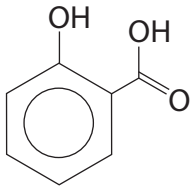
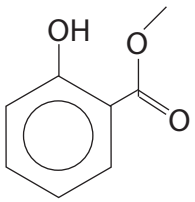
1 Salicylic acid is the active ingredient in one method of treatment of verrucas, warts and acne. The structure of salicylic acid is shown below.



A laboratory method of preparing salicylic acid is the hydrolysis of the ester, methyl salicylate, which is present in Oil of Wintergreen. A sample of the ester is initially refluxed with sodium hydroxide and salicylic acid is then precipitated by adding a strong acid.

(a) (i) Complete the equation for the alkaline hydrolysis of the ester group in methyl salicylate, using sodium hydroxide.

(1)



+ NaOH → ..... + ...

(ii) The salicylic acid is precipitated out of solution by the addition of dilute sulfuric acid until it is in excess.

How could you tell that the sulfuric acid is in excess?

(1)

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(b) Salicylic acid is sparingly soluble in water. Explain this observation in terms of intermolecular forces.

(2)

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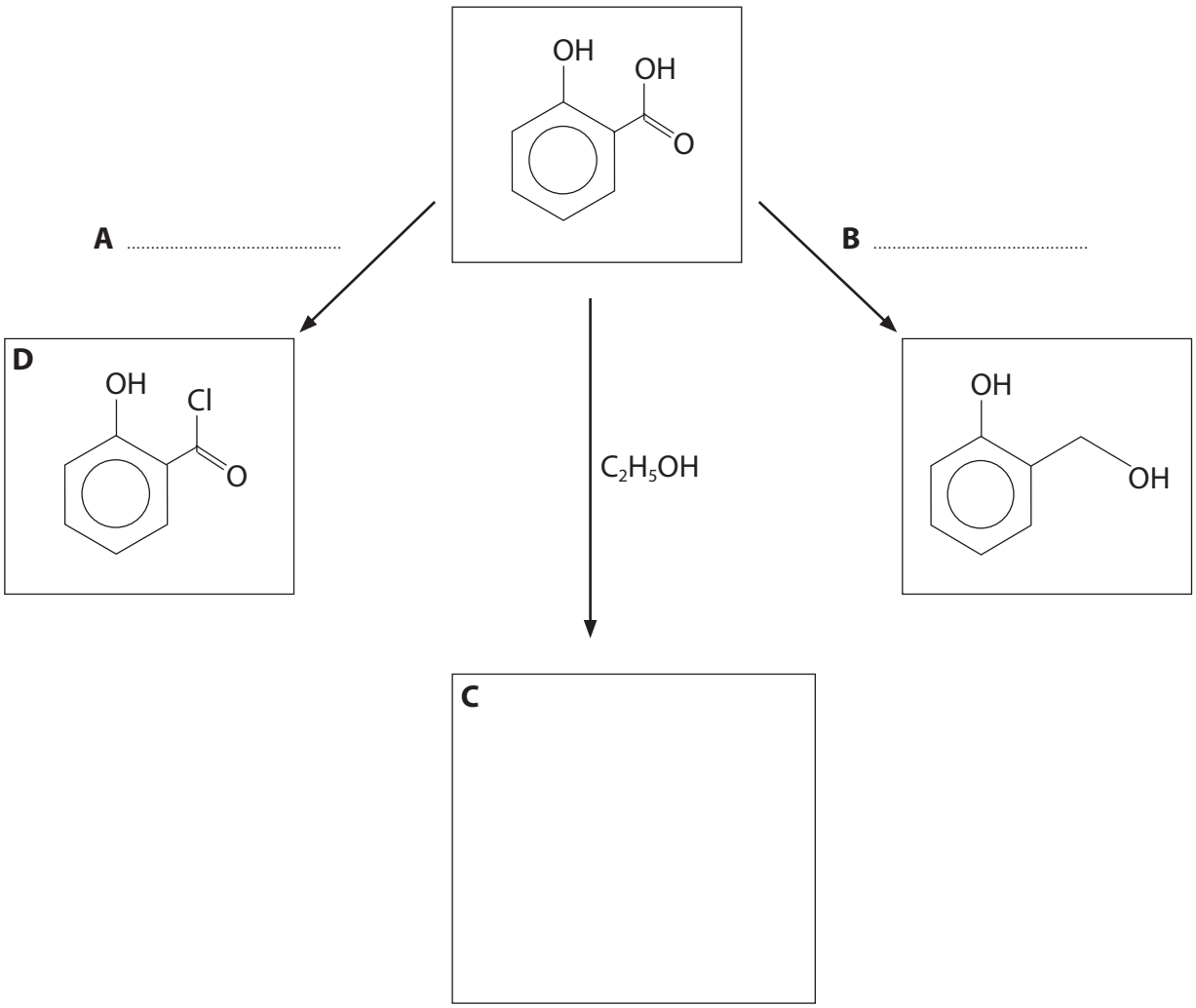
(c) State **three** ways in which the acid hydrolysis of an ester differs from the alkaline hydrolysis of an ester.

(3)

(d) Salicylic acid can undergo various reactions as outlined below.

(i) Give the **formula** of the reagents **A** and **B** and the **skeletal** formula of the product **C**.

(3)



(ii) Both compound **D** and salicylic acid react with ethanol. State **two** differences between these reactions.

(2)

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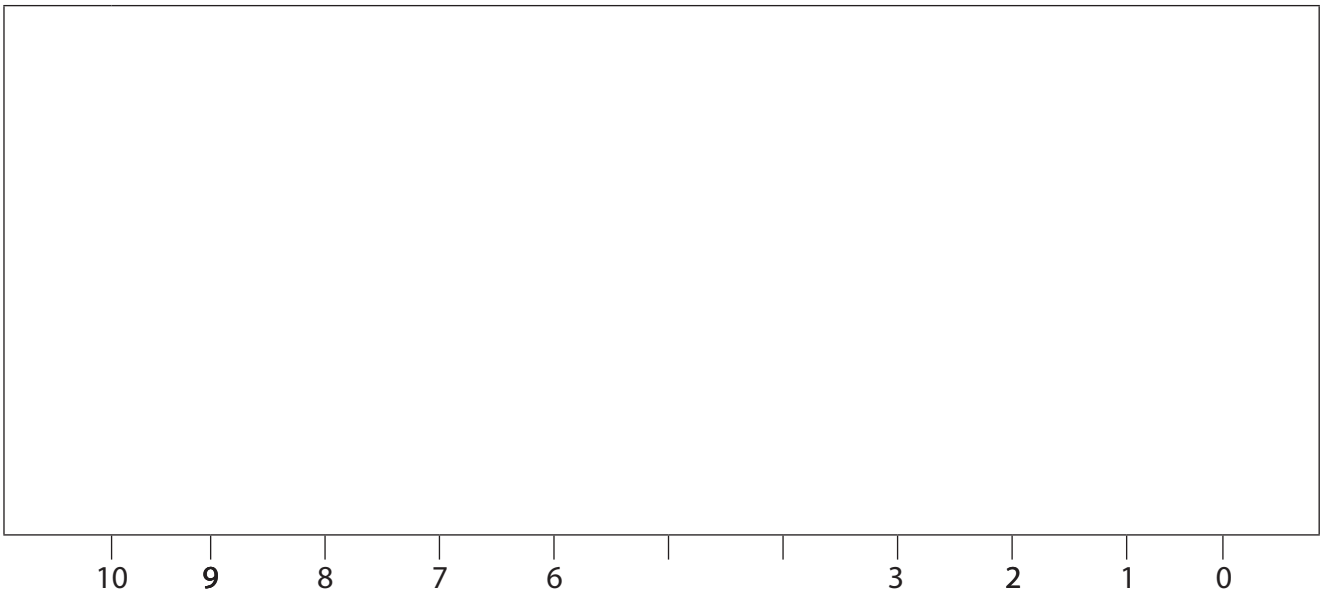
*(e) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for ethanol. The peaks do not overlap.

Explain the number of peaks, their splitting pattern and the ratio of the areas under each set of peaks.

(5)



(f) Tetramethylsilane, $Si(CH_3)_4$, is used as a reference standard in nmr spectra.

Suggest why it gives a very strong signal in the spectrum.

(1)

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(g) State the type of radiation that is used to create the nmr spectrum.

(1)

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.....

(h) Use the Data Booklet to state **two** differences between the infrared spectra of salicylic acid and compound **D**. Include the wave numbers of the relevant groups or bonds.

(2)

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(Total for Question = 21 marks)

2 This question is about the reactions of butanoic acid, $CH_3CH_2CH_2COOH$. It has a foul smell and behaves like a typical carboxylic acid.

(a) (i) The addition of sodium carbonate solution is often used as a chemical test to distinguish carboxylic acids, like butanoic acid, from other compounds, such as aldehydes.

Explain why old stocks of aldehydes often react with sodium carbonate solution.

(1)

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(ii) How would the result of this test distinguish between a carboxylic acid and an old stock of an aldehyde?

(1)

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(iii) Write the balanced chemical equation, including state symbols, for the reaction of sodium carbonate solution with butanoic acid.

(2)

*(iv) Infrared spectroscopy is a good physical method to distinguish carboxylic acids from other organic compounds. Give the wavenumbers of **two** characteristic absorptions for a carboxylic acid. Indicate the bond responsible for each absorption. Suggest why one of the absorptions is broad.

(3)

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(v) High resolution nuclear magnetic resonance spectroscopy is a suitable physical method to use alongside infrared spectroscopy to identify butanoic acid. State the total number of peaks and suggest the splitting pattern for each peak that you would expect for butanoic acid, $CH_3CH_2CH_2COOH$.

(3)

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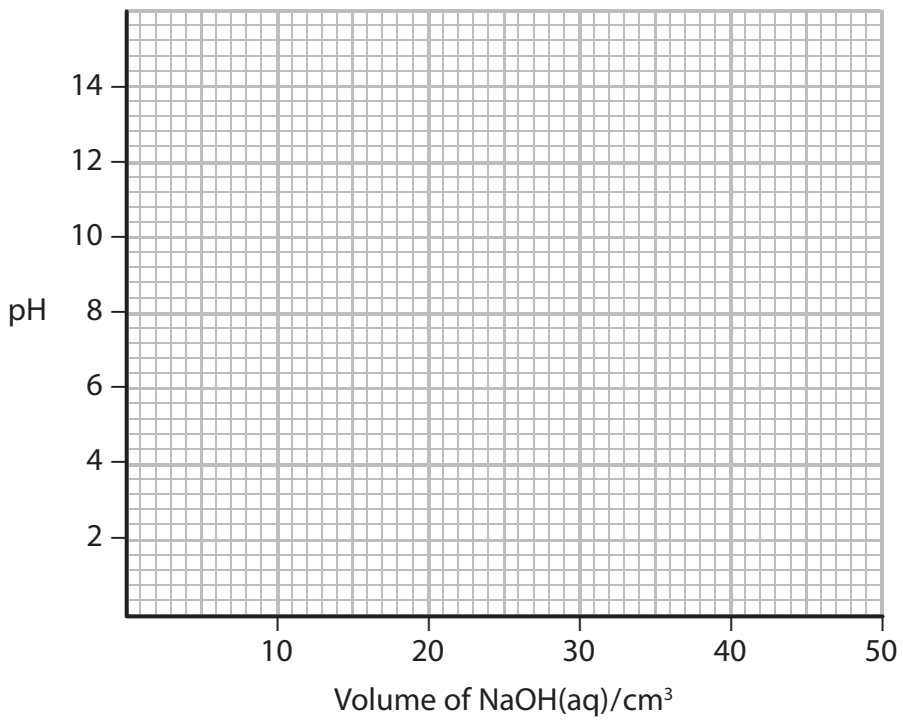
(b) Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

(4)



(c) (i) What would you see when phosphorus pentachloride, PCl_5, reacts with butanoic acid?

(1)

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.....

(ii) Give the structural formula and name of the organic product of this reaction.

(2)

Structural formula

Name .....

(d) (i) Give the name or formula of the organic product of the reaction between butanoic acid and lithium tetrahydridoaluminate (lithium aluminium hydride).

(1)

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(ii) Water cannot be used as the solvent in this reaction because it reacts with lithium tetrahydridoaluminate. Suggest a suitable solvent.

(1)

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(iii) State the type of reaction that takes place between butanoic acid and lithium tetrahydridoaluminate. Justify your classification.

(2)

Type .....

Justification .....

.....

.....

(e) (i) Butanoic acid can be reacted with methanol to make methyl butanoate. State **two** conditions that help to speed up this reaction.

(2)

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(ii) Draw the **displayed** formula of methyl butanoate.

(1)

(iii) Identify another chemical, by name or formula, which could be added to methanol to make methyl butanoate.

(1)

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*(iv) Give **two** advantages and **one** disadvantage of using the reaction occurring in (e)(iii), compared to the reaction in (e)(i), when making methyl butanoate.

(3)

Advantages .....

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Disadvantage .....

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(Total for Question = 28 marks)

3 The ester $CH_3CH_2COOCH_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

(a) (i) Name the ester.

(1)

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(ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)

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(b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c, for the reaction.

(3)

	CH_3CH_2COOH	CH_3OH	$CH_3CH_2COOCH_3$	H_2O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol			0.21	

(Total for Question 6 marks)