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.

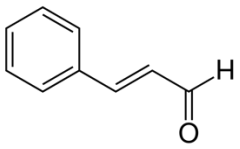
This document consists a total of **16** printed pages.

---

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

- Fehling's reagent, then warm.
- Ag_2O with warm aqueous NH_3.
- 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. [2]

(ii) Cinnamaldehyde was reduced by $LiAlH_4$ to trans-cinnamyl alcohol.

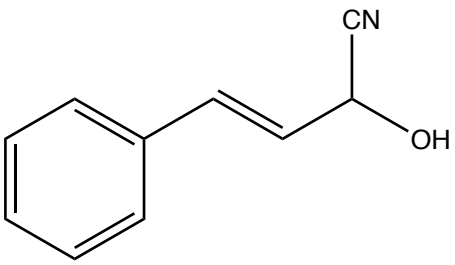
This reduction can be done by sodium borohydride too.

Explain the difference in the rate of reduction of cinnamaldehyde when $LiAlH_4$ is used compared to sodium borohydride. [2]

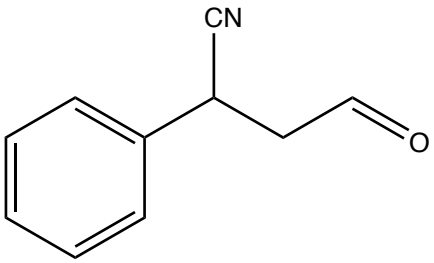
(iii) A brick-red precipitate is formed when cinnamaldehyde is reacted with 2,4-DNPH. Draw the skeletal structure of this precipitate. [1]

(iv) When cinnamaldehyde is reacted with aqueous potassium cyanide (KCN), 2 products are formed, with their structures shown on the next page:

Part (a) continues on the next page.



1



2

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

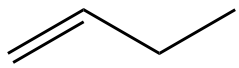
.....

.....

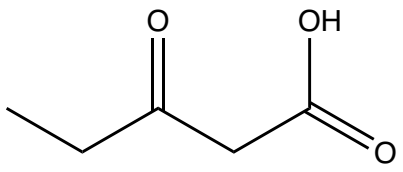
.....

.....

(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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(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]

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

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

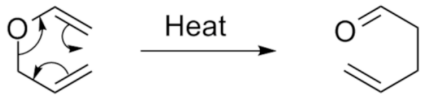
.....

.....

.....

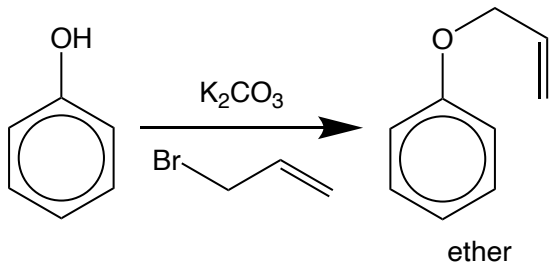
(d) A [3,3]-sigmatropic rearrangement reaction is a common reaction exploited by organic chemists to attach an alkyl side chain to the benzene ring of a phenol.

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



Part (d) continues on the next page.

(i) The first step proceeds as follows:



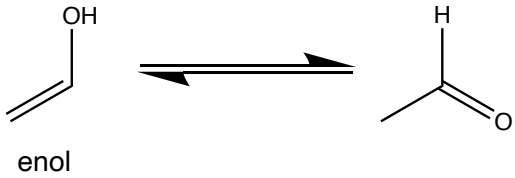
K_2CO_3 deprotonates phenol first.

Suggest a mechanism for this reaction. [2]

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

(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:



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]

(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]

(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]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

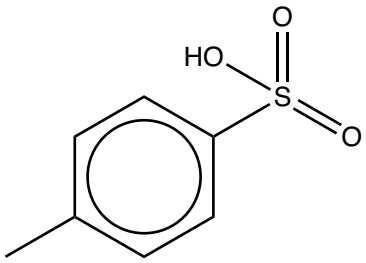
[Total: 25]

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]

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

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



tosylic acid

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

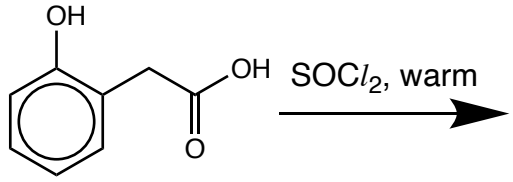
.....

.....

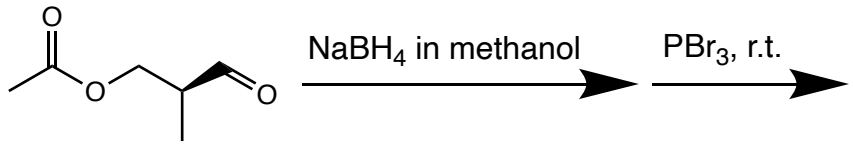
.....

(b) Draw the organic product(s) for the following: [3]

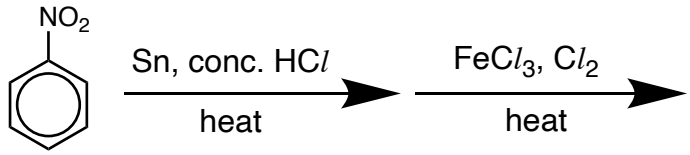
(i)



(ii)



(iii)



.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

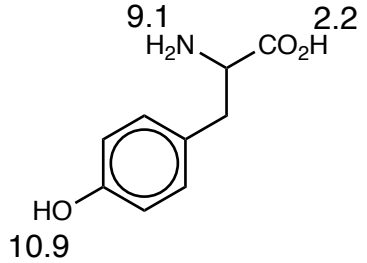
.....

.....

.....

.....

(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]

(ii) Define *zwitterion*. [1]

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(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**. From **Q** to **R**, the M_r decreased by approximately 63.

Given that the M_r of **P** is 145, **P** has 10 carbon atoms and 2 6-membered rings, 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]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(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.

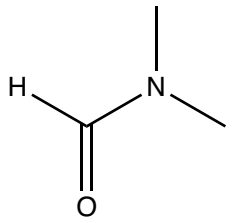
2 protons, **A** and **B**, are said to be chemically equivalent when **A** is replaced by say, a chlorine atom, the resultant molecule is the same if **B,** instead of **A**, is replaced by a chlorine atom. For example, ethene has 4 chemically equivalent protons.

Note that stereoisomers are considered as different molecules.

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

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

(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]

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

.....

.....

.....

.....

.....

.....

.....

[Total: 24]

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]

.....

.....

.....

.....

.....

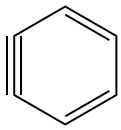
.....

.....

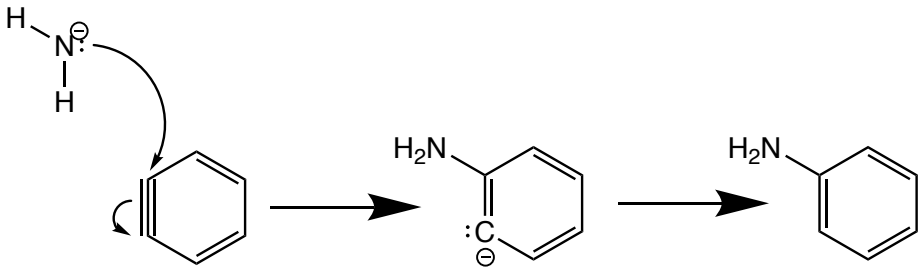
.....

(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.



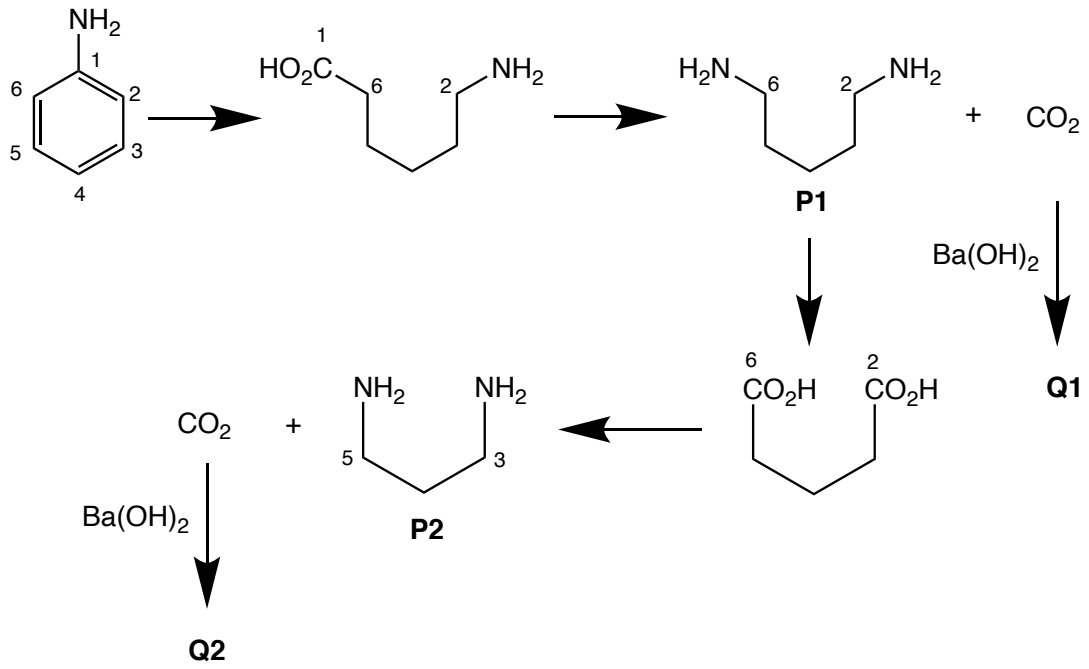
(i) Complete the mechanism based on the description above. [1]

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.

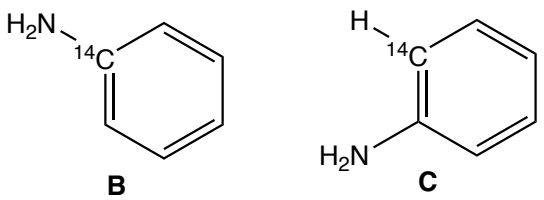


The numbers 1 to 6 are labelled on the carbon atoms of phenylamine to track the origin of the specific carbon atoms in the intermediates from phenylamine.

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]

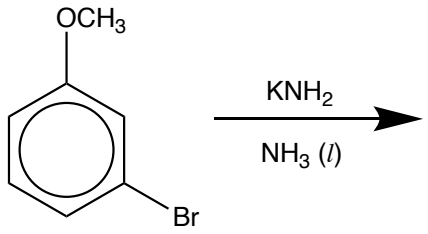


B **C**

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

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

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



.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 10]