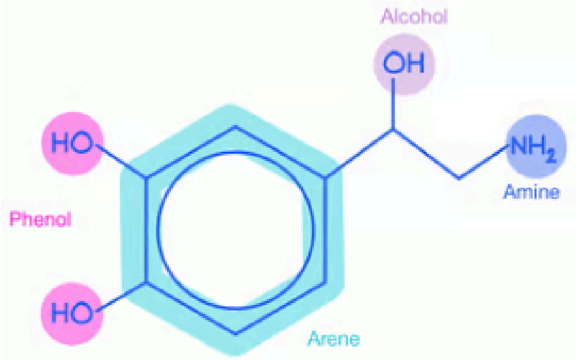
a) The three functional groups

Any **three** from the following

- Phenol; [1 mark]
- Primary alcohol; [1 mark]
- Amine; [1 mark]
- Arene / aryl / benzene; [1 mark]

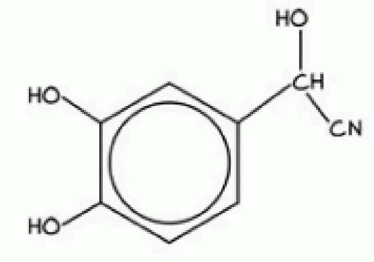
[Total: 3 marks]

- The groups in noradrenaline are:



b) Compound **Z** and the reagents for steps 1 and 2 are:

- Compound **Z** is:



; [1 mark]

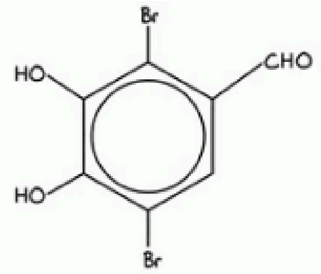
- Step 1: HCN and NaCN
  OR
  HCN and base; [1 mark]
- Step 2: H_2 and Ni
  OR
  $LiAlH_4$ in dry ether
  OR
  Na and ethanol; [1 mark]

[Total: 3 marks]

- To convert the functional group from dihydroxybenzaldehyde to noradrenaline the carbon chain needs to extend
- Therefore, a nitrile group CN needs to be added to the carbonyl carbon
- Then, reduction takes place to form the amine group

c) The observation and product of this reaction are:

- Bromine decolourises
  OR
  Bromine changes from orange to colourless
  OR
  A white precipitate is formed; [1 mark]
- The structure is:



OR

; [1 mark]

[Total: 2 marks]

- When drawing the structure you will gain a mark for including either two or three bromine atoms
- Phenols react readily with bromine and this reaction occurs at room temperature
- Dihydroxybenzaldehyde decolourises the orange bromine solution to form a white precipitate via electrophilic substitution
  - More than one hydrogen atom on the ring can be substituted as this

Answer 10.

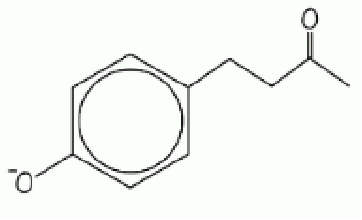
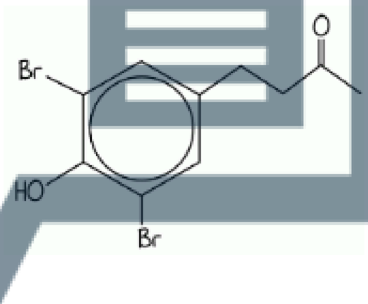
a) The functional groups present in compound **G** are:

- Phenol; [1 mark]
- Ketone; [1 mark]

[Total: 2 marks]

- When an -OH group is bonded to a benzene ring it is a phenol group
- The C=O group in the carbon chain is a ketone group

b) The completed table is:

Reagent	Observation	Structure of organic product	Type of reaction
Na (s)	Effervescence / bubbles / fizzing; [1 mark]	 ; [1 mark]	Redox; [1 mark]
Br_2 (aq)	Decolourises or white ppt.; [1 mark]	 ; [1 mark]	Electrophilic substitution; [1 mark]
I_2 / NaOH (aq)	Yellow ppt. ; [1 mark]	 ; [1 mark]	Oxidation; [1 mark]

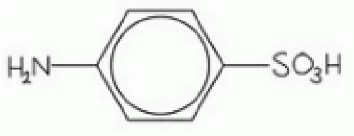
[Total: 9 marks]

- Na (s) will react with the -OH group to form an O^-
  - The oxygen-hydrogen bond in the hydroxy group breaks
- Aqueous bromine reacts with phenol and a hydrogen atom is substituted for a bromine atom in the 2 and 6 positions
  - There is a group already on the 4th carbon atom in the ring so the bromine atom does not substitute here
  - The -OH group is 2,4,6 directing
  - The ketone group is also 3,5 directing so this corresponds to where the bromine atoms have been substituted
- I_2 / NaOH (aq) are the reagents involved in the iodoform reaction, the ketone group in the compound will react with these reagents
  - The reaction involves a halogenation and hydrolysis step
    - In the halogenation step, all three H-atoms in the R group are replaced with iodine atoms, forming a $-CI_3$ group
    - The intermediate compound is hydrolysed by an alkaline solution to form a sodium salt (RCO_2^- Na^+) and a yellow precipitate of CHI_3

c)

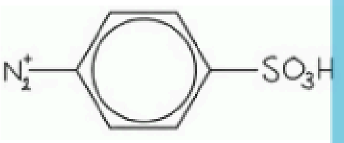
i) The structures are:

Compound **J**:

- 

; [1 mark]

Compound **K**:

- 

; [1 mark]

ii) The reagents and conditions required are:

Step 1

- $NaNO_2$ + HCl
  OR
  HNO_2; [1 mark]
- T < 10 °C; [1 mark]

Step 2

- (Add K to a solution of **G**) in NaOH (aq); [1 mark]

[Total: 5 marks]

- You are told that compound **J** is an amine and is converted to compound **K** which then forms an azo dye
- In order to form an azo dye, the amine group must be converted to a diazonium ion
- This then can bond with compound **G** to form the azo dye **H**
  - This must take place in alkaline conditions, hence the requirement for NaOH (aq)
- **Remember:** HNO_2 must be formed 'in situ' in the reaction vessel as it is very unstable
  - So, $NaNO_2$ and HCl must be used to form the acid
  - This also must take place at a low temperature, below 10 °C

d) Dye **H** is very stable because:

- Delocalised electrons in the π bonding systems of the two benzene rings; [1 mark]
- Extended through the -N=N- which acts as a bridge between the two rings; [1 mark]

[Total: 2 marks]

- Azo dyes contain benzene rings
- In azo compounds, the R groups are arene rings
    - The structures of these are more stable than if the R groups are alkyl groups
- Arenes are very stable compounds due to the delocalisation of π electrons in the ring
- This is because the negative charge is spread out over the molecule instead of being confined to a small area

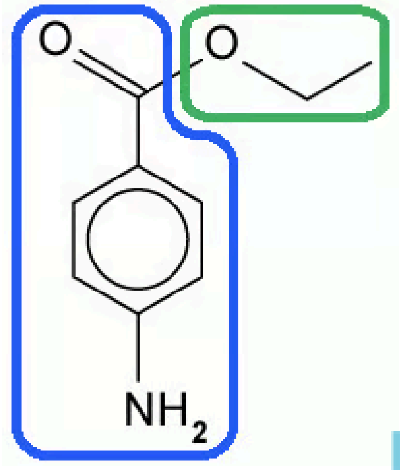
Answer 11.

a) The systematic name of benzocaine is:

- Ethyl 4-aminobenzoate; [1 mark]

[Total: 1 mark]

- The question tells you that benzocaine is an ester
    - This means that the name will follow the general alkyl alkanoate format for naming esters
- **Remember:** The direct formation of an ester involves the reaction of an alcohol and a carboxylic acid
    - Alcohol + acid → Ester



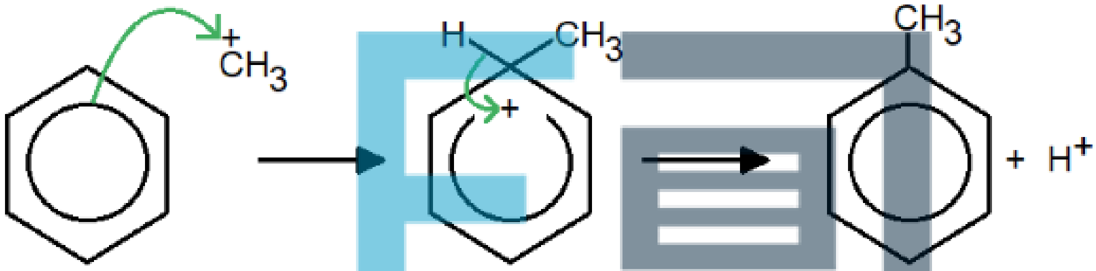
  - The alcohol (green) used gives the alkyl / first portion of the name
    - The alcohol contains two carbons and is, therefore, ethanol
  - The carboxylic acid (blue) used gives the alkanoate / second portion of the name
    - The carboxylic acid is benzoic acid with an amine group in the 4-position on the benzene ring
    - Therefore, the acid is 4-aminobenzoic acid
- So, to form benzocaine directly from an alcohol and a carboxylic acid:
  - Ethanol + 4-aminobenzoic acid → Ethyl 4-aminobenzoate + water

b)

i) A suitable catalyst for step 1 is:

- $AlBr_3$ / aluminium tribromide
  OR
  $FeBr_3$ / iron tribromide; [1 mark]

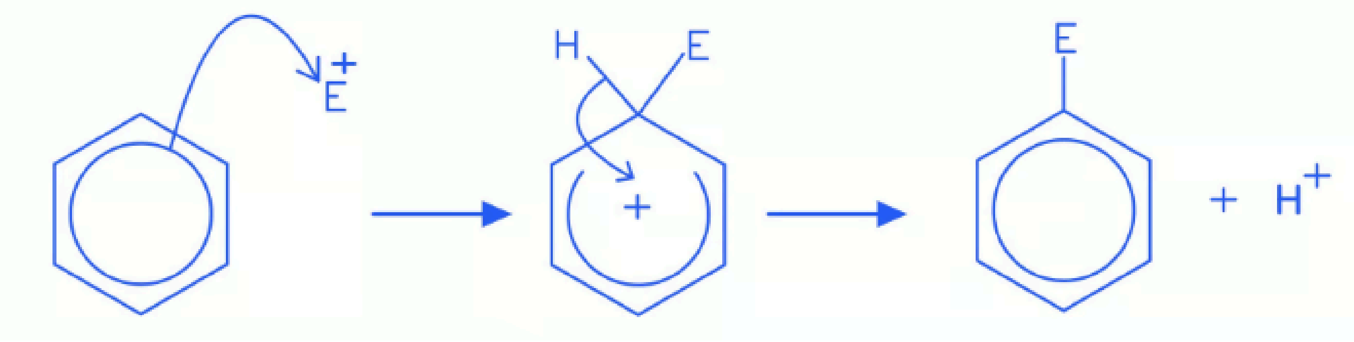
ii) The mechanism for step 1, including all necessary curly arrows and charges, is:



- Curly arrow from the ring inside benzene to the + carbon / C+; [1 mark]
- Correct intermediate structure with horseshoe covering more than half of the benzene but not extending past carbon 2 or 6; [1 mark]
- Curly arrow from the C-H bond back to the + within the ring
  AND
  Correct structure of **A** / methylbenzene; [1 mark]

[Total: 4 marks]

- The reaction of benzene with bromomethane is a Friedel-Crafts alkylation reaction
  - **Careful:** This is most commonly performed with a chloroalkane and an $AlCl_3$ catalyst
    - But the question tells you that one of the reactants is bromomethane, which means that an $AlBr_3$ or $FeBr_3$ is required
- The catalyst is required to form the $^+CH_3$ electrophile for this reaction
  - $CH_3Br + AlBr_3 \rightarrow {}^+CH_3 + AlBr_4^-$
- The mechanism then continues as a standard electrophilic substitution reaction



  - The electrophile bonds to the benzene ring
  - This forms an intermediate with a partially delocalised electron system which is shown as a horseshoe with + inside
  - The intermediate loses a proton, restoring the delocalised electron system and regenerating the catalyst
- There are extra marking points for electrophilic substitution mechanisms:
  - The + must be on the correct carbon in the $^+CH_3$ electrophile
  - The first arrow must start touching the ring, not start inside the ring
  - The horseshoe in the ring must be centred about carbon 1 and not extend past carbon 2 or 6

c)

i) The roles of each acid are:

- Sulfuric acid is acting as an (Brønsted-Lowry) acid
  AND
  Because it is donating a proton / hydrogen ion / H+; [1 mark]
- Nitric acid is acting as a (Brønsted-Lowry) base
  AND
  Because it is accepting a proton / hydrogen ion / H+; [1 mark]

ii) Comparing the strengths of the acids:

- Sulfuric acid is stronger than nitric acid (because it loses / donates a proton)
  OR
  Nitric acid is weaker than sulfuric acid (because it gains / accepts a proton); [1 mark]

iii) The structure of isomer **B** is:

- 

  ; [1 mark]
- The methyl / CH_3 group on methylbenzene (is electron donating which) activates the 2, 4 and 6 positions on the benzene ring
  AND
  The nitro / NO_2 group must attach / bond to carbon-4 (to form the product of step 3); [1 mark]

[Total: 5 marks]

- The reversible arrow in this reaction is irrelevant
- The reaction to form the nitronium ion occurs in a number of steps but the overall equation for the formation of the nitronium ion is
  - $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
- For part (i)
  - You are basically being asked what the roles of the acids are
  - The sulfuric acid is losing / donating a proton
    - This means that the sulfuric acid is acting as a Brønsted–Lowry acid
  - The nitric acid is gaining / accepting a proton
    - This means that the nitric acid is acting as a Brønsted–Lowry base
  - One of the first definitions of an acid is about being a proton donor - this is the definition
- For part (ii)
  - Both acids would normally lose / donate a proton
    - Therefore, sulfuric acid must be a stronger acid as it is losing / donating a proton to nitric acid
    - **Careful:** Since you are being asked to suggest the relative strengths, your answer must include comparative language e.g. sulfuric acid is strong<u>**er**</u> than nitric acid
- For part (iii)
  - The methyl / CH_3 group of methylbenzene donates electron density to the π-system of the benzene ring
  - This activates the 2, 4 and 6 positions for possible attack
  - Looking at the product of step 3, the nitro / NO_2 group must have reacted at carbon-4

d) The reagents and conditions for steps 4 and 5 of the synthesis are:

Step 3

- Reflux with potassium manganate(VII) / $KMnO_4$ / MnO_4^-
  AND
  Reflux; [1 mark]

Step 4

- Warm with ethanol; [1 mark]
- Concentrated sulfuric acid catalyst; [1 mark]

Step 5

Alternative reagents 1

- Tin and concentrated hydrochloric acid **OR** Sn / HCl
  AND
  Under reflux; [1 mark]

Alternative reagents 2

- Iron and concentrated hydrochloric acid **OR** Fe / HCl
  AND
  Under reflux; [1 mark]

Alternative reagents 3

- Nickel and hydrogen
  OR
  Ni / H_2; [1 mark]

[Total: 4 marks]

- Step **3** is the complete oxidation of an alkyl arene
    - Alkyl side-chains in alkyl arenes will oxidise to carboxylic acids when refluxed with alkaline potassium manganate(VII)
    - They are then acidified with dilute sulfuric acid (H_2SO_4) but this is not required for the mark
- Step **4** is an esterification reaction
    - This means that you need the corresponding alcohol to form the ester
    - From the reaction scheme, you can see that the alcohol must have an ethane-based carbon chain
    - Esterification also requires warming with a concentrated sulfuric acid catalyst
- Step **5** is the reduction of a nitro compound to its corresponding amine
    - This is done using Sn / HCl or Fe / HCl or Ni / H_2
    - **Careful:** $LiAlH_4$ and $NaBH_4$ are not suitable for this reduction reaction

e)

i) This reaction scheme is an improvement because:

- There are fewer / less steps (reaction scheme); [1 mark]

ii) This reaction scheme may not work because:

- The nitration step / nitration of benzoyl chloride may / does not happen at carbon 4 of the benzene ring; [1 mark]

[Total: 2 marks]

- Chemists aim to have fewer steps in any reaction scheme
    - This typically improves efficiency / overall atom economy
- The key changes in Fig. 1.2 are the first two steps with the Friedel Crafts acylation of benzene and the nitration of the resulting benzoyl chloride
- Fig. 1.1 has the extra step of converting the 4-nitromethylbenzene into 4-nitrobenzoic acid - you are not expected to know the reagents, conditions or mechanism for this step
- The final two esterification and reduction steps of both reaction schemes are the same
    - Therefore, the difference **must** be in those first two steps
- The first step of both reaction schemes might use different chemicals to form different products but it is ultimately an electrophilic substitution reaction
- In the second step in Fig. 1.1, nitrating the methylbenzene will produce 4-nitromethylbenzene
- In the second step in Fig. 1.2, nitrating the benzoyl chloride does **not** preferentially form 4-nitrobenzoyl chloride
    - It forms 3-nitrobenzoyl chloride as the acyl chloride group directs attack to carbon 3

Answer 12.

a) The reagents and conditions for each step are:

Step 1

- Ethanolic / alcoholic sodium hydroxide / NaOH
  OR
  Ethanolic / alcoholic potassium hydroxide / KOH; [1 mark]
- Heated under reflux; [1 mark]

Step 2

- Water vapour / H_2O (g) / Water at 300 °C; [1 mark]
- Concentrated sulfuric acid / H_2SO_4 catalyst
  OR
  Concentrated phosphoric acid / H_3PO_4 catalyst; [1 mark]

Step 3

- Heat / distil with (acidified) potassium dichromate (VI) / $K_2Cr_2O_7$ solution; [1 mark]

[Total: 5 marks]

- You are told that step 1 is not completed in acidic conditions
    - If you complete step 1 in alkaline / basic conditions, then you can:
        - Form propene via an elimination reaction - this would then allow for two further steps to form propanone
        - Form propan-2-ol via a nucleophilic substitution reaction - this would only require one further step to form propanone
    - Therefore, step 1 is the elimination reaction of 2-bromopropane to form propene
        - This requires refluxing with alcoholic a base like sodium hydroxide or potassium hydroxide
- Step 2 converts propene into propan-2-ol
    - This is a hydration reaction to form the secondary alcohol which requires water with a concentrated H_2SO_4 or H_3PO_4 catalyst at 300 °C (and 7 MPa)
- Step 3 is the reduction of propan-2-ol into propanone
    - This is an oxidation reaction which requires heating / distilling with acidified potassium dichromate(VI) solution
    - You do not need to specify distillation as a secondary alcohol will oxidise to a ketone with no further oxidation using acidified potassium dichromate

b) **One** reaction to replace steps 1 and 2 is:

- Nucleophilic substitution; [1 mark]
- Using aqueous sodium hydroxide / NaOH (aq) heated under reflux; [1 mark]

[Total: 2 marks]

- **Careful:** Take your time, this question has the distraction of compound **A** in the middle of where you need to look
- **Tip:** Remove the distraction of the reaction scheme by drawing the 2-bromopropane reactant and the propan-2-ol product
  - You should see that the bromine has been substituted by a hydroxyl group
- **Remember:** Aqueous conditions favour substitution
  - This means that you are using nucleophilic substitution from AS Chemistry with aqueous sodium hydroxide, heated under reflux

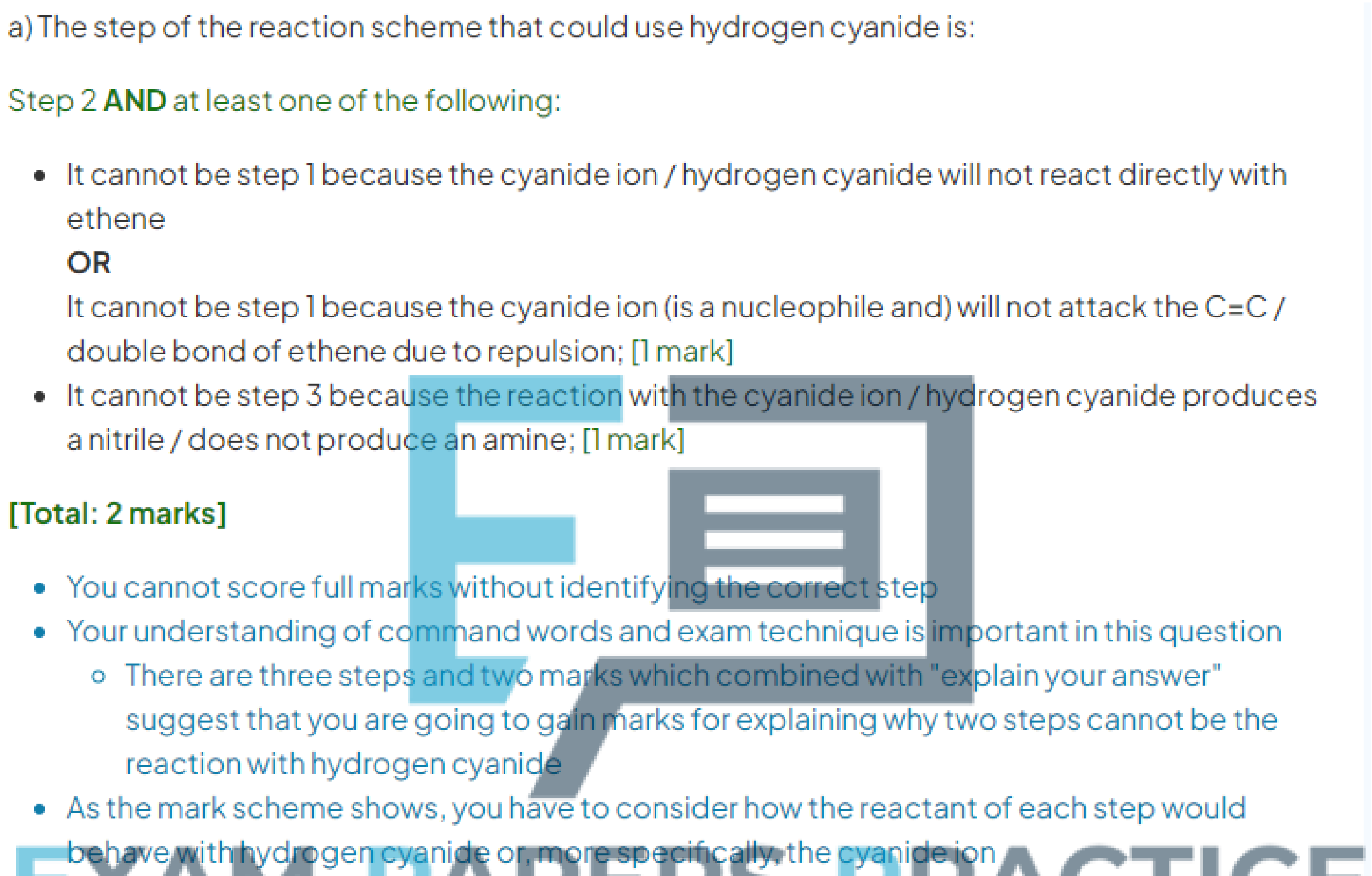
c) The equation for the reaction of compound **B** with an oxidising agent, [O], to form propanone is:

- $CH_3CHOHCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$; [1 mark]

[Total: 1 mark]

- **Careful:** The question asks for structural formulae
  - Compound **B** is propan-2-ol with the structural formula $CH_3CHOHCH_3$
  - Propanone has the structural formula CH_3COCH_3
- Step 3 is an oxidation reaction where the oxidising agent, [O], removes hydrogen from the secondary alcohol to form a ketone
  - The second product is water

Answer 13.



a) The step of the reaction scheme that could use hydrogen cyanide is:

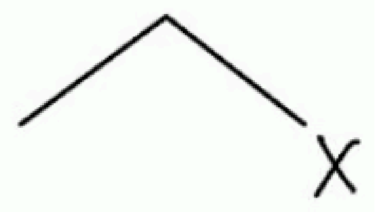
Step 2 **AND** at least one of the following:

- It cannot be step 1 because the cyanide ion / hydrogen cyanide will not react directly with ethene
  OR
  It cannot be step 1 because the cyanide ion (is a nucleophile and) will not attack the C=C / double bond of ethene due to repulsion; [1 mark]
- It cannot be step 3 because the reaction with the cyanide ion / hydrogen cyanide produces a nitrile / does not produce an amine; [1 mark]

[Total: 2 marks]

- You cannot score full marks without identifying the correct step
- Your understanding of command words and exam technique is important in this question
  - There are three steps and two marks which combined with "explain your answer" suggest that you are going to gain marks for explaining why two steps cannot be the reaction with hydrogen cyanide
- As the mark scheme shows, you have to consider how the reactant of each step would behave with hydrogen cyanide or, more specifically, the cyanide ion

b) The skeletal structure of compound **A** is:



- Correct skeletal formula of compound **A** with any appropriate halogen; [1 mark]
- Reagent = corresponding hydrogen halide compound to match the skeletal formula; [1 mark]

[Total: 2 marks]

- Compound **A** must be able to react with the cyanide ion
- Ethene is likely to undergo electrophilic addition
  - This means that you should automatically be thinking H_2, HX, X_2, H_2SO_4
  - As the next reaction is likely to be a nucleophilic substitution with CN^-, compound **A** needs to be monosubstituted and contain **one** polar bond
  - Therefore, the only realistic option is the reaction with HX
    - **Remember:** The X stands for a halide ion

c) Compound **B** is:

- Propanenitrile; [1 mark]

The type of reaction that compound **B** undergoes to form propylamine is:

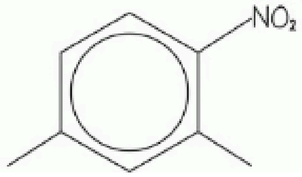
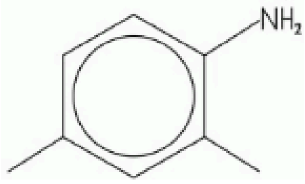
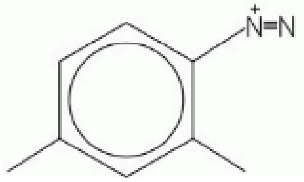
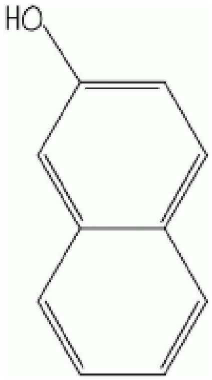
- Reduction
  AND
  The nitrogen / nitrile group has gained hydrogen; [1 mark]

[Total: 2 marks]

- Examiners often comment about the apparent difficulty that some students have naming compounds
  - Nitriles are an examiner favourite for this because:
    - The carbon chain increases, e.g. eth- to prop-
    - Students forget the letter "e" and sometimes it is marked as essential
    - So, make sure you can name nitriles correctly
- The nitrile group has gained hydrogen as it converted into an amine
  - **Remember**: Look for the GCSE identifiers of oxidation and reduction first because it can save time when identifying types of reaction

Answer 14.

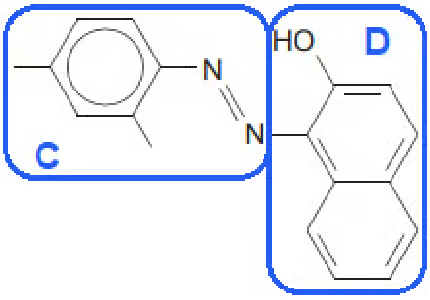
a) The structures of the organic compounds **A**, **B**, **C** and **D** are:

A	B	C	D
			

- Correct structure for compound **A**; [1 mark]
- Correct structure for compound **B**; [1 mark]
- Correct structure for compound **C** including positive charge on the correct nitrogen atom; [1 mark]
- Correct structure for compound **D**; [1 mark]

[Total: 4 marks]

- The first reaction with concentrated sulfuric acid and concentrated nitric acid is nitration
    - From the structure of the final product, the nitro group must add to carbon-4
- The second reaction with Sn / concentrated HCl is the reduction of a NO_2 group to an NH_2 group
- The third reaction with $NaNO_2$ and HCl below 10 °C is the formation of a diazonium ion from the NH_2 group
- Compound **D** can be deduced from the structure of compound **C** and the final Sudan II product:

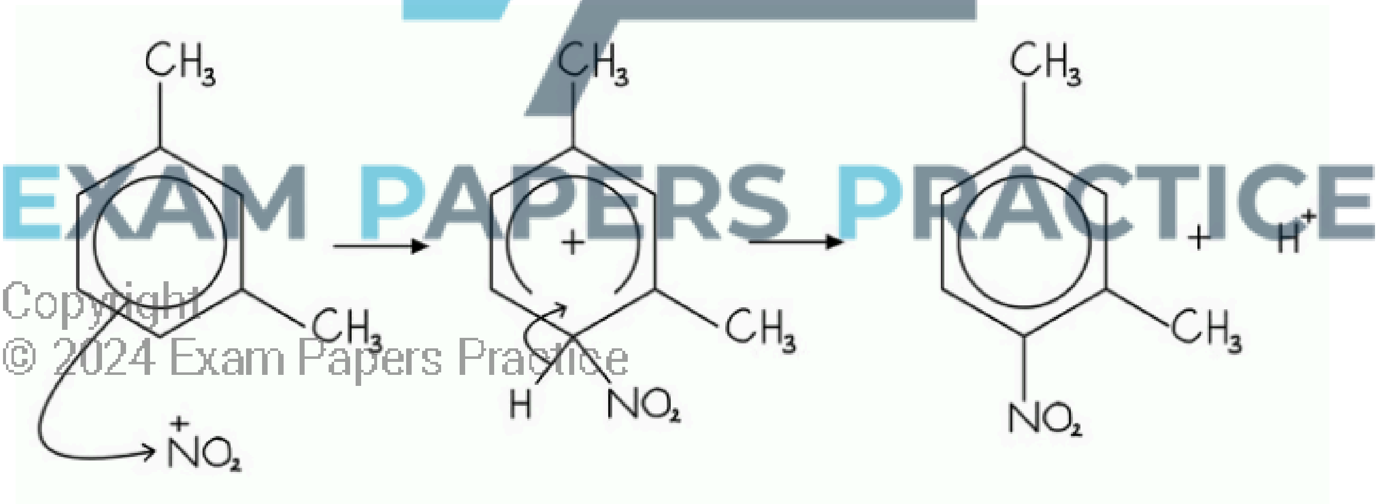


b)

i) The equation to form an appropriate reactive species is:

- $HNO_3 + H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$; [1 mark]

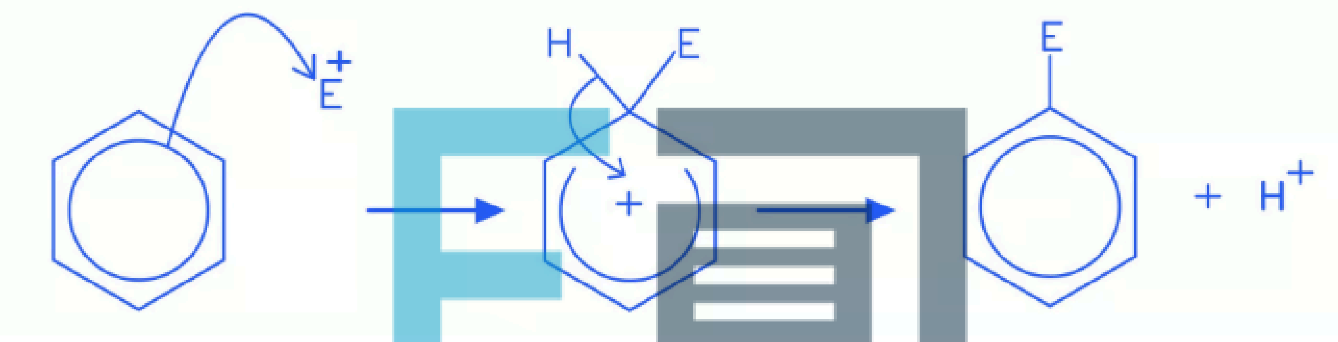
ii) The mechanism for the formation of compound A from 1,3-dimethylbenzene and an appropriate reactive species is:



- Curly arrow from the pi ring to the NO_2^+ electrophile; [1 mark]
- Correct intermediate structure; [1 mark]
- Curly arrow from the C-H bond to the + charge within the ring
  AND
  H^+ as a product; [1 mark]

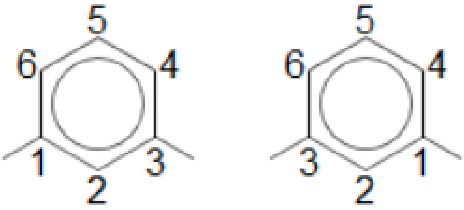
[Total: 3 marks]

- The reaction of benzene with concentrated sulfuric acid and concentrated nitric acid is nitration
  - **Careful:** This means that the appropriate reactive species is the NO_2^+ group
  - You need to know how the NO_2^+ group is formed from concentrated sulfuric acid and concentrated nitric acid
- The mechanism then continues as a standard electrophilic substitution reaction



  - The electrophile bonds to the benzene ring
  - This forms an intermediate with a partially delocalised electron system which is shown as a horseshoe with + inside
  - The intermediate loses a proton, restoring the delocalised electron system and regenerating the catalyst
- There are extra marking points for electrophilic substitution mechanisms:
  - The + must be on the correct carbon in the $^+NO_2$ electrophile
  - The first arrow must start touching the ring, not start inside the ring
  - The horseshoe in the ring must be centred about carbon 1 and not extend past carbon 2 or 6

c) 1,3-dimethyl-5-nitrobenzene is likely to be the more abundant product because:

- Methyl / CH_3 groups direct attacks to the 2, 4 and 6 positions (on the ring); [1 mark]
- 

  AND

  The 2, 4, 5, and 6 positions of both rings are the same; [1 mark]

[Total: 2 marks]

- **Remember:** Alkyl groups activate the 2, 4 and 6 positions on a benzene ring
- As the diagrams in the mark scheme show, the 2, 4, 5, and 6 positions of both rings are the same regardless of which methyl carbon is labelled as carbon-1
- Although mononitration is theoretically possible on any of the other non-substituted carbons, it is more likely on the 2, 4 or 6 position
  - The 4 and 6 positions will form compound **A**
  - This means that the 2 position is the next most likely structural isomer and, therefore, should have the next highest abundance