Mastering Chemistry

Book 3B

Topic 8 Chemistry of Carbon

Compounds







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32.1 Planning a synthesis (p.155)

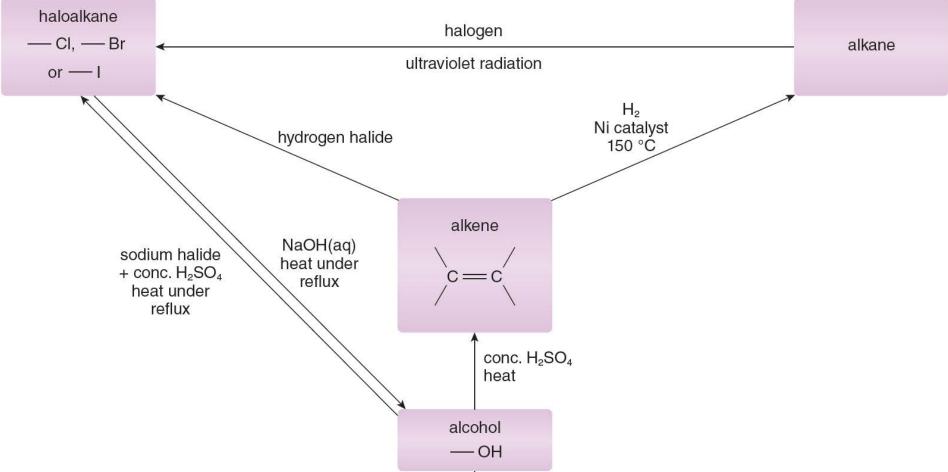
 A synthetic route is a series of reactions that can be used to change a starting chemical into a desired compound.
 Functional group interconversions are important in planning synthetic routes.





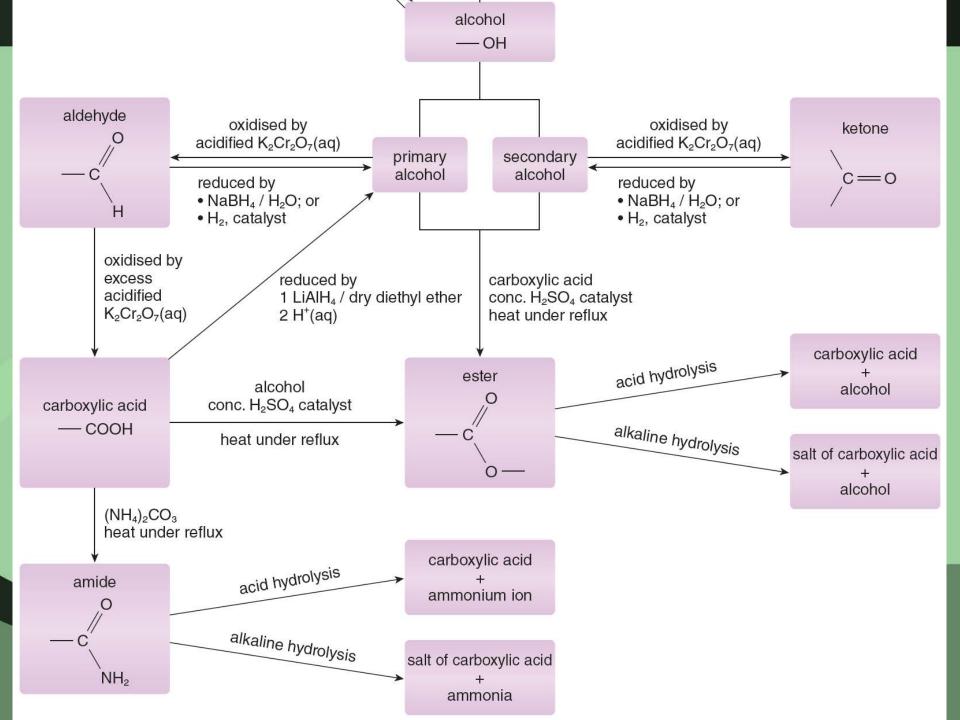


32.1 Planning a synthesis (p.155)





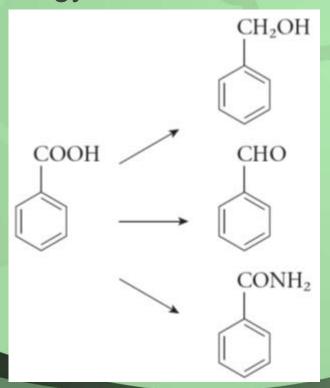


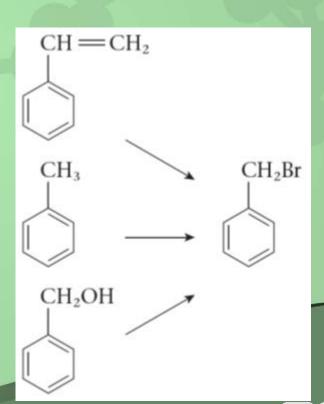




 Suppose you need to design a synthesis of (bromomethyl)benzene from benzoic acid:

The strategy:





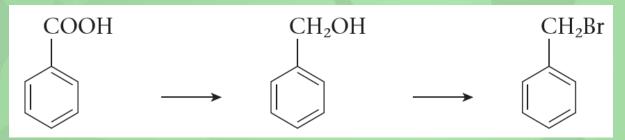




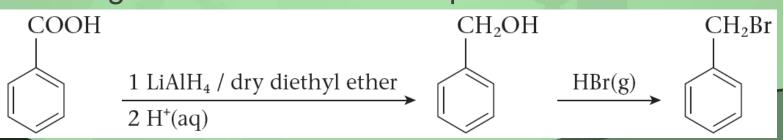


◆ сн₂он is common to the left and right lists.

A viable route would have this alcohol as an intermediate:



The reagents and conditions required:







Q (Example 32.1)

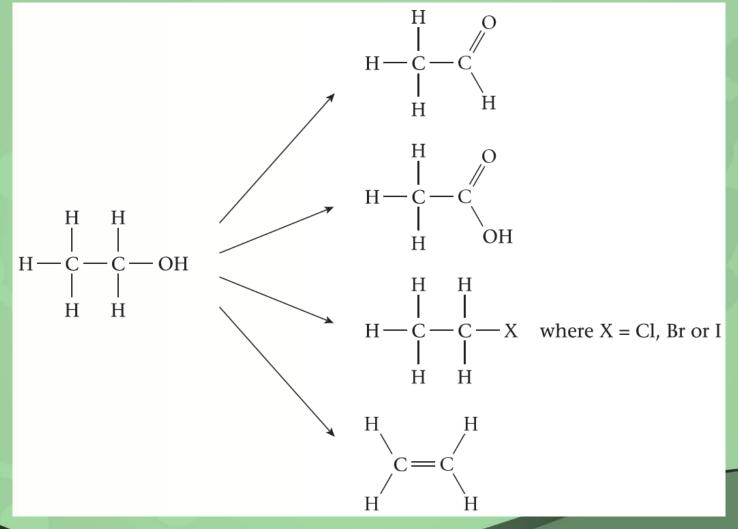
Outline a synthetic route to accomplish the following conversion.



The structures of all the compounds that can be made from ethanol in one step are shown below:













Ethanamide can be made from a carboxylic acid.

Thus, a viable synthetic route would have a carboxylic acid as an

intermediate:

Give the reagents and reaction conditions.

$$H \xrightarrow{H} \xrightarrow{H} \xrightarrow{H} \xrightarrow{H} \xrightarrow{\text{acidified } K_2Cr_2O_7(aq)} \xrightarrow{\text{heat under reflux}} H \xrightarrow{H} \xrightarrow{C} \xrightarrow{C} \xrightarrow{\text{NH}_4)_2CO_3} \xrightarrow{\text{heat under reflux}} H \xrightarrow{C} \xrightarrow{C} \xrightarrow{\text{NH}_2}$$





Q (Example 32.2)

Outline a synthetic route to accomplish the following conversion.

$$\begin{array}{cccc}
OH & & & \\
& & & \\
O & & \\$$

A

contains an ester functional group which can be made by the reaction between an –OH group and a –COOH group.

The –CONH₂ group in by hydrolysis.

can be converted to a -COOH group







Thus, a viable synthetic route would have a carboxylic acid as an intermediate:

Give the reagents and reaction conditions required.







Q (Example 32.3)

Outline a synthetic route to accomplish the following conversion.

A

The starting compound contains an ester functional group. An –OH group and a –COOH group are produced upon hydrolysis.

A –COOH group can be converted to an –OH group via reduction.





Thus, a viable synthetic route would be as follows:

Give the reagents and reaction conditions required.





Practice 32.1

Outline a two-step synthetic route to accomplish each of the following conversions. Give the reagents, reaction conditions (as appropriate) and the structures of organic products.

a) CH₃CH₃ → CH₃CH₂OH

$$CH_{3}CH_{3} \xrightarrow{Br_{2}(I)} CH_{3}CH_{2}Br \xrightarrow{NaOH(aq)} CH_{3}CH_{2}OH$$

$$+ CH_{3}CH_{2}Dr \xrightarrow{heat under reflux} CH_{3}CH_{2}OH$$

CH=CHCHO
$$\xrightarrow{\text{H}_2(g)}$$
 CH₂CH₂CH₂CH₂OH







c) CH₃COOCH₃ → CH₃CH₂OH

$$CH_{3}COOCH_{3} \xrightarrow{\text{heat}} CH_{3}COOH \xrightarrow{\text{dilute sulphuric acid}} CH_{3}COOH \xrightarrow{\text{1 LiAlH}_{4} / \text{dry diethyl ether}} CH_{3}COOH \xrightarrow{\text{2 H}^{+}(aq)} CH_{3}CH_{2}OH$$





32.3 More complicated synthetic routes (p.162)

 Methyl phenylethanoate is an ester used in food and perfume industries to produce a honey-like smell and flavour.

$$CH_2-C$$
O
 CH_3

 A convenient starting material for the synthesis of the compound could be (2-bromoethyl)benzene.





32.3 More complicated synthetic routes (p.162)

- ◆ The desired product is an ester. It is formed from the reaction between an alcohol and a carboxylic acid. Thus, CH₂CH₂B
 - needs to be converted into a carboxylic acid. This cannot be done directly.
- CH₂CH₂Br can be converted into an alcohol, and the alcohol can be converted into a carboxylic acid.
- So, the synthesis can be achieved in the following way:

$$\begin{array}{c} & & \\ & \\ & \\ & \\ \end{array} \begin{array}{c} & \\ \end{array} \begin{array}{c} & \\ \\ \end{array} \begin{array}{c} & \\ \end{array} \begin{array}{c} & \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c}$$





32.3 More complicated synthetic routes (p.162)

Practice 32.2

Outline a synthetic route to accomplish each of the following conversions. Give the reagents, reaction conditions (as appropriate) and the structures of organic products.

a) CH₃CH₂CH=CH₂ → CH₃CH₂COCH₃

$$CH_{3}CH_{2}CH=CH_{2} \xrightarrow{HBr(g)} CH_{3}CH_{2}CHBrCH_{3} \xrightarrow{NaOH(aq)} CH_{3}CH_{2}CH(OH)CH_{3} \xrightarrow{acidified \ K_{2}Cr_{2}O_{7}(aq)} CH_{3}CH_{2}COCH_{3}$$

$$+ CH_{3}CH_{2}CH_{2}CH(OH)CH_{3} \xrightarrow{acidified \ K_{2}Cr_{2}O_{7}(aq)} CH_{3}CH_{2}COCH_{3}$$

$$+ CH_{3}CH_{2}COCH_{3}$$

$$+ CH_{3}CH_{2}CH_{2}CH(OH)CH_{3} \xrightarrow{acidified \ K_{2}Cr_{2}O_{7}(aq)} CH_{3}CH_{2}COCH_{3}$$

$$CH_2CONH_2 \longrightarrow CH_2CH_2Br$$

moderately concentrated

$$CH_2CONH_2 \xrightarrow{H_2SO_4 \text{ or } HCI} \longrightarrow CH_2COOH$$

$$1 \text{ LiAlH}_4 \text{ / dry dimethyl ether}$$

$$2 \text{ H}^+(aq) \longrightarrow CH_2CH_2OH \xrightarrow{\text{heat under reflux}} \longrightarrow CH_2CH_2Br$$





32.4 Stages in the preparation of a carbon

compound (p.163)

 In Stage 1, chemists need to devise a series of reactions that will give the desired product from readily available reagents.

• In Stage 2, when carrying out the reaction, one of the more common techniques is to heat the reaction mixture in a flask fitted with a reflux condenser.











32.4 Stages in the preparation of a carbon compound (p.163)

- In Stage 3, when separating the crude product from the reaction mixture, solids are normally separated by filtration. Liquids can often be separated by simple or fractional distillation.
- In Stage 4, the crude product is usually contaminated with unreacted reagents or with by-products and hence purification is required. The method of purifying this crude product depends on whether it is a solid or a liquid.
- ◆ In Stage 5, the percentage yield (百分產率) can be obtained by comparing the actual yield (實際產率) with the theoretical yield (理論產率).

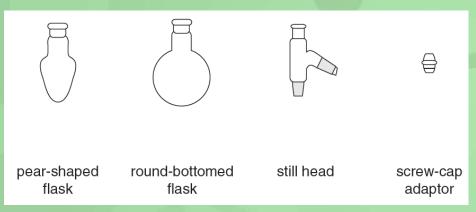




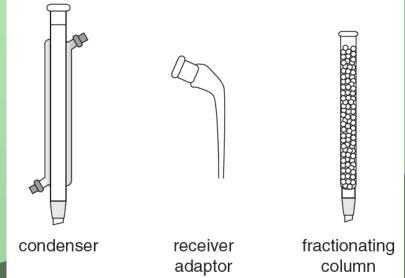
32.4 Stages in the preparation of a carbon

compound (p.163)

 Glassware called Quickfit apparatus is needed:















32.4 Stages in the preparation of a carbon compound (p.163)

• For heating, chemists, for safety reasons, often use an electric heating mantle, a hot water bath or a hot oil bath instead of the direct flame of a Bunsen burner.





32.5 Separation and purification methods in liquid carbon compound preparations (p.152)

- The techniques discussed will be:
 - simple distillation;
 - fractional distillation;
 - by using a separating funnel;
 - drying.







32.5 Separation and purification methods in liquid carbon compound preparations (p.152)

Simple distillation

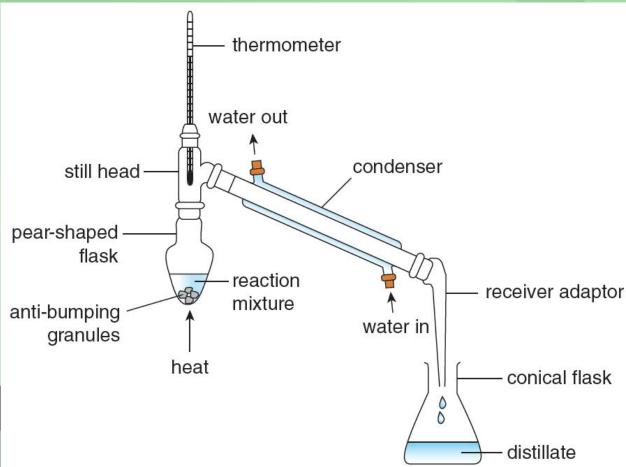
 Suppose a liquid product has a boiling temperature much lower than the other substances in the reaction mixture. Simple distillation can be used to separate the liquid product from the reaction mixture.







32.5 Separation and purification methods in liquid carbon compound preparations (p.152)











- 32.5 Separation and purification methods in liquid carbon compound preparations (p.152)
- When the pear-shaped flask is heated, the mixture in the flask starts to boil. The liquid with the lowest boiling point is the most volatile and boils first.
- The vapour moves out of the flask up into the other parts of the apparatus, leaving behind the less volatile components of the mixture. When the vapour reaches the cold condenser, it condenses and becomes a liquid. This liquid then drips into the collecting flask.







- 32.5 Separation and purification methods in liquid carbon compound preparations (p.152)
- The advantages of using simple distillation, rather than fractional distillation, are that simple distillation is easier to set up and is quicker.
- The disadvantage is that simple distillation does not separate the liquids as finely as fractional distillation does.
- Simple distillation should only be used if the boiling temperature of the liquid product is very different from the other liquids in the mixture, ideally a difference of more than 25 °C.





32.5 Separation and purification methods in liquid carbon compound preparations (p.152)

Fractional distillation

- ◆ Fractional distillation (分餾) separates mixtures of liquids with different boiling points.
- Fractional distillation uses an apparatus similar to simple distillation, but with a fractionating column between the pearshaped flask and the still head.
- The column is usually filled with glass beads or pieces of broken glass. This provides a larger surface area for vaporisation and condensation of the liquid mixture. The column is hotter at the bottom and cooler at the top.

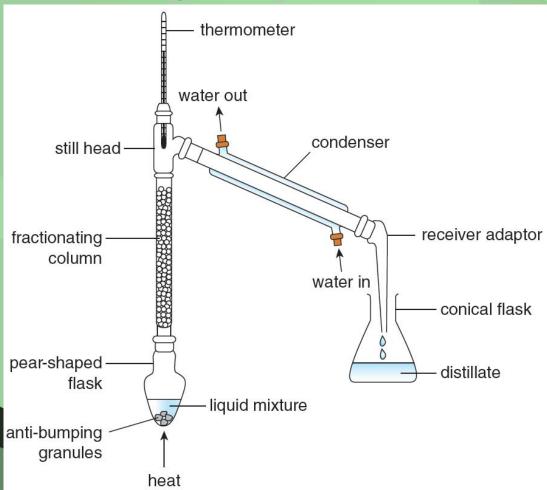








32.5 Separation and purification methods in liquid carbon compound preparations (p.152)







- 32.5 Separation and purification methods in liquid carbon compound preparations (p.152)
- When the flask containing a mixture of liquids is heated, the mixture produces a vapour which is richer in the most volatile component of the liquids present. Most of the vapour condenses in the column and runs back. As it does so, it meets more of the rising vapour. Some of the condensed liquid becomes vapour again.
- In this way, the mixture vaporises and condenses repeatedly as it rises up the column. But every time it does so, the vapour becomes richer in the most volatile liquid present. At the top of the column, the vapour contains 100% of the most volatile liquid.







- 32.5 Separation and purification methods in liquid carbon compound preparations (p.152)
- During fractional distillation, the most volatile liquid with the lowest boiling point is distilled off first, then the liquid with the next lowest boiling point and so on.
- Fractional distillation takes longer than simple distillation. It is best used when the difference in boiling temperatures is small, and when there are several liquids to be separated from a mixture.





32.5 Separation and purification methods in liquid carbon compound preparations (p.152)

By using a separating funnel

- The organic layer and the aqueous layer possibly obtained in a product mixture can be separated using a separating funnel.
 - 1 Pour the mixture of liquids into the separating funnel, place a stopper in the top of the funnel, and shake to mix the contents.
 - 2 Allow the layers to settle.
 - 3 Place a conical flask under the separating funnel, remove the stopper and open the tap until the whole of the lower layer has left the funnel.
 - 4 Place a second conical flask under the separating funnel to collect the other layer.



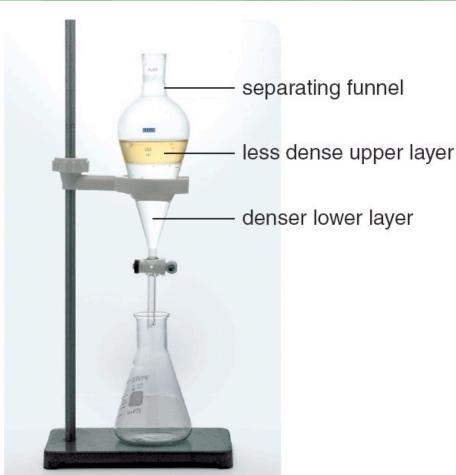




32.5 Separation and purification methods in liquid carbon compound preparations

(p.152)









- 32.5 Separation and purification methods in liquid carbon compound preparations (p.152)
- When you prepare an organic liquid using acids, your crude product may contain acid impurities. These impurities can be removed by adding sodium carbonate solution and shaking the mixture in the separating funnel.
- Any residual acid will react with the sodium carbonate, releasing carbon dioxide gas. The tap needs to be slowly opened at intervals to release any gas pressure that may build up.
- Finally, the sodium carbonate layer is removed and the organic layer washed with pure water to remove all inorganic impurities.







32.5 Separation and purification methods in liquid carbon compound preparations (p.152)

Drying the product

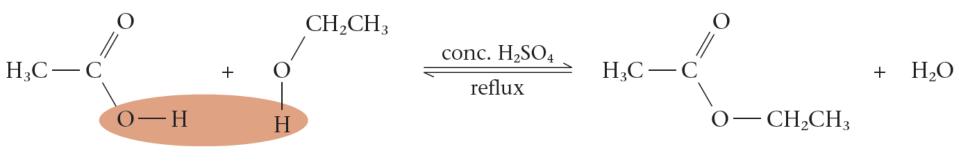
- There may be some water left in the liquid product. Traces of water are removed by adding a drying agent to the liquid product.
- Common drying agents include:
 - anhydrous calcium chloride;
 - anhydrous magnesium sulphate; and
 - anhydrous sodium sulphate.







 You can prepare ethyl ethanoate, an ester, by the reaction between ethanoic acid and ethanol in the presence of an acid catalyst.



ethanoic acid ethanol ethyl ethanoate

 This ester preparation has three stages — reaction, separation and purification.

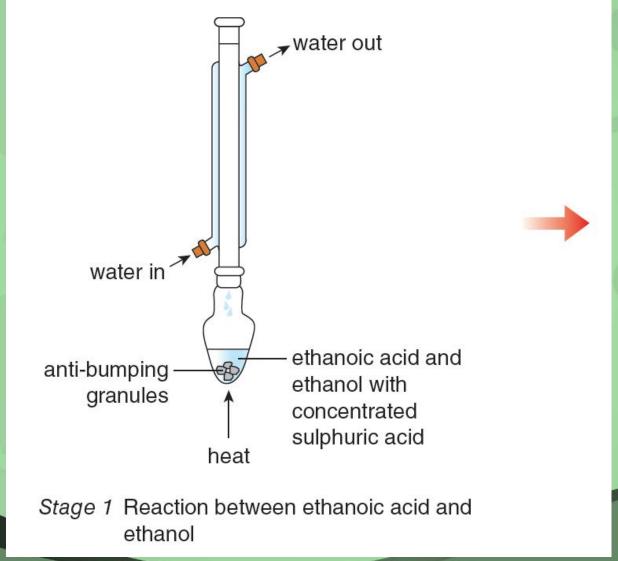


Preparing and purifying 2-chloro-2-methylpropane <u>Ref.</u>







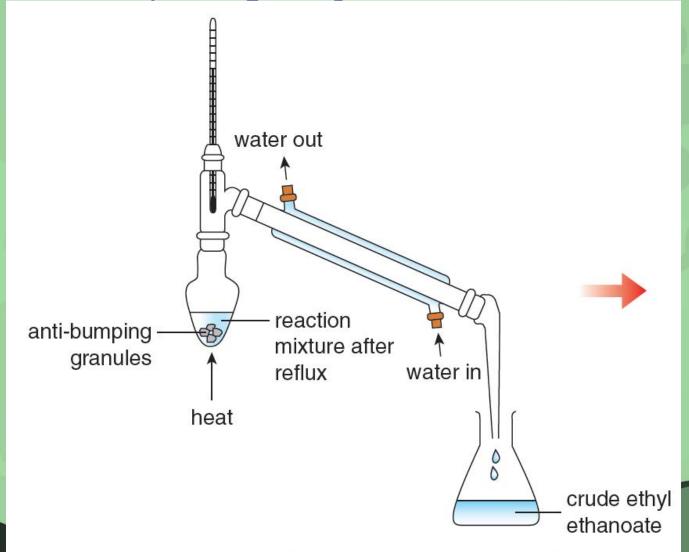










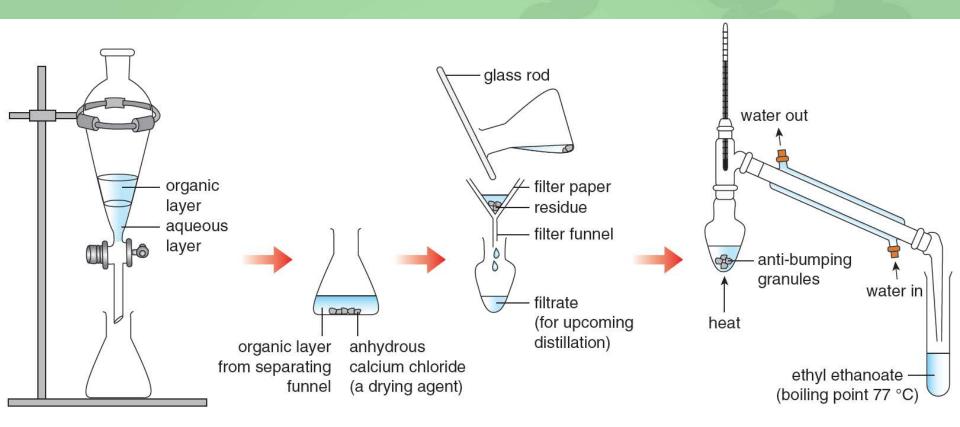


Stage 2 Separation of crude ethyl ethanoate from reaction mixture









Stage 3 Purification of ethyl ethanoate







Q (Example 32.4)

2-chloro-2-methylpropane is prepared by shaking methylpropane-2-ol and excess concentrated hydrochloric acid in a separating funnel. Two layers of liquids can be observed in the separating funnel after the reaction has taken place. The equation for the reaction is:





Use the data in the table below to answer the following questions.

Compound	Relative molecular mass	Density (g cm ⁻³)	Boiling point (°C)
Methylpropan-2-ol	74.0	0.78	82
2-chloro-2-methylpropane 92.5		0.84	51
Water	18.0	1.00	100







- a) Suggest ONE advantage of using a separating funnel to carry out the experiment.
- b) One of liquid layers in the separating funnel is aqueous and the other contains the organic product. Suggest whether the upper or lower layer is likely to contain the organic product. Explain your reasoning.
- c) The crude product of 2-chloro-2-methylpropane is washed with 10% NaHCO₃(aq).
 - i) A gas is produced in the washing process. Identify this gas.
 - ii) Suggest the chemical that could have reacted with NaHC03(aq) to form the gas.
- d) Suggest a suitable reagent for drying the washed product from (c).
- e) Name a suitable method for the purification of the dried product from (d).









- a) Any one of the following:
 - Allow better mixing of the reactants by vigorous shaking of the separating funnel.
 - Allow easy isolation of the product by draining out the aqueous layer from the separating funnel.
- b) The upper layer is likely to contain the organic product because the organic product is less dense than water.
- c) i) Carbon dioxide
 - ii) Concentrated hydrochloric acid
- d) Any one of the following:
 - Anhydrous calcium chloride
 - Anhydrous sodium sulphate
- e) Simple distillation / fractional distillation





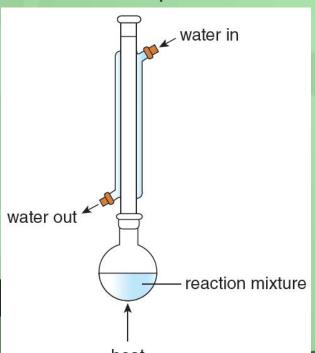




Practice 32.3

1 The diagram shows a proposed experimental set-up for heating a reaction mixture under reflux. Identify TWO improvements that should be made to this set-up. Give a reason for each improvement made. You may assume

suitable clamps are used.



Improvement 1

Swap the water inflow and outflow in the condenser.

To improve the efficiency of the condensing process.

Improvement 2

Add anti-bumping granules to the flask.

To promote smooth boiling / to prevent material from escaping from the top of the condenser.



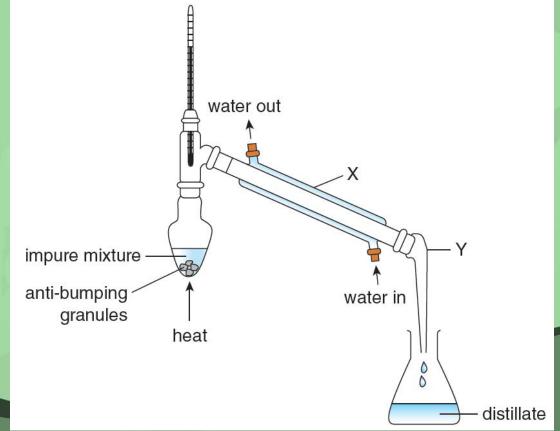






2 A student prepared a carbon compound and distilled the crude product using the apparatus below. The crude distillate was obtained over the range 105 °C to 125 °C. The boiling point of the pure carbon compound is

116 °C.









- a) Name the apparatus labelled X and Y.X: condenser; Y: receiver adaptor
- b) The distillate contained an aqueous layer and an organic layer. The densities of the layers are shown below. Describe briefly how you would obtain a dry, pure sample of the organic product, starting from the two layers.

Layer	Aqueous layer	Organic layer
Density (g cm ⁻³)	1.05	0.72

Place the two layers in a separating funnel.

Allow the layers to separate and discard the lower aqueous layer.

Collect the organic layer. Add a drying agent.

Redistil the dried organic layer.









- The theoretical yield is the amount of product that would be made if all the reactants were converted into the product.
- However, many chemical reactions do not give the amount of product you would expect and the amount of product you actually obtain is called the actual yield.
- Percentage yield = $\frac{actual\ yield\ of\ product}{theoretical\ yield\ of\ product}$ x 100%







- Percentage yield varies from 0 to 100%. It may be less than 100% because
 - some of the product may be lost due to mechanical transfer (transferring from one container to another);
 - some of the product may be lost during the separation process (for example, filtration or using a separating funnel);
 - there may be side reactions in which the reactants form different products;
 - the reaction may not go to completion.







Q (Example 32.5)

A student carried out an experiment to prepare benzoic acid from ethyl benzoate.

Step 1 Place 5.0 cm³ of ethyl benzoate into a round-bottomed flask. Add 30 cm³ of 2.0 mol dm⁻³ sodium hydroxide solution followed by 3 or 4 anti-bumping granules to the ethyl benzoate in the flask.

Step 2 Heat the flask under reflux gently.

Step 3 When all of the oily drops of ester have disappeared, stop heating and cool the mixture to room temperature.

Step 4 Treat the mixture with dilute hydrochloric acid until no more solid benzoic acid forms.









- a) Why is the reaction mixture refluxed rather than heated in an open beaker?
- b) Name the type of reaction that occurs between ethyl benzoate and sodium hydroxide solution.
- c) Write equations leading to the formation of benzoic acid from ethyl benzoate.
- d) Describe briefly how a dry benzoic acid sample can be obtained after Step 4.
- e) In this experiment, 5.0 cm³ of ethyl benzoate (density = 1.047 g cm⁻³) reacted with excess NaOH(aq). 3.532 g of benzoic acid was produced. Calculate the percentage yield of benzoic acid.
 - (Relative molecular masses: ethyl benzoate = 150.0, benzoic acid = 122.0)

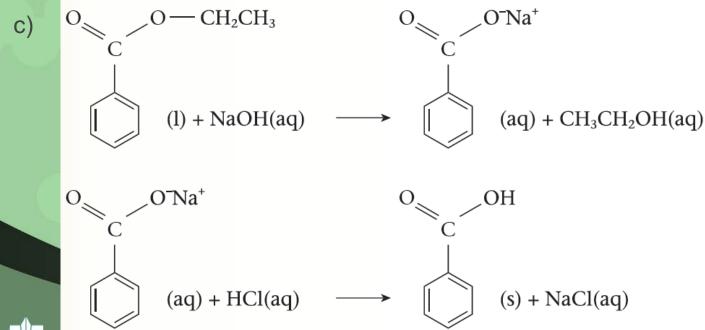






<u>A</u>

- a) Any one of the following:
 - To prevent the reactants / products escaping.
 - Ethyl benzoate / ethanol is flammable.
- b) Alkaline hydrolysis of ester









- d) Filter the mixture to obtain the solid benzoic acid. Wash it with deionised water and then dry in an oven.
- e) Mass of ethyl benzoate used = 5.0 cm 3 x 1.047 g cm⁻³ = 5.235 g Number of mole of ethyl benzoate used = $\frac{5.235 g}{150.0 g mol^{-1}}$ = 0.0349 mol

Theoretical yield of benzoic acid = $0.0349 \text{ mol } \times 122.0 \text{ g mol}^{-1} = 4.258 \text{ g}$ Percentage yield of benzoic acid = $\frac{3.532 \text{ g}}{4.258 \text{ g}} \times 100\% = 82.95\%$







Practice 32.4

1 Aspirin is made when salicylic acid reacts with ethanoic anhydride.

The chemical equation for this reaction is:

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + CH_3COOH$$
 salicylic acid ethanoic anhydride aspirin

(Relative molecular masses: salicylic acid = 138.0, aspirin = 180.0)

a) Calculate the maximum mass of aspirin that could be made from 85.0 g of salicylic acid.

$$C_7H_6O_3 \rightarrow C_9H_8O_4$$
 salicylic acid aspirin

Number of mole of salicylic acid = $\frac{85.0 \text{ g}}{138.0 \text{ g mol}^{-1}}$ = 0.616 mol

= number of moles of aspirin made Mass of aspirin made = 0.616 mol x 180.0 g mol⁻¹ = 111 g







- b) In an experiment, a student obtained 70.5 g of aspirin from 85.0 g of salicyclic acid.
 - i) Calculate the percentage yield of aspirin.

Percentage yield of aspirin =
$$\frac{70.5 g}{111 g}$$
 x 100% = 63.5%

ii) Suggest ONE possible reason why the student did NOT have a percentage yield of 100%.

Any one of the following:

- Reversible reaction
- Some of the product may be lost due to mechanical transfer / during the separation process.





2 120 g of ethanoic acid reacted with 230 g of ethanol to yield 132 g of ethyl ethanoate. What was the percentage yield of ethyl ethanoate? (Relative molecular masses: ethanoic acid = 60.0, ethanol = 46.0, ethyl ethanoate = 88.0)

Ethanoic acid and ethanol react according to the equation below: CH₃COOH + CH₃CH₂OH ⇒ CH₃COOCH₂CH₃ + H₂O 120 g 230 g

Number of moles of $CH_3COOH = \frac{120 \text{ g}}{60.0 \text{ g mol}^{-1}} = 2.00 \text{ mol}$

Number of moles of $CH_3CH_2OH = \frac{230 \text{ g}}{46.0 \text{ g mol}^{-1}} = 5.00 \text{ mol}$







According to the equation, 1 mole of CH₃COOH reacts with 1 mole of CH₃CH₂OH to produce 1 mole of CH₃COOCH₂CH₃.

In this reaction, 2.00 moles of CH₃COOH react with 2.00 moles of CH₃CH₂OH to produce 2.00 moles of CH₃COOCH₂CH₃.

Theoretical yield of the ester = $2.00 \text{ mol } \times 88.0 \text{ g mol}^{-1} = 176 \text{ g}$

Percentage yield of the ester = $\frac{132 \text{ g}}{176 \text{ g}} \times 100\% = 75.0\%$









Key terms (p.178)

percentage yield	百分產率	theoretical yield	理論產量
actual yield	實際產量	fractional distillation	分餾

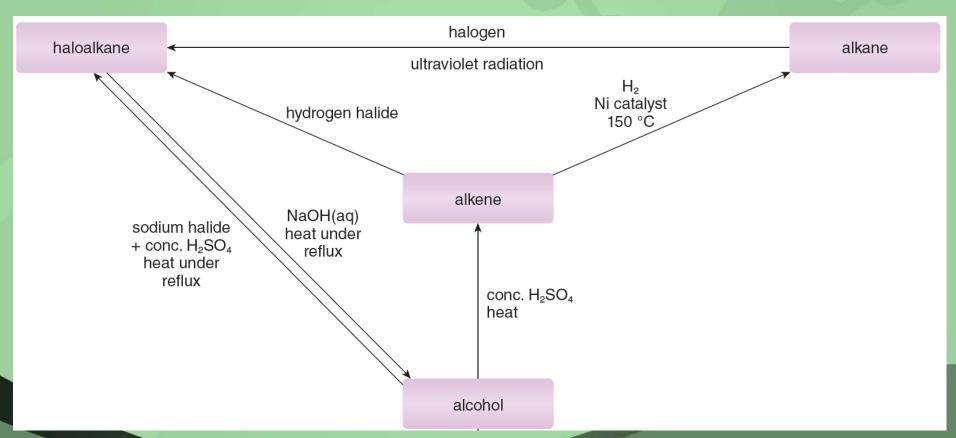






Summary (p.179)

The following chart summarises important reactions of some homologous series.







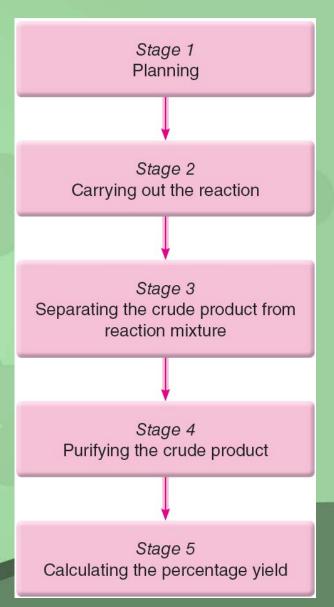






Summary (p.179)

2 The laboratory preparation of a carbon compound involves five stages:







Summary (p.179)

- 3 Separation and purification methods in liquid carbon compound preparations include:
 - simple distillation;
 - fractional distillation;
 - by using a separating funnel;
 - drying.
- 4 The percentage yield is the percentage of the theoretical yield which is achieved in the reaction.

Percentage yield =
$$\frac{actual\ yield\ of\ product}{theoretical\ yield\ of\ product} \times 100\%$$







Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

question targeted at level 3 and above;

question targeted at level 4 and above;

question targeted at level 5.

" * 'indicates 1 mark is given for effective communication.







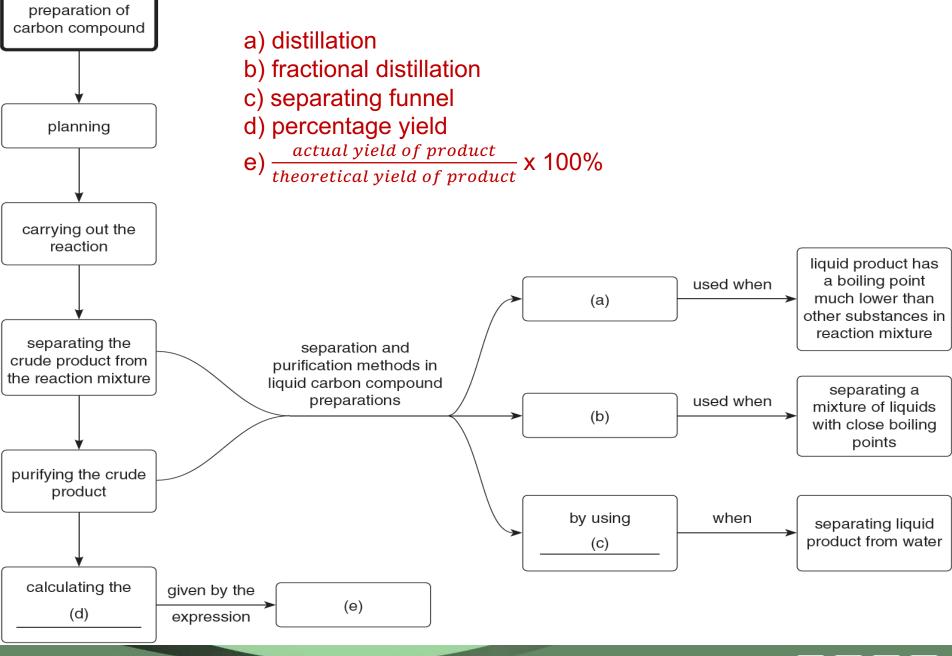
PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.











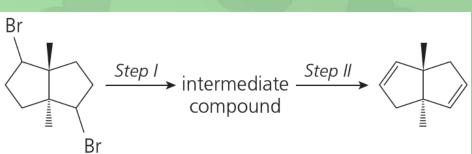




PART II MULTIPLE CHOICE QUESTIONS

2 Consider the following conversion:

Which of the following combinations can achieve the above conversion?



	Reagent used	Reagent used
	in Step I	in Step II
Α	aqueous ammonia	dilute sulphuric acid
В	aqueous potassium	dilute sulphuric acid
	hydroxide	Answer: D
С	aqueous ammonia	concentrated sulphuric
		acid
D	aqueous potassium	concentrated sulphuric
	hydroxide	acid
		(HKDSE Paper 14 2018 30)









3 Consider the following organic reactions where P, Q and R are the major organic products formed.

$$CH_3CH_2COOH \xrightarrow{LiAlH_4} P \xrightarrow{conc. H_2SO_4} Q \xrightarrow{HBr(g)} R$$

Which of the following combinations is correct?

Answer: A

Explanation:

CH₃CH₂COOH is reduced by LiAlH₄ to CH₃CH₂CH₂OH (P).

CH₃CH₂CH₂OH (P) is dehydrated by concentrated sulphuric acid to give CH₃CH=CH₂ (Q).

When CH₃CH=CH₂ (Q) reacts with HBr(g), the products are CH₃CHBrCH₃ and CH₂CH₂CH₂Br. According to Markovnikov's rule, the hydrogen atom attaches mainly to the carbon atom already carrying the larger number of hydrogen atoms, i.e. CH₃CHBrCH₃ is the major product.







4 Consider the following conversion:

Which of the following combinations of reagents can achieve the above conversion?

A NaOH(aq) and CH₃OH(l)

B CH₃OH(I) and CH₃COOH(I)

C NaOH(aq), H₂SO₄(aq) and CH₃OH(l)

D H₂SO₄(aq), NaOH(aq) and CH₃COOH(I)

Answer: C

(HKDSE, Paper 1A, 2015, 29)

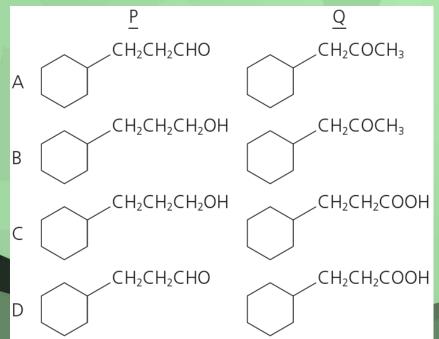






5 Consider the following organic reactions where P and Q are the major organic products formed.

Which of the following combinations is correct?



Answer: C









The molecular formula of compound X is $C_5H_{10}O$. Compound Z is synthesised from compound X as below:

$$X \xrightarrow{\text{acidified } K_2Cr_2O_7(aq)} Y \xrightarrow{\text{ethanol / conc. } H_2SO_4} Z$$
heat under reflux

What could be the chemical formula of Z?

Answer: D

A CH₃COO(CH₂)₄CH₃ B CH₃CH₂COO(CH₂)₃CH₃ C CH₃(CH₂)₃COCH₂CH₃ D CH₃(CH₂)₃COOCH₂CH₃

Explanation:

Y is probably a carboxylic acid as it reacts with ethanol to give an ester Z.

CH₃(CH₂)₃COOCH₂CH₃ is an ester formed from the reaction of a carboxylic acid containing 5 carbon atoms with ethanol.

The carboxylic acid is formed via the oxidation of X, an alcohol containing 5 carbon atoms.









7 Aspirin can be produced from salicylic acid according to the following equation:

What mass of salicylic acid is needed to produce 10.8 g of aspirin, assuming a 40.0% yield?

(Relative molecular masses: salicylic acid = 138.0, aspirin = 180.0)

Explanation:

A 3.13 g B 5.64 g

C 20.7 g

D 29.5 g

Theoretical yield of aspirin = $\frac{10.8 \text{ g}}{40.0\%}$ = 27.0 g

Mass of salicylic acid needed to produce 27.0 g of aspirin

= 27.0 g x
$$\frac{138.0}{180.0}$$
 = 20.7 g







Consider the following organic conversion:

CH₃CH₂CH₂OH → CH₃CH₂CH₂I

Which of the following reagents can X be?

- $(1) I_2(s)$
- $(2) Pl_3(I)$
- (3) NaI(s) and concentrated H₂SO₄(I)

A (1) only

B(2) only

C (1) and (3) only

D (2) and (3) only

Explanation:

(3) Concentrated H₃PO₄(I) reacts with NaI(s) to produce HI(g), which reacts with CH₃CH₂CH₂OH to give CH₃CH₂CH₂I.

Concentrated H₂SO₄(I) is NOT used because the acid oxidises iodide ions to iodine and produces very little HI(g).





Answer: B



9 In order to prepare 1-bromopropane, a mixture of propan-1-ol, sodium bromide, water and concentrated sulphuric acid is heated under reflux.

CH₃CH₂CH₂OH → CH₃CH₂CH₂Br

Which of the following statements about the preparation are correct?

- (1) The crude product can be separated from the reaction mixture by fractional distillation.
- (2) The crude product should be washed with sodium hydrogencarbonate solution.
- (3) The crude product can be dried by anhydrous sodium sulphate.

A (1) and (2) only

B (1) and (3) only

C (2) and (3) only

D (1), (2) and (3)

Explanation:

(2) Washing the crude product with sodium hydrogencarbonate solution can remove acidic impurities.



Answer: D



10 Consider the following conversion of carbon compounds:

$$CH_{3}CH_{2}CH_{2}Br \xrightarrow{Step 1} CH_{3}CH_{2}CH_{2}OH$$

$$\xrightarrow{Step 2} CH_{3}CH_{2}COOH \xrightarrow{Step 3} CH_{3}CH_{2}CONH_{2}$$

Which of the following reagents and reaction conditions is / are correct?

(1) Step 1 Heating with water

- Answer: B
- (2) Step 2 Heating with acidified K₂Cr₂O₇(aq) under reflux
- (3) Step 3 Mixing with NH₄Cl(s) at room temperature

A (1) only

B (2) only

Explanation:

- (1) CH₃CH₂CH₂Br is heated with NaOH(aq) under reflux in Step 1.
- C (1) and (3) only (3) CH₃CH₂COOH reacts with NH₃(aq) to give D (2) and (3) only CH₃CH₂COO-NH₄+. Heat the mixture under reflux to produce CH₃CH₂CONH₂.









11 Which of the following processes can form ethanol?

- (1) Heating ethanoic acid with NaBH₄
- (2) Heating bromoethane with KOH(aq)
- (3) Heating ethyl butanoate with NaOH(aq) under reflux

A (1) and (2) only

B (1) and (3) only

C (2) and (3) only

D (1), (2) and (3)

Answer: C

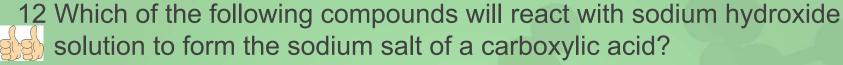
(HKDSE, Paper 1A, 2017, 35)











- (1) (CH₃)₂CHCOOH
- (2) HCOOCH₂CH₂CH₃
- (3) CH₃CH₂CH₂CONH₂

Answer: D

A (1) and (2) only B (1) and (3) only C (2) and (3) only D (1), (2) and (3)

Explanation:

(1) (CH₃)₂CHCOOH undergoes neutralisation when mixed with sodium hydroxide solution, forming (CH₃)₂CHCOO-Na⁺. (2) HCOOCH₂CH₂CH₃ undergoes alkaline hydrolysis when heated with sodium hydroxide solution, forming HCOO-Na⁺. (3) CH₃CH₂CH₂CONH₂ undergoes alkaline hydrolysis when heated with sodium hydroxide solution, forming CH₃CH₂CH₂COO-Na⁺.









PART III STRUCTURED QUESTIONS

13 A student proposed the following route for synthesising propanoic acid from propene.



- a) Identify X. CH₃CH₂CH₂OH (1)
- b) Give the reagents and reaction conditions needed to carry out Step 2 and Step 3. Step 2: NaOH(aq), heat under reflux (1)

Step 3: acidified K₂Cr₂O₇(aq), heat under reflux (1)

- c) Name the type of reaction that takes place in each step.
 - Step 1: addition reaction (1)
 - Step 2: substitution reaction / hydrolysis (1)
 - Step 3: oxidation (1)
- d) Explain why the student's choice of reaction for *Step 1* would lead to a low overall yield. The <u>major product</u> from the reaction between propene and HBr(g) is 2-bromopropane. (1)



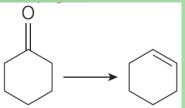


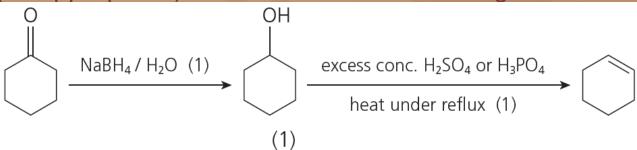


14 Outline a synthetic route, with *no more than three steps*, to accomplish each of the following conversions. For each step, give the reagent(s), reaction conditions (as appropriate) and the structure of the organic

product.

a)





b) CH₃CONH₂ → CH₃COOCH₃

$$CH_{3}CONH_{2} \xrightarrow{HCl(aq)} CH_{3}COOH \xrightarrow{CH_{3}OH} CH_{3}COOCH_{3}$$

$$(1) \xrightarrow{conc. H_{2}SO_{4}, heat under reflux} (1)$$

c) CH₃CHO → CH₃CH₂CI

$$CH_{3}CHO \xrightarrow{NaBH_{4} / H_{2}O (1)} \rightarrow CH_{3}CH_{2}OH \xrightarrow{HCl(g)} \rightarrow CH_{3}CH_{2}CI$$

$$(1) \xrightarrow{ZnCl_{2} catalyst (1)} \rightarrow CH_{3}CH_{2}CI$$









$$\begin{array}{c} \mathsf{d}) \\ \downarrow \\ \mathsf{OH} \\ \downarrow \\ \mathsf{O} \end{array} \longrightarrow \begin{array}{c} \mathsf{O} \\ \downarrow \\ \mathsf{O} \\ \mathsf{O} \end{array}$$

e) CH₃CH₂CHBrCH₃ → CH₃CH₂COCH₃

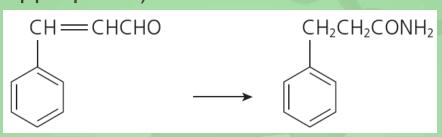
$$CH_{3}CH_{2}CHBrCH_{3} \xrightarrow{NaOH(aq)} CH_{3}CH_{2}CH(OH)CH_{3} \xrightarrow{acidified K_{2}Cr_{2}O_{7}(aq)} \rightarrow CH_{3}CH_{2}COCH_{3}$$
heat under reflux (1)

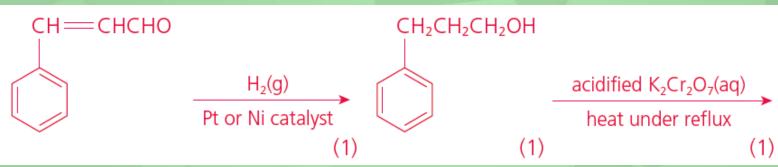


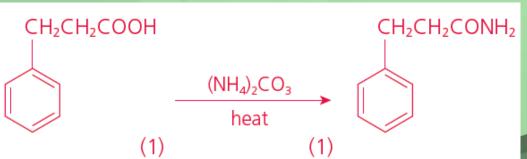




15 Outline a synthetic route, with *no more than four steps*, to accomplish the following conversion. For each step, give the reagent(s), reaction conditions (as appropriate) and the structure of the organic product.





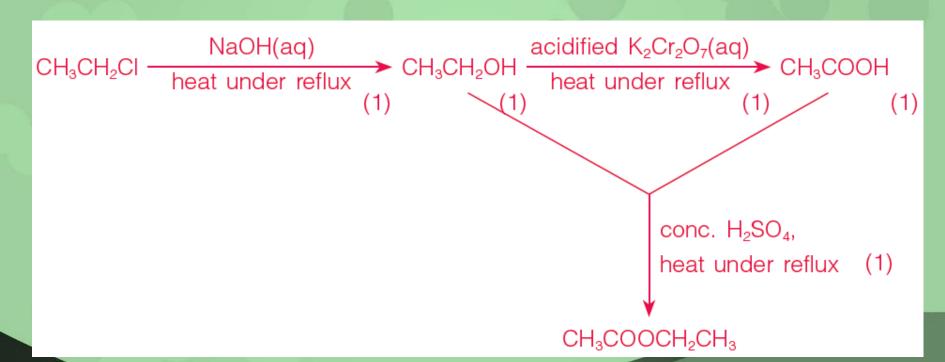








16 You are provided with chloroethane, inorganic reagents and organic solvents. Outline a synthetic route, with *no more than four steps*, to obtain ethyl ethanoate. For each step, give the reagent(s), reaction conditions (as appropriate) and the structure of the organic product.











17 Outline a synthetic route, with *no more than three steps*, to accomplish the following conversion. For each step, give the reagent(s), reaction conditions (as appropriate) and the structure of the organic product.

(HKDSE, Paper 1B, 2017, 13)





18 Benzamide, benzoic acid and benzyl bromide are commonly used organic compounds. Their structures are shown below:





- a) In an experiment, benzoic acid is prepared from benzamide in two steps:
 - Step 1: Benzamide is added to excess 1 M NaOH(aq) and the mixture is heated gently. An organic compound X is formed.
 - Step 2: The resulting mixture is then treated with reagent Y until no more solid benzoic acid is given out.
 - i) Name the type of reaction involved in Step 1.
 - ii) Draw the structure of X.
 - iii) Suggest what Y would be.
 - iv) Suggest why X is more soluble than benzoic acid in water.
 - v) Describe briefly how a dry benzoic acid sample can be obtained after Step 2.
- b) Outline a synthetic route, with *no more than three steps*, to accomplish the conversion of benzoic acid to benzyl bromide. For each step, give the reagent(s), reaction conditions (as appropriate) and the structure of the organic product.

(HKDSE, Paper 1B, 2014, 12)

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).







19 This is a brief method written by a student for preparing ethyl ethanoate.



- Heat under reflux together 0.45 mole of ethanoic acid with an equimolar quantity of ethanol.
- Add 5 cm³ of concentrated sulphuric acid.
- Distil off the crude product boiling up to 82 °C.
- Shake the distillate with sodium hydrogencarbonate solution in a separating funnel.
- Collect the organic layer and dry it.
- Distil off the dried ethyl ethanoate and collect the fraction boiling at 75–78 °C.









a) Give the equation for this reaction.

conc.
$$H_2SO_4$$

 $CH_3COOH + CH_3CH_2OH \Rightarrow CH_3COOCH_2CH_3 + H_2O$

b) Describe what happens to the vapour when a mixture is heated under reflux and give ONE reason why reflux is used in this reaction.

The <u>vapour</u> is condensed <u>into liquid</u>. (1) Any one of the following:

- Reflux is used so that no reactants or products are lost. (1)
- Reflux is used as the <u>mixture</u> needs to be <u>heated for a long time</u>. (1)
- c) State an important detail that is missing from the first point.

There is no indication of the time necessary to heat the mixture under reflux. (1)







d) State why concentrated sulphuric acid should have been added at the refluxing stage.

Concentrated sulphuric acid acts as a catalyst. (1)

e) What is the purpose of adding sodium hydrogencarbonate solution to the distillate?

To react with any remaining ethanoic acid (1)

f) Suggest a drying agent for the organic product.

Anhydrous calcium chloride (1)







- 20 The following procedure may be used to prepare 2-chloro-2-methylpropane.
 - Step 1 Place 15 cm³ of methylpropan-2-ol in a separating funnel and slowly add 30 cm³ of concentrated hydrochloric acid (an excess), while swirling the funnel.
 - Step 2 When all the hydrochloric acid has been added, leave the mixture to stand for 20 minutes, shaking it gently at intervals.
 - Step 3 Once the organic and aqueous layers have been completely separated, discard the aqueous layer.
 - Step 4 Add saturated sodium hydrogencarbonate solution, a little at a time, to the organic layer. After each addition, invert the separating funnel and open the tap.
 - Step 5 Discard the aqueous layer.
 - Step 6 Transfer the organic layer to a small flask, add a solid drying agent and swirl the flask.
 - Step 7 Decant the liquid into a clean flask and distil it to collect pure 2-chloro-2-methylpropane.



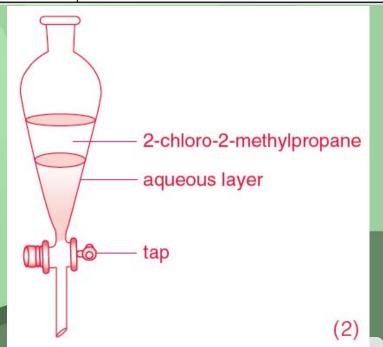




Some data on the organic reactant and product are given in the table.

Data	Methylpropan-2-ol	2-chloro-2-methylpropane
Molar mass (g mol ⁻¹)	74.0	92.5
Boiling temperature (°C)	82	51
Density (g cm ⁻³)	0.79	0.84

a) Draw a diagram of a separating funnel, labelling the aqueous layer and the layer of 2-chloro-2-methylpropane that would be observed at the end of *Step 2*.





b) Give the reason why sodium hydrogencarbonate solution is added to the organic layer in *Step 4* and why it is important to open the tap after adding this solution.

To react with any unreacted hydrochloric acid. (1)

To release the build-up of pressure due to the carbon dioxide produced. (1)

c) Which anhydrous compound may be used as a drying agent in Step 6?

Any of the following:

- Anhydrous calcium chloride (1)
- Anhydrous magnesium sulphate (1)
- Anhydrous sodium sulphate (1)

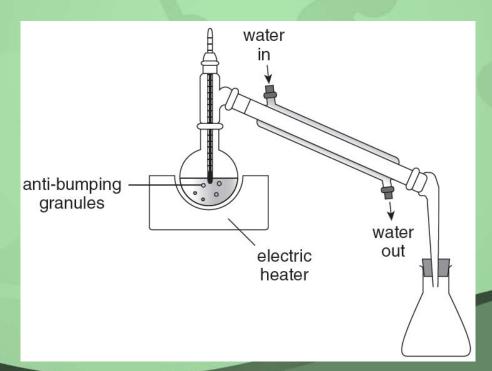






- d) A student set up this apparatus for distillation in Step 7 as shown.
 - i) Describe THREE ways in which this apparatus must be modified for safe and efficient use. Assume the apparatus is suitably clamped.
 - ii) Give a suitable temperature range over which to collect the final product during the distillation.

(Edexcel Advanced Subsidiary GCE, Unit 2, Jun. 2016, 5)









- i) The bulb of the thermometer should be opposite to the opening of the condenser. (1)

 The water in and out of the condenser should be reversed. (1)

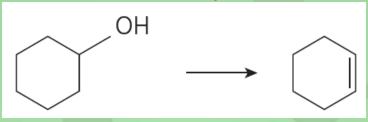
 But a vent after the condenser / Leave a gap between the condenser.
 - Put a vent after the condenser. / Leave a gap between the condenser and the receiver. / The conical flask must be open. (1)
- ii) 50–52 °C (1)







21 Cyclohexanol can be converted into cyclohexene.



a) Suggest a dehydrating agent that could be used for the conversion.

Concentrated sulphuric acid / concentrated phosphoric acid / aluminium oxide (1)







- b) In an experiment, a student obtained 2.86 g of cyclohexene from 4.05 g of cyclohexanol.
 - i) Calculate the percentage yield of cyclohexene.
 - ii) Give a reason why the percentage yield is NOT 100%.

(Relative molecular masses: cyclohexanol = 100.0, cyclohexene = 82.0)

i)

Number of moles of cyclohexanol used = $\frac{4.05 \text{ g}}{100.0 \text{ g mol}^{-1}}$ = 0.0405 mol

= number of moles of cyclohexene obtained theoretically

Theoretical yield of cyclohexene = $0.0405 \text{ mol } \times 82.0 \text{ g mol}^{-1} = 3.32 \text{ g}$ (1)

Percentage yield of cyclohexene = $\frac{2.86 \text{ g}}{3.32 \text{ g}} \times 100\% = 86.1\%$ (1)









- ii) Any one of the following:
 - Some of the product may be lost due to mechanical transfer. (1)
 - Some of the product may be lost during the separation process. (1)
 - There may be <u>side reactions</u> in which the reactants form different products. (1)
 - The reaction may not go to completion. (1)







22 In the preparation of 2-chloro-2-methylpropane from methylpropan-2-ol, 15.0 cm³ of methylpropan-2-ol produced 6.9 cm³ of 2-chloro-2-methylpropane.

The equation for the reaction is: $(CH_3)_3COH(I) + HCI(aq) \rightarrow (CH_3)_3CCI(I) + H_2O(I)$

Calculate the percentage yield of 2-chloro-2-methylpropane, using data from the table.

Compound	Molar mass (g mol ⁻¹)	Density (g cm ⁻³)
Methylpropan-2-ol	74.0	0.79
2-chloro-2-methylpropane	92.5	0.84





Mass of $(CH_3)_3COH$ used = 15.0 cm³ x 0.79 g cm⁻³ = 11.9 g

Number of moles of $(CH_3)_3COH$ used = $\frac{11.9 \text{ g}}{74.0 \text{ g mol}^{-1}}$ = 0.161 mol = number of moles of $(CH_3)_3CCI$ formed theoretically

Mass of $(CH_3)_3CCI$ formed theoretically = 0.161 mol x 92.5 g mol⁻¹ = 14.9 g (1)

Actual mass of $(CH_3)_3CCI$ formed = 6.9 cm³ x 0.84 g cm⁻³ = 5.8 g

Percentage yield of $(CH_3)_3CCI = \frac{5.8 \text{ g}}{14.9 \text{ g}} \times 100\% = 39\%$ (1)



