**1.** Consider the following reaction scheme in which all of the compounds have straight chains.

$$\mathbf{A} \xrightarrow[\text{STEP 1}]{\text{Mg}} CH_3MgBr \xrightarrow[\text{STEP 2}]{C_4H_8O} \underset{\mathbf{B}}{C_5H_{12}O} \xrightarrow[\text{STEP 3}]{K_2Cr_2O_7/H_2SO_4} \underset{\mathbf{C}}{C_5H_{10}O} \xrightarrow[\text{STEP 4}]{I_2/NaOH} \text{Yellow ppt.} + \underset{\mathbf{D}}{\mathbf{E}}$$

(a) (i) Give the structural formula of **A**.

**(1)**

(ii) State the conditions under which the reaction in step 1 is carried out.

……

**(2)**

(b) After giving consideration to the sequence of reactions in steps 2, 3 and 4,

(i) write the *structural* formula of $C_4H_8O$;

**(1)**

(ii) write the *structural* formula of **B**.

**(1)**

(c) (i) Identify the yellow precipitate **D** formed in step 4.

……

**(1)**

(ii) Give the structural formula of **E**.

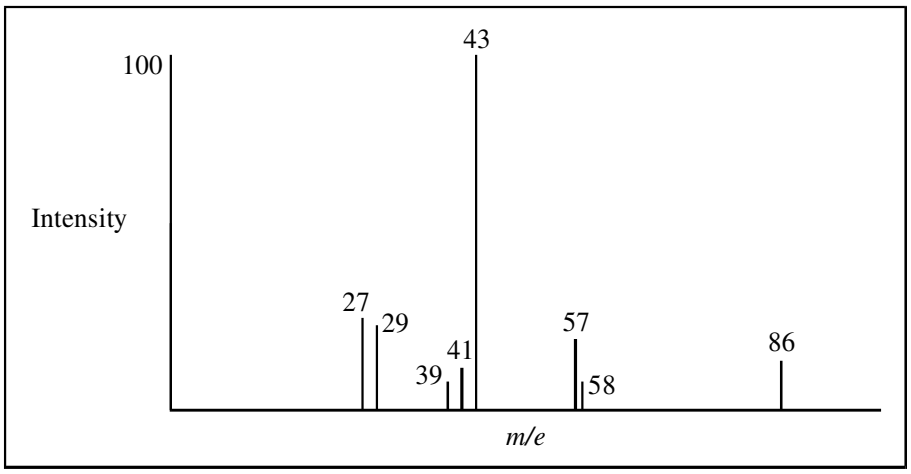
**(1)**

(d) Give the structural formula for **C.**

**(1)**

(e) The mass spectrum and infra–red spectrum of **C** are shown below.

(i) Mass spectrum of **C**



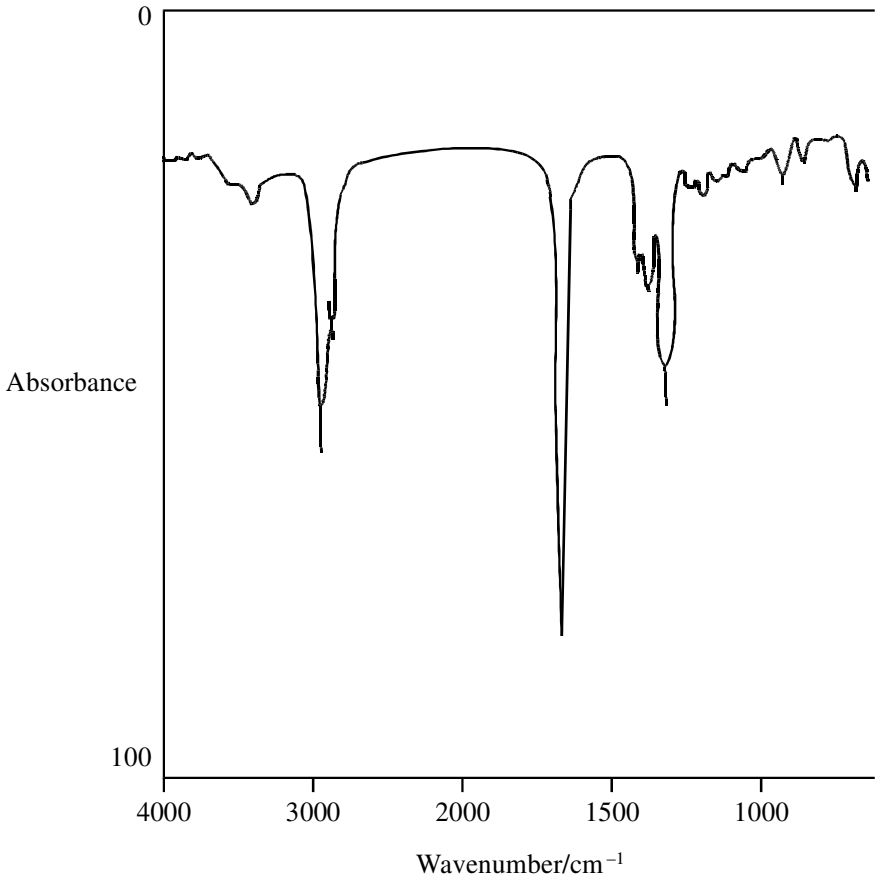
Referring to the mass spectrum, suggest the identities of the species giving rise to the peaks at *m/e* values of

86 ……..……

43 (two species) ……

**(3)**

(ii) Infra–red spectrum of **C**




–

| **Bond** | **Absorption wavenumber/cm⁻¹** |
|---|---|
| C–H | 2850–3300 |
| C—O | 1000–1300 |
| O–H | 2500–3500 |
| C==O | 1680–1750 |

Explain how the infra–red spectrum is consistent with the identity of **C**.

...……...……

...……...……

...……...……

**(2)**
**(Total 13 marks)**

**2.** The following is a modified account of a method for the preparation of phenylethanone, $C_6H_5COCH_3$.

Place 3 g of finely powdered anhydrous aluminium chloride and 7.5 $cm^3$ (6.6 g) of dry benzene in a 50 $cm^3$ round–bottomed flask.

Fit the flask with a reflux condenser and place in a cold water bath in a fume cupboard.

Slowly add, down the condenser, 2 $cm^3$ (2.2 g) of ethanoyl chloride.

Heat the flask in a water bath at 50 ºC for 30 minutes, or until no further hydrogen chloride is evolved.

Pour the reaction mixture into a 100 $cm^3$ flask containing 20 $cm^3$ of water, and shake vigorously.

Transfer to a separating funnel and discard the lower aqueous layer.

Add a dilute solution of sodium hydroxide to the separating funnel. Shake the mixture, and again discard the aqueous layer.

Dry the organic layer with anhydrous calcium chloride and fractionally distil, collecting the fraction boiling between 195 ºC and 205 ºC.

The yield of phenylethanone is 2 g.

(a) (i) Give the equation for the reaction between ethanoyl chloride and benzene, using structural formulae.

**(2)**

(ii) Suggest a mechanism for this reaction.

**(3)**

(b) Suggest reasons for each of the following steps in the preparation:

(i) *finely powdering* the aluminium chloride:

……

**(1)**

(ii) *drying* the benzene:

……

**(1)**

(iii) adding the ethanoyl chloride *slowly*:

……

**(1)**

(iv) using a fume cupboard:

……

**(1)**

(v) shaking the product with sodium hydroxide solution:

……

**(1)**

(c) The benzene is in excess in this preparation, being used as the solvent also.

(i) Calculate the mass of phenylethanone which could theoretically be obtained from this preparation based on the mass of ethanoyl chloride used.

(The molar mass of ethanoyl chloride is 78.5 g and that of phenylethanone is 120 g).

**(3)**

(ii) What is the percentage yield in this preparation?

**(1)**

(iii) Suggest reasons why the actual yield for organic reactions generally is significantly less than the theoretical yield.

……

……

**(2)**

**(Total 16 marks)**

**3.** This question concerns the addition polymer poly(propene), and the condensation polymer nylon.

(a) (i) Draw a structural formula for part of the poly(propene) chain showing clearly the repeating unit.

**(2)**

(ii) Suggest why, when poly(propene) is heated, it softens over a range of temperature rather than melting sharply at a particular temperature.

……

……

**(2)**

(b) Nylon–6,6 is made from a diamine, $H_2N(CH_2)_6NH_2$, and a diacid chloride, $ClOC(CH_2)_4COCl$.

(i) Draw the structural formula of a representative length of the polymer chain.

**(2)**

(ii) Using nylon–6,6 and poly(propene) as examples, explain the essential difference between condensation and addition polymerisation reactions.

……

……

……

……

**(3)**

(iii) Suggest why a diacid chloride is employed to make nylon rather than the corresponding dicarboxylic acid.

……

……

**(1)**

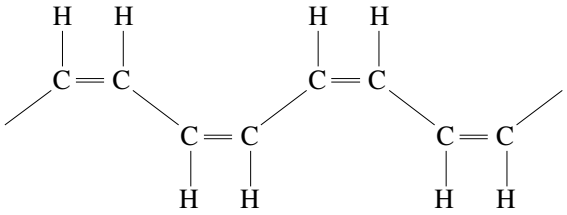
(iv) Nylon fibre is about twice as strong as poly(propene) fibre. Suggest in terms of the **intermolecular** forces in the polymers why this is so.

……

……

**(2)**

(c) Nylon is an extremely good electrical insulator. Conducting polymers can however be made by polymerising ethyne, HC CH. Poly(ethyne) shows stereoisomerism. A section of the *cis*– form is shown below:



(i) Draw a diagram of a section of the trans–form of poly(ethyne).

**(2)**

(ii) Suggest why poly(ethyne) conducts electricity.

……

……

**(2)**

**(Total 16 marks)**

**4.** (a) Phenylamine is formed by the reduction of nitrobenzene. Mixtures of phenylamine and nitrobenzene could be separated by fractional distillation, but another way is to shake the mixture with dilute hydrochloric acid, separate the aqueous and organic layers, and make the aqueous layer strongly alkaline with sodium hydroxide solution.

(i) Give the reagents and conditions which are used to reduce nitrobenzene to phenylamine.

……

……

……

**(3)**

(ii) Give the structural formula of the organic substance which is found in the **aqueous** phase after shaking with acid.

**(1)**

(iii) What is the effect on the organic species of making this aqueous layer strongly alkaline?

……

……

**(1)**

(b) Phenylamine is used to make azo dyes. It is first converted to benzenediazonium chloride.

(i) State the reagents and the conditions needed to convert phenylamine into benzenediazonium chloride.

……

……

**(2)**

(ii) Give reasons for the temperature conditions employed.

……

……

**(2)**

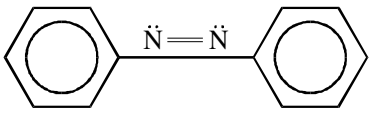
(iii) Write an equation, using structural formulae, to represent the reaction.

**(2)**

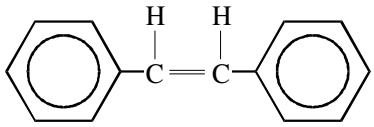
(iv) Addition of the benzenediazonium chloride solution to an alkaline solution of 2–naphthol gives the scarlet dye phenylazo–2–naphthol. Give the structural formula of phenylazo–2–naphthol.

**(2)**

(c) Phenylazo–2–naphthol has structural similarities to the compound azobenzene:



Azobenzene has the same *electronic* structure as 1,2–diphenylethene:



Comment on any isomerism which could be shown by the compound azobenzene, and hence comment on its possible shape.

**(2)**

**(Total 15 marks)**