16 HYDROXY COMPOUNDS

Learning outcomes

Candidates should be able to:

1. recall the reactions (reagents and conditions) by which alcohols can be produced:
   (a) electrophilic addition of steam to an alkene, $H_2O(g)$ and H_3PO_4 catalyst
   (b) reaction of alkenes with cold dilute acidified potassium manganate(VII) to form a diol
   (c) substitution of a halogenoalkane using NaOH(aq) and heat
   (d) reduction of an aldehyde or ketone using $NaBH_4$ or $LiAlH_4$
   (e) reduction of a carboxylic acid using $LiAlH_4$
   (f) hydrolysis of an ester using dilute acid or dilute alkali and heat
2. describe:
   (a) the reaction with oxygen (combustion)
   (b) substitution to halogenoalkanes, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$
   (c) the reaction with Na(s)
   (d) oxidation with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ to:
   (i) carbonyl compounds by distillation
   (ii) carboxylic acids by refluxing
   (primary alcohols give aldehydes which can be further oxidised to carboxylic acids, secondary alcohols give ketones, tertiary alcohols cannot be oxidised)
   (e) dehydration to an alkene, by using a heated catalyst, e.g. Al_2O_3 or a concentrated acid
   (f) formation of esters by reaction with carboxylic acids and concentrated H_2SO_4 or H_3PO_4 as catalyst as exemplified by ethanol
3. (a) classify alcohols as primary, secondary and tertiary alcohols, to include examples with more than 1 -OH group
   (b) state characteristic distinguishing reactions, e.g. mild oxidation with acidified $K_2Cr_2O_7$, colour change from orange to green
4. deduce the presence of a $CH_3CH(OH)–$ group in an alcohol, $CH_3CH(OH)–R$, from its reaction with alkaline $I_2(aq)$ to form a yellow precipitate of tri-iodomethane and an ion, RCO_2^-
5. explain the acidity of alcohols compared with water

Initial assessment

1. Which statement below describes what happens to an organic compound when it is reduced and then oxidised?
   Discuss with a partner how to:
   A It loses hydrogen, then loses oxygen
   B It gains hydrogen, then gains oxygen
   C It gains hydrogen, then loses oxygen
   D It loses hydrogen, then gains oxygen

2. complete these general equations

   a. acid + base →

   b. acid + metal →

   c. acid + carbonate →

3. Give the skeletal formula for:
   a. propan-2-ol
   b. butanone

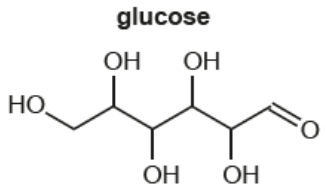
   d. ethanal
   c. ethanoic acid.

Introduction

1. **S** is a secondary alcohol with molecular formula $C_4H_{10}O$.
   Draw the displayed formula of **S**. [1]

2. Draw the structure of the tertiary alcohol that is an isomer of pentan-3-ol. [1]

3. The structure of glucose, $C_6H_{12}O_6$, is shown in figure below



Complete the following table to identify the number of primary, secondary and tertiary alcohol groups present in the structure shown in figure above. [1]

type of alcohol group	Primary	secondary	tertiary
number of groups			

1. How many structurally isomeric secondary alcohols exist with the molecular formula $C_5H_{12}O$?

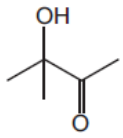
A 1 B 2 C 3 D 4

2. How many tertiary alcohols have the molecular formula $C_6H_{14}O$?

A 1 **B** 2 **C** 3 **D** 4

3. Compound X contains an alcohol group and a carbonyl group

compound X



Which row is correct?

	type of alcohol group	type of carbonyl group
A	Primary	Ketone
B	Primary	Aldehyde
C	Tertiary	Ketone
D	Tertiary	Aldehyde

4. Structural isomerism and stereoisomerism should be considered when answering this question.
If a molecule contains two non-identical chiral carbon atoms, four optical isomers exist.
How many isomers are there with:
• molecular formula $C_7H_{14}O$ and
• a five-membered ring and
• a tertiary alcohol group?

A 5 B 4 C 9 D 13

Preparation

Addition of steam to alkenes (studied in alkenes)

Alkenes with cold dilute acidified potassium manganate(VII)(studied in alkenes)

Substitution of a halogenoalkanes (studied in halogenoalkanes)

Reduction of an aldehyde or ketone with $NaBH_4$ or $LiAlH_4$

There are three common methods of reducing carbonyl compounds.

» By hydrogen on a nickel catalyst:

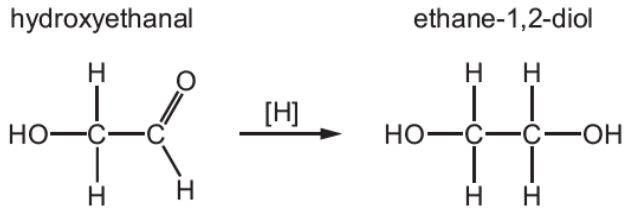
» By sodium tetrahydridoborate(III) (sodium borohydride) in alkaline methanol:

» By lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether:

Lithium tetrahydridoaluminate(III) is a dangerous reagent, producing heat and hydrogen gas (which usually catches fire) with any water, and ether is a hazardous solvent being very volatile and flammable. Hence this method is usually avoided.

Because these reagents ($LiAlH_4$ and $NaBH_4$) are nucleophilic, needing a $\delta+$ carbon to react with, they do not reduce C=C double bonds, in contrast to catalytic hydrogenation.

4. Hydroxyethanal can be reduced to ethane-1,2-diol, $(CH_2OH)_2$, as shown.

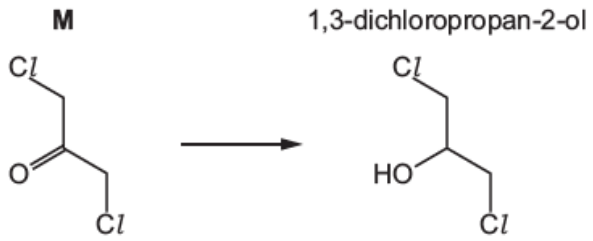


(i) Write an equation for the reduction of hydroxyethanal to $(CH_2OH)_2$.
Use [H] to represent an atom of hydrogen from the reducing agent. [1]

(ii) Identify a reagent for this reduction reaction. [1]

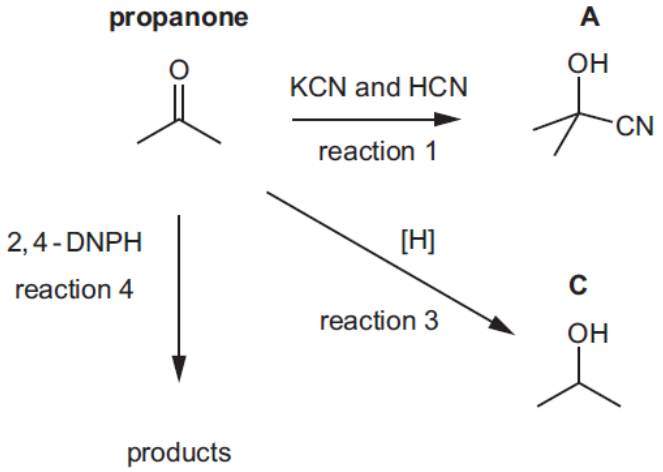
(iii) $(CH_2OH)_2$ also forms, when an alkene **A** reacts with cold, dilute, acidified manganate(VII) ions.
Name **A**. [1]

5. 1,3-dichloropropan-2-ol can be made by reacting M.



(ii) State a suitable reagent for this reaction. [1]

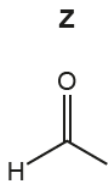
6. Reaction 3 is a reduction reaction.
(i) Construct an equation to represent reaction 3.



Use [H] to represent one atom of hydrogen from the reducing agent.

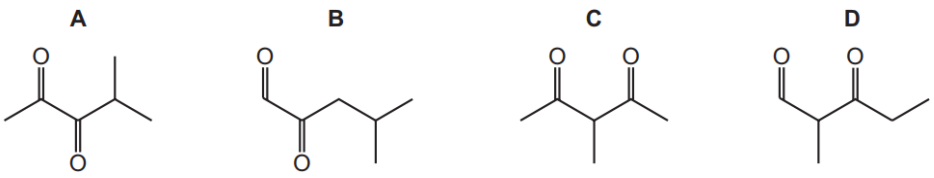
..... [1]

7. Construct an equation for the reaction of Z with $NaBH_4$.



Use [H] to represent an atom of hydrogen from the reducing agent.

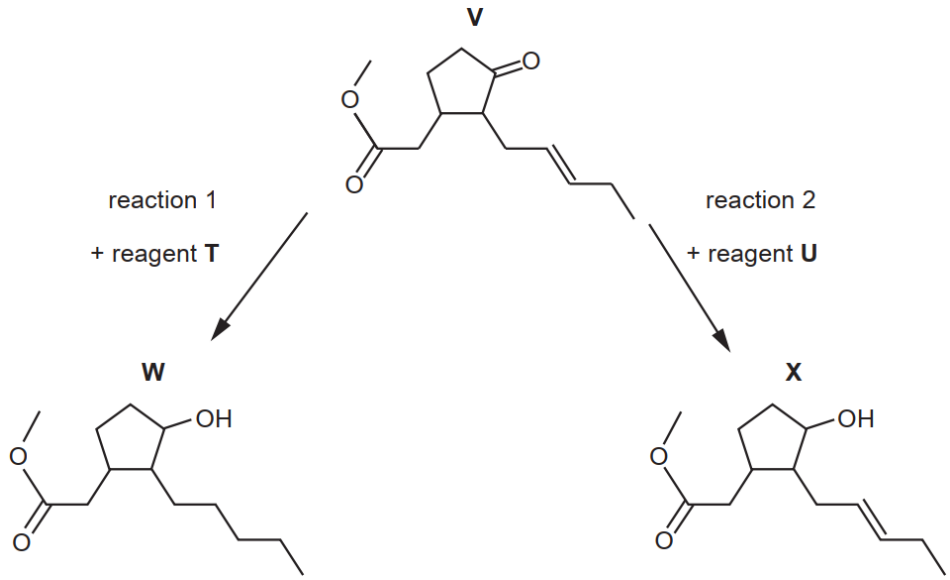
5. Reduction of compound R with $LiAlH_4$ gives the compound 4-methylpentane-2,3-diol.
What could be the identity of compound R?



6. Structural isomerism and stereoisomerism should be considered when answering this question.
Each of the following carbonyl compounds is reacted with $NaBH_4$. The product of each reaction is heated with Al_2O_3 at 600°C, giving either only one isomer or a mixture of isomers.
Which carbonyl compound will produce the most isomers?

A	Butanal
B	Butanone
C	pentan-3-one
D	Propanone

8. Fig. 6.2 shows two reactions involving **V**.



(i) Identify the role of reagent **T** for each functional group that reacts in reaction 1.

.....

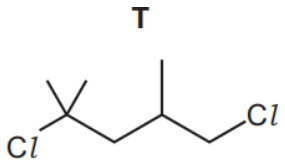
..... [1]

(ii) Suggest the identity of reagent **U** in reaction 2.

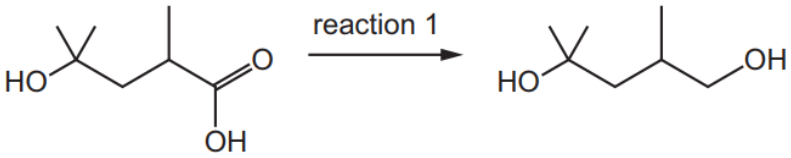
..... [1]

<u>Reduction of a carboxylic acid</u> (using $LiAlH_4$)

9. PCl_3 is used to convert alcohols to chloroalkanes, such as compound T.



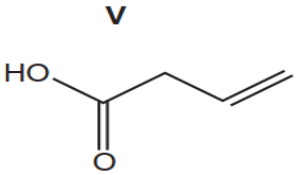
A possible synthesis of **T** is shown.



(i) Identify a reagent that could be used in reaction 1.

..... [1]

10. V is a colourless liquid.



V reacts with an excess of $LiAlH_4$ to form W.

(i) Draw the structure of W. [1]

(ii) Identify the role of $LiAlH_4$ in the reaction with V. [1]

7. A student suggests two uses of $LiAlH_4$.

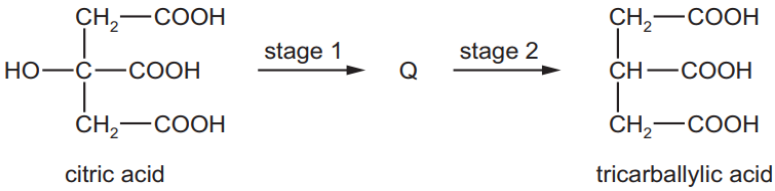
reaction 1 $CH_3—CH=CH_2 \xrightarrow{LiAlH_4} CH_3—CH_2—CH_3$

reaction 2 $CH_3CO_2H \xrightarrow{LiAlH_4} CH_3CH_2OH$

Which reactions would give the product shown?

A both reactions **B** reaction 1 only **C** reaction 2 only **D** neither reaction

8. Citric acid can be converted into tricarballylic acid in two stages. An intermediate, Q, is formed.

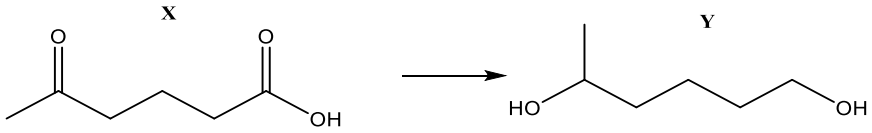


citric acid tricarballylic acid

Which reagents are needed for each stage?

	stage 1	stage 2
A	concentrated H_2SO_4	H_2(g) and Ni
B	concentrated H_2SO_4	$LiAlH_4$
C	$LiAlH_4$	H_2SO_4(aq)
D	NaOH(aq)	H_2(g) and Ni

11. Y is formed from X in a single-step reaction, as shown in Fig. 5.1



The formation of **Y** from **X** requires the addition of a suitable reducing agent.
(i) Construct an equation using molecular formulae and [H] for the reaction in Fig. 5.1. Use [H] to represent one atom of hydrogen from the reducing agent. [1]

(ii) Identify a suitable non-gaseous reducing agent for the formation of **Y** from **X**. [1]

9. Which compound will react with $LiAlH_4$ to form two optical isomers?

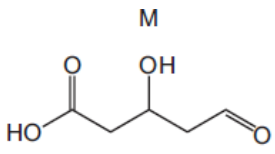
A $CH_3CH_2COCH_3$

B $CH_3CH_2CH_2CHO$

C $CH_3CH_2COCH_2CH_3$

D $CH_3CH(CH_3)CH_2CO_2H$

10. The skeletal formula of M is shown.



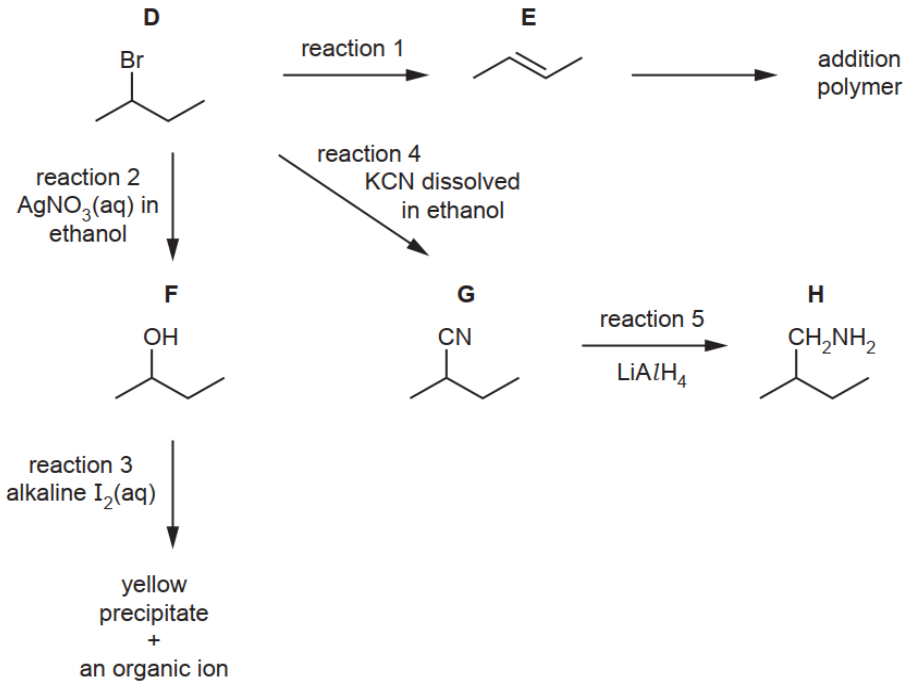
M is reacted with an excess of $LiAlH_4$. Dilute acid is then added.
What is the molecular formula of the final organic product?

A $C_5H_6O_5$ **B** $C_5H_{10}O_4$ **C** $C_5H_{10}O_3$ **D** $C_5H_{12}O_3$

11. Which reaction mixture produces a primary alcohol as the major product?

A propanone with $NaBH_4$
B propene with steam in the presence of H_3PO_4
C butanoic acid with $LiAlH_4$
D ethene with hot concentrated acidified $KMnO_4$

12. Fig. 4.1 shows some reactions of compound **D**, 2-bromobutane.



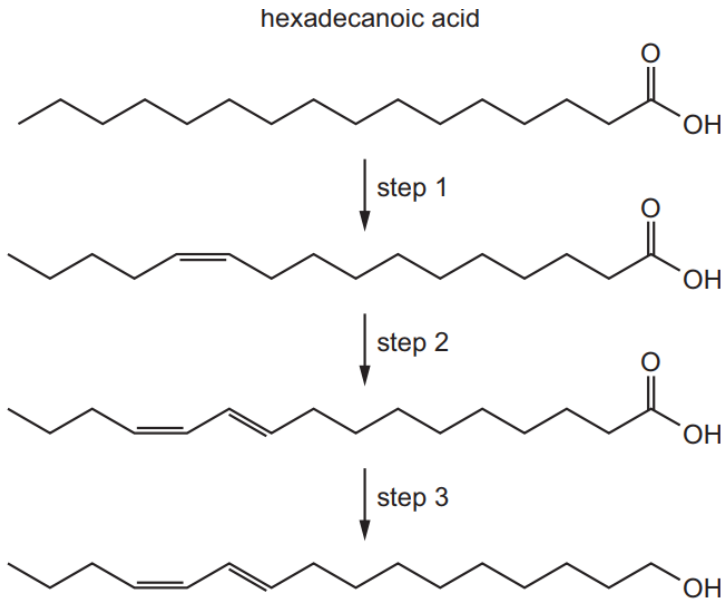
(i) State the reagent and conditions used to form **E** in reaction 1.

(ii) State the type of reaction that occurs in reaction 4.

(iii) Predict what is observed in reaction 2.

(iv) Reaction 5 is similar to the reaction of $LiAlH_4$ with carboxylic acids to form alcohols. Suggest the role of $LiAlH_4$ in reaction 5. [1]

12. Hexadeca-10,12-dien-1-ol is produced by silk moths from hexadecanoic acid in a three-step enzymic process.



Which row contains correct descriptions of the three steps?

	step 1	step 2	step 3
A	elimination	elimination	dehydration
B	elimination	reduction	reduction
C	oxidation	elimination	oxidation
D	oxidation	oxidation	reduction

13. $LiAlH_4$ cannot be used in aqueous solution because it reacts with water to produce LiOH(aq), $H_2(g)$ and a white precipitate which is soluble in excess sodium hydroxide.
Identify the white precipitate.

..... [1]

Hydrolysis of an ester

a. Acid hydrolysis

13. Which compound produces butan-2-ol and ethanoic acid on hydrolysis?

A $CH_3CO_2CH(CH_3)_2$

B $CH_3CO_2CH(CH_3)CH_2CH_3$

C $CH_3CH(CH_3)CO_2CH_2CH_3$

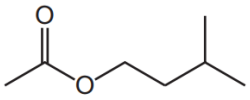
D $CH_3CH_2CO_2CH(CH_3)CH_2CH_3$

14. The structural formula of an ester is $(CH_3)_2CHOCO(CH_2)_2CH_3$.
This ester is boiled with aqueous hydrochloric acid.
Which two products are formed?

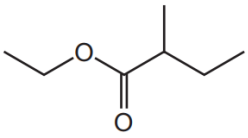
A propan-1-ol and butanoic acid
B propan-2-ol and butanoic acid
C propan-1-ol and propanoic acid
D propan-2-ol and propanoic acid

15. The diagrams show the structures of two esters, X and Y, that are formed in ripening apples.

ester X



ester Y



Which carboxylic acids are formed when these esters are hydrolysed by $H_2SO_4(aq)$?

	ester X	ester Y
A	CH_3COOH	CH_3CH_2COOH
B	CH_3COOH	$CH_3CH_2CH(CH_3)COOH$
C	$CH_3CH(CH_3)CH_2COOH$	CH_3CH_2COOH
D	$CH_3CH(CH_3)CH_2COOH$	$CH_3CH_2CH(CH_3)COOH$

16. Two reactions are shown.

$$(CH_3)_2CHCO_2H \xrightarrow{LiAlH_4} \text{alcohol P}$$

$$CH_3CO_2CH(CH_3)_2 \xrightarrow{\text{hydrolysis}} \text{alcohol Q + acid R}$$

To which classes of alcohol do P and Q belong?

	P	Q
A	primary	primary
B	primary	secondary
C	secondary	primary
D	secondary	secondary

17. Which ester may be hydrolysed to produce two products, one of which may be reduced to the other?

A $CH_3CH_2CO_2CH_3$

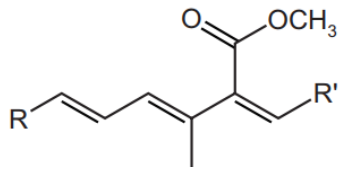
B $CH_3CH(CH_3)CO_2CH_2CH(CH_3)_2$

C $CH_3CH_2CO_2CH(CH_3)_2$

D $(CH_3)_2CHCO_2CH(CH_3)_2$

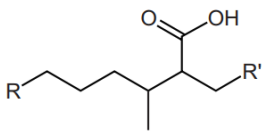
18. Part of the structure of strobilurin is shown. R and R' are inert groups.

strobilurin

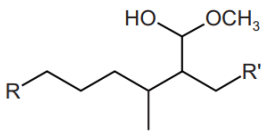


Strobilurin is warmed with aqueous sulfuric acid, producing compound X. Compound X is then treated with hydrogen in the presence of a nickel catalyst, producing compound Y.
What could be the structure of compound Y?

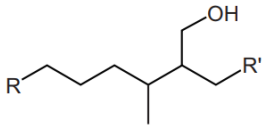
A



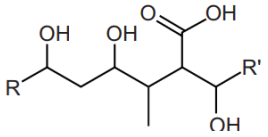
B



C



D



b. Basic hydrolysis

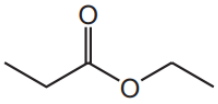
19. The ester ethyl butanoate can be hydrolysed using an excess of dilute sodium hydroxide solution.
Which substance is a product of this reaction?

A	$CH_3CH_2CH_2CO_2Na$
B	CH_3CO_2Na
C	CH_3CH_2ONa
D	H_2O

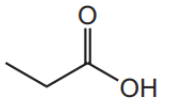
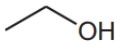
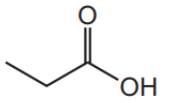
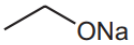
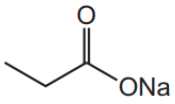
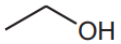
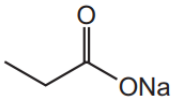
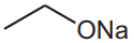
20. The compound cetyl palmitate, $C_{15}H_{31}CO_2C_{16}H_{33}$, is a waxy solid.
Cetyl palmitate is heated under reflux with an excess of aqueous sodium hydroxide.
Which products will be formed?

A $C_{15}H_{31}ONa$ and $C_{16}H_{33}CO_2Na$
B $C_{15}H_{31}CO_2Na$ and $C_{16}H_{33}ONa$
C $C_{15}H_{31}OH$ and $C_{16}H_{33}CO_2Na$
D $C_{15}H_{31}CO_2Na$ and $C_{16}H_{33}OH$

21. The diagram shows an ester. It is heated under reflux with an excess of NaOH(aq).

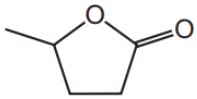


Which row shows the 2 products of the reaction?

	product 1	product 2
A		
B		
C		
D		

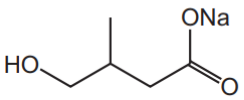
22. The structure of compound X is shown.

X

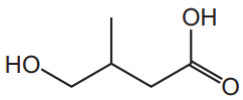


What is produced when X is heated with NaOH(aq)?

A



B



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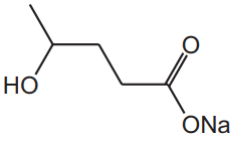

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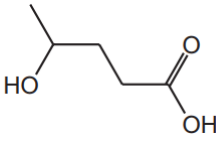
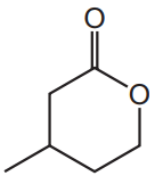


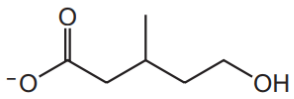
23. Compound X is treated with an excess of dilute aqueous potassium hydroxide.

X



What is the structure of the organic product?

A



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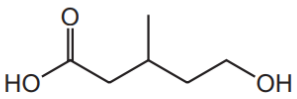

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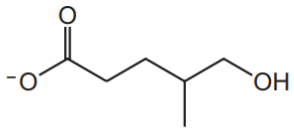

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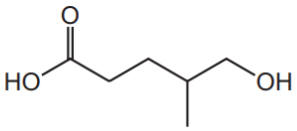
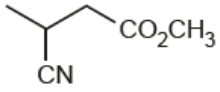


24. The ester $CH_3CH_2CO_2CH_3$ is hydrolysed by boiling with aqueous sodium hydroxide.
Which compound is one of the products?

A ethanol
B propan-1-ol
C sodium methanoate
D sodium propanoate

14. $Ba(OH)_2$ is used to hydrolyse organic compounds.
Fig. 2.2 shows the reaction of **B** with $Ba(OH)_2$, followed by acidification.
Draw the structures of the organic products of the process shown in Fig. 2.2.

B



$Ba(OH)_2$ then HNO_3

organic product 1	+	organic product 2	+ $Ba(NO_3)_2$

25. Which reaction gives butanoic acid as one of its products?
A acid hydrolysis of butyl ethanoate
B alkaline hydrolysis of butyl ethanoate
C acid hydrolysis of ethyl butanoate
D alkaline hydrolysis of ethyl butanoate

26. Esters can be hydrolysed with an aqueous alkali or an aqueous acid to form two products.
The table compares the two methods.
Which row is correct?

	aqueous alkali	aqueous acid
A	complete conversion to a salt and an organic acid	forms an equilibrium mixture with an organic acid and an alcohol
B	forms an equilibrium mixture with a salt and an organic acid	complete conversion to a salt and an alcohol
C	complete conversion to a salt and an alcohol	forms an equilibrium mixture with an organic acid and an alcohol
D	complete conversion to a salt and an alcohol	complete conversion to an organic acid and an alcohol

27. A sample of propyl ethanoate is hydrolysed by heating under reflux with aqueous NaOH. The two organic products of the hydrolysis are separated, purified and weighed.
Out of the total mass of products obtained, what is the percentage by mass of each product?

A 32.4% and 67.6%
B 38.3% and 61.7%
C 42.3% and 57.7%
D 50.0% and 50.0%

28. $C_2H_5COOCH_3$ is reacted with aqueous acid.
The products from this reaction are reacted with $LiAlH_4$ to form two molecules Y and Z.
What are the identities of molecules Y and Z?

A both molecules are C_2H_5OH
B CH_3OH and $CH_3CHOHCH_3$
C CH_3OH and C_2H_5OH
D CH_3OH and $C_2H_5CH_2OH$

Properties

Reaction with oxygen

29. 17.6 g of pentan-1-ol is completely combusted.
Which volume of gaseous products is formed when measured at s.t.p.?

A 22.4 dm^3 B 24.0 dm^3 C 49.3 dm^3 D 52.8 dm^3

30. In an experiment, 0.100mol of propan-1-ol is burnt completely in 12.0dm^3 of oxygen, measured at room conditions.
What is the final volume of gas, measured at room conditions?

A 7.20dm^3 B 8.40dm^3 C 16.80dm^3 D 18.00dm^3

31. How many moles of oxygen gas are needed for the complete combustion of mol of $(CH_3)_3COH$?

A 6 **B** 6.5 **C** 12 **D** 13

32. A mixture of ethanol and methanol is burned in oxygen to produce 35 cm^3 of CO_2 and 55 cm^3 of H_2O.
Complete combustion occurs, and the volumes of both products are measured at 101 kPa and 120 ^{0} C.
What is the molar ratio of ethanol: methanol in the mixture?

A 1 : 3 B 2 : 3 C 3 : 2 D 3 : 1

Substitution (studied in halogenoalkanes)

to halogenoalkanes, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PC*l*$_3$ and heat; or with PCl_5; or with SOC*l*$_2$

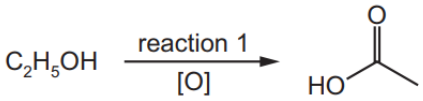
Reaction with Na

33. When ethanol reacts with sodium metal, ethoxide ions, $CH_3CH_2O^-$, are produced.
When water reacts with sodium metal, OH^- ions are produced.
Which statement about these reactions and the ethoxide ion is correct?

A At the same temperature, the rate of reaction between sodium and ethanol is greater than that between sodium and water.
B $CH_3CH_2O^-$, is a stronger base than OH^- due to the electron-donating effect of the ethyl group.
C The negative charge on the oxygen in an ethoxide ion is delocalised.
D It is easier to deprotonate ethanol as it is more acidic than water.

Oxidation

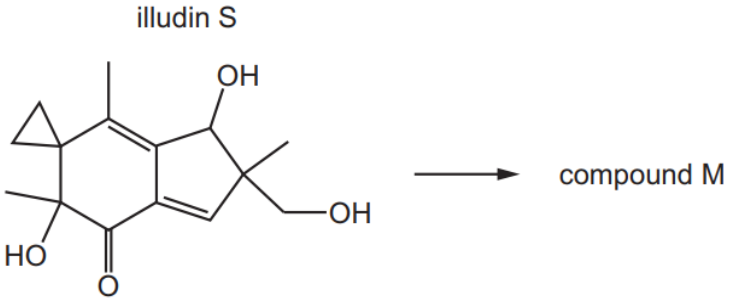
15. Reaction 1 is an oxidation reaction.



(i) Give the reagent(s) and conditions required for reaction 1. [2]

(i) Construct an equation to represent reaction 1.
Use [O] to represent an oxygen atom from the oxidising agent in this reaction. [1]

34. When illudin S is heated under reflux with an excess of acidified potassium dichromate**(VI)**, compound M is formed.

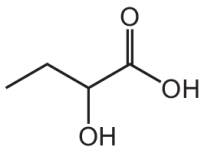


What is the molecular formula of compound M?

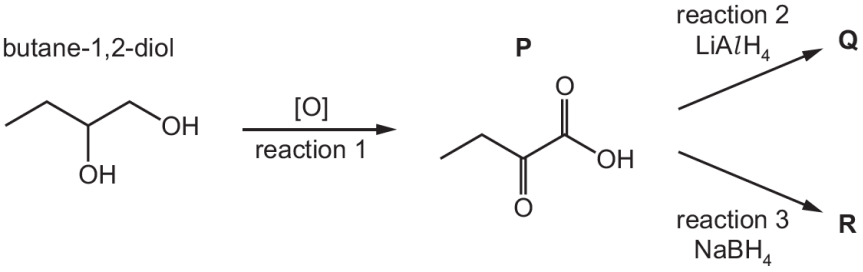
A $C_{15}H_{16}O_4$ **B** $C_{15}H_{16}O_5$ **C** $C_{15}H_{18}O_4$ **D** $C_{15}H_{18}O_5$

16. Two students try to prepare 2-hydroxybutanoic acid in the laboratory.

2-hydroxybutanoic acid



Both students oxidise butane-1,2-diol to form P in reaction 1.
One student then reduces P using LiAl H_4. Q is formed.
The other student reduces P using $NaBH_4$. R is formed.



i) State the reagents and conditions required for reaction 1. [2]

ii) Only one of the students successfully prepares 2-hydroxybutanoic acid.
Identify which of **Q** or **R** is 2-hydroxybutanoic acid and explain the difference between reactions 2 and 3. [2]

35. Primary alcohols can be oxidised to aldehydes using either acidified potassium dichromate(VI) or acidified potassium manganate(VII). The reaction mixtures change colour as the oxidising agent is reduced.
What are the colour changes seen?

	acidified potassium dichromate(VI)		acidified potassium manganate(VII)	
	before	after	before	after
A	green	orange	purple	colourless
B	orange	green	colourless	purple
C	orange	green	purple	colourless
D	purple	colourless	orange	green

36. Which compound produces a ketone when refluxed with an acidified solution of potassium dichromate(VI)?

A pentan-1-ol

B 2-methylbutan-1-ol

C 2-methylbutan-2-ol

D 3-methylbutan-2-ol

37. A sample of 2.30 g of ethanol is mixed with an excess of aqueous acidified potassium dichromate(**VI**). The reaction mixture is boiled under reflux for one hour. The required organic product is then collected by distillation. The yield of the product is 60.0%.
Which mass of product is collected?

A 1.32 g B 1.38 g C 1.80 g D 3.00 g

38. Crotyl alcohol, $CH_3CH=CHCH_2OH$, is a colourless liquid which is used as a solvent.
Crotyl alcohol will react separately with Br_2, $K_2Cr_2O_7/H^+$, conc. $KMnO_4/H^+$ and PCl_5 under suitable conditions.
Which row is correct?

	reactant	conditions	main product
A	Br_2	room temperature	$CH_3CH=CHCH_2Br$
B	$K_2Cr_2O_7$ / H^+	heat under reflux	$CH_3CH=CHCHO$
C	conc. $KMnO_4$ / H^+	heat under reflux	$CH_3CH=CHCO_2H$
D	PCl_5	room temperature	$CH_3CH=CHCH_2Cl$

39. Compound P is heated under reflux with an excess of acidified potassium dichromate(**VI**) to form compound Q.
Compound Q has a **lower** boiling point than compound P.
What could be compound P?

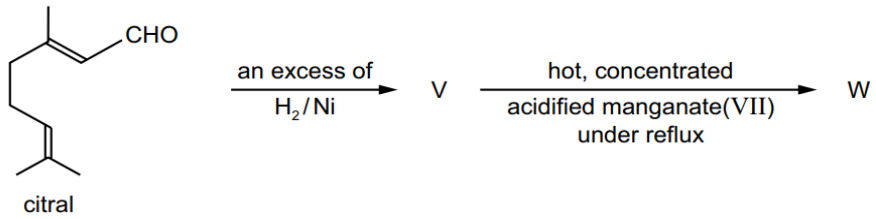
A 2-methylbutan-1-ol

B 2-methylbutan-2-ol

C pentan-1-ol

D pentan-2-ol

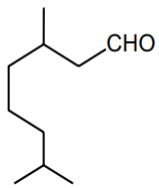
40. Citral is found in lemongrass oil. It can react to give compound W.



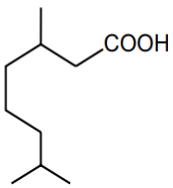
citral

What could compound W be?

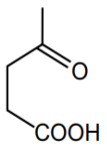
A



B

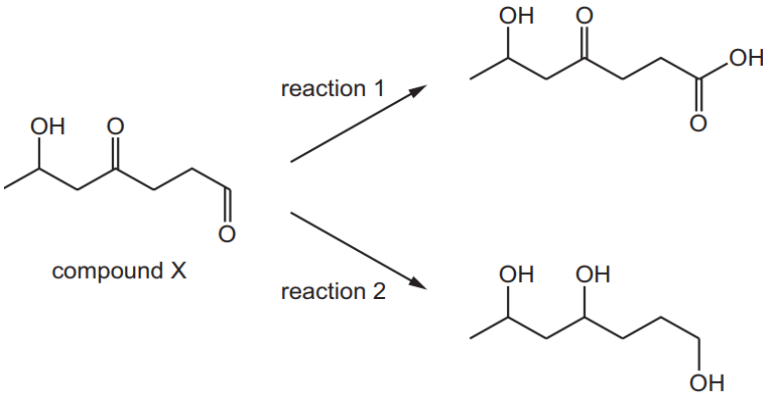


C



D

41. Two samples of compound X were treated separately with different reagents which were added in excess.
The products of these two reactions are shown.



Which reagents could be used for reaction 1 and reaction 2?

	reaction 2	reaction 1
A	Na	hot acidified sodium dichromate VI
B	$NaBH_4$	hot acidified sodium dichromate VI
C	Na	Tollens'reagent followed by HC/ (aq)
D	$NaBH_4$	Tollens'reagent followed by HC/ (aq)

42. $HOCH_2CHO$ is heated under reflux with an excess of acidified $K_2Cr_2O_7$ until there is no further reaction.
What is the final product of this reaction?

A HOOCCHO
B $HOCH_2COOH$
C HOOCCOOH
D HOOCCH2COOH

43. In this question you can assume that $_1H$ and $_3H$ have the same chemical properties.
A sample of ethanal contains only one isotope of hydrogen, $_1H$.
It is reduced to compound Z, C_2H_6O, in a nucleophilic addition reaction using $NaBH_4$. All the hydrogen atoms in the $NaBH_4$ are the $_3H$ isotope.

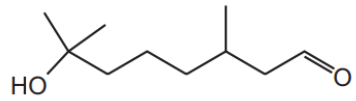
$$CH_3CHO \xrightarrow{NaBH_4} \underset{\text{compound Z}}{C_2H_6O}$$

Compound Z is then oxidised back to ethanal and water.
$C_2H_6O + [O] \rightarrow CH_3CHO + H_2O$
Which statement about the final mixture of products is correct?

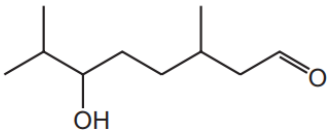
A Both ethanal and water contain $_3H$ atoms.
B Ethanal is the only product containing $_3H$ atoms.
C Neither ethanal nor water contain $_3H$ atoms.
D Water is the only product containing $_3H$ atoms.

17. Separate samples of **Q** and **R** are added to separate test-tubes containing acidified $K_2Cr_2O_7$(aq) and heated.

Q



R



Predict the observations for each test-tube. Explain your answer in terms of the functional groups present in **Q** and **R**. [3]

18. Hydroxyethanal is converted to ethanedioic acid, $(CO_2H)_2$, when it reacts with excess acidified dichromate(VI) ions, $Cr_2O_7^{2-}$.

(i) State the role of acidified $Cr_2O_7^{2-}$ in this reaction. [1]

(ii) State and explain any other necessary conditions for this reaction to be successful. [2]

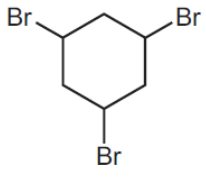
44. Compound R can be formed from 1-bromopropane using a nucleophilic substitution reaction followed by an oxidation reaction.
What is the identity of R?

A propanoic acid
B propanone
C propylamine
D propyl ethanoate

45. When an organic compound, Q, is treated with phosphorus pentachloride, fumes of hydrogen chloride are evolved.
When Q is warmed with acidified aqueous potassium dichromate(**VI**), the solution turns green.
What is Q?

A CH_3CH_2CHO
B $CH_3CH_2CO_2H$
C $CH_3CH(OH)CH_3$
D $(CH_3)_3COH$

46. The diagram shows the structure of compound X.



X

X undergoes hydrolysis to form product Y in which all of the bromine atoms are replaced by hydroxyl groups. Product Z is formed by oxidation of Y.
Two suggestions are listed.
1 Y is a secondary alcohol.
2 Z is a ketone.
Which suggestions are correct?

A both 1 and 2
B 1 only
C 2 only
D neither 1 nor 2

47. Write an equation for the oxidation of lactic acid to pyruvic acid, the third step of Fig. 4.4.

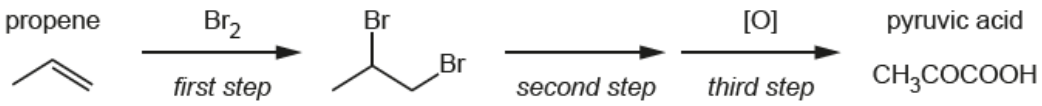


Fig. 4.3

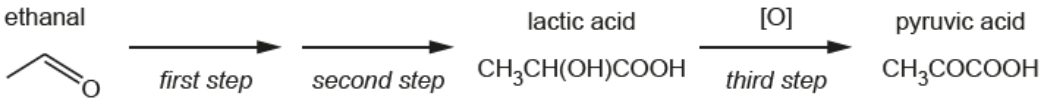


Fig. 4.4

(i) Use [O] to represent one atom of oxygen from an oxidising agent.

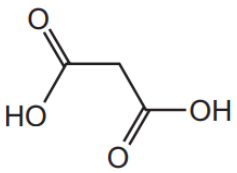
CH3CH(OH)COOH + ... [1]

(ii) Complete the following table to give details of the reagents and conditions used in each of the two syntheses shown in Fig. 4.3 and Fig. 4.4. [4]

		synthesis from propene (shown in Fig. 4.3)	synthesis from ethanal (shown in Fig. 4.4)
reagents and conditions used	*first step*	Br_2	
	second step		
	third step		

48. Hydroxyethanal, $HOCH_2CHO$, is heated under reflux with an excess of acidified $K_2Cr_2O_7$ until no further oxidation takes place.
What is the skeletal formula of the organic product?

A



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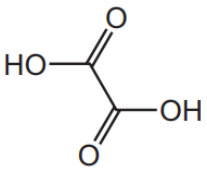

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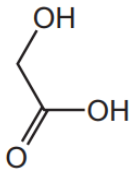

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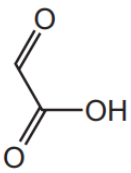
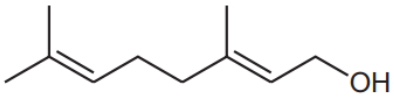


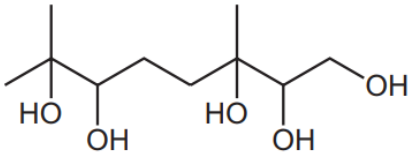
49. A molecule of geraniol is shown.

geraniol

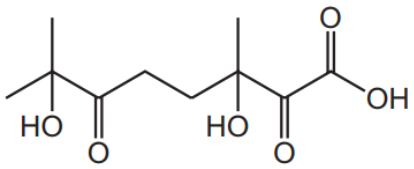


What is formed when geraniol is reacted with an excess of cold, dilute acidified MnO_4^-?

A



B



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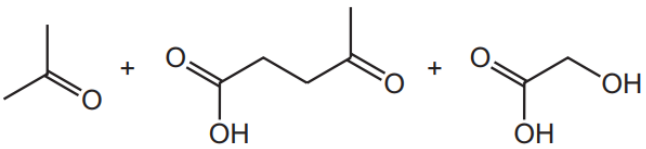
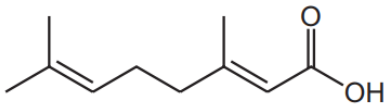


D



50. When an organic compound is oxidised, any oxygen atom gained by the organic molecule is considered to be from a water molecule also producing $2H^+ + 2e^-$. Any hydrogen atom lost may be considered to be lost as $H^+ + e^-$.
These changes can be represented by the following two equations.

$H_2O \rightarrow [O] + 2H^+ + 2e^-$
$[H] \rightarrow H^+ + e^-$

Compound X is oxidised by heating under reflux with hot, acidified potassium dichromate(VI) for one hour.
The half-equation for the reduction reaction is shown.
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Under these conditions, one mole of potassium dichromate(VI) oxidises three moles of X.
What could X be?

A propanal **B** propan-1-ol **C** propan-1,2-diol **D** propan-1,3-diol

51. The compound 'leaf alcohol' is partly responsible for the smell of new-mown grass.

leaf alcohol
$CH_3CH_2CH=CHCH_2CH_2OH$

What will be formed when 'leaf alcohol' is oxidised using an excess of hot acidified $K_2Cr_2O_7(aq)$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CO_2H$

B $CH_3CH_2COCOCH_2CO_2H$

C $CH_3CH_2CH=CHCH_2CO_2H$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

52. Which alcohol gives only one possible oxidation product when warmed with dilute acidified potassium dichromate(VI)?

A butan-1-ol

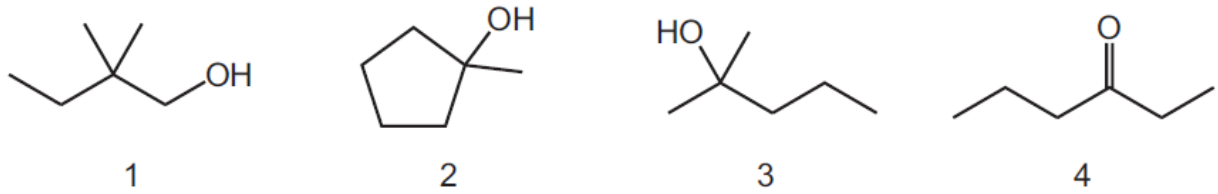
B butan-2-ol

C 2-methylpropan-1-ol

D 2-methylpropan-2-ol

53. Some properties of compound X are listed.
- 1.0 mol X reacts with exactly 8.5 mol oxygen when completely combusted.
- X does not react when heated with acidified $KMnO_4$.

What are the possible identities of X?



A 1 and 3 B 2 and 4 C 3 only D 4 only

19. Fig. 4.1 shows how propane, C_3H8, can be converted to propanoic acid, CH_3CH_2COOH.

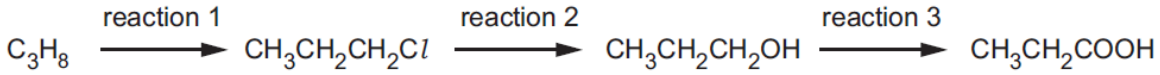


Fig. 4.1

(b) State the reagent and solvent required for reaction 2.

..... [1]

(c) Reaction 3 takes place when $CH_3CH_2CH_2OH$ is heated under reflux with acidified potassium dichromate(VI) solution.
(i) State the colour change that takes place in the reaction mixture.

..... [1]
(ii) Construct an equation to represent reaction 3. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]

Dehydration (studied in the preparation of alkenes)

54. Which row describes the type of reaction that occurs when propan-1-ol reacts to form the named carbon-containing product?

	carbon-containing product	type of reaction
A	1-chloropropane	addition to propan-1-ol
B	carbon monoxide	complete combustion of propan-1-ol
C	propene	dehydration of propan-1-ol
D	propanal	reduction of propan-1-ol

55. Two reactions are shown. Only one product is identified in each reaction.
ethanol + acidified $Cr_2O_7^{2-} \rightarrow$ ethanal
ethanol + sodium $\rightarrow$ sodium ethoxide
Which statement about these reactions is correct?
A The formations of both ethanal and sodium ethoxide are redox reactions.
B The formations of both ethanal and sodium ethoxide result in colour changes.
C The formation of ethanal is catalysed by potassium dichromate.
D The formation of sodium ethoxide is a dehydration reaction.

56. Two reactions are shown. Only one product is identified in each reaction.
ethanol + acidified $Cr_2O_7^{2-} \rightarrow$ ethanal
ethanol + sodium $\rightarrow$ sodium ethoxide
Which statement about these reactions is correct?

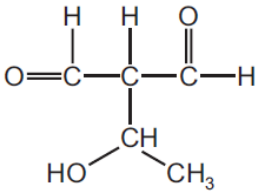
A The formations of both ethanal and sodium ethoxide are redox reactions.
B The formations of both ethanal and sodium ethoxide result in colour changes.
C The formation of ethanal is catalysed by potassium dichromate.
D The formation of sodium ethoxide is a dehydration reaction.

57. The balanced equation for the reaction of X with an excess of acidified $K_2Cr_2O_7$ is shown.

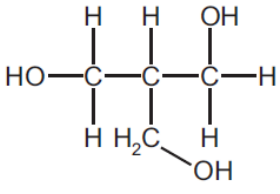
$X + 3\ [O] \rightarrow Y + H_2O$

Compound Y is the only organic product of the reaction.
Which compound is X?

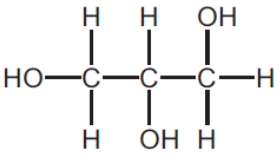
A



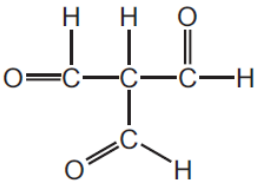
B



C

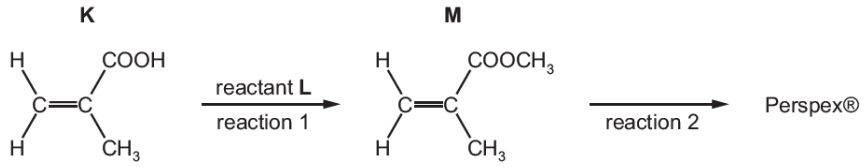


D



Formation of ester (esterification)

20. **K** is used to make the addition polymer Perspex®. A synthesis of Perspex® is shown in the following figure.



(i) Identify **L**. State the conditions required for reaction 1.

L= .....

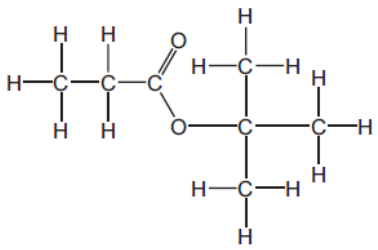
conditions =..... [2]

(ii) Draw **one** repeat unit of the addition polymer Perspex®. [2]

58. The structural formula of compound P is $CH_3CH_2COOCH_2CH_3$.
P can be formed by reacting together two organic compounds in the presence of a suitable catalyst.
Which pair of compounds could react together to produce P?

A ethanoic acid and propanoic acid
B ethanoic acid and propan-1-ol
C ethanol and propanoic acid
D ethanol and propan-1-ol

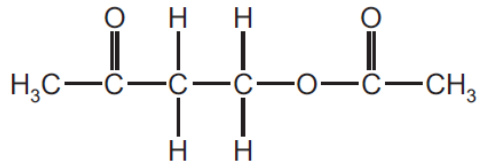
59. An ester is shown.



Which two compounds react to form this ester?

A 2-methylpropan-1-ol and propanoic acid
B 2-methylpropan-2-ol and propanoic acid
C propan-1-ol and 2-methylpropanoic acid
D 2-methylpropan-2-ol and ethanoic acid

60. Compound X reacts with ethanoic acid in the presence of an H^+ catalyst to produce the compound shown.

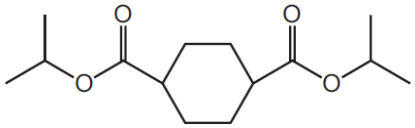


What is the molecular formula of compound X?

A C_2H_4O **B** $C_2H_6O_2$ **C** C_4H_8O **D** $C_4H_8O_2$

61. An alcohol, X, reacts with a dicarboxylic acid, Y, to form a double ester, Z.
The diagram shows the structure of the ester.

Z



Which row about the reactants forming ester Z is correct?

	the class of alcohol X	the shape of the ring in Y
A	secondary	non-planar
B	secondary	planar
C	tertiary	non-planar
D	tertiary	planar

62. A carboxylic acid, P, has no chain isomers. It reacts with an alcohol, Q, that has only one positional isomer.
What could be the ester formed from a reaction between P and Q?

A butyl propanoate
B ethyl butanoate
C pentyl ethanoate
D propyl pentanoate

63. Q is a compound with the molecular formula $C_4H_{10}O$. Q can be oxidised with acidified potassium dichromate(VI). Q cannot be made by reducing a carboxylic acid with $LiAlH_4$.
What is the structure of Q?

A $CH_3CH(OH)CH_2CH_3$
B $CH_3CH_2CH_2CH_2OH$
C $(CH_3)_3COH$
D $(CH_3)_2CHCH_2OH$

21. A sample of 2.30g of ethanol is mixed with an excess of aqueous acidified potassium dichromate(VI). The reaction mixture is then boiled under reflux for one hour. The required organic product is then collected by distillation. The yield of product is 60.0%.
Which mass of product is collected?

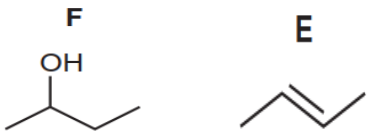
A 1.32g B 1.38g C 1.80g D 3.00g

22. CH_3CH_2COOH can also be formed from propan-1-ol and potassium dichromate(**VI**).
State the conditions required. [1]

64. Which reagent will react with pentan-3-ol to give a mixture of stereoisomers?

A acidified potassium dichromate
B concentrated sulfuric acid
C ethanoic acid in the presence of a little concentrated H_2SO_4
D hydrogen chloride

65. **E** also forms when **F** is heated strongly in the presence of an Al_2O_3 catalyst.



Write an equation for this reaction. [1]

66. X, Y and Z are three isomeric alcohols.

X $CH_3CH_2CH_2CH_2CH_2OH$
Y $CH_3CH_2CH(OH)CH_2CH_3$
Z $(CH_3)_2C(OH)CH_2CH_3$

Separate samples of each alcohol are warmed with a mild oxidising agent and the results noted.
One of these alcohols, when dehydrated, will give a pair of cis-trans isomers with molecular formula C_5H_{10}.
Which row is correct?

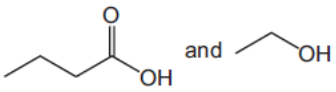
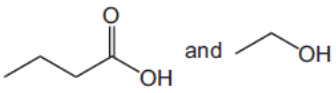
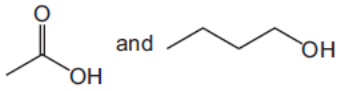
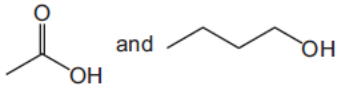
	gives cis/trans isomers	reacts with mild oxidising reagents
A	Y only	X, Y and Z
B	Z only	X, Y and Z
C	Y only	X and Y only
D	Z only	X and Y only

67. Which two-step process converts cyclohexanol into cyclohexane-1,2-diol?

cyclohexanol cyclohexane-1,2-diol

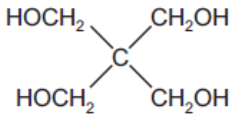
	step 1	step 2
A	heat strongly with Al_2O_3	add cold dilute $KMnO_4$ and H_2SO_4
B	heat strongly with Al_2O_3	heat with steam and H_2SO_4
C	reflux with ethanolic NaOH	add cold dilute $KMnO_4$ and H_2SO_4
D	reflux with ethanolic NaOH	heat with steam and H_2SO_4

68. Ethyl butanoate is a flavouring, with a fruity flavour.
Which row is correct?

	alcohol and acid that react to form ethyl butanoate	the mass of water formed when 2.32 g of ester is formed
A		0.36 g
B		0.40 g
C		0.36 g
D		0.40 g

69. Pentaerythritol is used as an intermediate in the manufacture of paint.

pentaerythritol



Which statement is correct?

A Pentaerythritol can be dehydrated by concentrated sulfuric acid to form an alkene.
B The empirical formula and molecular formula of pentaerythritol are different.
C Pentaerythritol does not react with acidified potassium manganate(VII).
D One mole of pentaerythritol gives two moles of hydrogen gas on reaction with an excess of sodium.

23. Lactones are cyclic esters. Under suitable conditions, lactones form from molecules that have both an alcohol and a carboxylic acid functional group.
Equation **1** shows an example of the formation of a lactone.

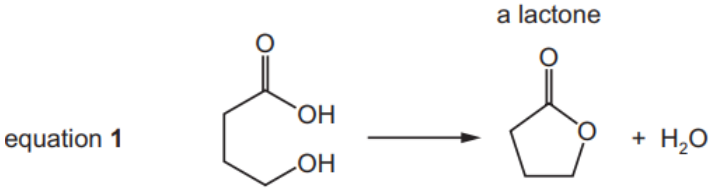
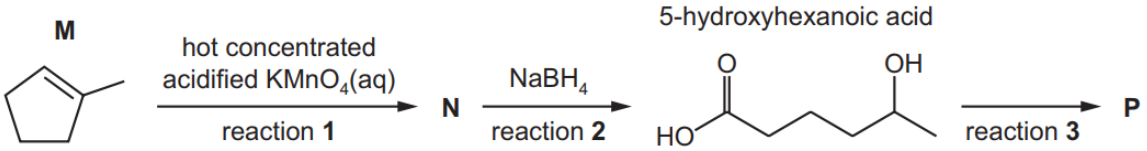


Fig. 5.1 shows the synthesis of lactone **P** from compound **M**.



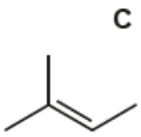
(a) (i) M reacts with hot concentrated acidified $KMnO_4(aq)$ to form **N**, $C_6H_{10}O_3$, in reaction **1**. Draw the structure of **N**. [1]

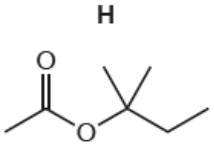
(ii) N **is reduced by $NaBH_4$ to form 5-hydroxyhexanoic acid in reaction** 2**.**
Construct an equation for reaction 2 **using molecular formulae.**
In the equation, use [H] to represent one atom of hydrogen from the reducing agent. **[1]**

(iii) Reaction **2** is a nucleophilic addition.
Suggest why reaction **2** creates a mixture of two organic compounds.

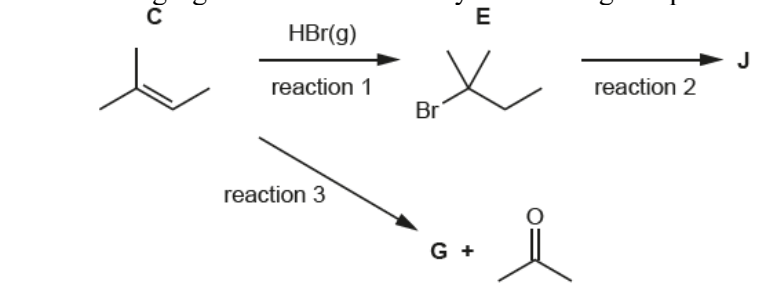
(iv) Draw lactone **P**, the product of reaction **3**.

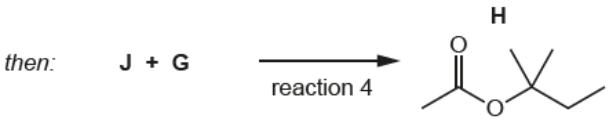
24. C can be used to form H.





One possible synthesis of **H** is shown in Fig. 4.5. Different portions of **C** are used in reactions 1 and 3. Some of the products are then combined to produce **H**.
The following figure does not show any of the inorganic products of the reactions.



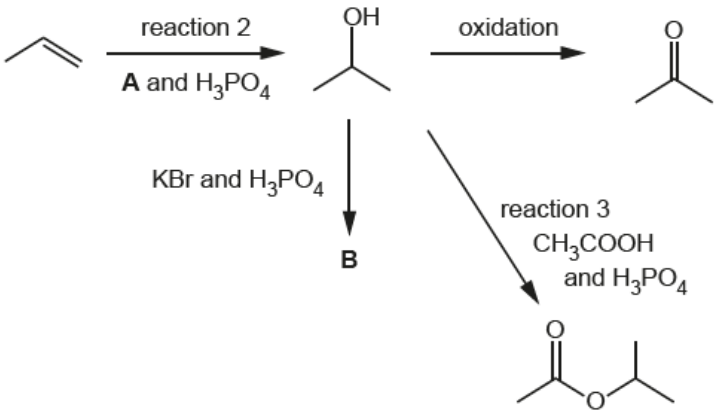


Complete the following table with the reagents and conditions required for each of the reactions shown in Fig. 4.5.

	reagent and conditions
reaction 1 **C** → **E**	HBr(g)
reaction 2 **E** → **J**	
reaction 3 **C** → **G** + 	
reaction 4 **J** + **G** → **H**	

[3]

25. The following figure shows a reaction scheme that involves H_3PO_4 in several reactions.

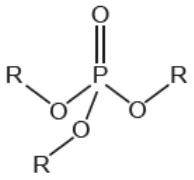


(i) Identify **A**, which reacts with propene in the presence of H_3PO_4 in reaction 2. [1]

(ii) Draw the structure of B. [1]

(iii) Name the type of reaction that occurs in reaction 3. [1]

26. H_3PO_4 also reacts with alcohols to form organophosphates.
Organophosphates are compounds similar to esters. They have the general structure shown in Fig. 3.2.



R = alkyl group

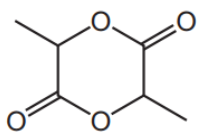
Fig. 3.2

Complete the equation to suggest the products of the reaction of H_3PO_4 with methanol, CH_3OH.

$H_3PO_4 + 3CH_3OH \rightarrow$ ..... [1]

70. Lactide is an intermediate in the manufacture of a synthetic fibre.

lactide

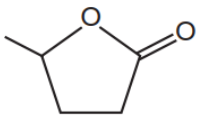


Which compound, on heating with an acid catalyst, can produce lactide?

A hydroxyethanoic acid
B 2-hydroxybutanoic acid
C 2-hydroxypropanoic acid
D 3-hydroxypropanoic acid

27. **D** reacts in the presence of a sulfuric acid catalyst to form **E** and water. The structure of **E** is shown below.

E

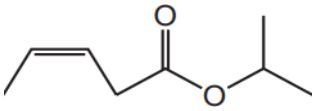


(i) Name the functional group present in **E**. [1]

(ii) Identify the type of reaction that occurs when **D** reacts to form **E**. [1]

(iii) Draw the structure of **D** in the box. [1]

71. An unsaturated carboxylic acid reacts with alcohol X to form an ester.
The structure of the ester is shown.

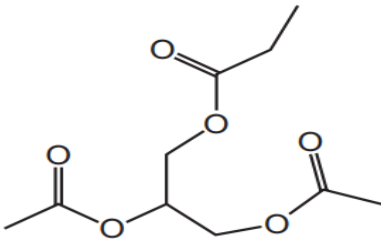


Which geometrical isomer is shown in this ester and to which class of alcohol does X belong?

	geometrical isomer	class of alcohol X
A	*cis*	secondary
B	*cis*	tertiary
C	*trans*	secondary
D	*trans*	tertiary

72. Two compounds, X and Y, are mixed and a little concentrated H_2SO_4 is added.
Ester Z is found in the resulting mixture of products.

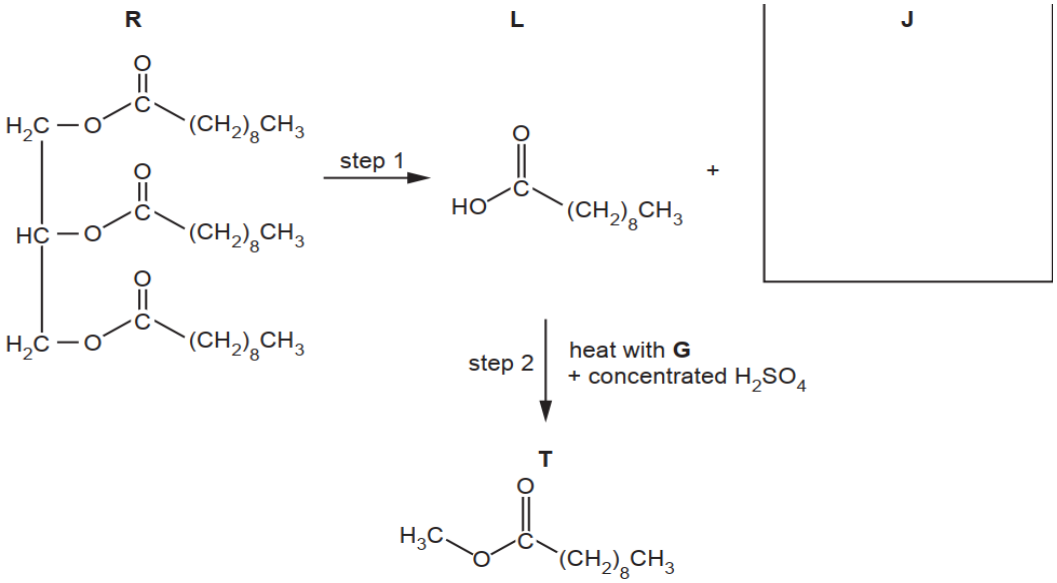
ester Z



Which two compounds could be X and Y?

	X	Y
A	CH_3CH_2OH	$CH(CO_2H)_3$
B	CH_3CH_2OH	$CH_3CO_2CH_2CH(OH)CH_2OCOCH_2CH_3$
C	CH_3CO_2H	$CH_3CH_2CO_2CH_2CH(OH)CH_2OH$
D	CH_3CO_2H	$CH_2(OH)CH(OH)CH_2(OH)$

28. Biodiesel **T** is a fuel made from vegetable oil R. Fig. 5.1 shows the production of **T** from **R** in a two-step process.



(i) In step 1 all three ester groups in **R** react. Suggest a suitable reagent and conditions for step 1. [1]

(ii) Draw the structural formula of **J** in the box in the above figure. [1]

(iii) Name the type of reaction that occurs in step 2. [1]

(iv) Name the organic reagent **G** used in step 2. [1]

(v) L is called decanoic acid. Use systematic nomenclature to deduce the name of **T**. [1]

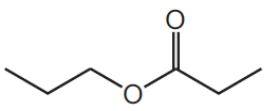
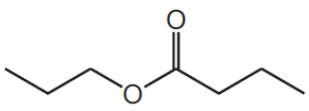
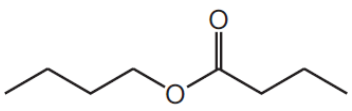
73. How many esters with the molecular formula $C_5H_{10}O_2$ can be made by reacting a primary alcohol with a carboxylic acid?

A 4 **B** 5 **C** 6 **D** 8

74. When an organic acid reacts with an alcohol, a reversible reaction takes place producing an ester and water.
0.40 mol of an organic acid and 0.30 mol of an alcohol are mixed and allowed to stand at 25 °C until equilibrium is reached.
At equilibrium, 0.20 mol of ester is produced.
What is the value of the equilibrium constant, *K*c, under the conditions used?

A 0.33 **B** 0.50 **C** 2.0 **D** 10

75. Compound Z has the molecular formula $C_4H_8O_2$.
Compound Z reacts with propan-1-ol in the presence of concentrated H_2SO_4.
The diagram shows the skeletal formulae of three compounds, S, T and U.

S  T  U 

What are the possible skeletal formulae of the products of the reaction between compound Z and propan-1-ol?

A S and T **B** U only **C** S and U **D** T only

Iodoform test

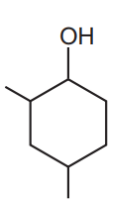
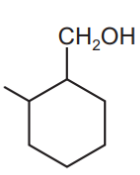
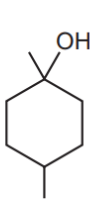
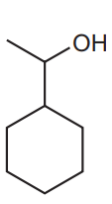
76. Which alcohol reacts with alkaline $\mathbf{I}_2$(aq) to produce ethanoate ions?

A ethanol B methylpropan-2-ol C propan-2-ol D butan-2-ol

77. Compound G gives a pale yellow precipitate with alkaline I_2(aq).
What could be compound G?

A pentan-1-ol B pentan-2-ol C pentan-3-ol D 2-methylpentan-2-ol

78. Alcohol X gives a yellow precipitate with alkaline I_2(aq).
What is the structure of X?

A 
B 
C 
D 

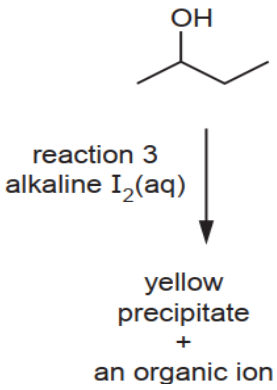
79. Which alcohol reacts with alkaline $I_2(aq)$ to produce ethanoate ions?

A ethanol B methylpropan-2-ol C propan-2-ol D butan-2-ol

80. Four different alcohols are treated with alkaline $I_2(aq)$.
Which row is correct?

	name of alcohol	formulae of products
A	butan-2-ol	CH_3COO^- and CH_3CI_3
B	propan-1-ol	CH_3COO^- and CHI_3
C	propan-2-ol	CH_3COO^- and CHI_3
D	butan-2-ol	$CH_3CH_2COO^-$ and CH_3I

29. Identify the yellow precipitate and the organic ion formed in reaction 3. [2]



30. Two bottles labelled **Q** and **M** each contain a straight-chain halogenoalkane with molecular formula C_4H_9X, where **X** represents Cl, Br or **I**.
A sample from each bottle is added to separate samples of equal amounts of aqueous silver nitrate in ethanol. In each reaction, the same organic product, **T**, and a precipitate are made, as shown in Fig. 4.2.

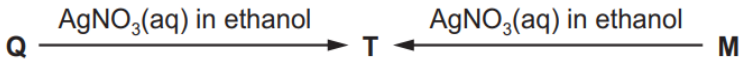


Table 4.1 describes the colour of each of the precipitates made.

Table 4.1

halogenoalkane added to $AgNO_3(aq)$ in ethanol	colour of precipitate
Q	white
M	yellow

(i) Identify the functional group present in **T** and name the type of reaction that occurs using the information in Fig. 4.2 and Table 4.1. [2]

(ii) Construct an ionic equation to describe the formation of the yellow precipitate produced when **M** reacts with $AgNO_3(aq)$ in ethanol. [1]

(iii) Describe which reagent, **Q** or **M**, will produce a precipitate more quickly when each is added to $AgNO_3(aq)$ in ethanol. Explain your answer. [1]

(iv) When pure **T** is added to alkaline $I_2(aq)$, a yellow precipitate and an anion, **L**, are made. Identify the anion **L**. [1]

(v) Deduce the structure of the straight-chain halogenoalkane **M**. [2]

81. Compound Y reacts with alkaline $I_2(aq)$. When the products of this reaction are acidified, a dicarboxylic acid is produced. The formula of the dicarboxylic acid is HOOC–R–COOH where R consists of one or more CH_2 groups.
Which compound is Y?

A pentan-1,4-diol **B** pentan-1,5-diol **C** pentan-2,3-diol **D** pentan-2,4-diol

31. Fig. 4.1 shows a possible synthesis of propene, C_3H6.

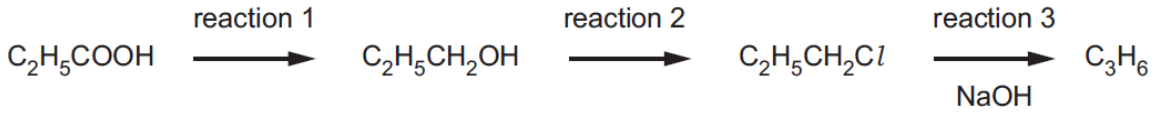


Fig. 4.1

(a) (i) Identify the type of reaction that occurs in reaction 1.

..... [1]

(ii) Suggest a suitable reagent for reaction 2.

..... [1]

(iii) Reaction 3 is an elimination reaction.
Write an equation for this reaction and identify the solvent and conditions used.

equation .....

solvent and conditions ..... [2]

(iv) $C_2H5CH2OH$ can be directly converted to C3H6.
Suggest the reagent and conditions for this conversion.

..... [1]

32. Propan-2-ol, $(CH_3)_2CHOH$, is sometimes added to fuel to help it burn.
Fig. 3.1 shows some reactions of propan-2-ol.

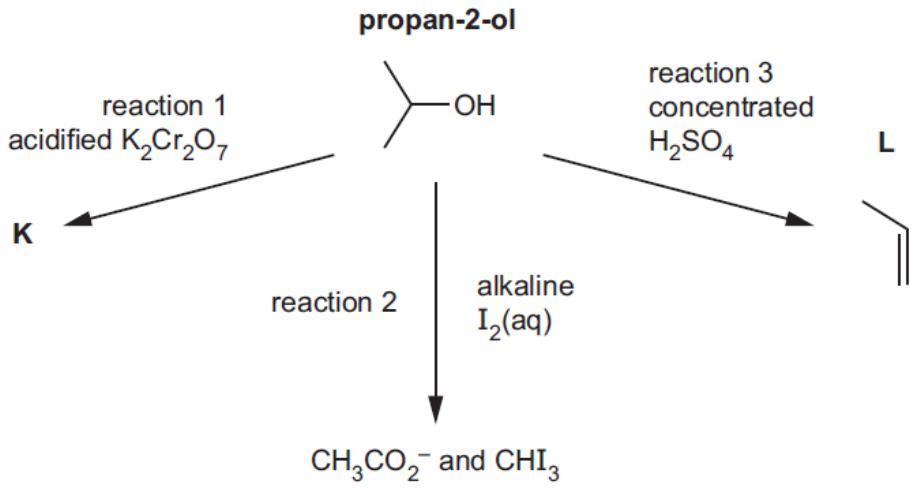


Fig. 3.1

(i) Draw the structure of organic compound K. [1]

(ii) State an observation you would make in reaction 2.

..... [1]

(iii) State the type of reaction that is shown in reaction 3.

..... [1]

33. Propan-2-ol reacts with sodium to produce $(CH_3)_2CH–O^-$ anions.
These anions react with 2-bromopropane to form compound N, as shown in Fig. 3.3. [3]

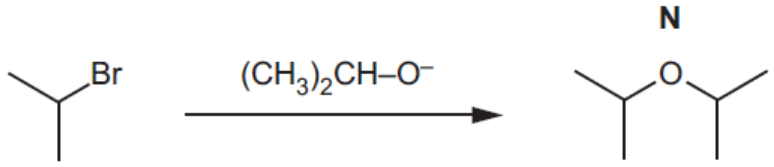


Fig. 3.3

(i) Write an equation for the reaction of propan-2-ol with sodium.

..... [1]

(ii) The reaction of 2-bromopropane with $(CH_3)_2CH–O^-$ anions follows an SN1 mechanism.
Complete Fig. 3.4 to show this mechanism. Include charges, dipoles, lone pairs of electrons and curly arrows, as appropriate.

Fig. 3.4

(iii) Suggest how the rate of the SN1 reaction would change, if at all, if 2-chloropropane were used instead of 2-bromopropane.
Explain your answer.

.....

.....

..... [2]

(iv) N is also added to petrol to make it burn more smoothly.
Construct an equation for the complete combustion of N, $C_6H_{14}O$.

$C_6H_{14}O$ ..... [1]

Comparing the acidity of alcohols and water

Once dissolved in water, ethanol molecules do not dissociate (split up) to any great extent, although there is a very small **degree of dissociation**:

$$\underset{\text{ethanol}}{C_2H_5OH(aq)} \rightleftharpoons \underset{\text{ethoxide ion}}{C_2H_5O^-(aq)} + H^+(aq)$$

The position of equilibrium lies well over to the left, favouring the undissociated C_2H_5OH molecules. Even compared to the dissociation of water molecules:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

the concentration of $H^+(aq)$ ions is much lower. So, we can say that ethanol is a weaker acid than water: its molecules are less likely to dissociate and form H^+ ions. This is because of the electron-donating alkyl (ethyl) group bonded to the negatively charged oxygen atom in the ethoxide ion. The positive inductive effect of the ethyl group has the effect of concentrating more negative charge on this oxygen atom. So, the ethoxide ion more readily accepts an H ion than the hydroxide ions, OH^-, from the dissociation of water. The hydroxide ion only has a hydrogen atom bonded to its negatively charged oxygen, and no alkyl groups.