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 **17** printed pages.

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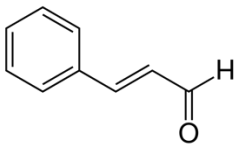
1 This Question tests up to, and mainly Chapter 16 and 17 (Alcohols, Phenols and Carbonyl compounds).

(a) Cinnamaldehyde is an aromatic compound that has a cinnamon like smell.

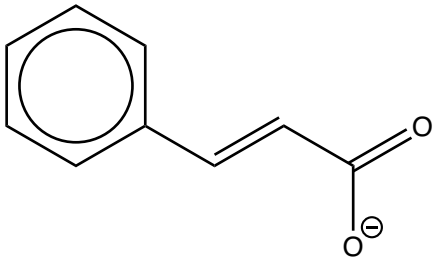
The structure of cinnamaldehyde is shown below.



(i) Draw the skeletal structure of the organic product when cinnamaldehyde is reacted separately under these conditions

B2 (0.5 pts each)

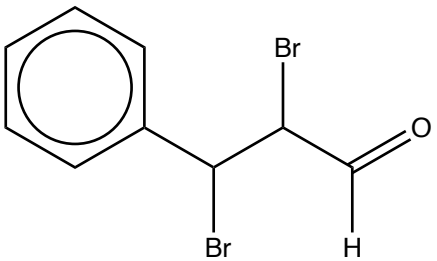
- For BOTH Fehling's reagent, then warm AND Ag_2O with warm aqueous NH_3.



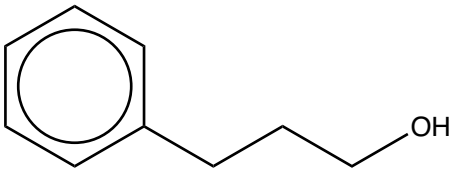
[2]

No marks if the carboxylic acid is written

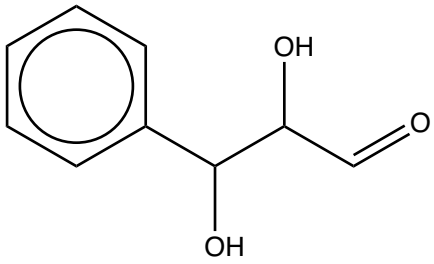
- Br_2 in tetrachloromethane at room temperature.



- 10 atm H_2 in presence of a nickel catalyst at room temperature.



- $KMnO_4$ with dilute NaOH at 10 degrees Celsius.



(ii) Cinnamaldehyde was reduced by LiA/H_4 to trans-cinnamyl alcohol.

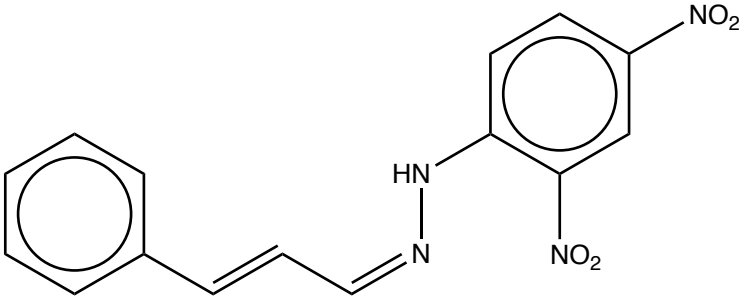
This reduction can be done by sodium borohydride too.

Explain the difference in the rate of reduction of cinnamaldehyde when LiA/H_4 is used compared to sodium borohydride. [2]

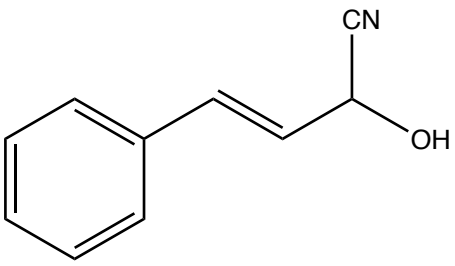
B1 – The rate of reduction is faster when lithium aluminium hydride is used.
B1 – Since aluminium is less electronegative than boron, the A*l*—H bond is more polarised in which the hydrogen atom is more nucleophilic which makes the reduction happen faster.
(An attempt to explain the candidate's answer is needed for the first B1 mark to be awarded)
Note: Hydrogen is more electronegative than aluminium and boron!

(iii) A brick-red precipitate is formed when cinnamaldehyde is reacted with 2,4-DNPH. Draw the skeletal structure of this precipitate. [1]

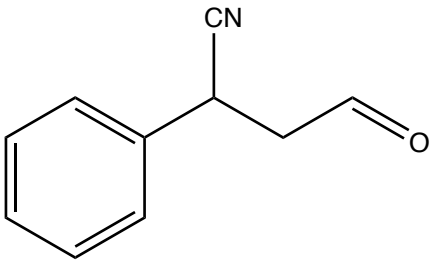
B1 – Correct structure



(iv) When cinnamaldehyde is reacted with aqueous potassium cyanide (KCN), 2 products were formed, with their structures shown below:



1



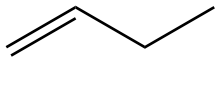
2

Using concepts of electronegativity and delocalisation, explain why product **2** can be formed. [2]

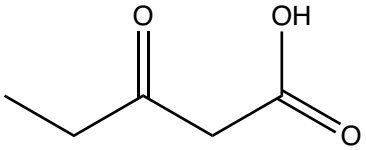
B1 – Explains why the beta-carbon is an electrophilic centre (the carbon in **bold purple** is the beta-carbon FYI)
In the **C**=C—C=O conjugated system, since oxygen is more electronegative than carbon, electron density at the C=C bond decreases due to the delocalisation of pi-electrons into the electrophilic C=O group.

B1 – Explains that the nucleophile will attack the beta-carbon
Hence, the cyanide ion can attack the beta-carbon since it is electron deficient.

(b) Propose a 3-step synthetic route to convert **X** to **Y**. Include the structures of all intermediates, and reagents and conditions for each step. [5]

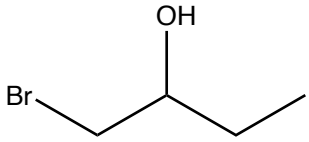


X

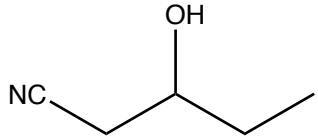


Y

B1 each
Step 1: aqueous bromine at room temperature
Intermediate after step 1:



Step 2: KCN in ethanol, heat
Intermediate after step 2:



Step 3: $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat OR $KMnO_4$ can be used in place of $K_2Cr_2O_7$

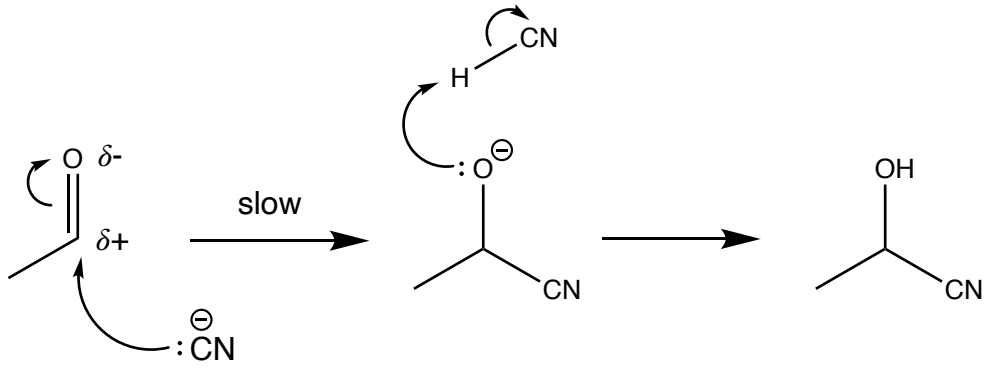
(c) Lactic acid is produced as a byproduct during anaerobic respiration. A build-up of lactic acid causes muscle aches and cramps.

A common route for the synthesis of lactic acid is through the starting material, ethanal.

(i) Ethanal is reacted with cold aqueous HCN with a few drops of aqueous NaOH to form a racemic product.

Describe the mechanism of this reaction. [3]

B1 – Nucleophilic addition
B2 – Mechanism
Generation of nucleophile: $HCN + NaOH \rightarrow H_2O + Na^+ + CN^-$



- Partial charges
- Slow step indicated
- Generation of nucleophile must be stated
- Correct curly arrows

(ii) Explain the purpose of adding a few drops of aqueous NaOH. [1]

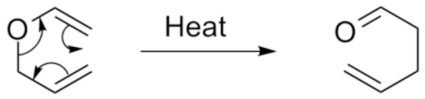
B1 – NaOH undergoes an acid-base reaction with HCN to form the cyanide ion, thus creating the catalyst for the nucleophilic addition reaction to occur.

(iii) Explain why this reaction produces a racemic product. [1]

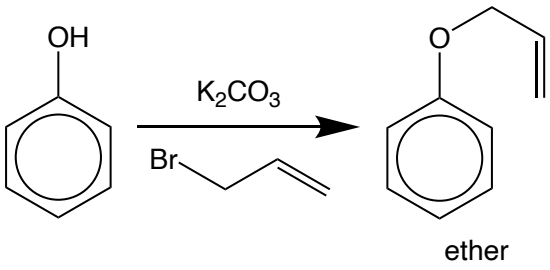
B1 – The carbonyl carbon has trigonal planar geometry, so the cyanide nucleophile can attack the carbon from the top and bottom of the plane with equal probability.

(d) A [3,3]-sigmatropic rearrangement reaction is a common reaction exploited by organic chemists to attach an alkyl side chain to the benzene ring of a phenol.

One example of the [3,3]-sigmatropic rearrangement reaction is shown below:



(i) The first step proceeds as follows:

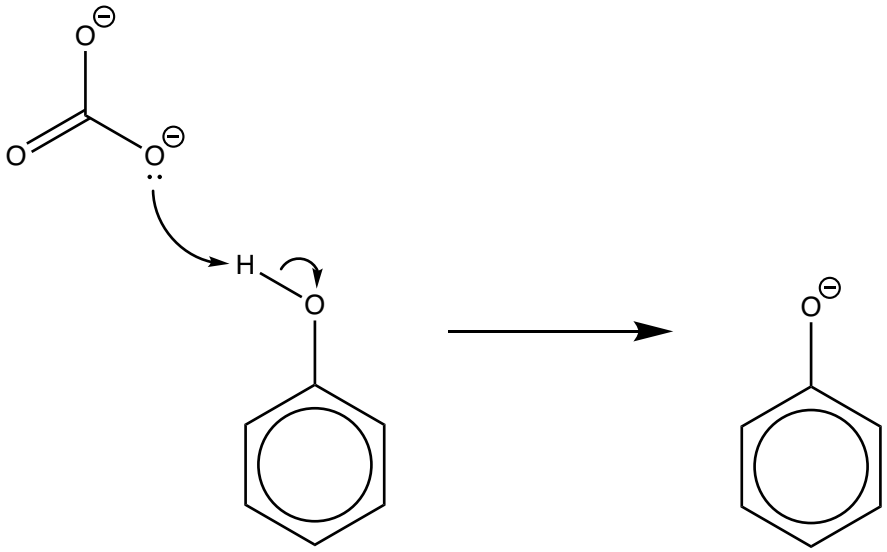


ether

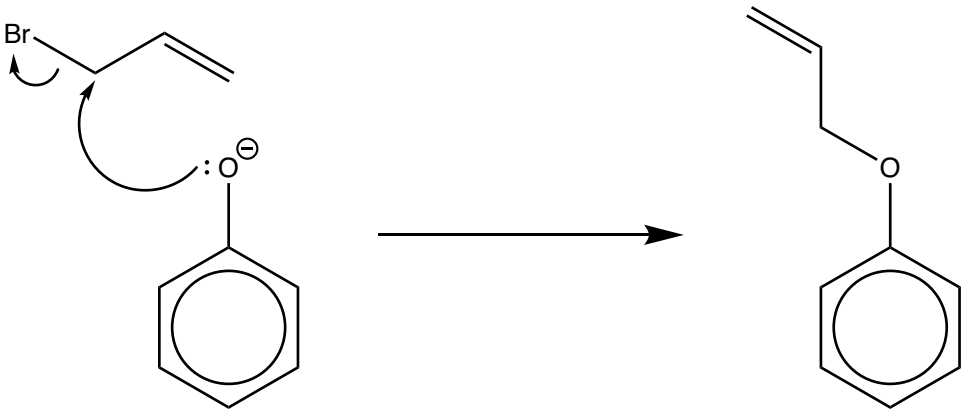
K_2CO_3 deprotonates phenol first.

Suggest a mechanism for this reaction. [2]

B1 – Acid-base reaction (no curly arrows are needed, but the generation of the phenoxide must be clearly shown)



B1 – Substitution (accept both S_N1 and S_N2 mechanism pathways), details are not required as this is not the main point of the question.

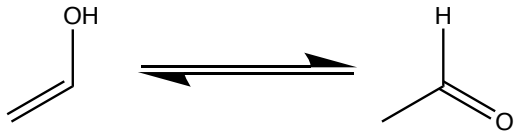


(ii) Suggest why the base KOH is not used to deprotonate phenol. [1]

B1 – A nucleophilic substitution reaction may occur with 3-bromoprop-1-ene and the hydroxide ion instead since the hydroxide ion, not the phenoxide ion, is a stronger nucleophile. (The idea of the side reaction must be present, the reason doesn't need to be stated.)

(iii) The ketone-enol tautomerisation reaction is a reversible reaction that explains the conversion of an enol to a ketone or aldehyde (or vice versa).

One such example is shown below:

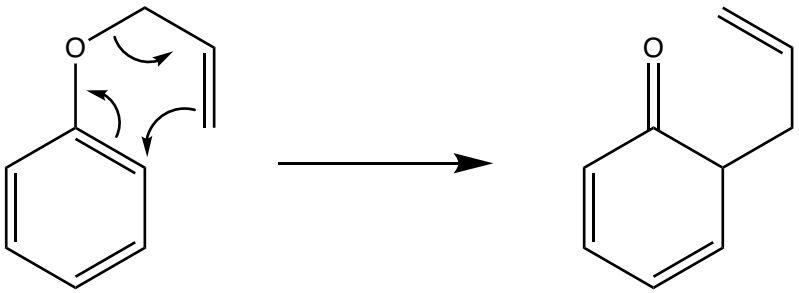


enol

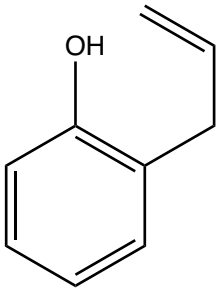
After the ether product in **(i)** is obtained, a [3,3]-sigmatropic rearrangement occurs, followed by a ketone-enol tautomerisation reaction.

Using curly arrows, show how the [3,3]-sigmatropic rearrangement occurs, and therefore draw the final product of the reaction. [2]

B1 – Sigmatropic rearrangement shown with 1 resonance structure for the benzene ring



B1 – Correct final product (a phenol)



Either the benzene ring or one of its canonical structures (an example above) is accepted.

(iv) In most scenarios, the enol tautomer is disfavoured because it is less stable. Explain why in **(iii)**, the final product, an enol tautomer, is favoured. [1]

B1 – The enol tautomer happens to be a phenol, which is stabilised by aromaticity to a large extent. The ketone tautomer is not aromatic however.

(v) State 2 simple tests to confirm that the final product is still a phenol, and that the alkene-containing side-chain is present. [2]

The **only** acceptable combination of tests
B1 – Test 1: neutral $FeCl_3$ (aq). Expected observation: violet colouration
B1 – Test 2: cold $KMnO_4$ (aq), NaOH (aq). Expected observation: Brown precipitate (with decolourisation of purple $KMnO_4$).

Note to markers:
The usage of Br_2 (aq)/(*l*) will be capped at 1 mark, regardless of any other correct tests written from the above.

- Positive tests apply to both a phenol and alkene; but…
  - The product can be an alkene but not a phenol
  - The product can be a phenol but not an alkene

Other tests that will **not** be given credit:

- $KMnO_4$ (aq), H_2SO_4 (aq), heat
  - Side chain oxidation gives a positive result too
- Na (s)

2 (a) Both 4-methylbenzoic acid and tosylic acid are stronger acids than phenol.

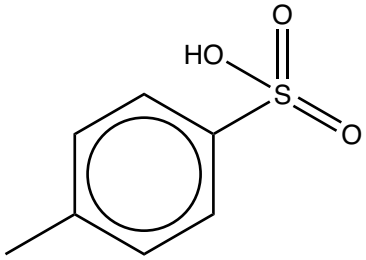
(i) Explain why 4-methylbenzoic acid is a stronger acid than phenol. [2]

B1 – The negative charge on 4-methylbenzonate is delocalised over 2 highly electronegative oxygen atoms (making them a good bearer of a negative charge from an extra electron)
B1 – But the negative charge on phenoxide is delocalised over 1 oxygen atom and less electronegative carbon atoms only
Thus 4-methylbenzonate is stabilised by a greater extent than the phenoxide io.

(ii) Explain the difference in the K_a values of phenol, water and ethanol. [2]

K_a phenol > water > ethanol
B1 – phenol is more acidic than water because the negative charge is delocalised over the benzene ring which stabilises the phenoxide ion by resonance, while the hydroxide ion's negative charge is localised.
B1 – The ethoxide ion's negative charge is intensified by the electron-donating ethyl group which destabilises the ethoxide ion, thus ethanol is a weaker acid.

(iii) Suggest why 4-methylbenzoic acid is less acidic than tosylic acid. [1]

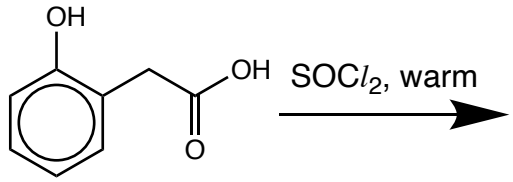


tosylic acid

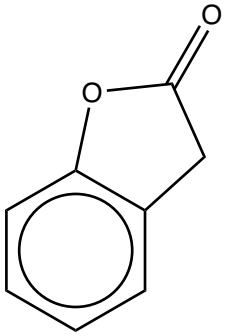
B1 – More electron-withdrawing =O groups in tosylic acid than 4-methylbenzoic acid
OR
B1 – Tosylate ion is stabilised by a greater extent due to resonance since there's more =O groups for the negative charge to be delocalised in.

(b) Draw the organic product(s) for the following: [4]

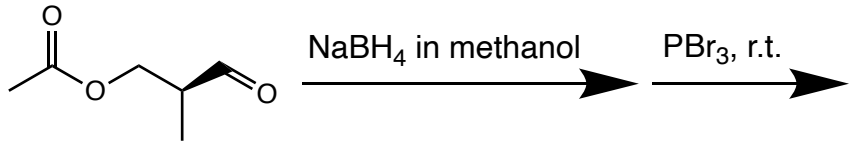
(i)



B1 for the following



(ii)



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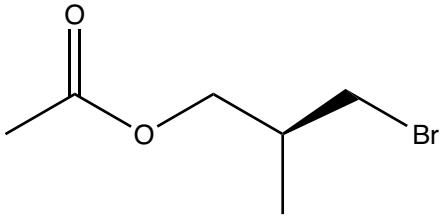
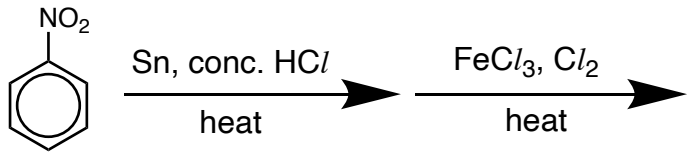
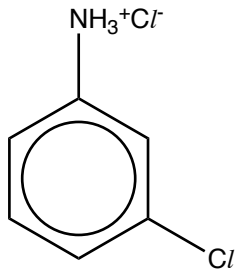


(iii)

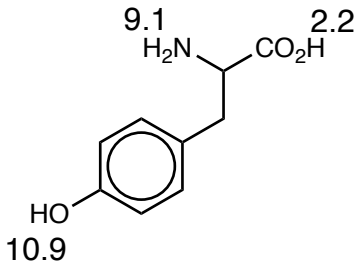


B1 for the following



The counterion (chloride ion) can be omitted.

(c) Tyrosine is an amino acid with a phenol group.

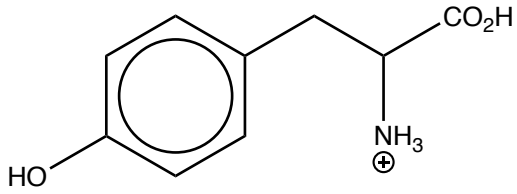


The numbers written near basic or acidic groups represent their respective pK_a values.

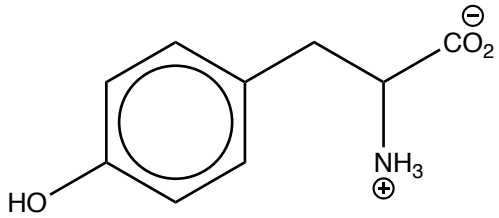
(i) Draw the predominant species of tyrosine when some tyrosine is dissolved separately in a solution of pH 1, 4, 10 and 12. [2]

B2 (0.5 pts for each correct species)

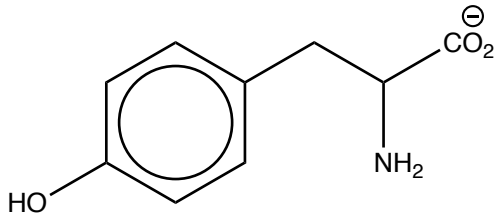
pH 1:



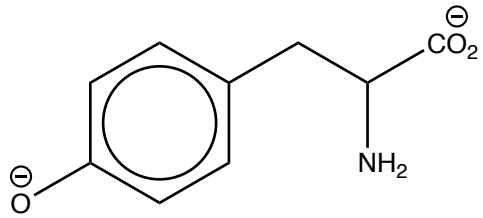
pH 4:



pH 10:



pH 12:



(ii) Define *zwitterion*. [1]

B1: Zwitterion is a species that is dipolar but has a net zero charge.

(iii) Explain why tyrosine tends to exist as a zwitterion at its isoelectric point. [1]

B1 – Favourable **ion-dipole interactions** of the tyrosine zwitterion with water.

(d) An unknown organic molecule **P** was treated with aqueous bromine in the dark. A precipitate was observed immediately after addition, yielding product **Q**. To **Q**, neutral iron(III) chloride solution was added. There was no colouration. **Q** was also treated with aqueous sodium hydroxide under heating, yielding compound **R**. Analysis shows that the M_r decreased by approximately 63 from **Q** to **R**.

Given that the M_r of **P** is 145, **P** has 10 carbon atoms, and that only 1 carbon atom in **P** is covalently bonded to a heteroatom (an atom that is neither C nor H), deduce the structures of **P**, **Q** and **R**. In your answer, you should include the name of any reactions that took place. (If there are multiple answers, you may just show 1 answer.) [6]

B3 – Deductions (award 1 pt per deduction)

Deduction	Evidence with explanation
Electrophilic substitution of Br onto a phenylamine	Precipitate after treatment of **P** with aqueous bromine **Q** is not a phenol due to negative neutral iron(III) chloride test
Nucleophilic substitution of 1 -OH replacing a Br atom	M_r of the product decreased by approximately 63 A_r Br = 79.9, M_r OH = 17.0, difference is about 63. Hence 1 -OH group replaced 1 -Br group.
P is an alkene AND electrophilic addition occurred too when aqueous Br_2 is added	Since **P** has 10 carbon atoms, the remaining non carbon atoms have a M_r of 25.0. Since A_r Br > 25.0, **P** must have no bromine atoms. But since **Q** has a Br atom attached to a sp^3 carbon (hence allowing for a nucleophilic substitution), the only way this is possible is that **P** is an alkene, which electrophilic addition occurred to produce a substitutable Br atom.

B3 – Correct structures for **P**, **Q** and **R**
Molecular formula for **P**: $C_{10}H_{11}N$
The following combinations are accepted.

P	**Q**	**R**

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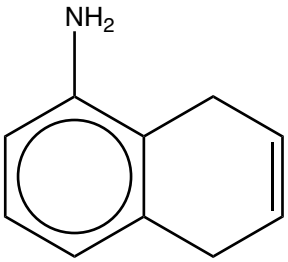
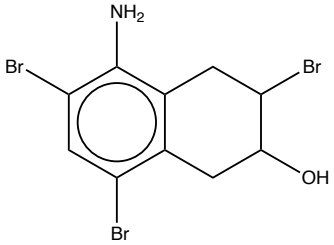
<td>  </td>
<td> 
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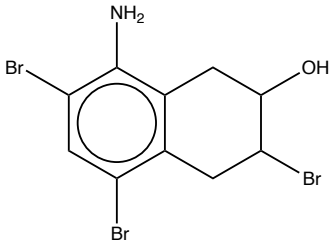
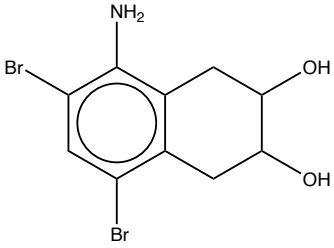
  </td>
<td>  </td>
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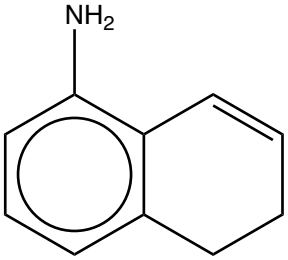
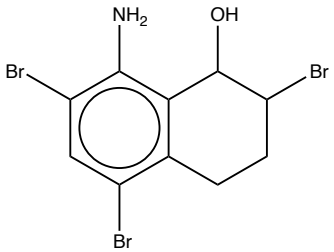
<td>  </td>
<td> 
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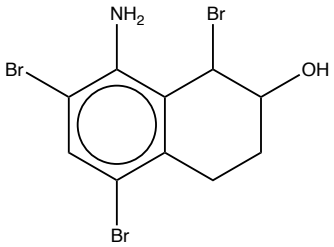
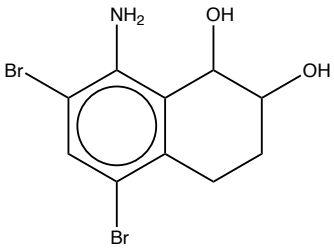
  </td>
<td>  </td>
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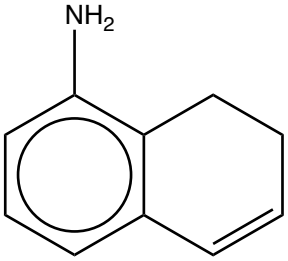
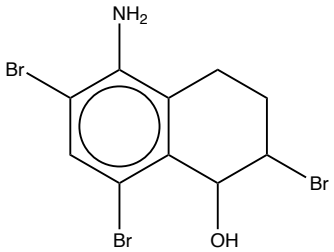
<td>  </td>
<td> 
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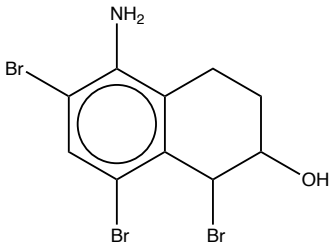
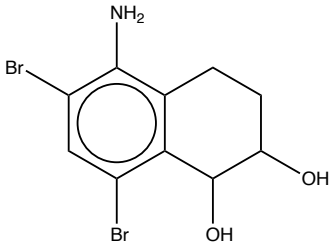
  </td>
<td>  </td>
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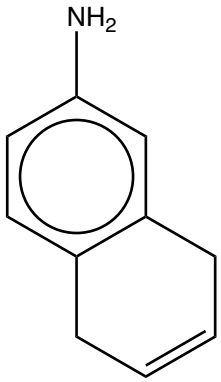

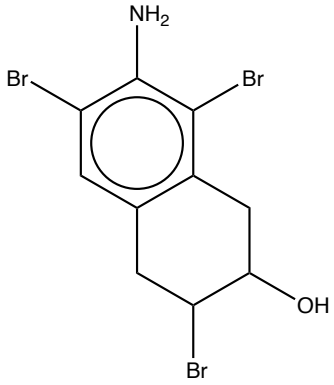

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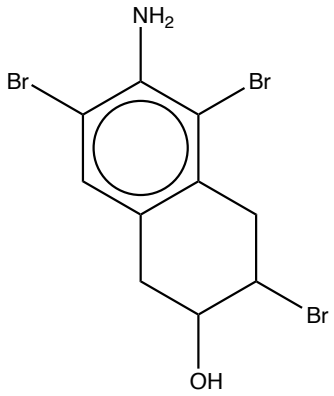
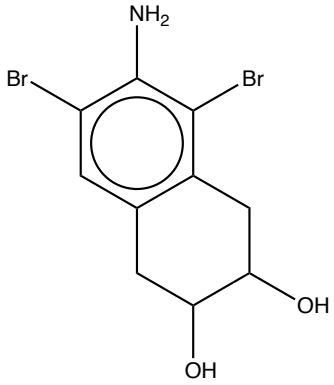




And all positional isomers for the alkene functional group for **P**, which yield their corresponding products.

There are no other answers for P.

(e) Nuclear Magnetic Resonance (NMR) is a go-to for organic chemists to deduce unknown organic structures.

A proton in the molecule will be detected through a peak in the NMR spectrum. The area under the peak (integration ratio) is proportional to the number of protons contributing to that peak.

When a molecule is analysed in proton (1H) NMR, protons that are chemically equivalent be reflected under 1 peak in the spectrum.

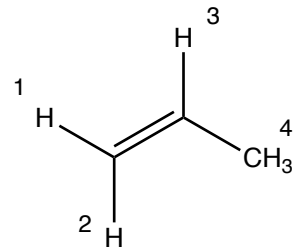
2 protons, **A** and **B**, are said to be chemically equivalent when **A** is replaced by say, a chlorine atom, the resultant molecule is the same if **B** instead of **A** is replaced by a chlorine atom. For example, ethene has 4 chemically equivalent protons.

Note that stereoisomers are considered as different molecules.

(i) State the number of peaks observed when phenol is analysed by 1H NMR. [1]

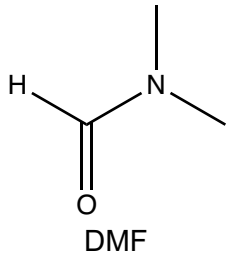
B1 – 4 peaks

(ii) Explain why propene has 4 peaks in its 1H NMR spectrum. [2]



B1 – It is clear that protons 1, 3 and 4; and 2, 3 and 4 are different.
B1 – 1 and 2 are different because there are 2 different groups attached to the other carbon in the C=C bond. Hence, if proton 1 or 2 were to be replaced with another atom, cis-trans isomerism will occur. (Explanation of why proton 1 and 2 are different)

(iii) DMF (dimethylformaldehyde) has 3 peaks in its 1H NMR spectrum.



DMF

By considering your answer in **(ii)**, suggest a reason for this observation. [2]

B1 – Explains partial double-bond character of the C—N bond

The lone pair from N will be delocalised into the C=O bond. Through resonance, the C—N bond will hence have partial double-bond character.

B1 – This partial double-bond character means that the protons in each methyl group are (somewhat) chemically different as implied from (ii). Taking into account the proton on the left of the structure of DMF, there are 3 chemically different protons.

(iv) State how DMF can be synthesised from N,N-dimethylamine. [1]

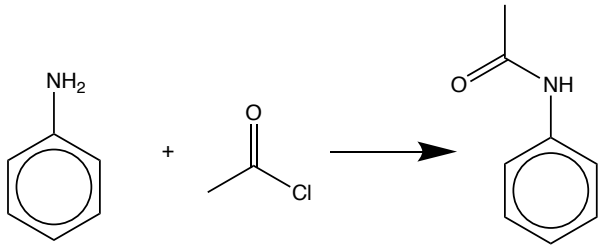
B1 – add HCOC*l* at room temperature

3 (a) When phenylamine is treated with aqueous bromine at room temperature, a tribrominated product is obtained.

However, when phenylamine is treated with ethanoyl chloride first, then aqueous bromine at room temperature, a monobrominated product is obtained.

Explain the following observation above. [2]

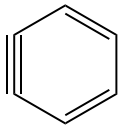
B1 – Explains that lone pair on nitrogen is the reason for the activation of the benzene ring



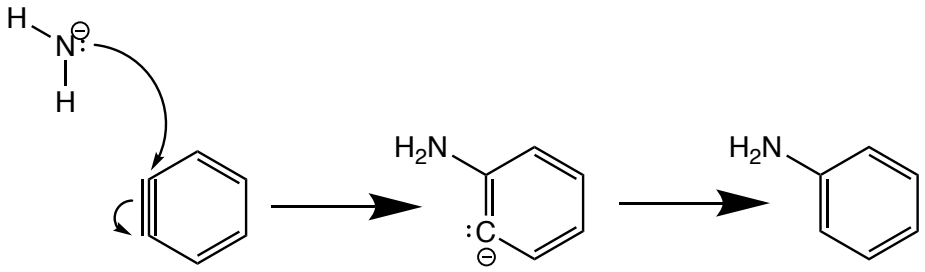
B1 – Explains why the amide group is not as activating compared to the amine
The lone pair is delocalised into the carbonyl side too. This makes the lone pair on N less available to the benzene ring, thus the amide group is not as activating as compared to the corresponding amine.

(b) Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant radioactive labelling experiments by John D. Roberts and co-workers.

Benzyne has the following structure below.

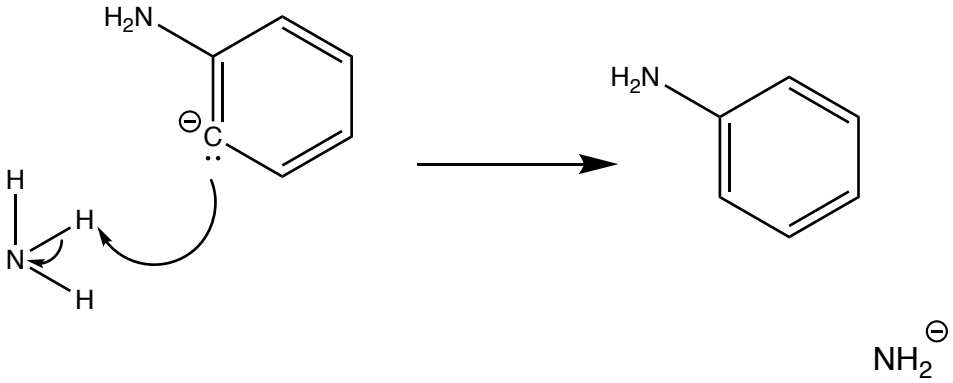


When chlorobenzene is treated with a strong base $NaNH_2$, benzyne is first formed. Subsequently, the NH_2^- nucleophile attacks one of the carbons with a triple bond. A Bronsted-Lowry acid-base exchange with liquid ammonia takes place afterwards, reforming the NH_2^- ion.



(i) Complete the mechanism based on the description above. [1]

B1 – Correct Bronsted-Lowry Acid-base reaction and NH_2^- ion shown

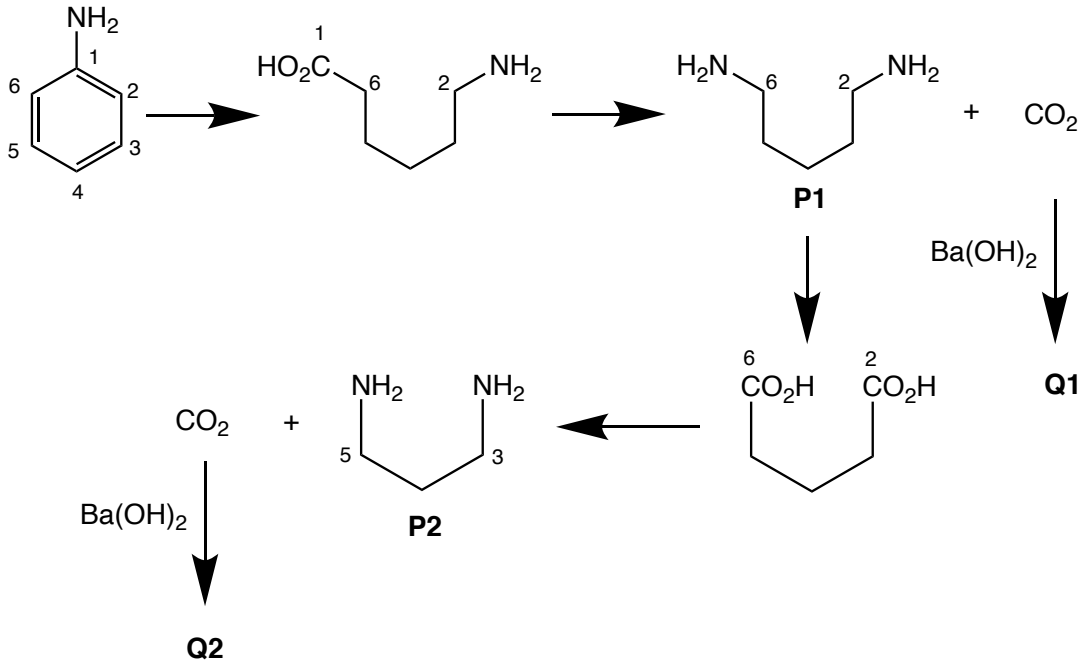


In order to prove that benzyne was formed, radioactive isotopic labelling was conducted.

Roberts concluded that if benzyne was formed, then there would be no preference for a nucleophile in attacking any one of the carbon in the C—C triple bond.

Roberts first started with **A**, a radioactive isotope of chlorobenzene. Only the carbon covalently bonded to the chlorine atom is ^{14}C, which is radioactive.

A was reacted with KNH_2 in liquid NH_3. The product, radioactive phenylamine, was subjected to the following conversions below.

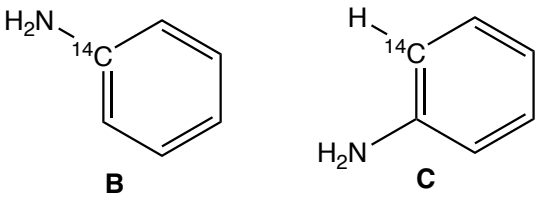


The numbers 1 to 6 are labelled on the carbon atoms of phenylamine to track the origin of the specific carbon atoms in the intermediates from phenylamine.

It was concluded that intermediate **P1**, and products **Q1** and **Q2** exhibited radioactivity. Furthermore, the results show that there are almost equal amounts of radioactive **Q1** and **Q2**.

You should assume that the yield for every conversion is 100%.

(ii) Explain how these results can lead you to conclude that almost equal amounts of radioactive phenylamine, **B** and **C**, were formed. [3]



B1 – Relating the relevant carbon atoms to the final $BaCO_3$ isolate
Q1 is radioactive → carbon-1 is radioactively labelled (^{14}C)
Q2 is radioactive → carbon-2 is radioactively labelled (or carbon-6 is radioactively labelled, since carbon-2 and carbon-6 are chemically equivalent)

B1 – Linking **Q1** and **Q2** to the respective phenylamine isotopes
B1 – Identifying **B** and **C** (B1 mark scored after previous B1 marks are scored)

Since almost equal amounts of **Q1** and **Q2** were formed, phenylamine with carbon-1 radioactively labelled (that is, **B**) will be in equal amount with phenylamine with carbon-2 (or 6) radioactively labelled (that is, **C**).

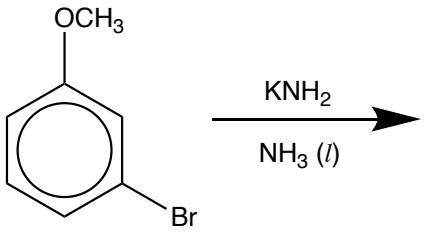
(iii) If **B** was formed only, which intermediate(s) and/or product(s) (from **P1**, **P2**, **Q1**, **Q2**) will exhibit radioactivity? [1]

B1 - **Q1** only

(iv) Give the chemical formula of **Q1** and **Q2**. [1]

B1 - $BaCO_3$

(v) By using results of this study, draw the products of the reaction below. [2]



B2 – all 3 correct (award 1 pt for 2 correct)