CONTENTS

HOMEWORK

DATE	PARTICULARS

DATE	PARTICULARS

NOTES

NOTES

NOTES

8
NOTES

Alcohols

a recall the chemistry of alcohols, exemplified by ethanol, in the following reactions: ☐

(i) combustion

(ii) substitution to give halogenoalkanes

(iii) reaction with sodium

(iv) oxidation to carbonyl compounds and carboxylic acids

(v) dehydration to alkenes

(vi) formation of esters by esterification with carboxylic acids

(vii) formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples

b (i) classify hydroxy compounds into primary, secondary and tertiary alcohols ☐

(ii) suggest characteristic distinguishing reactions, e.g. mild oxidation

c deduce the presence of a CH3CH(OH)– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane ☐

ALCOHOLS

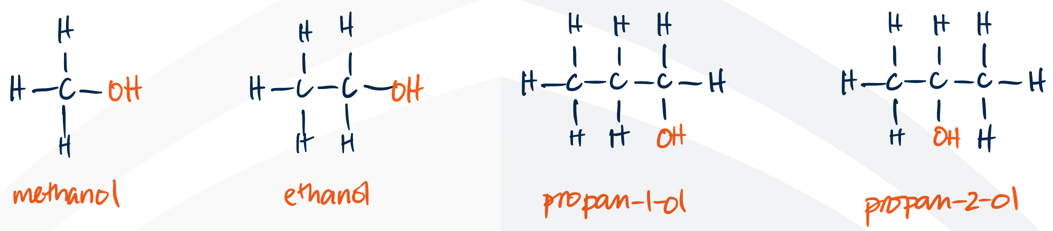
17.1 Alcohols	a)	recall the chemistry of alcohols, exemplified by ethanol, in the following reactions: (i) combustion (ii) substitution to give halogenoalkanes (iii) reaction with sodium (iv) oxidation to carbonyl compounds and carboxylic acids (v) dehydration to alkenes (vi) formation of esters by esterification with carboxylic acids **(vii) formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples**
	b)	(i) classify hydroxy compounds into primary, secondary and tertiary alcohols (ii) suggest characteristic distinguishing reactions, e.g. mild oxidation
	c)	deduce the presence of a $CH_3CH(OH)–$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

ALCOHOLS

The simplest alcohols form a homologous series of **general formula $C_nH_{2n+1}OH$ –** *provided there are no rings.*

Named as substituted alkanes by removing the final –e and adding –ol

For isomers the position of the OH is given by a number – *propan-1-ol and propan-2-ol*

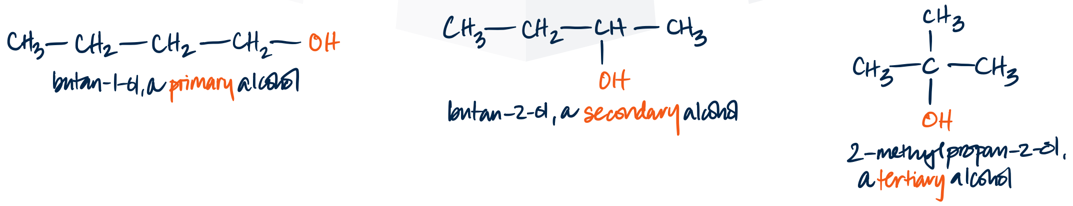


1

ALCOHOLS

The —OH group is called the hydroxyl group. When drawing alcohols always make sure the bond goes to the O.

The functional group, however, is referred to as primary/secondary/tertiary alcohol as chemical behavior of alcohols, especially with oxidation, often depends on the structure of the alcohol.



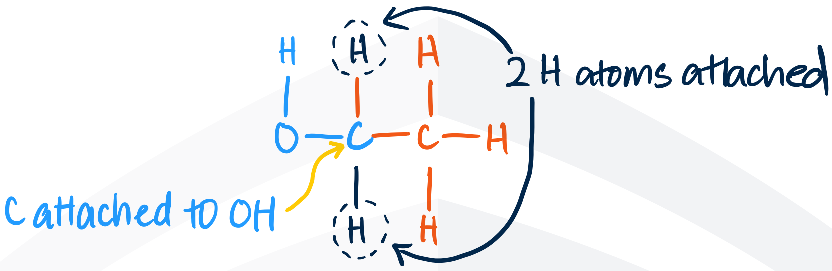
Alcohols may be described as primary, secondary or tertiary, depending on the number of H atoms attached to the carbon with the –OH group on it.

2

PRIMARY ALCOHOLS

Ethanol is a primary alcohol, as it has two hydrogens attached to the C with the –OH attached.

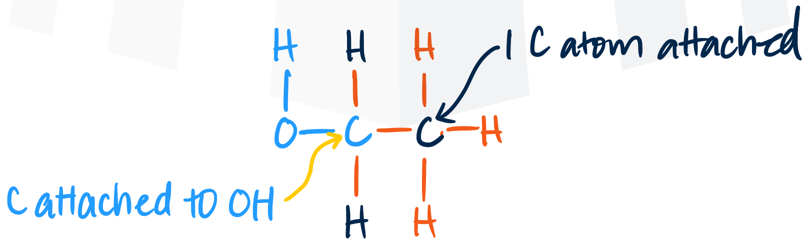
A primary alcohol thus contains the **$-CH_2OH$ group**.



PRIMARY ALCOHOLS

Another way of looking at this is that the C with the –OH attached has one other C attached to it.

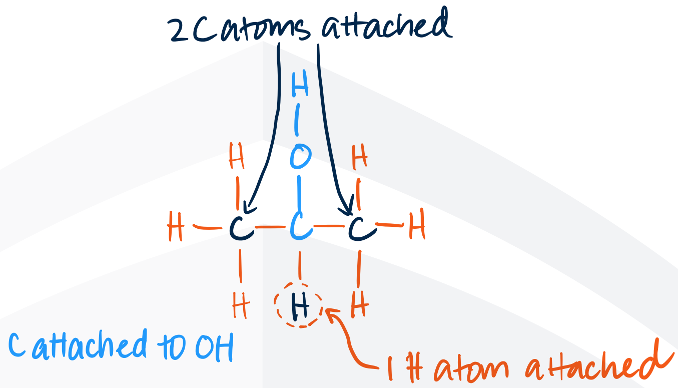
One C attached = primary.



SECONDARY ALCOHOLS

Propan-2-ol is a secondary alcohol, as it has one H atom attached to the C with the –OH attached.

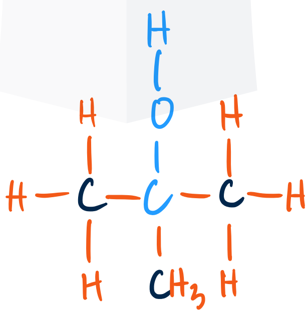
A secondary alcohol contains the **–CHOH** group.



5

TERTIARY ALCOHOLS

2-methylpropan-2-ol is a tertiary alcohol, as there are no H atoms (or three C atoms) attached to the C with the –OH attached.



6

PROPERTIES

Alcohols are useful solvents and are key intermediates in the production of esters, which are important solvents for the paints and plastics industries.

The polar —OH group readily forms hydrogen bonds to similar groups in other molecules.

This accounts for the following major differences between the alcohols and the corresponding alkanes.

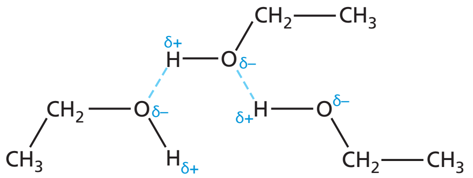
7

PROPERTIES

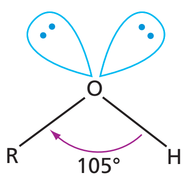
Alcohols have higher boiling points than other organic molecules with similar relative molecular masses.

Methanol, with the lowest molar mass, is a liquid at room temperature.

This is because of hydrogen bonding along with van der Waals' forces between alcohol molecules. This also explains why smaller alcohol molecules mix and dissolve so well in water.



Intermolecular hydrogen bonding in ethanol



The oxygen atom in an alcohol has two lone pairs of electrons

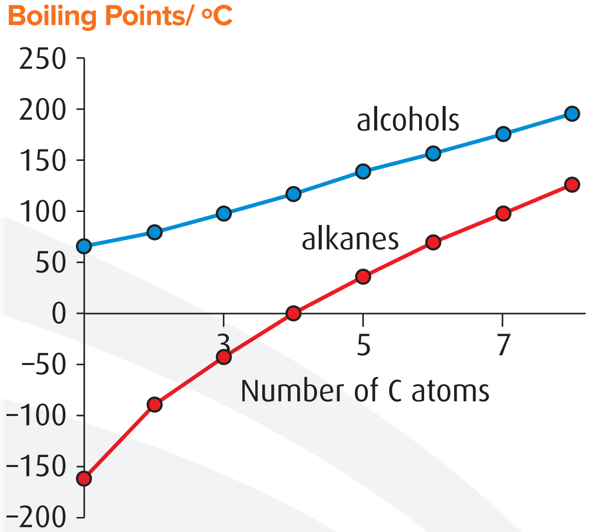
8

BOILING POINTS

The forces between molecules must be broken for the liquid to boil.

In alcohols, hydrogen bonding is the strongest intermolecular force, therefore, more energy is needed to break the hydrogen bonds.

And so the boiling points of alcohols is higher.



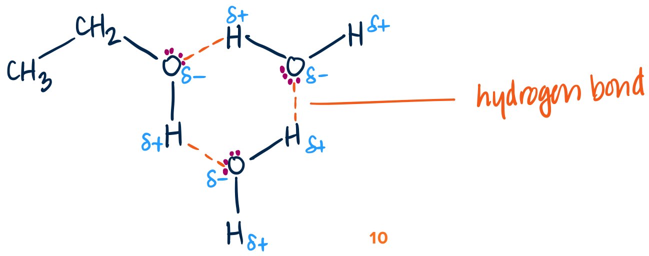
9

SOLUBILITY

The lower members of the series are very soluble in water because of the hydrogen bonding.

For example, ethanol is soluble in water in all proportions, and this is because the –OH group allows it to hydrogen bond to water.

However, solubility decreases as the length of the hydrocarbon chain increases so that pentan-1-ol and hexan-1-ol are only sparingly soluble in water.



10

COMBUSTION OF ALCOHOLS

In a plentiful supply of oxygen, alcohols burn to produce carbon dioxide and water:

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

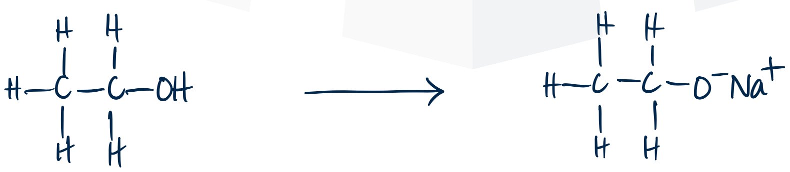
$$2\,C_3H_7OH + 9O_2 \longrightarrow 6CO_2 + 8H_2O$$

11

REACTION WITH SODIUM

Reagent Sodium metal, Na
Condition room temperature

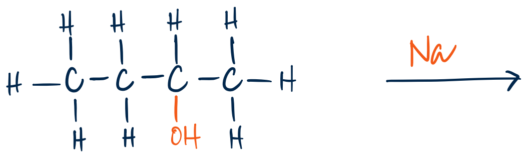
$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^- Na^+ + \tfrac{1}{2}H_2$$



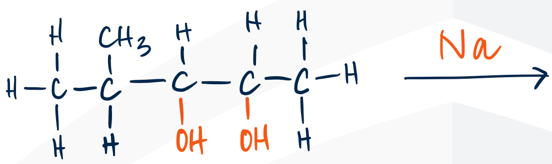
Alcohols are organic chemistry's equivalent of water; water reacts with sodium to produce hydrogen and so do alcohols. The reaction is slower with alcohols.

12

REACTION WITH SODIUM



$CH_3CH_2CH(OH)CH_3$



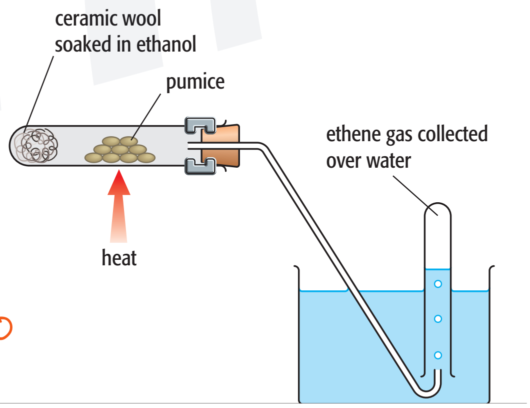
$(CH_3)_2CHCH(OH)CH(OH)CH_3$

13

ALCOHOLS TO ALKENES

When an alcohol is heated with excess concentrated sulphuric acid at around 200 °C an alkene is formed. (Refer to the notes on Alkenes).

Dehydration of the alcohol can also be carried out by passing the alcohol vapour over alumina at 350 °C.

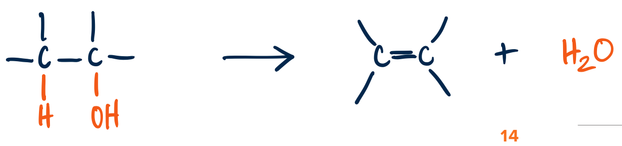


Reagent conc H_2SO_4

Condition 200 °C

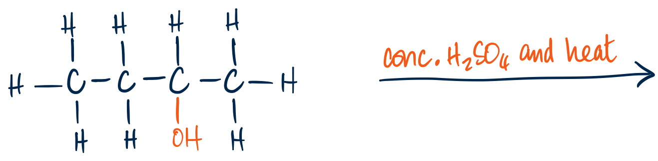
Alternatively Alumina at 350°C.

Type Elimination

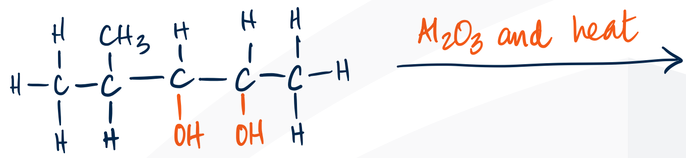


14

ALCOHOLS TO ALKENES



$CH_3CH_2CH(OH)CH_3$



$(CH_3)_2CHCH(OH)CH(OH)CH_3$

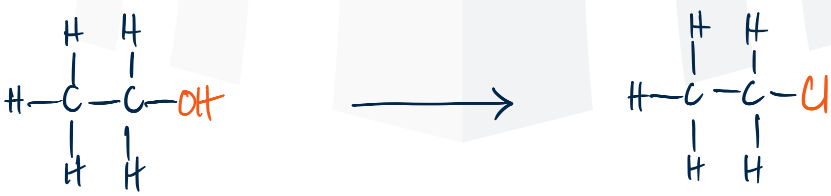
15

ALCOHOLS TO HALOGENOALKANES

Reagent PCl_5, (PCl_3 or $SOCl_2$)

Condition room temperature (heat for PCl_3 and $SOCl_2$)

Type nucleophilic substitution



The reaction releases white fumes of HCl with PCl_5

NOTE: This is another test for the "OH" group in alcohols and carboxylic acids

16

ALCOHOLS TO HALOGENOALKANES

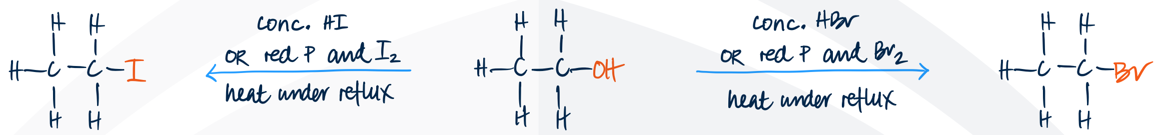
Reagent conc. HBr or conc. HI

Condition heat under reflux

Type nucleophilic substitution

Alternatively Red Phosphorous and Br_2 or Red Phosphorous and I_2 can also be used.

Conc H_2SO_4 and NaBr can also be used to produce conc HBr.



17

ALCOHOL TO ESTERS

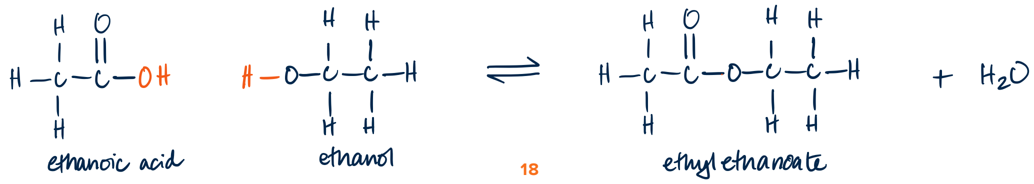
When an alcohol is heated with a carboxylic acid in the presence of a small amount of concentrated sulfuric acid as a catalyst, an ester is formed.

Reagent carboxylic acid and conc. sulfuric acid, H_2SO_4

Condition 60°C / heat

Type esterification / condensation / nucleophilic substitution

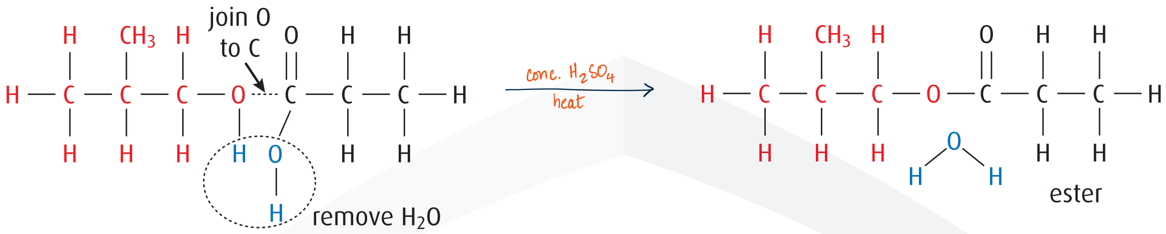
$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$



18

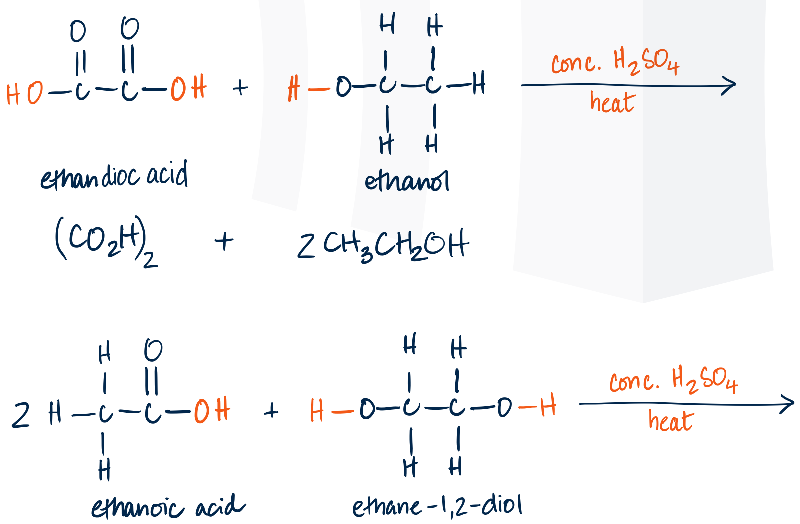
ALCOHOL TO ESTERS

The alcohol and the carboxylic acid have been joined together and water has been eliminated (one H atom from the alcohol and –OH from the carboxylic acid molecule).



19

ALCOHOL TO ESTERS



20

OXIDATION

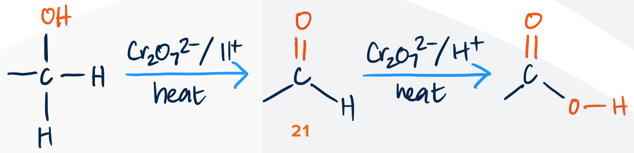
Primary and secondary alcohols may be oxidised using an oxidising agent, such as:

acidified potassium dichromate(VI) ($K_2Cr_2O_7/H^+$), or

acidified potassium manganate(VII) ($KMnO_4/H^+$).

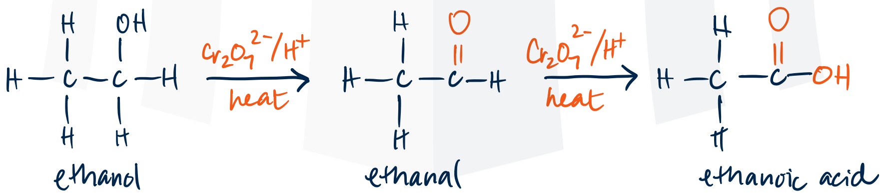
Primary alcohols are oxidised first of all to an aldehyde (partial oxidation), and then the aldehyde is oxidised further to a carboxylic acid (complete oxidation).

$$\text{primary alcohol} \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} \text{aldehyde} \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} \text{carboxylic acid}$$



OXIDATION OF PRIMARY ALCOHOLS

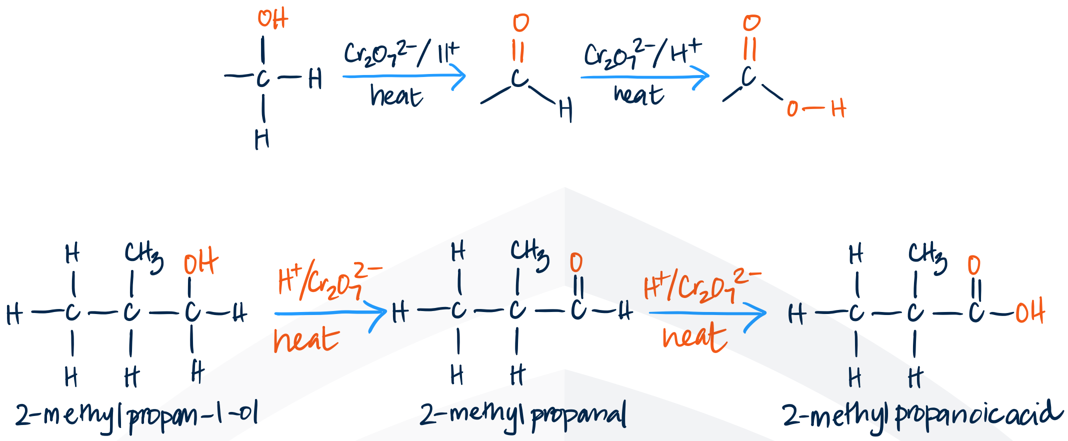
Primary alcohols are oxidised to aldehydes, which, in turn, are even more easily oxidised to carboxylic acids. For example:



$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + [O] \longrightarrow CH_3CO_2H$$

OXIDATION OF PRIMARY ALCOHOLS



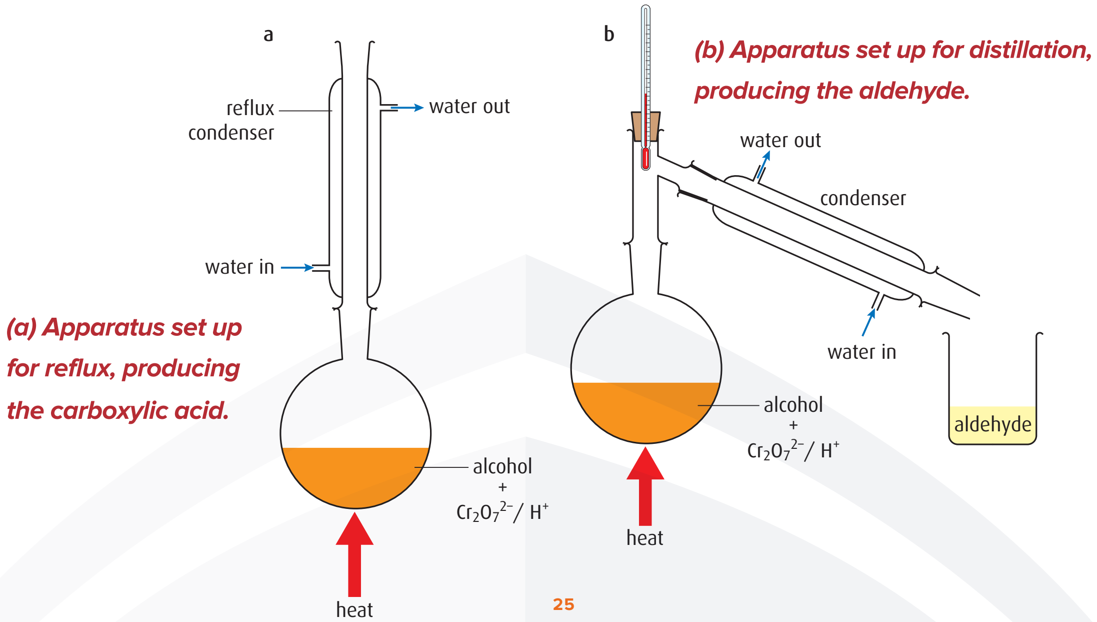
OXIDATION OF PRIMARY ALCOHOLS

As soon as any aldehyde is formed it can be oxidised further by the oxidising agent, to the carboxylic acid, and so special techniques are needed to stop the oxidation at the aldehyde stage.

One such method makes use of the lower volatility of the alcohol (due to hydrogen bonding) compared with the aldehyde. The reaction mixture is warmed to a temperature that is above the boiling point of the aldehyde, but below that of the alcohol.

The aldehyde is allowed to distill out as soon as it is formed, thus avoiding any further contact with the oxidising agent.

OXIDATION OF PRIMARY ALCOHOLS

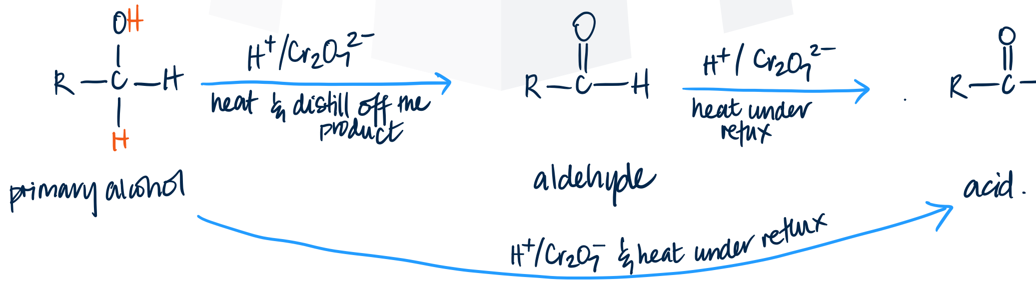


25

OXIDATION OF PRIMARY ALCOHOLS

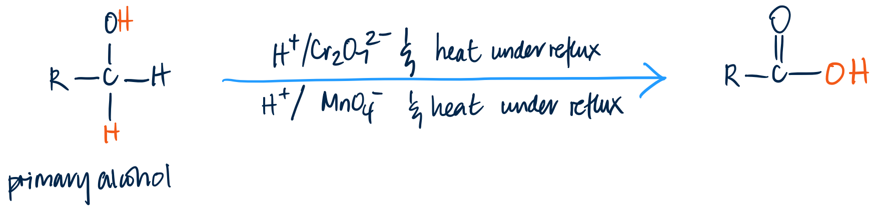
If the reaction mixture is heated under reflux, carboxylic acid is obtained as the main product and the aldehyde is not usually isolated.

However, it is possible to set up the experiment so that the aldehyde is distilled off as soon as it is formed and before it can be oxidised further.



26

OXIDATION OF PRIMARY ALCOHOLS



Using an excess of oxidising agent and heating the reaction under reflux to prevent any escape of the aldehyde before distillation, allows the alcohol to be oxidised all the way to the carboxylic acid.

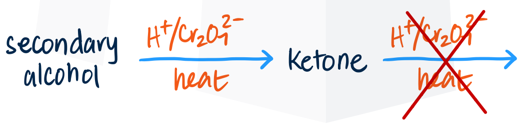
This oxidation reaction can be used to distinguish between primary, secondary and tertiary alcohols.

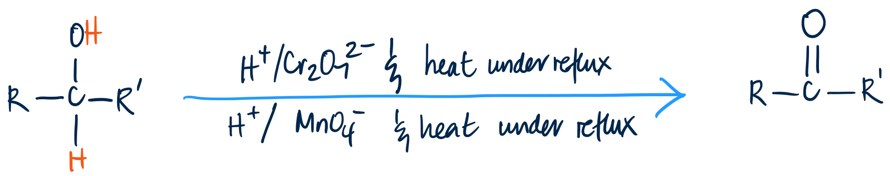
27

OXIDATION OF SECONDARY ALCOHOLS

Secondary alcohols are also oxidised by heating with acidified potassium dichromate(VI) (or acidi ed potassium manganate(VII)).

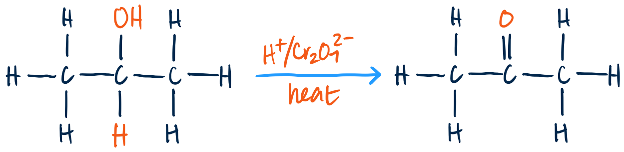
They are oxidised to ketones, which cannot be oxidised any further.





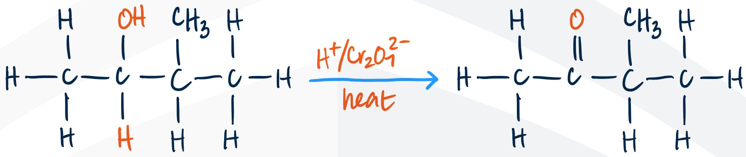
28

OXIDATION OF SECONDARY ALCOHOLS



propan-2-ol   propanone

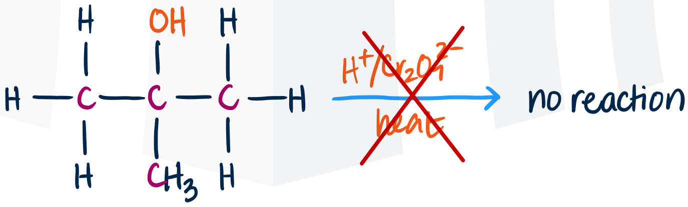
$$CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$$



3-methylbutan-2-ol   3-methylbutanone

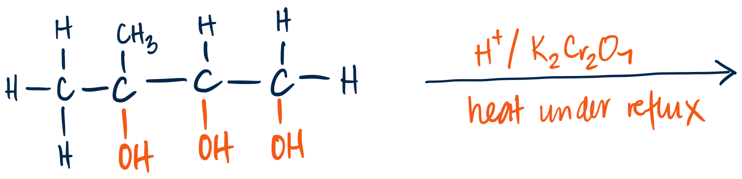
OXIDATION OF TERTIARY ALCOHOLS

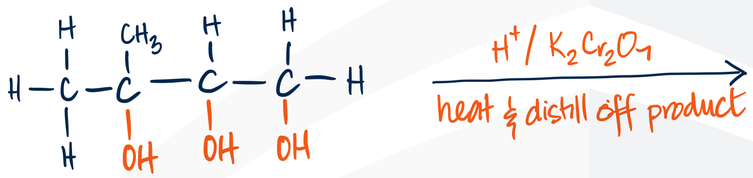
Tertiary alcohols are resistant to oxidation.



2-methylpropan-2-ol

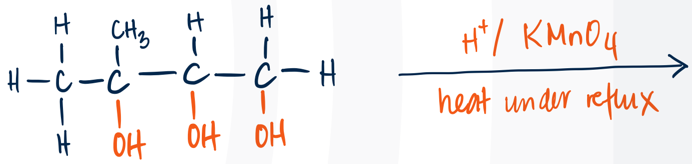
OXIDATION EXAMPLES

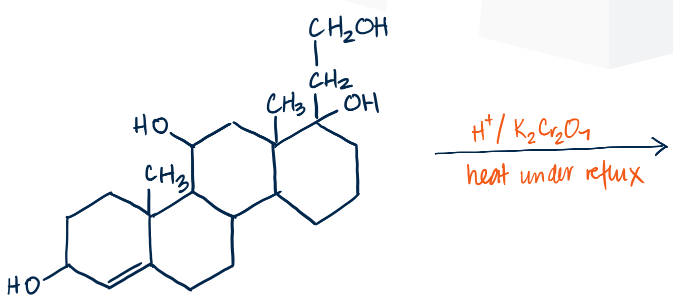




31

OXIDATION EXAMPLES

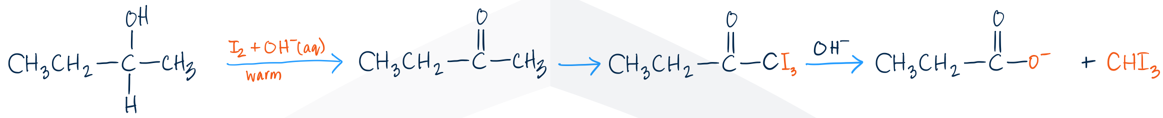




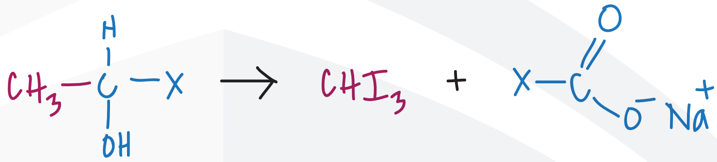
32

IODOFORM REACTION

Alcohols that contain the group CH3CH(OH)-, that is, those that have a methyl group and a hydrogen atom on the same carbon atom that bears the OH group, can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound CH3C(O)-, which is further oxidised a salt of a carboxylic acid (with one less carbon) and a pale yellow ppt of tri-iodomethane.



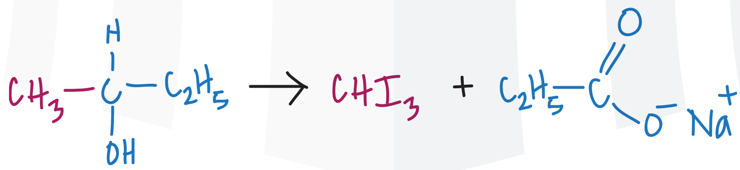
The overall reaction is:

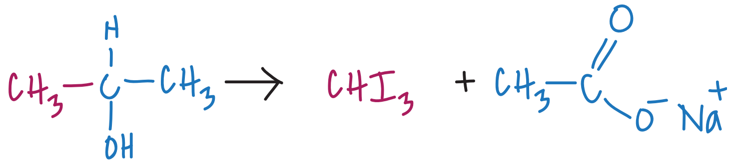


33

IODOFORM REACTION

Except for ethanol, all the alcohols that undergo this reaction are secondary alcohols, with the OH group on the second carbon atom of the chain, that is, they are alkan-2-ols.

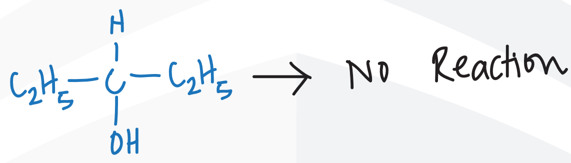




34

IODOFORM REACTION

The exception, ethanol, is the only primary alcohol to give the pale yellow precipitate of tri-iodomethane (iodoform) with alkaline aqueous iodine:



35

IODOFORM REACTION

Which of these alcohols will undergo the iodoform reaction?

36

TESTS FOR THE PRESENCE OF 'OH' GROUP

1. With phosphorous pentachloride, PCl_5, gives white fumes (of HCl)

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

2. With sodium, gives out bubbles of gas that gives a pop sound with a lighted splinter (hydrogen).

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2ONa + \tfrac{1}{2} H_2$$

37

TESTS TO DIFFERENTIATE BETWEEN ALCOHOLS

Warm the alcohol with acidified sodium dichromate. If the orange color of dichromate turns green, distill off the product and then warm it with Fehling's solution.

Tertiary alcohol: The orange color remains unaffected.

Secondary alcohol: The orange color turns green but Fehling's solution is unaffected.

Primary alcohol: The orange color turns green and with Fehling's gives a brick-red precipitate.

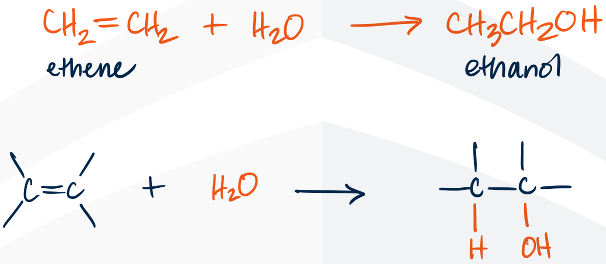
Note: Tollen's reagent can also be used instead of Fehling's solution. The result would be a silver mirror or silver ppt.

38

ALCOHOLS FROM ALKENES

Alkenes react with acid catalyst and steam at temperatures of around 350°C and pressures over 100 atm to form alcohols.

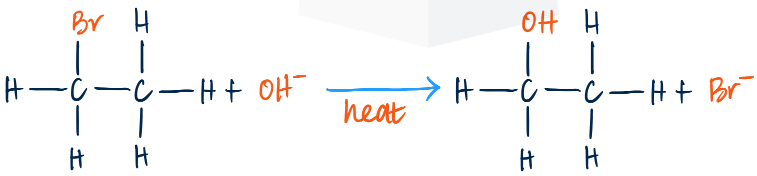
Reagent Steam and dil phosphoric acid (H_3PO_4)
Condition 350 °C and 100 atm
Type Electrophilic addition



ALCOHOLS FROM HALOGENOALKANES

Hydrolysis of halogenoalkanes via NaOH (aq) produces alcohols.

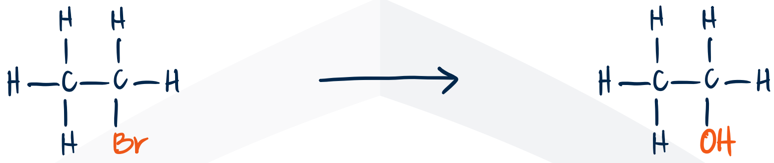
Reagent **Aqueous** sodium (or potassium) hydroxide.
Condition heat under reflux in **aqueous** solution
Type nucleophilic substitution



ALCOHOLS FROM HALOGENOALKANES

$$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$$

$$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$$



41

ALCOHOLS FROM CARBONYLS

Reagent sodium borohydride, $NaBH_4$(aq) or lithium aluminiumhydride, $LiAlH_4$, in ether.

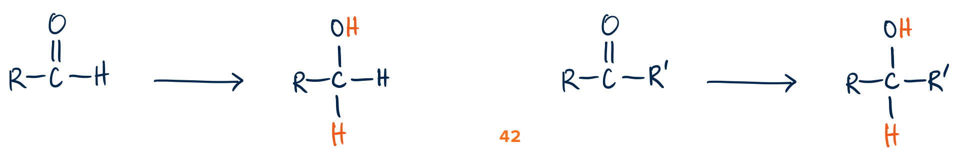
Condition heat

Type Reduction

Alternate hydrogen gas over a nickel or platinum catalyst and heat

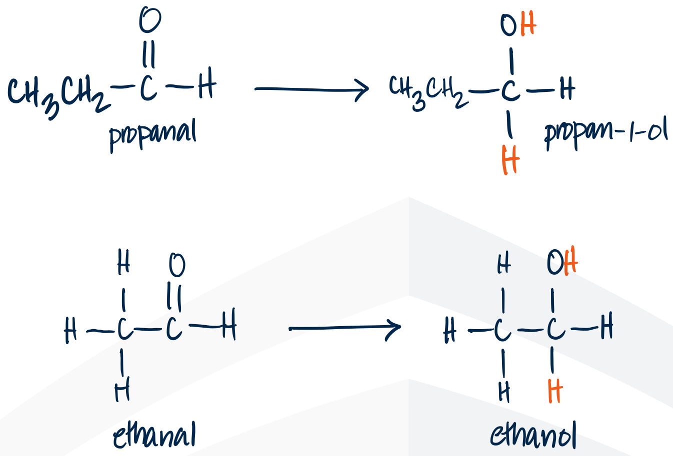
Aldehydes give primary alcohols, while ketones give secondary alcohols.

$$RCHO + 2[H] \longrightarrow RCH_2OH \qquad RCOR' + 2[H] \longrightarrow RCH(OH)R'$$



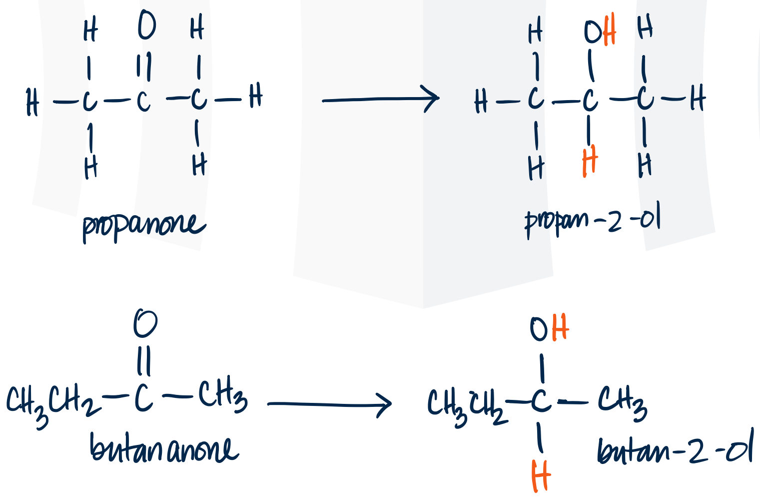
42

PRIMARY ALCOHOLS FROM ALDEHYDES



43

SECONDARY ALCOHOLS FROM KETONES



44

ALCOHOLS WS 1

SECTION A

1 Compound X has the molecular formula $C_4H_{10}O_2$. X has an unbranched carbon chain and contains two OH groups.

On reaction with an excess of hot, acidified, aqueous manganate(VII) ions, X is converted into a compound of molecular formula $C_4H_6O_4$.

To which two carbon atoms in the chain of X are the two OH groups attached?

A 1st and 2nd

B 1st and 3rd

C 1st and 4th

D 2nd and 3rd

[S'14 P11 Q28]

2 Which alcohol has a chiral centre **and** can be oxidised to a ketone?

A pentan-2-ol

B pentan-3-ol

C 3-methylhexan-1-ol

D 3-methylhexan-3-ol

[S'14 P12 Q22]

3 Compound **X** produces a carboxylic acid when heated under reflux with acidified potassium dichromate(VI). Compound **X** has no reaction with sodium metal.

What could be the identity of compound **X**?

A propanal

B propanone

C propan-1-ol

D propan-2-ol

[S'14 P13 Q22]

4 Most alcohols can be dehydrated to give alkenes.

Which alcohol can be dehydrated to give three different isomeric alkenes?

A $CH_3(CH_2)_3CH_2OH$

B $CH_3(CH_2)_2CH(OH)CH_3$

C $CH_3CH_2CH(OH)CH_2CH_3$

D $CH_3C(CH_3)_2CH_2OH$

[S'14 P13 Q25]

5 Methylpropan-1-ol and butan-1-ol are structural isomers. Methylpropan-1-ol has a lower boiling point.

Which statement explains why the boiling point of methylpropan-1-ol is lower than that of butan-1-ol?

A Methylpropan-1-ol cannot form hydrogen bonds.

B Methylpropan-1-ol has weaker covalent bonds than butan-1-ol.

C Methylpropan-1-ol has weaker van der Waals' forces than butan-1-ol.

D Methylpropan-1-ol molecules have more surface area than butan-1-ol molecules.

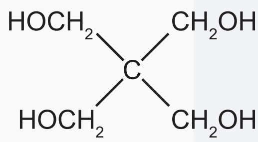
[W'14 P11 Q9]

6 Considering **only** structural isomers, what is the number of alcohols of each type with the formula $C_5H_{12}O$?

	primary	secondary	tertiary
A	3	3	2
B	4	2	2
C	4	3	1
D	5	2	1

[W'14 P11 Q23]

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



pentaerythritol

Which statement about pentaerythritol is correct?

A It can be dehydrated by concentrated sulfuric acid to form an alkene.

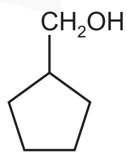
B Its empirical formula and its molecular formula are different.

C It does not react with acidified potassium manganate(VII).

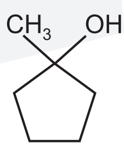
D One mole of it gives two moles of hydrogen gas on reaction with an excess of sodium.

[W'14 P13 Q22]

8 Which reagent will give a different observation with compounds W and X?



W



X

A hot $SOCl_2$

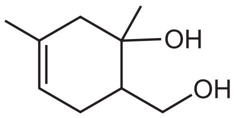
B hot acidified $K_2Cr_2O_7$

C NaOH(aq)

D warm Fehling's reagent

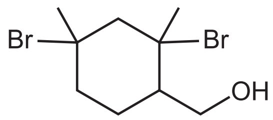
[S'15 P11 Q27]

9 What is the major product formed when compound Q is warmed with excess HBr?



Q

A



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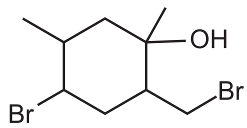

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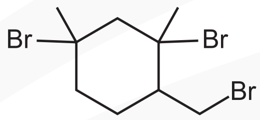

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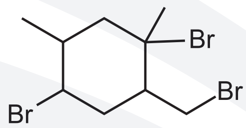


[S'15 P12 Q21]

10 2.40 g of propan-2-ol were mixed with excess acidified potassium dichromate(VI). The reaction mixture was then boiled under reflux for twenty minutes. The organic product was then collected by distillation. The yield of product was 75.0%.

What mass of product was collected?

A 1.74 g **B** 1.80 g **C** 2.22 g **D** 2.32 g

[S'15 P12 Q26]

11 Butan-2-ol can be made by reducing X with H_2/Ni.

Butan-2-ol can be dehydrated to form Y and Z which are structural isomers of each other.

Which row is correct?

	X is	*cis-trans* isomerism is shown by
A	an aldehyde	both Y and Z
B	an aldehyde	only one of Y and Z
C	a ketone	both Y and Z
D	a ketone	only one of Y and Z

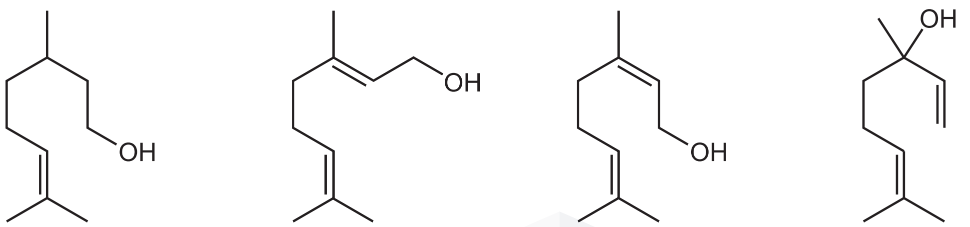
[W'15 P11 Q27]

12 The compounds below are all produced by plants.

Each compound is warmed with acidified potassium dichromate(VI).

Which compound will give a different observation to the other three?

A **B** **C** **D**



[W'15 P12 Q26]

13 Which compound **cannot** be oxidised by acidified potassium dichromate(VI) solution but **does** react with sodium metal?

A $(CH_3)_3COH$

B $CH_3COCH_2CH_3$

C $CH_3CH_2CH_2CH_2OH$

D $CH_3CH_2CH(OH)CH_3$

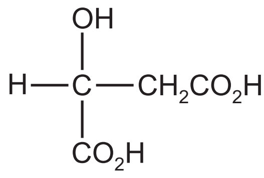
[W'15 P13 Q26]

14 Which row correctly shows a primary, a secondary and a tertiary alcohol?

	primary	secondary	tertiary
A	CH_2OH CH_2 CH_3	CH_2OH $CHOH$ CH_3	CH_2OH $CHOH$ CH_2OH
B	CH_2OH CH_3-C-H CH_3	CH_3 CH_3-C-OH CH_3	CH_3 CH_3-C-H CH_2OH
C	CH_2OH CH_3-C-H H	CH_2OH CH_3-C-CH_2OH H	CH_2OH CH_3-C-CH_2OH CH_2OH
D	H CH_3-C-OH H	CH_3 CH_3-C-OH H	CH_3 CH_3-C-OH CH_3

[M'16 P12 Q26]

15 Malic acid is found in apples.



malic acid

Which reagent will react with all three –OH groups present in the malic acid molecule?

A ethanol in the presence of concentrated sulfuric acid

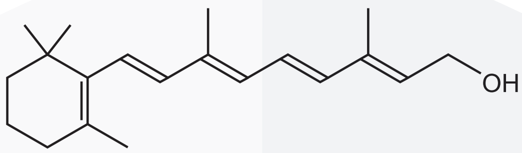
B potassium hydroxide

C sodium

D sodium carbonate

[S'16 P11 Q26]

16 Vitamin A contains retinol.



retinol

Under appropriate conditions, acidified $KMnO_4(aq)$ can be used to break apart C=C bonds.

After these bonds have been broken, further oxidation of the fragments may occur.

Under which conditions is the acidified $KMnO_4(aq)$ used and what do the final oxidation products include?

	conditions	final oxidation products
A	cold, dilute	aldehydes and carboxylic acids
B	cold, dilute	ketones and carboxylic acids
C	hot, concentrated	aldehydes and carboxylic acids
D	hot, concentrated	ketones and carboxylic acids

[S'16 P13 Q24]

17 X, Y and Z are three isomeric alcohols.

X $CH_3CH_2CH_2CH_2CH_2OH$

Y $CH_3CH_2CH(OH)CH_2CH_3$

Z $(CH_3)_2C(OH)CH_2CH_3$

Two or more of these alcohols react with mild oxidising agents.

One of these alcohols, when dehydrated, will give a pair of cis-trans isomers with molecular formula C_5H_{10}.

Which row is correct?

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

[W'16 P11 Q25]

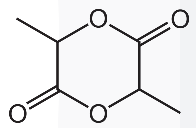
18 Propan-2-ol undergoes many reactions.

Which row is correct?

	reagent added to propan-2-ol	product
A	acidified $KMnO_4$	CH_3CH_2CHO
B	Cl_2	$CH_3CHClCH_3$
C	conc. H_2SO_4	CH_3CHCH_2
D	methanoic acid	$HCO_2CH_2CH_2CH_3$

[M'17 P12 Q26]

19 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

[S'17 P11 Q24]

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

Which mass of product was collected?

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

[S'17 P11 Q28]

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

Which mass of product was collected?

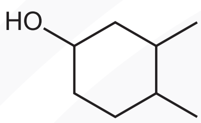
A 1.32 g **B** 1.38 g **C** 1.80 g **D** 3.00 g

[S'17 P11 Q28]

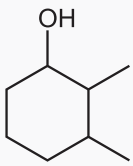
22 Compound X is a single, pure, optical isomer. X is heated with an excess of concentrated H_2SO_4. Only one organic product is formed.

What could X be?

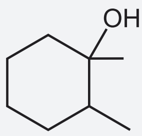
A



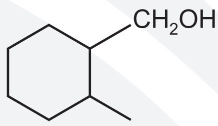
B



C



D

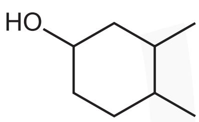


[S'17 P12 Q25]

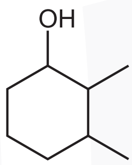
23 Compound X is a single, pure, optical isomer. X is heated with an excess of concentrated H_2SO_4. Only one organic product is formed.

What could X be?

A



B



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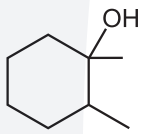

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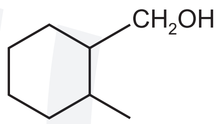


[S'17 P12 Q25]

24 Which statement about butan-1-ol, butan-2-ol, and 2-methylbutan-2-ol is **not** correct?

A They all react with methanoic acid to form an ester.

B They all react with sodium.

C They can all be dehydrated to form an alkene.

D They can all be oxidised to a carbonyl compound.

[S'17 P13 Q26]

25 2,3-dimethylpent-2-ene, $(CH_3)_2C{=}C(CH_3)CH_2CH_3$, is treated with cold, dilute $KMnO_4$. The product of this reaction is treated with an excess of concentrated H_2SO_4 at 180 °C, giving a mixture of isomeric hydrocarbons with molecular formula C_7H_{12}.

What is the name of one of the isomeric hydrocarbons?

A 2,3-dimethylpenta-1,2-diene

B cis-2,3-dimethylpenta-1,3-diene

C 2,3-dimethylpenta-1,4-diene

D 3,4-dimethylpenta-1,3-diene

[N'17 12 Q24]

26 Many, but not all, organic reactions need to be heated before a reaction occurs.

Which reaction occurs quickly at room temperature (20 °C)?

A $CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$

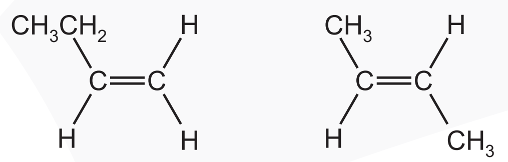
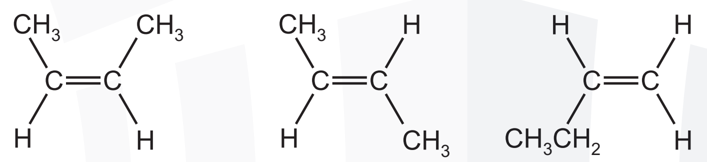
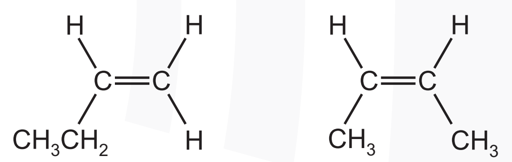
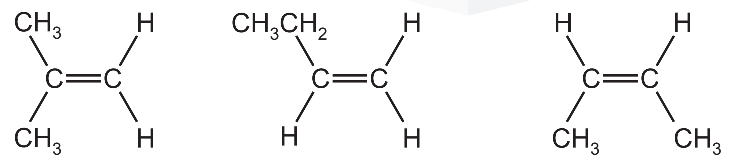
B $CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$

C $CH_3CH_2OH \rightarrow C_2H_4 + H_2O$

D $CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2CO_2H + NH_3$

[N'17 12 Q26]

27 What are the **only** structures formed when butan-2-ol is heated with concentrated H_2SO_4?

A	
B	
C	
D	

[N'17 12 Q28]

28 An ester with an odour of banana has the following formula.

$$CH_3CO_2CH_2\underset{\overset{|}{CH_3}}{C}HCH_2CH_3$$

Which pair of reactants, under suitable conditions, will produce this ester?

A $CH_3CH_2\underset{\overset{|}{CH_3}}{C}HCH_2CO_2H \;+\; CH_3OH$

B $CH_3CH_2\underset{\overset{|}{CH_3}}{C}HCO_2H \;+\; CH_3CH_2OH$

C $CH_3CO_2H \;+\; CH_3CH_2\underset{\overset{|}{CH_3}}{C}HCH_2OH$

D $CH_3CO_2H \;+\; CH_3\underset{\overset{|}{CH_3}}{C}HCH_2CH_2OH$

[N’17 12 Q30]

29 Ethene is reacted with steam in the presence of concentrated H_3PO_4. The product of this reaction is added to acidified potassium dichromate(VI) and heated under reflux for one hour. The final organic product is collected and labelled X.

But-2-ene is treated with hot, concentrated, acidified potassium manganate(VII). The final organic product is collected and labelled Y.

Which statement is correct?

A One molecule of X has more carbon atoms than one molecule of Y.

B One molecule of Y has more carbon atoms than one molecule of X.

C X and Y have different functional groups.

D X is the same compound as Y.

[N’17 13 Q29]

30 Structural isomerism and stereoisomerism should be considered when answering this question.

The molecular formula of compound X is $C_5H_{12}O$.

Compound X:

- reacts with alkaline aqueous iodine
- can be dehydrated to form two alkenes only.

What could be the identity of compound X?

A $CH_3CH_2CH(CH_3)CH_2OH$

B $CH_3CH_2CH(OH)CH_2CH_3$

C $(CH_3)_2CHCH(OH)CH_3$

D $CH_3CH_2CH_2CH(OH)CH_3$

[M’18 12 Q24]

31 Which alcohol will react with an acidified solution of potassium dichromate(VI) to produce a ketone containing six carbon atoms?

A 2,2-dimethylbutan-1-ol

B 2-methylpentan-3-ol

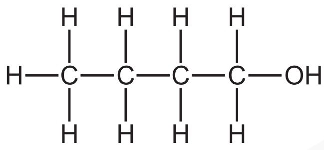
C 3,3-dimethylpentan-2-ol

D 3-methylpentan-3-ol

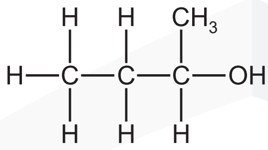
[S'18 P12 Q26]

32 Which alcohol can be dehydrated to give two products which are structural isomers of each other?

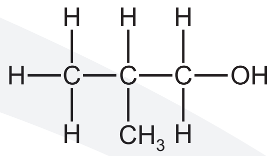
A



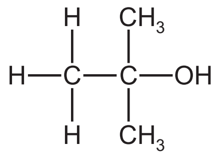
B



C



D



[J'18 P11 Q23]

33 Which alcohol will react with an acidified solution of potassium dichromate(VI) to produce a ketone containing six carbon atoms?

A 2,2-dimethylbutan-1-ol

B 2-methylpentan-3-ol

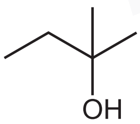
C 3,3-dimethylpentan-2-ol

D 3-methylpentan-3-ol

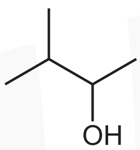
[J'18 P12 Q26]

34 Which compound is a secondary alcohol that can be dehydrated to form an alkene with $M_r = 70$?

A



B



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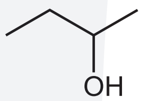

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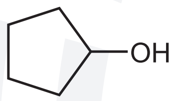


[J'18 P13 Q25]

35 When 0.0075 mol of alcohol X are completely burnt in excess oxygen and the gases produced are passed through an excess of limewater (calcium hydroxide solution), 3.0 g of calcium carbonate are produced.

When X is warmed with acidified potassium dichromate(VI) there is a colour change from orange to green.

What could be the identity of X?

A $CH_3CH(OH)CH_2CH_3$

B $(CH_3)_3COH$

C $CH_3CH_2CH_2OH$

D $CH_3CH(OH)CH_3$

[J'18 P13 Q26]

36 Considering **only** structural isomers, what is the number of alcohols of each type with the formula $C_5H_{12}O$?

	primary	secondary	tertiary
A	3	3	2
B	4	2	2
C	4	3	1
D	5	2	1

[J'18 P13 Q27]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 In an organic synthesis, a 62% yield of product is achieved.

Which of these conversions are consistent with this information?

1 74.00g of butan-2-ol → 44.64 g of butanone

2 74.00g of butan-1-ol → 54.56 g of butanoic acid

3 74.00g of 2-methylpropan-1-ol → 54.56 g of 2-methylpropanoic acid

[S'14 P11 Q40]

2 Which alcohols **cannot** be dehydrated to form alkenes?

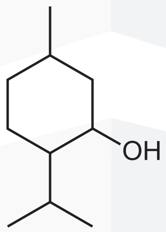
1 CH_3OH

2 $(CH_3)_3COH$

3 CH_3CH_2OH

[S'14 P12 Q37]

3 Menthol is a naturally-occurring alcohol found in peppermint oil.



menthol

Which reagents will react with menthol?

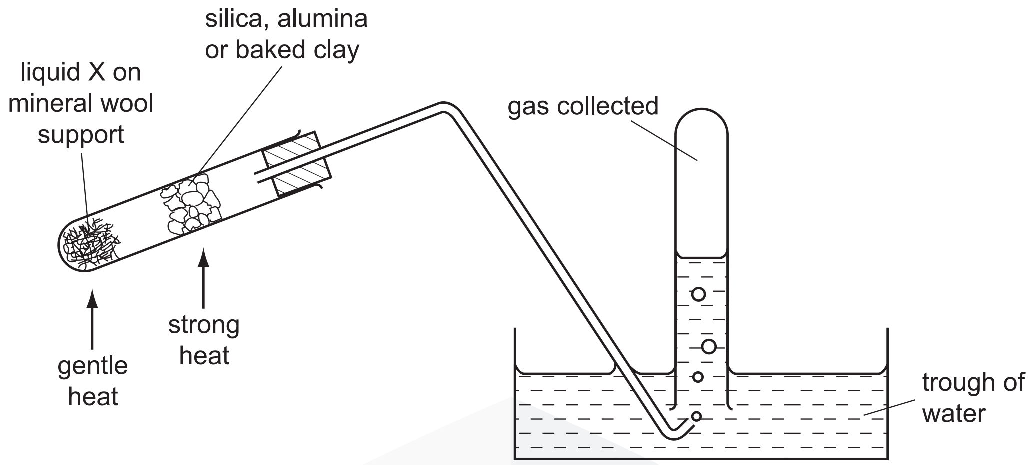
1 aqueous bromine

2 sodium metal

3 aqueous acidified manganate(VII)

[S'14 P12 Q38]

4 The diagram shows an experimental set-up which can be used in several different experiments.



Which processes could be demonstrated by using the above apparatus?

1 oxidation of ethanol (liquid X)

2 dehydration of ethanol (liquid X)

3 cracking of paraffin (liquid X)

[S'14 P13 Q40]

5 Which statements about 2-methylbutan-1-ol are correct?

1 It can give $HCl(g)$ on reaction with PCl_5.

2 It can be oxidised to give an aldehyde.

3 It exists in two optically active forms.

[S'15 P12 Q38]

6 Compound Q is obtained by adding H_2O across the double bond in compound P.

P Q

Which statements about these two compounds are correct?

1 P shows *cis-trans* isomerism.

2 Q contains two chiral centres.

3 Q is a tertiary alcohol.

[W'15 P12 Q37]

7 Several structural isomers of $C_3H_6O_3$ are listed below.

$HOCH_2COCH_2OH$

$HOCH_2CH(OH)CHO$

$HOCH_2CH_2CO_2H$

$CH_3CH(OH)CO_2H$

Which statements about these structural isomers are correct?

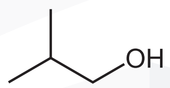
1 One mole of each reacts with two moles of sodium.

2 Only one of the isomers contains a tertiary alcohol group.

3 They all contain a primary alcohol group.

[W'16 P11 Q39]

8 An organic compound, X, has the following skeletal formula.



X

Which statements about X are correct?

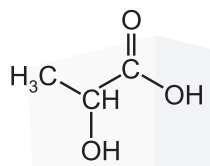
1 X is a primary alcohol.

2 X will dehydrate to give a single alkene.

3 X will undergo a substitution reaction with chloride ions.

[S'17 P12 Q39]

9 The structure of lactic acid is shown.

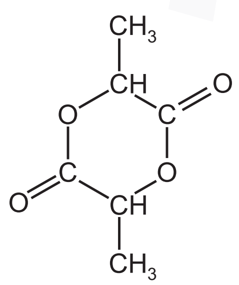


lactic acid

Which esters might form when lactic acid is heated?

1 $CH_3CH(OH)CO_2CH(CH_3)CO_2H$

2



3 $CH_3CH(OH)CO_2CH(OH)CH_3$

[M'18 12 Q40]

10 Which pairs of compounds may be distinguished from each other by testing with alkaline aqueous iodine?

1 ethane-1,2-diol and ethanol

2 propan-2-ol and methylpropan-2-ol

3 ethanol and butan-2-ol

[J'18 P12 Q38]

11 Which statements about 2-methylbutan-1-ol are correct?

1 It can give $HCl(g)$ on reaction with PCl_5.

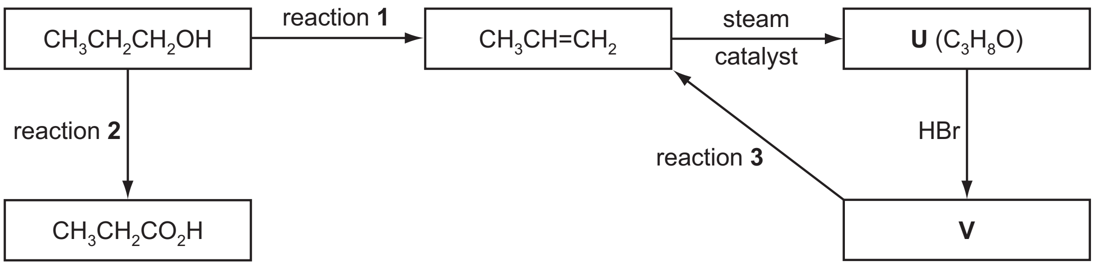
2 It can be oxidised to give an aldehyde.

3 It displays optical isomerism.

[N'18 P12 Q39]

ALCOHOLS WS 2

1 A series of reactions based on propan-1-ol is shown.



(a) Suggest a suitable reagent and conditions for reaction **1**.

.... [2]

(b) **(i)** Write an equation for reaction **2**, using [O] to represent the oxidising agent.

.... [1]

(ii) Suggest a suitable reagent and conditions for reaction **2**.

.... [2]

(c) Give the structural formulae of **U** and **V**.

U ....

V ....

[2]

(d) Suggest a suitable reagent and conditions for reaction **3**.

....

.... [2]

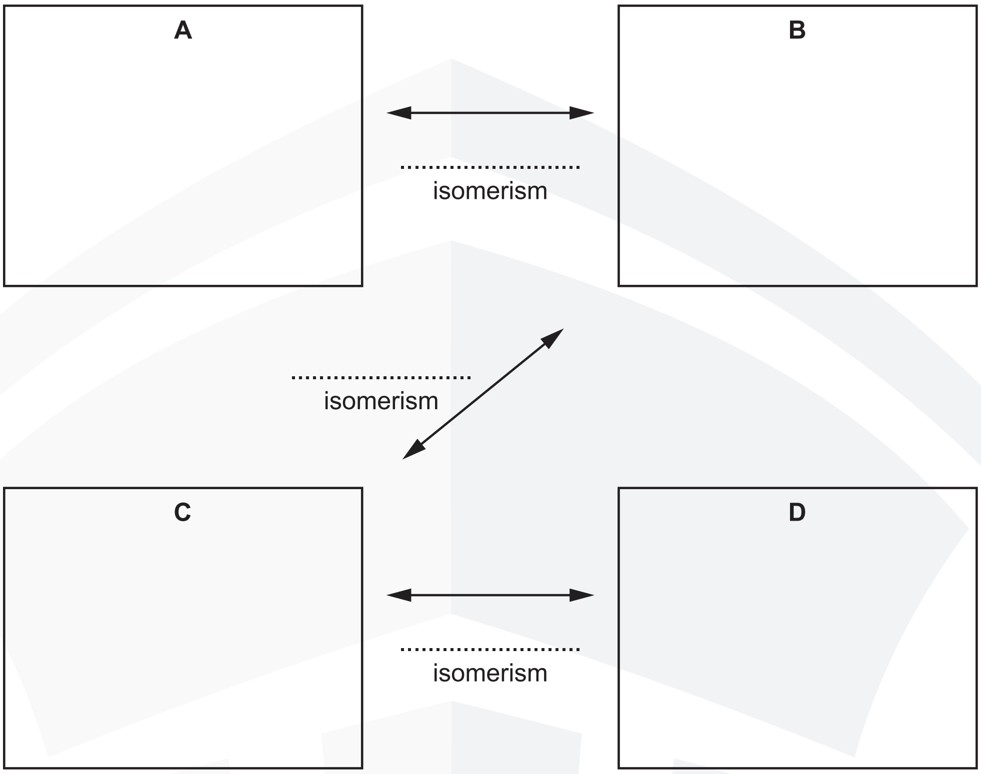
[N'14 P23 Q4]

2 There are four alcohols, **A**, **B**, **C** and **D**, which are structural isomers with the molecular formula $C_4H_{10}O$.

Alcohol **A** does not react with acidified potassium dichromate(VI) solution but **B**, **C** and **D** do.

All four alcohols react with hot, concentrated sulfuric acid to form products with the molecular formula C_4H_8. **A**, **C** and **D** each give a single product in this reaction. **B** gives a mixture of two structural isomers, one of which shows stereoisomerism.

(a) Give the **skeletal** formula for each of the four alcohols and complete the diagram with the names of the types of structural isomerism shown by each linked pair of compounds.



[7]

(b) **(i)** Give the names of the two structural isomers produced by the reaction of **B** with hot, concentrated sulfuric acid

.... [2]

(ii) State which of these two isomers shows stereoisomerism. Explain why this molecule is capable of showing stereoisomerism.

....

....

....

.... [2]

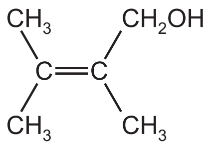
(iii) Draw **displayed** formulae to show the two stereoisomers.

stereoisomer 1	stereoisomer 2

[2]

[J'15 P21 Q4]

3 The structure of **H** is shown.



H

(a) **H** reacts with both cold, dilute, acidified potassium manganate(VII) and with hot, concentrated, acidified potassium manganate(VII).

(i) Give the structure of the organic product of the reaction of **H** with cold, dilute, acidified potassium manganate(VII).

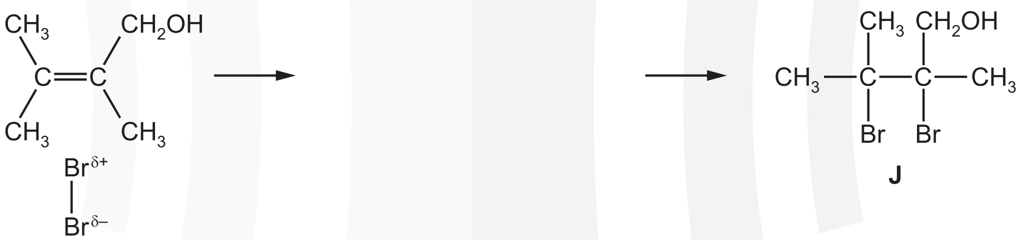
[1]

(ii) Give the structures of the organic products of the reaction of **H** with hot, concentrated, acidified potassium manganate(VII).

[2]

(b) **(i)** Complete the reaction scheme to show the mechanism of the reaction of **H** with bromine to form **J**.

Include all necessary curly arrows, lone pairs and charges.



[3]

(ii) Explain the origin of the dipole on the bromine molecule.

....

.... [1]

J is formed as an equimolar mixture of isomers.

(iii) State the type of isomerism shown by **J**.

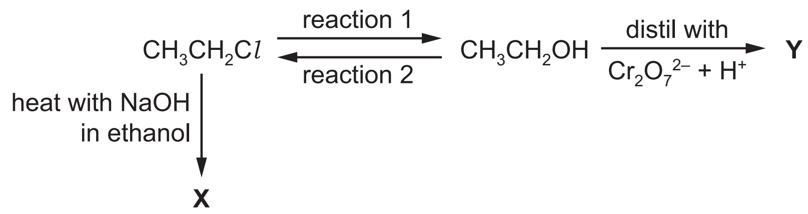
.... [1]

(iv) Draw the structures of the two isomers of **J**.

[2]

[J'15 P23 Q4]

4 Some reactions involving ethanol are shown.



(a) **(i)** Give an equation for reaction 2 including the reagent needed for the conversion.

.... [2]

(ii) State the reagent and conditions required for reaction 1.

.... [2]

(b) **(i)** Identify the organic product **X**.

.... [1]

(ii) Nitric acid is added to the products of reaction of CH_3CH_2Cl with NaOH in ethanol. Silver nitrate solution is then added to this mixture.

State what you would observe.

.... [1]

(iii) Write an ionic equation, including state symbols, for the reaction responsible for the observation in **(ii)**.

.... [1]

(c) **(i)** Identify the organic product **Y** which is distilled out of the reaction mixture.

.... [1]

(ii) Explain, in terms of the properties of and intermolecular forces in CH_3CH_2OH and **Y**, why the chosen conditions for the reaction ensure that **Y** is the product.

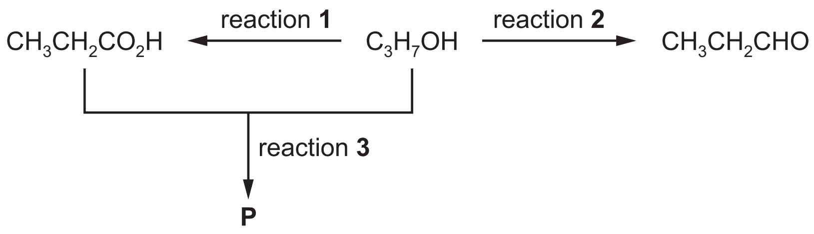
....

....

.... [3]

[N'15 P21 Q4]

5 A sequence of reactions is shown starting with an alcohol, C_3H_7OH.



(a) Draw the skeletal formula of the alcohol C_3H_7OH.

[1]

(b) State the reagents and conditions needed for reaction **1**.

....

.... [2]

(c) State the reagents and conditions needed for reaction **2**.

....

.... [2]

(d) Name **P**, the organic product of reaction **3**.

.... [1]

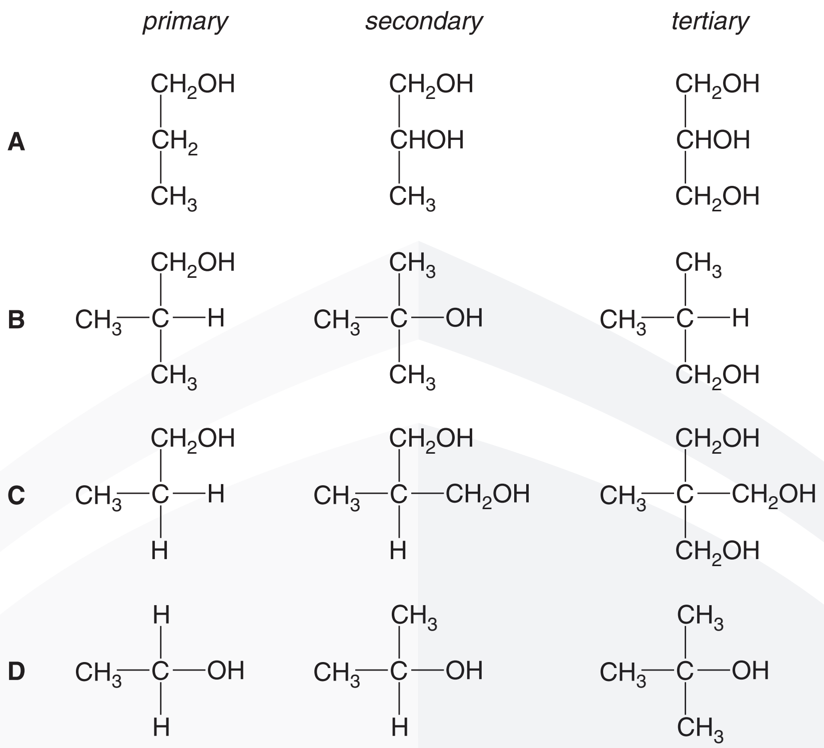
[Total: 6]

[N'16 P21 Q5]

ALCOHOLS WS 3

SECTION A

1 Which set of alcohols correctly shows a primary, a secondary and a tertiary alcohol?



[S'02 Q20]

2 An organic compound will decolorise dilute acidified aqueous potassium manganate(VII) on warming, but will not decolorise bromine water.

What could the organic compound be?

A butane

B ethanol

C ethene

D ethanoic acid

[S'02 Q26]

3 Compound **X** undergoes the following reactions.

$$\underset{\mathbf{X}}{C_4H_9Br} \xrightarrow{\text{NaOH(aq) / heat}} C_4H_{10}O \xrightarrow{Cr_2O_7^{2-},\ H^+\text{(aq) / heat}} C_4H_8O \text{ only}$$

What is **X**?

A 1-bromobutane

B 2-bromobutane

C 1-bromo-2-methylpropane

D 2-bromo-2-methylpropane

[W'02 Q24]

4 The compound hex-3-en-1-ol, **P**, has a strong 'leafy' smell of newly cut grass and is used in perfumery.

$CH_3CH_2CH{=}CHCH_2CH_2OH$

P

What is produced when **P** is treated with an excess of hot concentrated acidic $KMnO_4$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CH_2OH$

B $CH_3CH_2CH{=}CHCH_2CO_2H$

C CH_3CH_2CHO and $OCHCH_2CH_2OH$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

[S'03 Q22]

5 In a preparation of ethene, ethanol is added a drop at a time to a heated reagent **Y**. To purify the ethene it is bubbled through a solution **Z** and then collected.

What could reagent **Y** and solution **Z** be?

	reagent **Y**	solution **Z**
A	acidified $K_2Cr_2O_7$	dilute NaOH
B	concentrated H_2SO_4	dilute H_2SO_4
C	concentrated H_2SO_4	dilute NaOH
D	ethanolic NaOH	concentrated H_2SO_4

[S'03 Q29]

6 1,1-Dichloropropane reacts with aqueous sodium hydroxide in a series of steps to give propanal.

$$CH_3CH_2CHCl_2 \xrightarrow{NaOH(aq)} CH_3CH_2CHO$$

What is the mechanism of the first step of this reaction?

A electrophilic substitution

B elimination

C nucleophilic substitution

D oxidation

[W'03 Q25]

7 1,1-dichloropropane reacts with aqueous sodium hydroxide in a series of steps to give propanal.

$$CH_3CH_2CHCl_2 \xrightarrow{NaOH(aq)} CH_3CH_2CHO$$

Which term describes the first step of this reaction?

A electrophilic addition

B elimination

C nucleophilic substitution

D oxidation

[W'03 Q25]

8 What will react differently with the two isomeric pentanols, $(CH_3)_3CCH_2OH$ and $(CH_3)_2CHCH_2CH_2OH$?

A acidified aqueous potassium manganate(VII)

B concentrated sulphuric acid

C phosphorus pentachloride

D sodium

[W'03 Q27]

9 How many hydrogen atoms in a molecule of glycerol, $HOCH_2CH(OH)CH_2OH$, may be substituted by deuterium on dissolving it in an excess of D_2O?

A 2 **B** 3 **C** 5 **D** 8

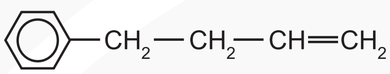
[W'03 Q28]

10 Compound **X**

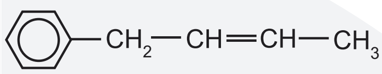
- has the molecular formula $C_{10}H_{14}O$;
- is unreactive towards mild oxidising agents.

What is the structure of the compound formed by dehydration of **X**?

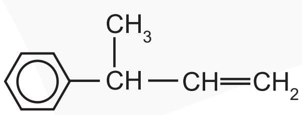
A



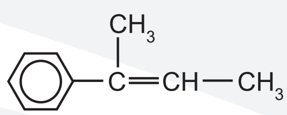
B



C



D



[S'04 Q28]

11 Bromomethane, CH_3Br, is used as a fumigant to destroy insect pests in grain that is to be stored. It can be made by reacting methanol with hydrogen bromide.

$$CH_3OH + HBr \rightarrow CH_3Br + H_2O$$

What type of reaction is this?

A condensation

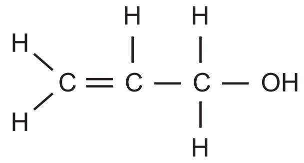
B electrophilic substitution

C free radical substitution

D nucleophilic substitution

[S'05 Q19]

12 Prop-2-en-1-ol (allyl alcohol) has the following structure.



Which reagent would react with prop-2-en-1-ol to form a product that could exist as optical isomers?

A bromine

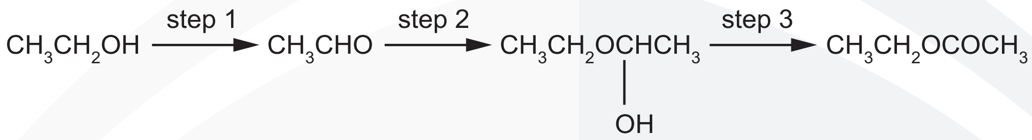
B hydrogen and nickel

C phosphorus pentachloride

D sodium

[S'05 Q20]

13 Ethyl ethanoate is a very important solvent in industry. Currently, researchers are investigating ways of producing the ester from cheap, low grade ethanol by the following process.



What types of reaction are steps 1 and 3?

	step 1	step 3
A	elimination	esterification
B	elimination	isomerisation
C	oxidation	esterification
D	oxidation	oxidation

[S'05 Q25]

14 Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid?

A propanal

B propanoic acid

C propanone

D propan–1–ol

[S'05 Q27]

15 In which reaction is the relative molecular mass of the organic product the largest?

A bromoethane + aqueous sodium hydroxide

B bromoethane + alcoholic sodium hydroxide

C ethane + bromine

D ethanol + phosphorus pentachloride

[S'06 Q23]

16 When (chloromethyl)benzene, $C_6H_5CH_2Cl$, is treated in succession with two reagents **X** and **Y**, it gives phenylethanoic acid, $C_6H_5CH_2CO_2H$.

What are reagents **X** and **Y**?

	X	Y
A	NaOH(aq)	$K_2Cr_2O_7$(aq)
B	Cl_2(aq)	NaOH(aq)
C	NaCN (in aqueous ethanol)	dilute H_2SO_4
D	NaOH(aq)	CO_2

[W'06 Q26]

17 An alcohol with molecular formula $C_nH_{2n+1}OH$ has a chiral carbon atom but does not react with MnO_4^- / H^+.

What is the least number of carbon atoms such an alcohol could possess?

A 5 **B** 6 **C** 7 **D** 8

[S'07 Q26]

18 When dangerous chemicals are transported by road, vehicles must carry signs that indicate what measures should be taken in the event of a spillage of the chemical carried.

Which material must be used if there were a spillage of metallic sodium?

A ethanol

B jets of water

C sand

D water spray

[W'07 Q12]

19 An alcohol of molecular formula $C_4H_{10}O_2$ contains two OH groups and has an unbranched carbon atom chain.

On reaction with an excess of hot MnO_4^- / H^+ this alcohol is converted into a compound of molecular formula $C_4H_6O_4$.

To which two carbon atoms in the chain of the alcohol are the two OH groups attached?

A 1st and 2nd

B 1st and 3rd

C 1st and 4th

D 2nd and 3rd

[S'08 Q26]

20 Compound **X**, $C_6H_{12}O$, is oxidised by acidified sodium dichromate(VI) to compound **Y**.

Compound **Y** reacts with ethanol in the presence of a little concentrated sulphuric acid to give liquid **Z**.

What is the formula of **Z**?

A $CH_3(CH_2)_2CH{=}CHCO_2H$

B $CH_3(CH_2)_4CH_2COCH_2CH_3$

C $CH_3(CH_2)_4CO_2CH_2CH_3$

D $CH_3CH_2CO_2(CH_2)_4CH_3$

[S'08 Q30]

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

$CH_3CH_2CH{=}CHCH_2CH_2OH$

leaf alcohol

Which two compounds will be formed when 'leaf alcohol' is oxidised using hot, concentrated manganate(VII) ions?

A CH_3CO_2H and $HOCH_2CH_2CH_2CO_2H$

B CH_3CO_2H and $HO_2CCH_2CH_2CO_2H$

C $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

D $CH_3CH_2CO_2H$ and $HOCH_2CH_2CO_2H$

[W'08 Q21]

22 The functional group in a primary alcohol is $–CH_2OH$.

Which reagent reacts with a primary alcohol, under suitable conditions, to give an organic product with the same number of oxygen atoms as the alcohol?

A Al_2O_3 **B** CH_3CO_2H **C** HBr **D** Na

[W'08 Q25]

23 Which ester is formed when the alcohol CH_3CH_2OH is reacted with $CH_3CH_2CH_2CO_2H$?

A ethyl propanoate

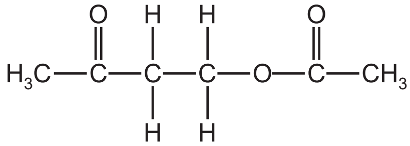
B ethyl butanoate

C propyl ethanoate

D butyl ethanoate

[S'09 P11 Q27]

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



What is the molecular formula of compound X?

A $C_2H_6O_2$ **B** $C_2H_6O_3$ **C** C_4H_8O **D** $C_4H_8O_2$

[W'10 P11 Q21]

25 Which alcohol gives only **one** 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

[W'10 P11 Q24]

26 Which sequence of reagents may be used in the laboratory to convert propan-1-ol into 2-bromopropane?

A concentrated sulfuric acid, followed by bromine

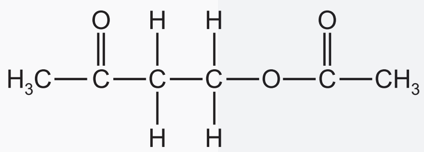
B concentrated sulfuric acid, followed by hydrogen bromide

C ethanolic sodium hydroxide, followed by bromine

D ethanolic sodium hydroxide, followed by hydrogen bromide

[W'10 P12 Q23]

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



What is the molecular formula of compound X?

A $C_2H_6O_2$ **B** $C_2H_6O_3$ **C** C_4H_8O **D** $C_4H_8O_2$

[W'10 P13 Q22]

28 In the reaction pathway below, an alkane is converted into a carboxylic acid through several stages.

$$C_{10}H_{22} \xrightarrow{\text{stage 1}} C_2H_4 \xrightarrow[\text{catalytic hydration}]{\text{stage 2}} C_2H_5OH \xrightarrow{\text{stage 3}} CH_3CO_2H$$

Which processes occur at stage 1 and at stage 3?

	stage 1	stage 3
A	condensation	combustion
B	cracking	dehydration
C	cracking	oxidation
D	dehydration	combustion

[S'11 P11 Q19]

29 Pentanol, $C_5H_{11}OH$, has four structural isomers that are primary alcohols.

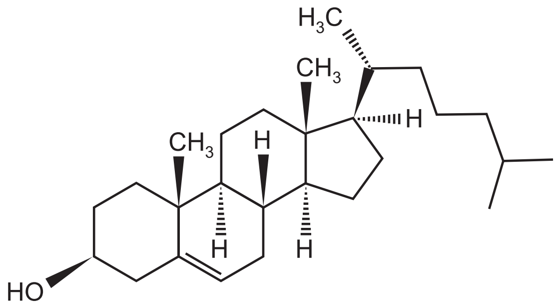
How many of these primary alcohols contain a chiral carbon atom?

A 0 **B** 1 **C** 2 **D** 3

[S'11 P11 Q23]

30 This question should be answered by considering the reactions of $KMnO_4$ with different functional groups under the stated conditions.

The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Cholesterol is separately treated with

- cold, dilute acidified $KMnO_4$,
- hot, concentrated acidified $KMnO_4$.

What is the change in the **number** of chiral carbon atoms in the molecule during each reaction?

	cold, dilute acidified $KMnO_4$	hot, concentrated acidified $KMnO_4$
A	+1	0
B	+1	–1
C	+2	0
D	+2	–1

[S'11 P12 Q29]

31 2.76 g of ethanol were mixed with an excess of aqueous acidified potassium dichromate(VI). The reaction mixture was then boiled under reflux for one hour. The organic product was then collected by distillation.

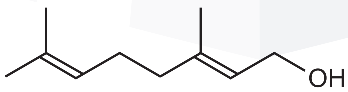
The yield of product was 75.0 %.

What mass of product was collected?

A 1.98 g **B** 2.07 g **C** 2.70 g **D** 4.80 g

[W'11 P11 Q25]

32 Geraniol is a constituent of some perfumes.



geraniol

Which statement about geraniol is **not** correct?

A Geraniol causes hot acidified potassium dichromate(VI) to change colour from orange to green.

B Geraniol decolourises bromine water.

C There are three methyl groups and three methylene (CH_2) groups in geraniol.

D There are two pairs of *cis-trans* isomers of geraniol.

[W'11 P11 Q29]

33 Buta-1,3-diene is currently obtained from fossil fuel sources. In future it may be obtained from ethanol, which can be produced from non-food agricultural crops. The sequence of reactions is as follows.

$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO \xrightarrow{\text{step 2}} CH_3CH(OH)CH_2CHO \xrightarrow{\text{step 3}} \underset{\text{buta-1,3-diene}}{CH_2{=}CHCH{=}CH_2}$$

Which term could be used to describe step 1?

A condensation

B dehydration

C dehydrogenation

D hydrogenation

[W'11 P12 Q21]

34 2.30 g of ethanol were mixed with aqueous acidified potassium dichromate(VI). The desired product was collected by immediate distillation under gentle warming.

The yield of product was 70.0 %.

What mass of product was collected?

A 1.54 g **B** 1.61 g **C** 2.10 g **D** 3.14 g

[W'11 P12 Q26]

35 Which reagent could best be used to distinguish between cyclohexene and cyclohexanol?

A $Ag(NH_3)_2^+$ in H_2O

B Br_2 in CCl_4

C 2,4-dinitrophenylhydrazine in CH_3OH

D $NaBH_4$ in CH_3OH

[W'11 P12 Q28]

36 When 1-bromopropane is treated in succession with two reagents, X and Y, it produces propanoic acid.

What are reagents X and Y?

	X	Y
A	NaOH(aq)	$H^+ / Cr_2O_7^{2-}$(aq)
B	NaOH(aq)	CO_2
C	KCN in ethanol	HCl(aq)
D	KCN in ethanol	NaOH(aq)

[S'12 P12 Q22]

37 An organic compound will decolorise dilute acidified aqueous potassium manganate(VII) on warming, but will not decolorise bromine water.

What could the organic compound be?

A butane

B ethanol

C ethene

D ethanoic acid

[S'12 P12 Q30]

38 Which compound is optically active and could also be oxidised to a ketone?

A 2-methylbutan-1-ol

B 3-methylhexan-3-ol

C 3-methylpentan-2-ol

D propan-2-ol

[W'12 P13 Q28]

39 2.30 g of ethanol were mixed with an excess of aqueous acidified potassium dichromate(VI). The reaction mixture was then boiled under reflux for one hour. The desired organic product was then collected by distillation. The yield of product was 60.0 %.

What mass of product was collected?

A 1.32 g **B** 1.38 g **C** 1.80 g **D** 3.20 g

[S'13 P11 Q26]

40 The compound hex-3-en-1-ol, **P**, has a strong 'leafy' smell of newly cut grass and is used in perfumery.

$$CH_3CH_2CH{=}CHCH_2CH_2OH$$

P

What is produced when **P** is treated with an excess of hot concentrated acidified $KMnO_4$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CH_2OH$

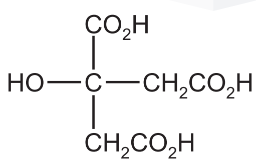
B $CH_3CH_2CH{=}CHCH_2CO_2H$

C CH_3CH_2CHO and $OCHCH_2CH_2OH$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

[S'13 P12 Q20]

41 How many moles of hydrogen, H_2, are evolved when an excess of sodium metal is added to one mole of citric acid?



citric acid

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

[W'13 P11 Q26]

42 Primary alcohols can be oxidised to aldehydes using either acidified potassium dichromate(VI) or acidified potassium manganate(VII). Both these oxidising agents change colour as they are reduced.

What is the colour of each oxidising agent before and after it has reacted?

	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

[W'13 P11 Q27]

43 An alcohol with molecular formula $C_nH_{2n+1}OH$ has a chiral carbon atom but does not react with hot, acidified $K_2Cr_2O_7$.

What is the smallest possible value for *n*?

A 5 **B** 6 **C** 7 **D** 8

[W'13 P13 Q27]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which alcohols on oxidation with acidified potassium dichromate(VI) give an organic product which causes an effervescence when reacted with sodium carbonate?

1 butan-1-ol

2 2-methylpropan-1-ol

3 2-methylpropan-2-ol

[S'02 Q40]

2 Which ions are present in a solution of ethanol in an excess of concentrated sulphuric acid?

1 $CH_3CH_2O^-$

2 $CH_3CH_2\overset{+}{O}H_2$

3 HSO_4^-

[W'02 Q39]

3 Chloroethane can be formed from bromoethane in two steps.

$$C_2H_5Br \xrightarrow{\text{step } \mathbf{X}} C_2H_5OH \xrightarrow{\text{step } \mathbf{Y}} C_2H_5Cl$$

Which statements about these steps are correct?

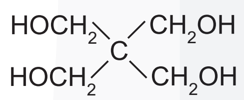
1 Step **X** involves nucleophilic substitution.

2 Hot aqueous sodium hydroxide is the reagent in step **X**.

3 Hot aqueous sodium chloride is the reagent in step **Y**.

[S'03 Q38]

4 Pentaerythritol is an intermediate in the manufacture of paint.



pentaerythritol

Which of the following statements about pentaerythritol are correct?

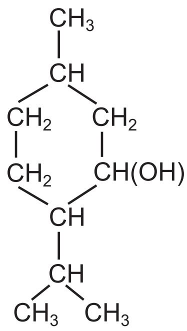
1 It reacts with metallic sodium.

2 It is dehydrated by concentrated sulphuric acid to an alkene.

3 Its empirical formula is CH_3O.

[W'04 Q39]

5 Menthol, from oil of mint, is used in soaps and perfumes.



menthol

Which statements about menthol are correct?

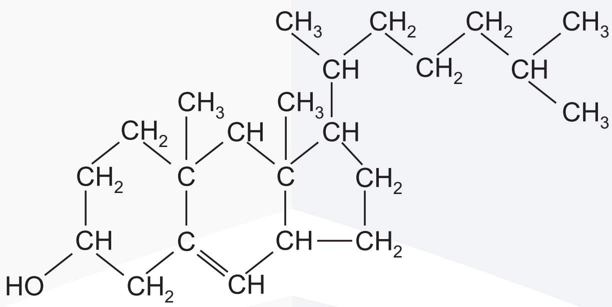
1 There is a total of two chiral centres present in the menthol molecule.

2 On reaction with concentrated sulphuric acid, menthol produces a mixture of two alkenes.

3 A solution of acidified potassium dichromate(VI), on warming with menthol, changes colour from orange to green.

[S'07 Q39]

6 The compound cholesterol has the following structure.



Which statements are correct?

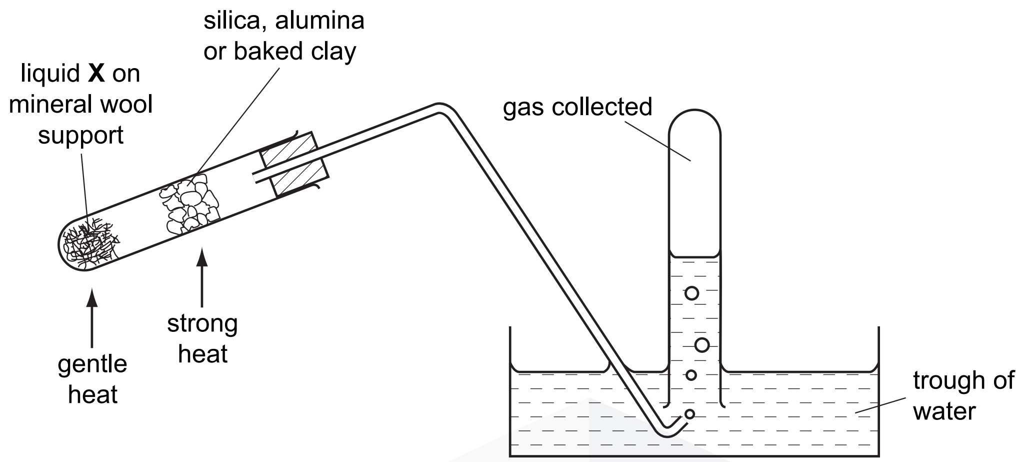
1 Cholesterol reacts with a mixture of ethanoic acid and concentrated sulphuric acid.

2 Cholesterol reacts with bromine to form a compound which has two new chiral centres.

3 Cholesterol is oxidised by acidified sodium dichromate(VI) to form an aldehyde.

[S'08 Q39]

7 The diagram shows an experiment.



Which processes could be demonstrated by using the above apparatus?

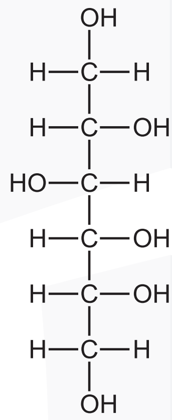
1 the oxidation of ethanol (the liquid **X**)

2 the dehydration of ethanol (the liquid **X**)

3 the cracking of paraffin (the liquid **X**)

[W'09 P12 Q38]

8 Sorbitol is an artificial sweetener used to sweeten chocolate which is suitable for diabetics.



sorbitol

Which functional groups can be produced when this molecule is subjected to oxidation under suitable conditions?

1 aldehyde

2 carboxylic acid

3 ketone

[S'11 P13 Q39]

9 A number of alcohols with the formula $C_4H_{10}O$ are separately oxidised. Using 70 g of the alcohols a 62 % yield of organic product is achieved.

What mass of product could be obtained?

1 42.2 g of butanone

2 51.6 g of butanoic acid

3 51.6 g of 2-methyl propanoic acid

[S'12 P11 Q38]

10 What can be produced when an aqueous solution of butan-2-ol is oxidised under suitable conditions?

1 butanone

2 butanoic acid

3 butanal

[S'13 P12 Q38]

ALCOHOLS WS 4

1 Pentan-1-ol, $C_5H_{11}OH$, is important in the synthesis of organic compounds.

(a) Give the structural formula of another primary alcohol which is an isomer of pentan-1-ol.

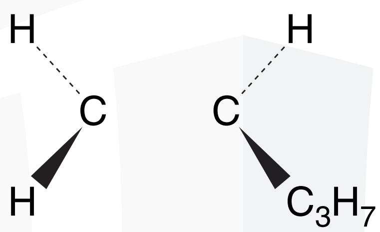
[1]

(b) **(i)** Write a balanced equation for the preparation of 1-bromopentane from pentan-1-ol.

(ii) This preparation gives a yield of 60%. Calculate the mass of pentan-1-ol required to produce 15.0 g of 1-bromopentane.

[3]

(c) Dehydration of pentan-1-ol produces pent-1-ene. Sketch on the diagram below the orbital overlap between the two carbon atoms. Label the bonds.



[2]

(d) The two compounds below are among many secreted by insects to attract members of the same species. Such compounds are used in traps to control insect populations. They need to be made synthetically.

For each synthesis outline how they could be prepared from pentan-1-ol, giving the necessary reagents and conditions.

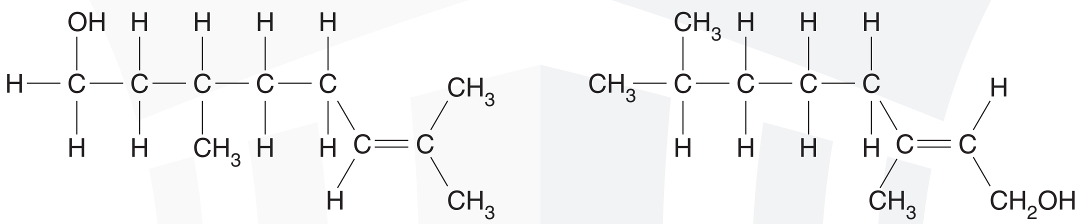
(i) $CH_3(CH_2)_3CO_2H$

(ii) $CH_3CO_2(CH_2)_4CH_3$

[4]

[N'02 Q6]

2 Some perfumes and scents of flowers and fruit contain compounds which are structural isomers. Two such examples are citronellol and geraniol.



citronellol geraniol

(a) Confirm that citronellol and geraniol are isomers by calculating their molecular formula and their relative molecular mass, M_r.

(i) Molecular formula ....

(ii) M_r ....[2]

(b) Name two functional groups present in **both** molecules.

(i) ....

(ii) ....[3]

Citronellol and geraniol also show stereo isomerism.

(c) On the diagram of the structure of citronellol above, draw a circle around a chiral carbon atom. [1]

(d) **(i)** Draw the other *cis-trans* isomer of geraniol. [In parts **(d)** and **(f)** use R – to represent a part of the molecule.]

(ii) Explain why geraniol has no optical isomers.

....

....[2]

(e) State what you would expect to see if citronellol was reacted with aqueous bromine.

....

....[1]

(f) Draw structures of the organic products when geraniol reacts with each of the following reagents.

(i) an excess of $H^+ / Cr_2O_7^{2-}$ under reflux

(ii) ethanoic acid in the presence of an acidic catalyst

(iii) hydrogen bromide, HBr

[4]

(ii) Leaf alcohol was reacted to form a product with an M_r value 18 units less.

Suggest a structure for this product and deduce the type of reaction that took place.

structure of product.

type of reaction ....[3]

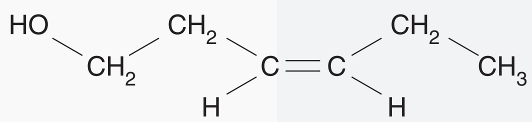
(d) Describe a simple chemical test to distinguish between leaf alcohol and your product in **(c)(ii)**.

test ....

observation ....[2]

[N'04 Q2]

3 **(b)** Leaf alcohol is a stereoisomer that can form when insects such as caterpillars eat green leaves.



(i) Draw the other stereo-isomer of leaf alcohol.

(ii) Draw the structure for the ester formed when leaf alcohol reacts with ethanoic acid. Show **all** the bonds in the ester group.

[3]

(c) **(i)** Deduce the relative molecular mass, M_r, for leaf alcohol.

[J'04 Q4]

4 Alcohols are widely used as solvents and in the manufacture of esters.

Butan-1-ol, $C_4H_{10}O$, is an example of a primary alcohol.

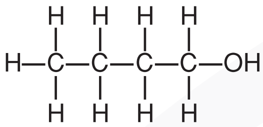
(a) What is meant by the term *primary alcohol*?

.... [1]

(b) There are three more alcohols with molecular formula $C_4H_{10}O$ that are **structural** isomers of butan-1-ol.

Complete the table below by drawing displayed formulae of **each** of these three compounds.

For **each** isomer, state whether it is a primary, secondary, or tertiary alcohol.

			
primary			
butan-1-ol	isomer 2	isomer 3	isomer 4

[6]

(c) Butan-1-ol can be oxidised to a carboxylic acid by heating with an acidified solution of potassium dichromate(VI).

(i) What colour change would be seen during this reaction?

from .... to ....

(ii) State which of the isomers you have drawn in **(b)** could also be oxidised to form a carboxylic acid.

....
[3]

[N'05 Q4]

5 Compounds containing the allyl group, $CH_2{=}CHCH_2{-}$, have pungent smells and are found in onions and garlic.
Allyl alcohol, $CH_2{=}CHCH_2OH$, is a colourless liquid which is soluble in water.

(a) Allyl alcohol behaves as an alkene and as a primary alcohol.

Give the structural formula of the organic compound formed when allyl alcohol is

(i) reacted with Br_2,

(ii) heated under reflux with an acidified solution of $Cr_2O_7^{2-}$ ions.

[2]

(b) When allyl alcohol is reacted with MnO_2 at room temperature, propenal, $CH_2{=}CHCHO$ is formed.

What type of reaction is this?

....[1]

(c) Allyl alcohol may be converted into propanal, CH_3CH_2CHO, by using a ruthenium(IV) catalyst in water.

$$CH_2{=}CHCH_2OH \xrightarrow{\text{ruthenium(IV) catalyst}} CH_3CH_2CHO$$

The reactant and the product are isomers.
What form of isomerism do they display?

....[1]

(d) Allyl alcohol can be converted into propanal in two steps **without** the use of a ruthenium(IV) catalyst.

$CH_2{=}CHCH_2OH \xrightarrow{\text{step I}} CH_3CH_2CH_2OH \xrightarrow{\text{step II}} CH_3CH_2CHO$

What reagents and conditions would be used for **each** step?

step I

reagent(s) ....

condition(s) ....

step II

reagent(s) ....

condition(s) ....[4]

(e) By considering your answers to **(b)** and **(d)**, suggest what is unusual about the single-step reaction in **(c)**.

....

....[1]

(f) Suggest the structural formula of the organic compound formed when allyl alcohol is

(i) reacted with cold, dilute MnO_4^- ions,

(ii) heated under reflux with acidified MnO_4^- ions.

[3]

[J'06 Q4]

6 Lactic acid, 2-hydroxypropanoic acid, $CH_3CH(OH)CO_2H$, occurs in sour milk.

Glycollic acid, 2-hydroxyethanoic acid, $HOCH_2CO_2H$, occurs in sugar cane.

(a) Lactic acid may be synthesised from propene by the following sequence.

$$CH_3CH{=}CH_2 \xrightarrow{\text{step I}} CH_3CH(OH)CH_2OH \xrightarrow{\text{step II}} CH_3CH(OH)CO_2H$$

(i) What reagent(s) and condition(s) are used for step **I**?

reagent(s) ....

condition(s) ....

(ii) What type of reaction is step **II**?

....

[3]

(b) Glycollic acid may be synthesised from ethanoic acid by the following sequence.

$$CH_3CO_2H \xrightarrow{\text{step III}} ClCH_2CO_2H \xrightarrow{\text{step IV}} HOCH_2CO_2H$$

(i) Suggest the reagent(s) and condition(s) that are used for step **III**.

reagent(s) ....

condition(s) ....

(ii) What reagents and conditions are used in step IV?

reagent(s) ....

condition(s) ....

[4]

(c) Lactic acid and glycollic acid react differently when heated under reflux with acidified dichromate(VI) ions.

Draw the structural formula of the organic product in **each** case.

product from lactic acid product from glycollic acid

[2]

(d) Lactic acid is chiral. Draw displayed formulae of the two optical isomers of lactic acid clearly showing their three-dimensional structures. Indicate with an asterisk (*) the chiral carbon atom in each.

[2]

Glycollic acid and lactic acid each give the reactions of an alcohol group and of a carboxylic acid group. Each compound will react with the other to give an ester.

(e) When one molecule of glycollic acid reacts with one molecule of lactic acid, it is possible to form two different esters.

Draw the structure of **each** of these esters.

[2]

Glycollic acid and lactic acid are reacted together to make the material for 'soluble stitches' (also known as 'soluble sutures') which are used in surgery.

In this material, many molecules of each acid have been reacted to form a long chain 'polyester' molecule which contains many ester groups.

This polyester is used in surgery to sew up wounds inside the body.

Over a period of time, the polyester undergoes a chemical reaction and breaks up to re-form the two individual hydroxy-acids.

(f) **(i)** This reaction occurs where the pH of the body is about pH5 to pH6. Suggest what type of chemical reaction causes the polyester material to break up.

....

(ii) Suggest why the products of this reaction are soluble in water.

....

....

[2]

[N'06 Q5]

7 Alcohols may be classified into primary, secondary and tertiary. Some reactions are common to all three types of alcohol. In other cases, the same reagent gives different products depending on the nature of the alcohol.

In the empty squares below give the structural formula of the organic compound formed in each of the reactions indicated.

If no reaction occurs, write 'no reaction' in the space.

reagent(s) and conditions \ alcohol	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH(OH)CH_3$	$(CH_3)_3COH$
red phosphorus and iodine heat under reflux			
concentrated H_2SO_4 heat			
$Cr_2O_7^{2-}/H^+$ heat under reflux			

[5]

[J'07 Q2]

8 The structural formulae of six different compounds, **A – F**, are given below.
Each compound contains four carbon atoms in its molecule.

$CH_3CH{=}CHCH_3$	$CH_3CH_2COCH_3$	$CH_2{=}CHCH_2CH_3$
A	**B**	**C**
$CH_3CH_2CH(OH)CH_3$	$HOCH_2CH_2CH_2CH_2OH$	$CH_3CH_2OCH_2CH_3$
D	**E**	**F**

(a) **(i)** What is the empirical formula of compound **E**? ………………

(ii) Draw the skeletal formula of compound **D**.

(iii) Structural formulae do not show all of the isomers that may exist for a given molecular formula. Which **two** compounds **each** show **different** types of isomerism and what type of isomerism does each compound show? Identify each compound by its letter.

compound	type of isomerism

[4]

Compound **D** may be converted into compound **C**.

(b) **(i)** What type of reaction is this?

………………………………………

(ii) What reagent would you use for this reaction?

………………………………………

(iii) What is formed when compound **E** undergoes the same reaction using an excess of the same reagent?

……………………………………… [3]

Compound **A** may be converted into compound **B** in a two-stage reaction.

$$CH_3CH{=}CHCH_3 \xrightarrow{\text{stage I}} \text{intermediate} \xrightarrow{\text{stage II}} CH_3CH_2COCH_3$$

(c) **(i)** What is the structural formula of the intermediate compound formed in this sequence?

(ii) Outline how stage **I** may be carried out to give this intermediate compound.

....

....

....

(iii) What reagent would be used for stage **II**?

.... [4]

(d) Compounds **D** and **F** are isomers.

What type of isomerism do they show?

.... [1]

[N'09 Q4]

9 The fermentation of starch or molasses using the bacterium *Clostridium acetobutylicum*, produces a mixture of propanone and butan-1-ol.

(b) What will be observed when a small piece of sodium metal is dropped into a dry sample of butan-1-ol? Write an equation for the reaction that takes place.

observation ....

equation .... [2]

The molecular formula $C_5H_{12}O$ represents a number of alcohols.
Three alcohols with molecular formula $C_5H_{12}O$ are straight chain pentanols.

(c) Draw the following formulae.

(i) the **structural** formula of pentan-1-ol

(ii) the **displayed** formula of pentan-2-ol

(iii) the **skeletal** formula of pentan-3-ol

[3]

When one of the three pentanols in **(c)** is dehydrated, alkenes with **two** different structural formulae are formed.

(d) Identify this alcohol and give the structural formula of **each** alkene.

name of alcohol ....

alkene 1	alkene 2

[3]

A number of alcohols with molecular formula $C_5H_{12}O$ are branched chain compounds and may be considered as derivatives of butanol or propanol with alkyl side chains.

(e) **(i)** Draw the structural formula of the **derivative of propanol** that has the molecular formula $C_5H_{12}O$.

(ii) Draw the structural formula of the organic compound that will be present when the derivative of propanol you have given in **(i)** is heated under reflux with acidified potassium dichromate(VI).

[2]

[N'09 Q5]

10 Fermentation of sugars by bacteria or moulds produces many different organic compounds.

One compound present in fermented molasses is 2-ethyl-3-methylbutanoic acid which gives a distinctive aroma to rum.

$$(CH_3)_2CHCH(C_2H_5)CO_2H$$

2-ethyl-3-methylbutanoic acid

(a) (i) What is the molecular formula of 2-ethyl-3-methylbutanoic acid?

(ii) How many chiral carbon atoms are present in a molecule of 2-ethyl-3-methylbutanoic acid? If none write 'none'.

....

[2]

A sample of 2-ethyl-3-methylbutanoic acid may be prepared in a school or college laboratory by the oxidation of 2-ethyl-3-methylbutan-1-ol, $(CH_3)_2CHCH(C_2H_5)CH_2OH$.

(b) (i) State the reagent(s) that would be used for this oxidation.
Describe what colour change would be seen.

reagent(s) ....

colour change from .... to ....

This reaction is carried out by heating the reacting chemicals together.

(ii) What could be the main organic impurity present in the sample of the acid?

Explain your answer.

....

....

....

(iii) State whether a distillation apparatus or a reflux apparatus should be used.

Explain your answer.

....

....

....

[6]

(c) A structural isomer of 2-ethyl-3-methylbutan-1-ol is 2-ethyl-3-methylbutan-2-ol, $(CH_3)_2CHC(OH)(C_2H_5)CH_3$.

What colour change would be seen if this were heated with the reagents you have given in **(b)(i)**?
Explain your answer as clearly as you can.

....

....

....[3]

An isomer of 2-ethyl-3-methylbutanoic acid which is an ethyl ester is a very strong smelling compound which is found in some wines.

(d) This ethyl ester contains a branched hydrocarbon chain and is chiral.

Draw the displayed formula of this ethyl ester.

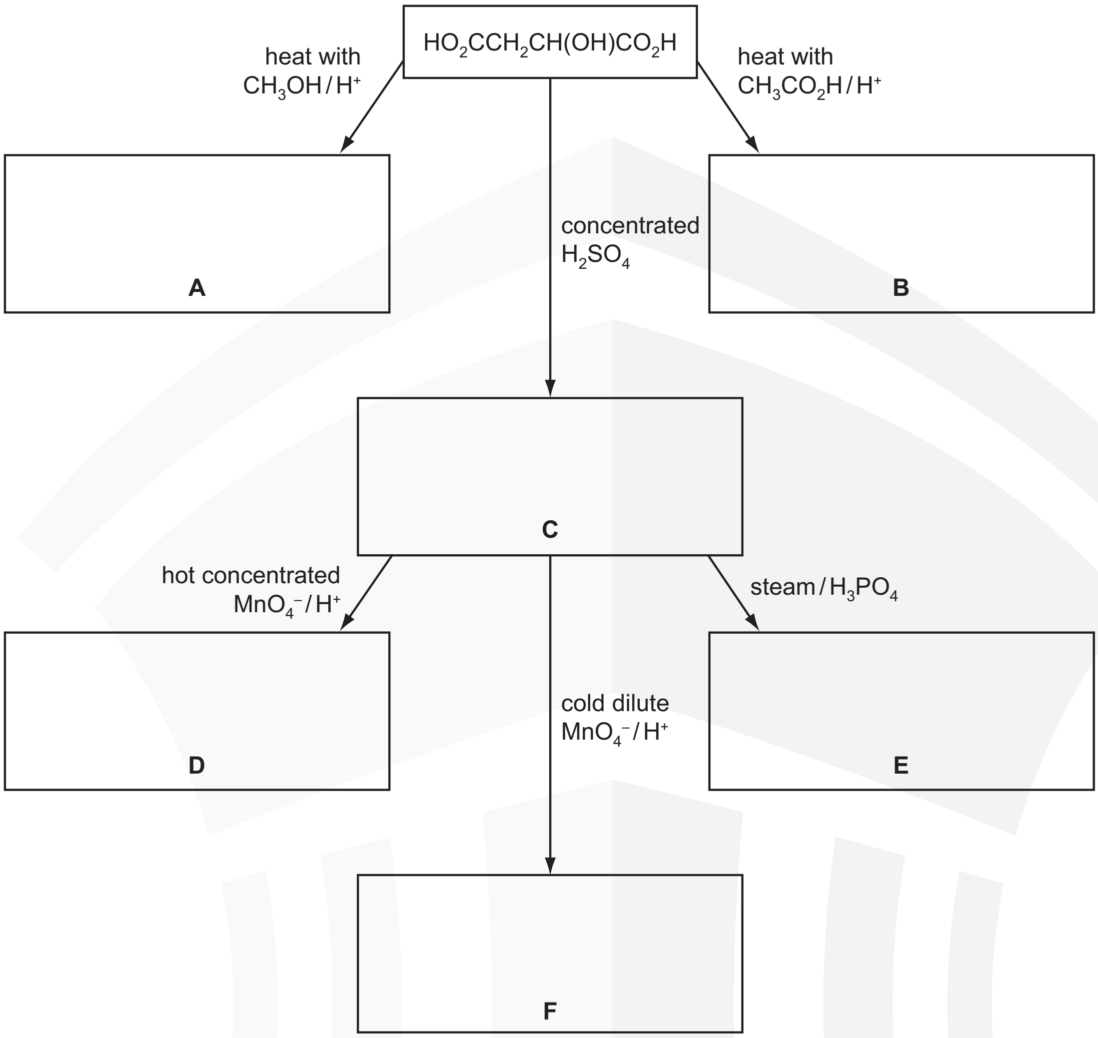
Identify the chiral carbon atom with an asterisk (*).

[3]

[J'11 P23 Q5]

11 Food additives are substances added to food to preserve the flavour or to improve its taste and appearance.
European Union legislation requires most additives used in foods to be labelled clearly in the list of ingredients, either by name or by an ‘E number’. E296 is malic acid which occurs in unripe fruit.
Malic acid has the structural formula $HO_2CCH_2CH(OH)CO_2H$.

(a) Some reactions of malic acid are shown below.
In the boxes below, give the **structural** formulae of organic compounds **A** to **F**.



[6]

(b) What *type of reaction* is **each** of the following conversions?

malic acid into **C** ....

C into **D** ....

C into **E** .... [3]

(c) Suggest **one** major commercial use of compounds such as **A** or **B**.

.... [1]

(d) **(i)** Malic acid is chiral.
Draw fully displayed formulae of the two optical isomers of malic acid.
Indicate with an asterisk (*) the chiral carbon atom.

(ii) Compound **C** also shows stereoisomerism.
Draw the skeletal formulae of **each** of the stereoisomers of **C**. Label **each** isomer.

[6]

(e) The food additive E330 is another organic compound which occurs naturally in fruit.
E330 has the following composition by mass: C, 37.5 %; H, 4.17 %; O, 58.3 %.
Calculate the empirical formula of E330.

[3]

[J'12 P22 Q3]

12 Compounds containing the allyl group, $CH_2{=}CHCH_2{-}$, have pungent smells and are found in onions and garlic.
Allyl alcohol, $CH_2{=}CHCH_2OH$, is a colourless liquid which is soluble in water.

(a) Allyl alcohol behaves as a primary alcohol and as an alkene.

Give the structural formula of the organic compound formed when allyl alcohol is reacted separately with each of the following reagents.

(i) acidified potassium dichromate(VI), heating under reflux

(ii) bromine in an inert organic solvent

(iii) cold, dilute, acidified potassium manganate(VII)

(iv) hot, concentrated, acidified potassium manganate(VII)

[5]

(b) Allyl alcohol undergoes the following reactions.

(i) When reacted with concentrated HCl at 100 °C, $CH_2{=}CHCH_2Cl$ is formed.

State as fully as you can what *type of reaction* this is.

....

(ii) When reacted with MnO_2 at room temperature, $CH_2{=}CHCHO$ is formed.

What *type of reaction* is this?

....

[2]

(c) Allyl alcohol can be converted into propanal in two steps.

$$CH_2{=}CHCH_2OH \xrightarrow{\text{step I}} CH_3CH_2CH_2OH \xrightarrow{\text{step II}} CH_3CH_2CHO$$

(i) What reagents and conditions would be used for **each** step?

step I

reagent(s) ....

condition(s) ....

step II

reagent(s) ....

condition(s) ....

(ii) Allyl alcohol and propanal are isomers.

What form of isomerism do they display?

....

[5]

(d) Allyl alcohol may also be converted into propanal by using a ruthenium(IV) catalyst in water.

$$CH_2{=}CHCH_2OH \xrightarrow{\text{ruthenium(IV) catalyst}} CH_3CH_2CHO$$

Suggest what is unusual about this single step reaction.

....

.... [1]

[J'13 P23 Q5]

13 The molecular formula C_4H_9OH represents four different alcohols, **W**, **X**, **Y** and **Z**.

W	**X**	**Y**	**Z**
$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH(OH)CH_3$	$(CH_3)_2CHCH_2OH$	$(CH_3)_3COH$

(a) Draw the **skeletal formula** of **Z**.

[1]

(b) Acidified potassium dichromate(VI) is used as an oxidising agent in organic chemistry.

Give the **structural formula** of the organic product formed when **each** of the four alcohols above is heated under reflux with acidified potassium dichromate(VI).
If you believe that no reaction occurs, write 'no reaction' in the box.

W	
X	
Y	
Z	

[4]

(c) One of the alcohols, **W**, **X**, **Y** or **Z**, can be dehydrated to give more than one organic product.

Identify this alcohol and give the structural formulae of **two** of the products.

alcohol	
product 1	
product 2	

[2]

[N'13 P23 Q5]

Carbonyls

This topic introduces the chemistry of the carbonyl compounds, aldehydes and ketones.

a describe: ☐

(i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$

(ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ or $LiAlH_4$

(iii) the reaction of aldehydes and ketones with HCN and NaCN

b describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones ☐

c describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds ☐

d deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation) ☐

e describe the reaction of CH3CO– compounds with alkaline aqueous iodine to give tri-iodomethane ☐

CARBONYLS

18 Carbonyl compounds

This topic introduces the chemistry of the carbonyl compounds, aldehydes and ketones.

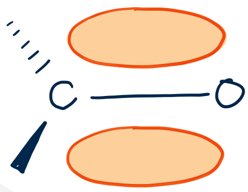
	Learning outcomes Candidates should be able to:
18.1 Aldehydes and ketones	a) describe: (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$ (ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ or $LiAlH_4$ (iii) the reaction of aldehydes and ketones with HCN and NaCN b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation) e) describe the reaction of $CH_3CO–$ compounds with alkaline aqueous iodine to give tri-iodomethane

INTRODUCTION

Collectively, aldehydes and ketones are known as carbonyl compounds.

The properties of aldehydes and ketones are very similar to each other: almost all the reactions of ketones are also shown by aldehydes. But aldehydes show additional reactions associated with their lone hydrogen atom.

The carbonyl double bond is formed by the sideways overlap of two adjacent p orbitals, one on carbon and one on oxygen. Because of its higher electronegativity, oxygen attracts the bonding electrons (in both the σ and the π bonds), creating an electron- deficient carbon atom.



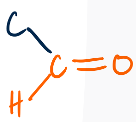
This unequal distribution of electrons is responsible for the ways in which carbonyl compounds react.

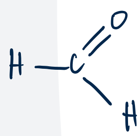
1

ALDEHYDES

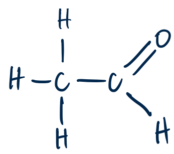
Aldehydes have at least one H attached to the carbonyl group.

Their names end in -al

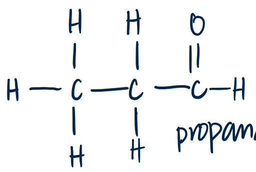




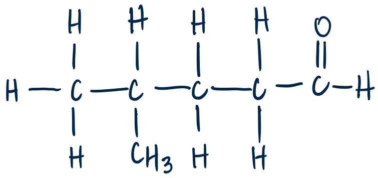
methanal
HCHO



ethanal
CH_3CHO



propanal



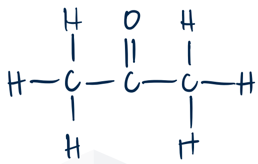
4-methylpentanal

2

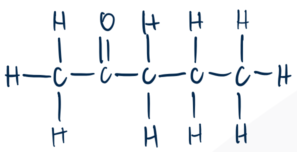
KETONES

Ketones have two carbons attached to the carbonyl group.

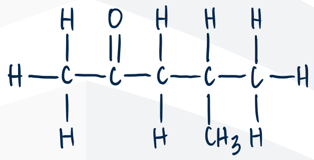
Their names end in **-one**



propanone



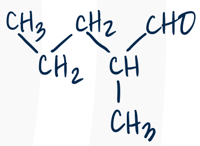
pentan-2-one

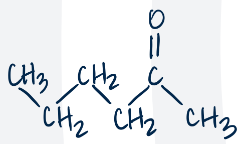


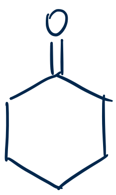
4-methylpentan-2-one

3

SKILL CHECK





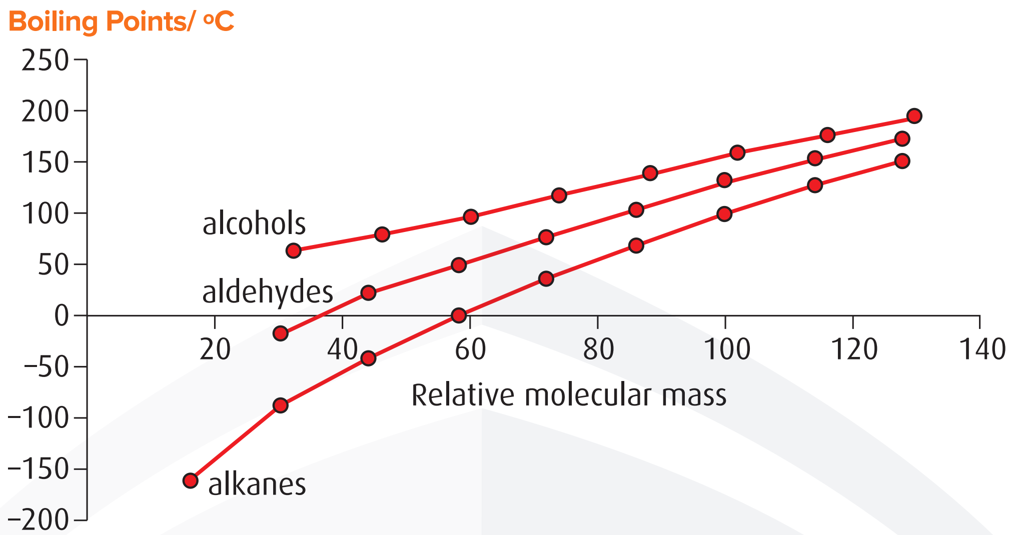


$(CH_3)_3C\,CHO$

$(CH_3CH_2CH_2)_2C=O$

4

BOILING POINTS



5

BOILING POINTS

Aldehydes have higher boiling points than alkanes, as aldehydes are polar whereas alkanes are non-polar. Aldehydes are polar because of the presence of the very electronegative O atom.

The intermolecular forces between aldehyde molecules are stronger than those between alkane molecules of similar relative molecular mass because of the presence of dipole–dipole interactions between the aldehyde molecules.

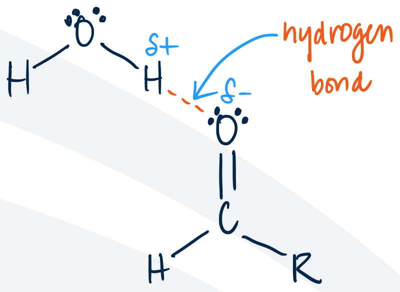
Alcohols are also polar molecules, but, because the O is joined directly to an H atom, they are also able to participate in hydrogen bonding. Hydrogen bonding is a stronger intermolecular force than dipole–dipole interactions.

6

SOLUBILITY

Lower members (methanal, ethanal, propanal, propanone, butanone) are soluble in water because of their polarity and also because they are able to hydrogen bond to water molecules.

The solubility decreases as the hydrocarbon chain gets longer, because of the non-polar nature of the hydrocarbon chain.



Note: aldehydes do not hydrogen bond to each other, but they are able to participate in hydrogen bonding with water.

7

FORMATION OF ALDEHYDES

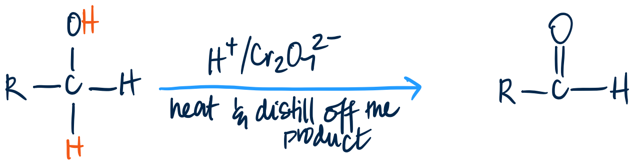
Aldehydes are prepared by the controlled oxidation of a primary alcohol.

Primary alcohols oxidize to aldehydes when heated with acidified potassium dichromate, K2Cr2O7, and the product distilled off. (It is essential to distill off the aldehyde before it gets oxidized to acid.)

Reagent acidified potassium dichromate, $K_2Cr_2O_7$

Condition heat and distill off the product

Type oxidation



8

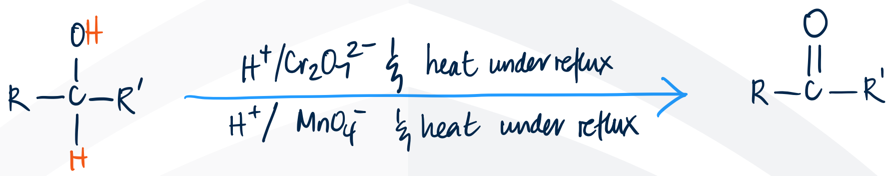
FORMATION OF KETONES

Secondary alcohols when heated (under reflux to get a good yield) with acidified potassium dichromate(VI) or potassium manganate(VII), form ketones.

Reagent acidified potassium dichromate, $K_2Cr_2O_7$
(OR acidified potassium manganate(VII), $KMnO_4$)

Condition heat under reflux

Type oxidation



9

REDUCTION OF ALDEHYDES & KETONES

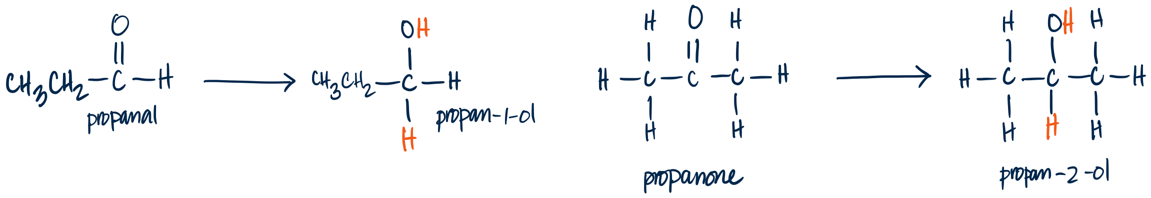
Reagent sodium borohydride, $NaBH_4$(aq) or lithium aluminiumhydride, $LiAlH_4$, in ether.

Condition heat

Type Reduction

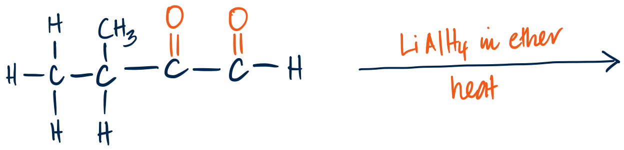
Alternate hydrogen gas over a nickel or platinum catalyst and heat

Aldehydes give primary alcohols, while ketones give secondary alcohols.



10

SKILL CHECK



Draw molecules **W** and **X.**

11

SKILL CHECK

Draw molecule Q and give the reagents and conditions for reactions **I** and **II**.

$$(CH_3)_2CO \xrightarrow{\text{I}} Q \xrightarrow{\text{II}} CH_3CH=CH_2$$

12

SKILL CHECK

Name the reagents and the conditions required for the following reactions:

(a) $CH_3-CH=CH-CHO \longrightarrow CH_3-CH=CH-CH_2OH$

(b) $CH_3-CH=CH-CHO \longrightarrow CH_3-CH_2-CH_2-CH_2OH$

13

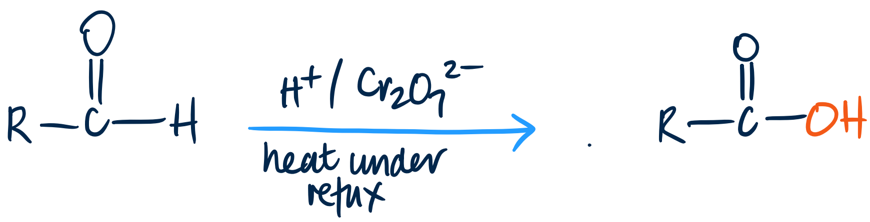
OXIDATION OF ALDEHYDES

Aldehydes are oxidized readily to their corresponding acids by acidified sodium dichromate or manganate (VII). Ketones do not undergo oxidation.

Reagent acidified potassium dichromate, $K_2Cr_2O_7$
(OR acidified potassium manganate(VII), $KMnO_4$)

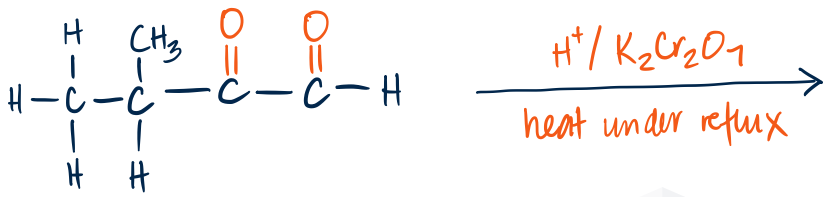
Condition heat under reflux

Type oxidation



14

SKILL CHECK

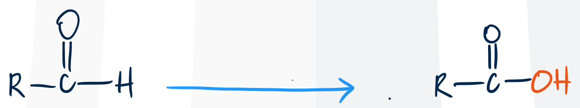


15

OXIDATION OF ALDEHYDES

OXIDATION provides a way of differentiating between aldehydes and ketones.

Aldehydes can be oxidized to carboxylic acids and ketones can not be oxidized.



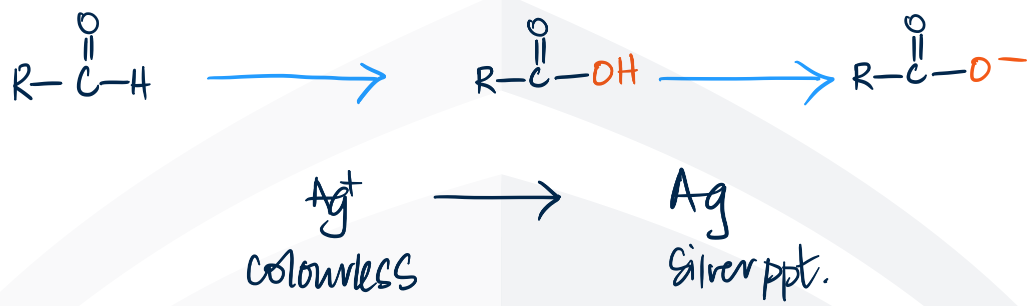
OXIDISING AGENTS	OBSERVATION with ALDEHYDES
Acidified Potassium Dichromate	color changes from orange to green
Acidified Potassium Permanganate	color changes from purple to colorless
Tollen's Reagent	forms a silver ppt.
Fehling's Solution	forms a brick red ppt.

16

TOLLEN'S REAGENT

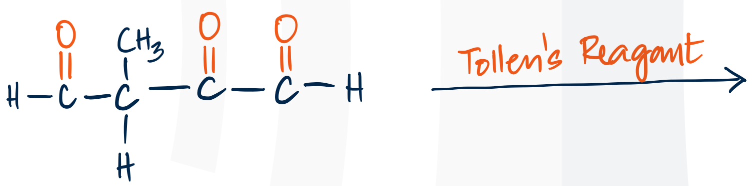
Tollen's Reagent – ammoniacal silver nitrate, contains the diammine silver(I) ion $[Ag(NH_3)_2]^+$ (ligand, complex ion), this acts as a mild oxidizing agent and will oxidize aldehydes but not ketones.

The silver(I) ion is reduced to silver.



17

SKILL CHECK



18

TOLLEN'S REAGENT

The reaction produce a silver ppt (as the silver(I) ion is reduced to silver.)

The test is known as THE SILVER MIRROR TEST.

Aldehydes are oxidised to salt of carboxylic acids as Tollen's reagent is alkaline.

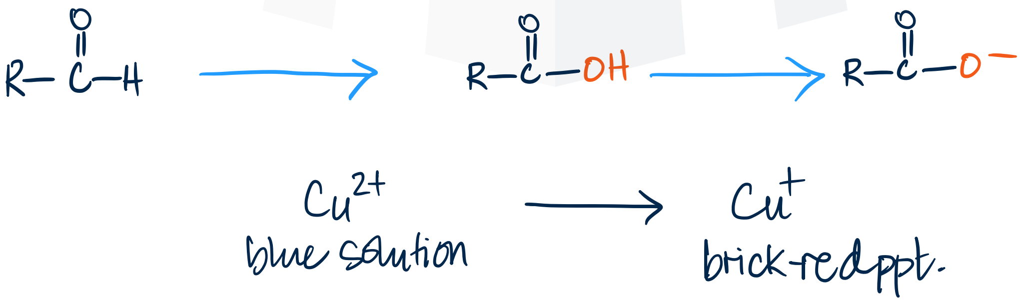
Note: if the container isn't clean, then a black ppt. forms

FEHLING'S SOLUTION

Fehling's Solution contains copper(II) ions, blue solution.

On warming it will oxidize aldehydes.

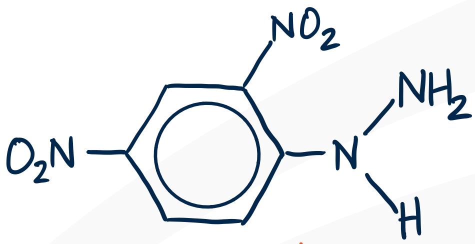
Copper(II) is reduced to a brick-red precipitate.



CONDENSATION REACTION

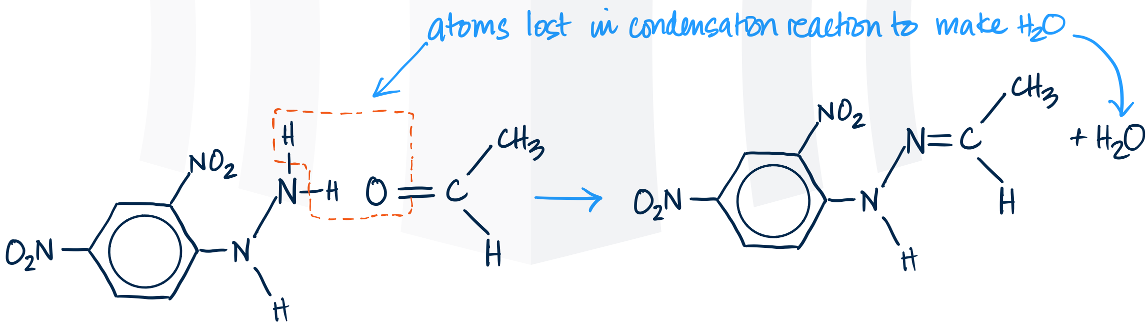
The most important condensation reaction of carbonyl compounds is that with 2,4-dinitrophenylhydrazine (2,4-DNPH).

The products are called hydrazones and are crystalline orange solids, which precipitate out of solution rapidly.



2,4-DNPH

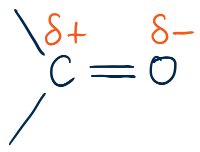
CONDENSATION REACTION



2,4-dinitrophenylhydrazine

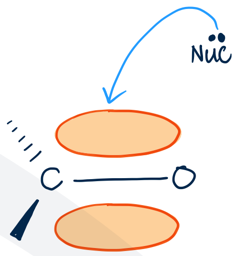
NUCLEOPHILIC ADDITION REACTION

The carbonyl group in aldehydes and ketones is polar because oxygen is much more electronegative than carbon.



The shared electrons in the double bond are drawn towards the oxygen atom. This leaves a slight positive charge on the carbon atom.

As a result, the carbon atom in a carbonyl group is open to attack by nucleophiles.



Both aldehydes and ketones undergo nucleophilic addition reactions.

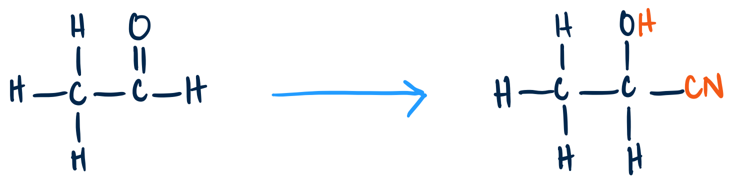
It involves addition to the **polar** C=O double bond. Nucleophiles attack the positive carbon centre.

NUCLEOPHILIC ADDITION REACTION

Carbonyl compounds add on to hydrogen cyanide (HCN) to give nitriles.

The reaction is carried out by treating the carbonyl compound with dilute HCN in an excess of $NaCN_{(aq)}$ (or $KCN_{(aq)}$).

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$$



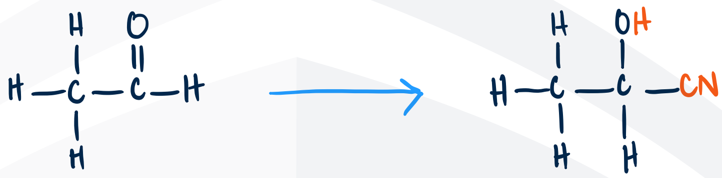
NUCLEOPHILIC ADDITION REACTION

Reagent dilute HCN in an excess of $NaCN_{(aq)}$ (or $KCN_{(aq)}$)
OR aqueous sodium cyanide and dilute sulphuric acid (or dilute HCl).

Condition heat under reflux

Type nucleophilic addition

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

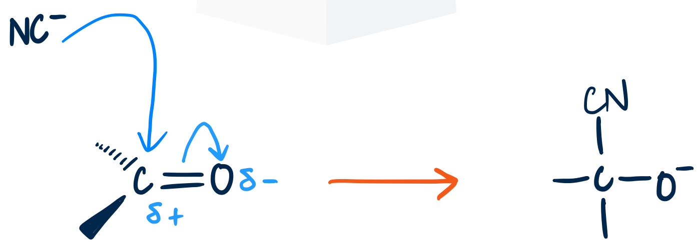


25

NUCLEOPHILIC ADDITION STEP 1

CN– (from NaCN or KCN) acts as a nucleophile and attacks the slightly positive carbon atom.

One of the C=O bonds breaks; a pair of electrons goes onto the O and gets a negative charge.



26

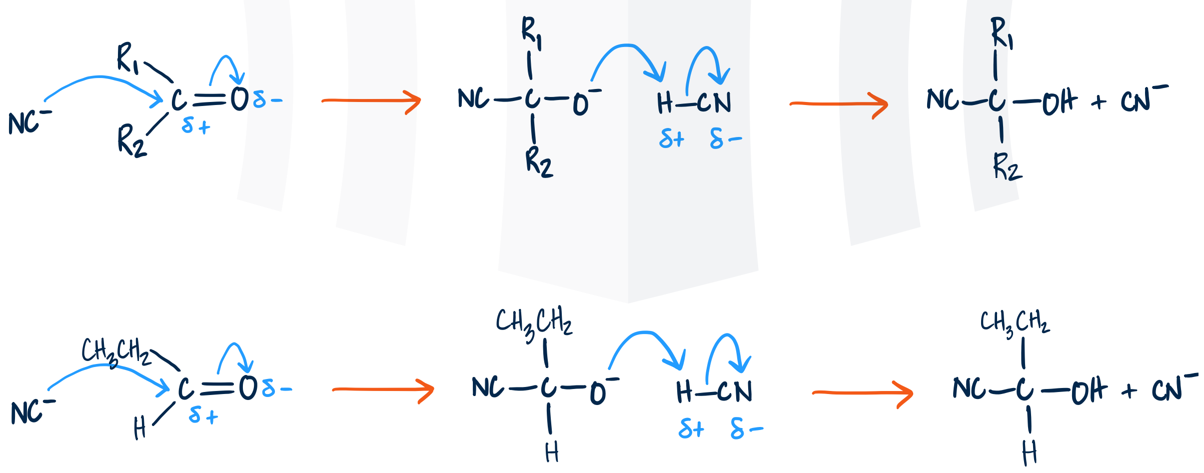
NUCLEOPHILIC ADDITION STEP 2

A pair of electrons from the O with a —ve charge is used to form a bond with H from HCN.

Overall, there has been an addition of HCN.

27

NUCLEOPHILIC ADDITION

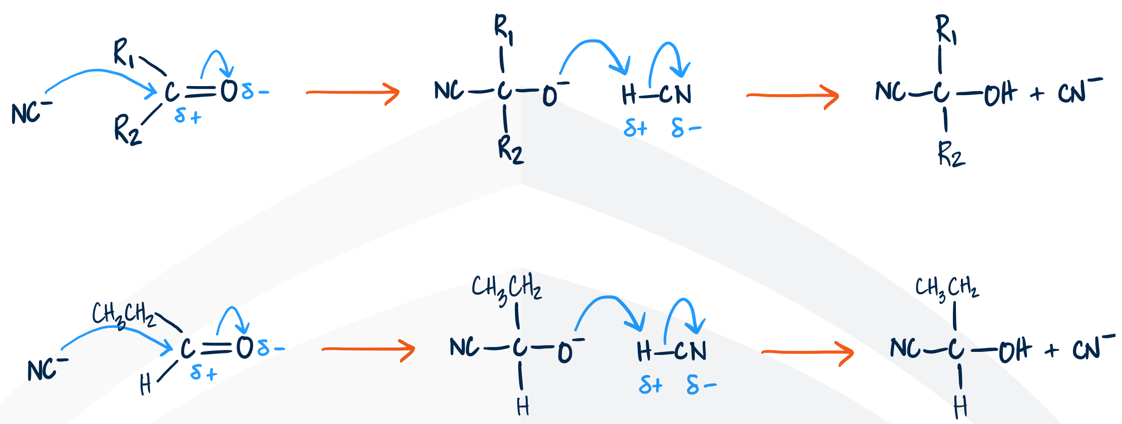


28

NUCLEOPHILIC ADDITION

Note: HCN is a **weak acid**; HCN $\rightleftharpoons$ H^+ + CN^- therefore, a **few CN^- ions** produced.

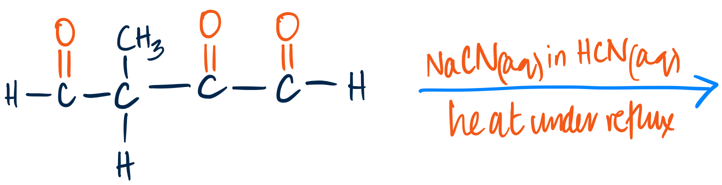
The reaction is catalyzed by CN^- ions from NaCN (or KCN).



29

SKILL CHECK

2-methylpropanal



30

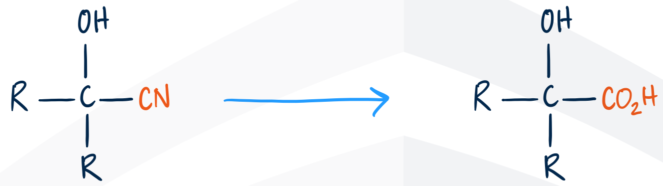
HYDROLYSIS

The product of nucleophilic addition, the hydroxy-nitrile, are hydrolyzed by heating under reflux with a dilute acid.

Reagent dilute hydrochloric acid, dil. HCl, (or dilute sulphuric acid)

Condition heat under reflux

Type hydrolysis



$$CH_3CH(OH)CN \;+\; 2H_2O \;+\; H^+ \longrightarrow CH_3CH(OH)CO_2H \;+\; NH_4^+$$

31

SKILL CHECK

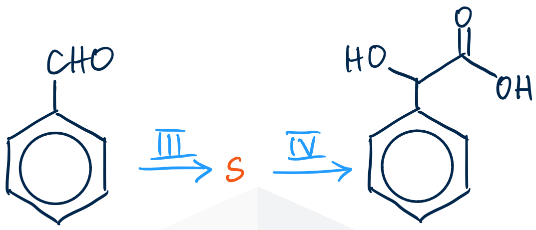
Draw molecules **A** and **B**.

$$(CH_3)_2CHCHO \xrightarrow{HCN + NaCN} A \xrightarrow{\text{heat with dil HCl}} B$$

32

SKILL CHECK

Draw molecule **S** and give the reagents and conditions for reactions **III** and **IV**.



33

SKILL CHECK

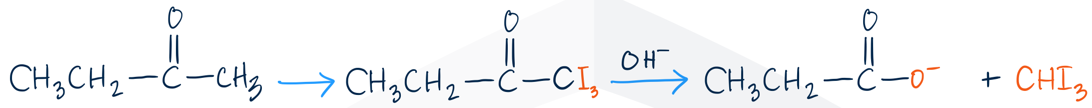
Compound **A** has the molecular formula C_4H_8O. It reacts with Fehling's solution. On treatment with sodium tetrahydridoborate(III) it gives **B**, which on warming with concentrated sulfuric acid gives 2-methylpropene. Identify **A** and **B**.

34

IODOFORM REACTION

Carbonyl compounds containing CH_3CO- group, that is, those that have a methyl group on the same carbon atom that bears the oxygen atom, can be oxidised by alkaline aqueous iodine to a salt of a carboxylic acid (with one less carbon) and a pale yellow ppt of tri-iodomethane.

The tri-iodomethane (iodoform) reaction is thus a very specific test for the CH_3CO— group (or the $CH_3CH(OH)$— group.



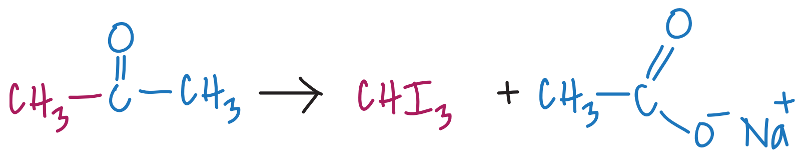
The overall reaction is:

35

IODOFORM REACTION

Except for ethanal, all the carbonyls that undergo this reaction are methyl ketones, with the carbonyl group on the second carbon atom of the chain, that is, they are alkan-2-ones.

The reaction can be use to obtain an acid having one carbon less.



36

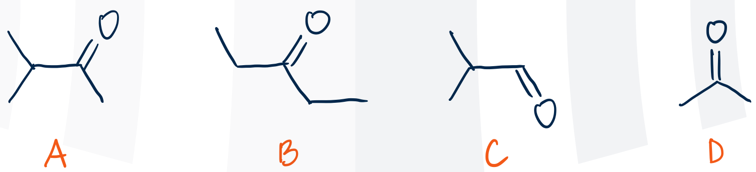
IODOFORM REACTION

The exception, ethanal, is the only aldehyde to give the pale yellow precipitate of tri-iodomethane (iodoform) with alkaline aqueous iodine:

37

SKILL CHECK

Which of these carbonyl compounds will undergo the iodoform reaction? Draw all the organic products.



38

CARBONYLS WS 1

SECTION A

1 Which reaction would **not** give ethanoic acid as a product?

A heating ethanenitrile under reflux with dilute sodium hydroxide

B heating ethanenitrile under reflux with dilute sulfuric acid

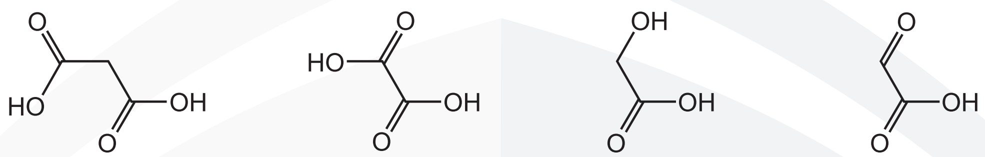
C heating ethanal under reflux with acidified sodium dichromate(VI)

D heating ethanol under reflux with acidified sodium dichromate(VI)

2 Hydroxyethanal, $HOCH_2CHO$, is heated under reflux with an excess of acidified potassium dichromate(VI) until no further oxidation takes place.

What is the skeletal formula of the organic product?

A **B** **C** **D**



3 $CH_3CH_2COCH_2CH_3$ reacts with hydrogen cyanide to form an organic product called a cyanohydrin.

Which feature applies to the cyanohydrin product?

A It has one chiral centre.

B It is formed by electrophilic addition.

C It is formed via an intermediate which contains the C–OH group.

D Its formation requires the use of cyanide ions as a catalyst.

4 Compound X, C_4H_8O, produces an orange precipitate when it is reacted with 2,4-dinitrophenylhydrazine reagent. Compound X produces a carboxylic acid when heated under reflux with an acidified solution of potassium dichromate(VI).

What could be compound X?

A butanal

B butanone

C 2-methylbutanal

D 4-hydroxybut-1-ene

5 Hept-4-enal is present in cow's milk.

$CH_3CH_2CH{=}CHCH_2CH_2CHO$

hept-4-enal

Which row correctly shows the product formed when hept-4-enal is treated with the given reducing agent?

	reducing agent	product
A	H_2 + Ni	$CH_3(CH_2)_5CH_2OH$
B	H_2 + Ni	$CH_3(CH_2)_5CH_3$
C	$NaBH_4$	$CH_3(CH_2)_5CH_2OH$
D	$NaBH_4$	$CH_3(CH_2)_5CHO$

6 Alcohol Y gives product Z after mild oxidation. Z gives a positive result with Tollens' reagent and with 2,4-dinitrophenylhydrazine reagent.

What could be the identity of alcohol Y?

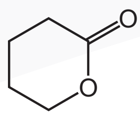
A butan-1-ol

B butan-2-ol

C butan-2,3-diol

D 2-methylbutan-2-ol

7 Cyclic esters are also known as lactones. *Delta* lactone is used as a solvent and in the manufacture of polyesters.



delta lactone

From which compound could *delta* lactone be made by a single reaction?

A $HOCH_2CH_2CH_2CH_2CHO$

B $HOCH_2CH_2CH_2CH_2CO_2H$

C $HOCH_2CH_2CH_2CH_2CH_2OH$

D $HOCH_2CH_2CH_2CH_2CH_2CO_2H$

8 An unknown organic compound reacts with sodium to give a combustible gas as one product but does **not** give a yellow precipitate with alkaline aqueous iodine.

What is a possible identity of the unknown organic compound?

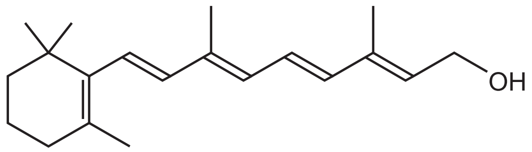
A propanal

B propan-1-ol

C propan-2-ol

D propanone

9 Vitamin A contains retinol.



retinol

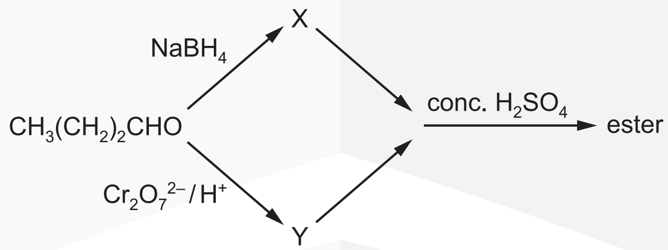
Under appropriate conditions, acidified $KMnO_4(aq)$ can be used to break apart C=C bonds.

After these bonds have been broken, further oxidation of the fragments may occur.

Under which conditions is the acidified $KMnO_4(aq)$ used and what do the final oxidation products include?

	conditions	final oxidation products
A	cold, dilute	aldehydes and carboxylic acids
B	cold, dilute	ketones and carboxylic acids
C	hot, concentrated	aldehydes and carboxylic acids
D	hot, concentrated	ketones and carboxylic acids

10 An ester with an aroma of pineapples can be synthesised in the laboratory from butanal using this reaction scheme.



What is the structural formula of the **ester**?

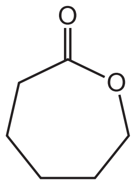
A $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$

B $CH_3(CH_2)_2CO_2(CH_2)_3CH_3$

C $CH_3(CH_2)_3CO_2(CH_2)_2CH_3$

D $CH_3(CH_2)_3CO_2(CH_2)_3CH_3$

11 Caprolactone is a cyclic ester. It is being used increasingly for the manufacture of specialist polymers.



caprolactone

From which compound could caprolactone be made by a single reaction?

A $OHCCH_2CH_2CH_2CH_2CHO$

B $HOCH_2CH_2CH_2CH_2CH_2CH_2OH$

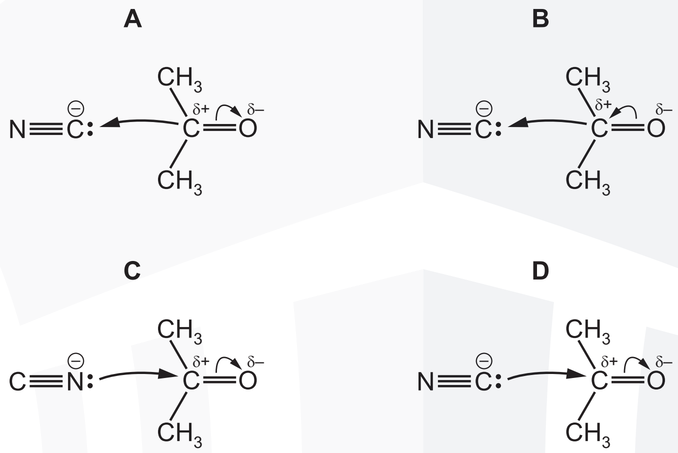
C $HOCH_2CH_2CH_2CH_2CH_2CO_2H$

D $HO_2CCH_2CH_2CH_2CH_2CO_2H$

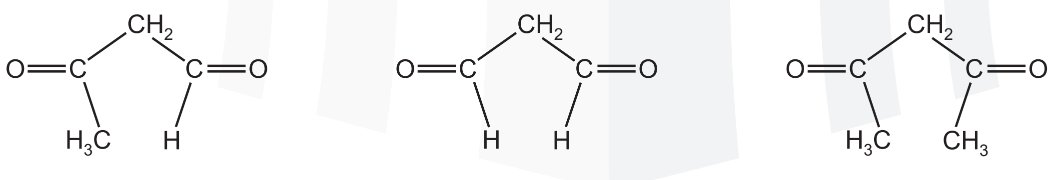
12 Propanone reacts with an aqueous mixture of HCN and NaCN by a nucleophilic addition mechanism.

The first stage of the mechanism involves attack by cyanide ions.

Which diagram correctly represents this?



13 P, Q and R are carbonyl compounds.



Fehling's solution can be used to help identify these compounds.

Which compounds form a red-brown precipitate on warming with Fehling's solution?

A P, Q and R **B** P and Q only **C** P only **D** Q only

14 Which reaction would **not** give ethanoic acid?

A heating ethanenitrile under reflux with dilute sodium hydroxide

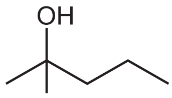
B heating ethanenitrile under reflux with dilute sulfuric acid

C heating ethanal under reflux with acidified sodium dichromate(VI)

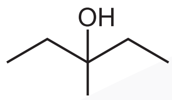
D heating ethanol under reflux with acidified sodium dichromate(VI)

15 Which compound can be oxidised by acidified potassium manganate(VII) to give 3-methylpentan-2-one?

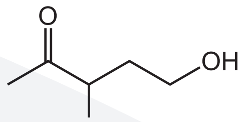
A



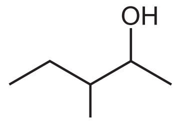
B



C



D



16 Compound **X** is heated with a mild oxidising agent. One of the products of the reaction will react with hydrogen cyanide, forming 2-hydroxybutanenitrile.

What is compound **X**?

A butan-1-ol

B butan-2-ol

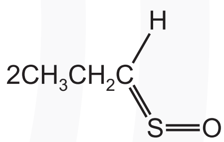
C propan-1-ol

D propan-2-ol

17 Which row correctly describes the reactivity of aldehydes and ketones?

	with $NaBH_4$	with $H^+ / Cr_2O_7^{2-}(aq)$
A	both react	both react
B	both react	only aldehydes react
C	only ketones react	both react
D	only ketones react	only aldehydes react

18 When onions are peeled in air, the reaction shown is thought to occur.



$$+ 2H_2O + 2[O] \rightarrow H_2SO_4 + H_2S + 2CH_3CH_2CHO$$

Which tests would give a positive reaction with the organic product?

1 warming with Tollens' reagent

2 warming with acidified potassium manganate(VII)

3 warming with alkaline aqueous iodine

19 A carbonyl compound **X** will react with HCN in the presence of NaCN to make a compound with M_r 85. Compound **X** does **not** react with Fehling's reagent.

What is **X**?

A butanal

B butanone

C propanal

D propanone

20 Which compound, when hydrolysed, gives propanoic acid and propan-2-ol?

A $CH_3CH_2CO_2CH_2CH(CH_3)CH_3$

B $(CH_3)_2CHCO_2CH_2CH_3$

C $CH_3CH_2CO_2CH(CH_3)CH_3$

D $CH_3CH_2CH_2CO_2CH(CH_3)CH_3$

21 Diols in which both hydroxy groups are bonded to the same carbon atom spontaneously eliminate a molecule of water to produce a carbonyl compound.

Which compound is hydrolysed to form a product that gives a positive reaction with 2,4-dinitrophenylhydrazine but **not** with Fehling's reagent?

A 1,1-dibromopropane

B 1,2-dibromopropane

C 1,3-dibromopropane

D 2,2-dibromopropane

22 **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**?

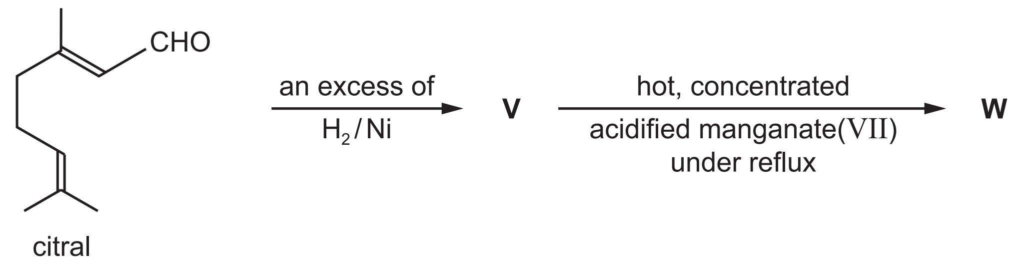
A $CH_3CH(OH)CH_2CH_3$

B $CH_3CH_2CH_2CH_2OH$

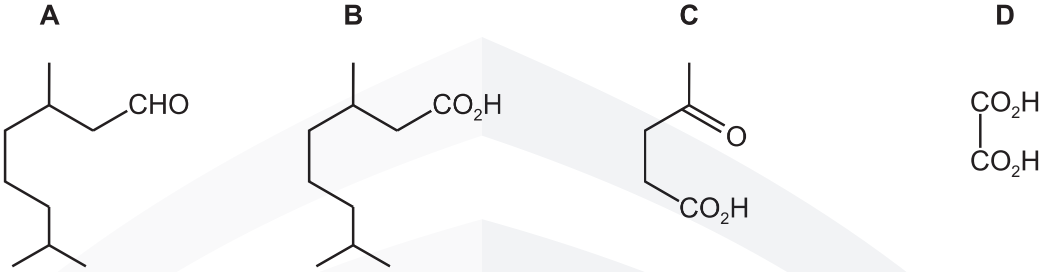
C $(CH_3)_3COH$

D $(CH_3)_2CHCH_2OH$

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



What could compound **W** be?



24 Diols in which both hydroxy groups are bonded to the same carbon can spontaneously eliminate a molecule of water to produce a carbonyl compound.

Which compound, after complete hydrolysis, gives a positive reaction with Tollens' reagent?

A 1,1-dibromobutane

B 1,2-dibromobutane

C 1,3-dibromobutane

D 2,2-dibromobutane

25 $CH_3CH_2COCH_2CH_3$ reacts with hydrogen cyanide to form an organic product called a cyanohydrin.

Which statement is correct?

A The cyanohydrin product has one chiral centre.

B The cyanohydrin product is formed by electrophilic addition.

C The cyanohydrin product is formed via an intermediate which contains a C–OH group.

D The formation of the cyanohydrin product requires the use of cyanide ions as a catalyst.

26 Compound X, $CH_3CH(OH)CH(CHO)CH_3$, is heated under reflux with an excess of acidified $K_2Cr_2O_7$ to form compound Y.

Both X and Y are separately warmed with Fehling's solution and the observations noted.

What are the observations?

A Both X and Y give a red precipitate.

B Only X gives a red precipitate.

C Only Y gives a red precipitate.

D Neither X nor Y gives a red precipitate.

27 **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 $(CH_3)_2CHCH_2OH$

28 Which compound will react with acidified potassium dichromate(VI) **and** with alkaline aqueous iodine?

A $CH_3COCH_2CH_3$

B $CH_3CH(OH)CH_2CH_3$

C $CH_3CH_2CH_2CHO$

D $CH_3CH_2CH_2CH_2OH$

29 The formulae of three compounds are shown.

C_3H_7CHO $C_2H_5COCH_3$ $CH_2CHCH_2CH_2OH$

Only one of these compounds will decolourise bromine water. Only one of these compounds will produce a silver mirror with Tollens' reagent.

Which row shows the correct results?

	decolourises bromine water	forms a silver mirror with Tollens' reagent
A	C_3H_7CHO	$C_2H_5COCH_3$
B	$C_2H_5COCH_3$	C_3H_7CHO
C	$CH_2CHCH_2CH_2OH$	$C_2H_5COCH_3$
D	$CH_2CHCH_2CH_2OH$	C_3H_7CHO

30 Which compound will react with acidified potassium dichromate(VI) **and** with alkaline aqueous iodine?

A $CH_3COCH_2CH_3$

B $CH_3CH(OH)CH_2CH_3$

C $CH_3CH_2CH_2CHO$

D $CH_3CH_2CH_2CH_2OH$

31 Which compound gives a positive test with alkaline aqueous iodine and does **not** show optical isomerism?

A $CH_3COCH_2CH_2OH$

B $CH_3CH_2CH(OH)CHO$

C $CH_3COCH(OH)CH_3$

D $(CH_3)_2C(OH)CHO$

32 When compound X is warmed with dilute, acidified potassium dichromate(VI) there is no colour change. X does not give an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

What could X be?

A butan-2-ol

B ethanal

C methylpropan-2-ol

D propanone

[N'17 P12 Q27]

33 Compound G

- has a chiral centre,
- gives a positive result with alkaline aqueous iodine,
- does not give a silver mirror with Tollens' reagent.

What could compound G be?

A 1-hydroxybutan-2-one

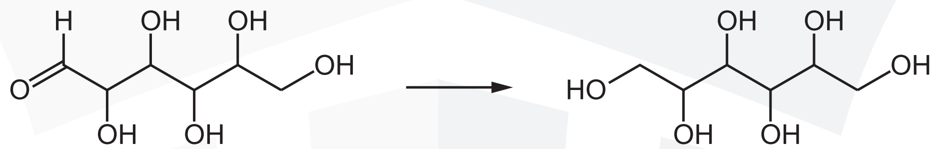
B 2-hydroxybutanal

C 3-hydroxybutanal

D 3-hydroxybutan-2-one

[N'17 P12 Q29]

34 Glucose can be used to prepare sorbitol, a compound used as a sugar substitute.



glucose sorbitol

Which reagent may be used for this conversion?

A acidified potassium dichromate(VI)

B sodium borohydride

C sodium hydroxide

D Tollens' reagent

[N'17 P13 Q26]

35 3-methylbutanone is treated with alkaline aqueous iodine. The mixture of products is then acidified.

Which compound is present in the final mixture of products?

A 3-methylbutanoic acid

B butanoic acid

C methylpropanoic acid

D propanoic acid

[N'17 P13 Q27]

36 Which compound reacts with 2,4-dinitrophenylhydrazine reagent but does **not** react with Tollens' reagent?

A CH_3COCO_2H

B $CH_3CH(OH)CHO$

C CH_3COCHO

D $CH_3CH(OH)CH_3$

[S'18 P12 Q23]

37 Compound X produces a carboxylic acid when heated under reflux with acidified potassium dichromate(VI). Compound X does not react with sodium metal.

What could be the identity of compound X?

A propanal

B propanone

C propan-1-ol

D propan-2-ol

[M'18 P12 Q26]

38 Alcohols, aldehydes and nitriles can each be converted into carboxylic acids.

Which descriptions of their conversions into carboxylic acids are correct?

	alcohols	aldehydes	nitriles
A	hydrolysis	hydrolysis	hydrolysis
B	hydrolysis	hydrolysis	oxidation
C	oxidation	oxidation	hydrolysis
D	oxidation	oxidation	oxidation

[M'18 P12 Q29]

39 Compound Q

- contains a chiral centre,
- gives a positive result with Fehling's reagent,
- gives a positive result with alkaline aqueous iodine.

What could compound Q be?

A 1-hydroxybutanone

B 2-hydroxybutanal

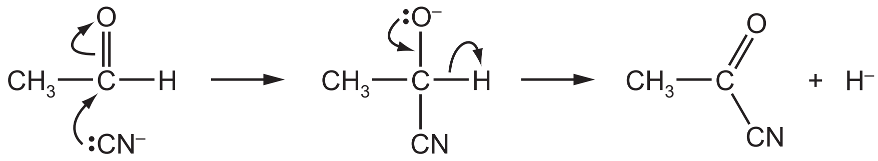
C 3-hydroxybutanal

D 3-hydroxybutanone

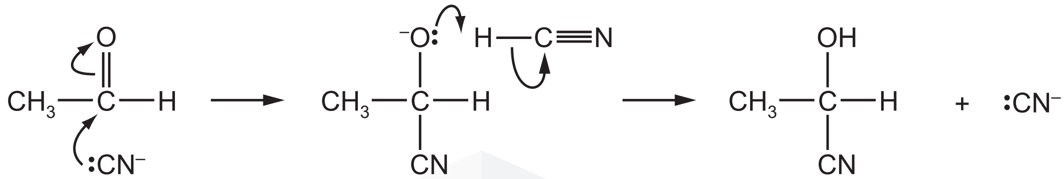
[J'18 P11 Q25]

40 What is the mechanism for the reaction of ethanal, CH_3CHO, with hydrogen cyanide, HCN, in the presence of NaCN?

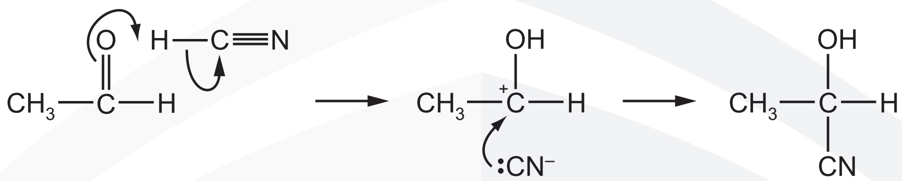
A



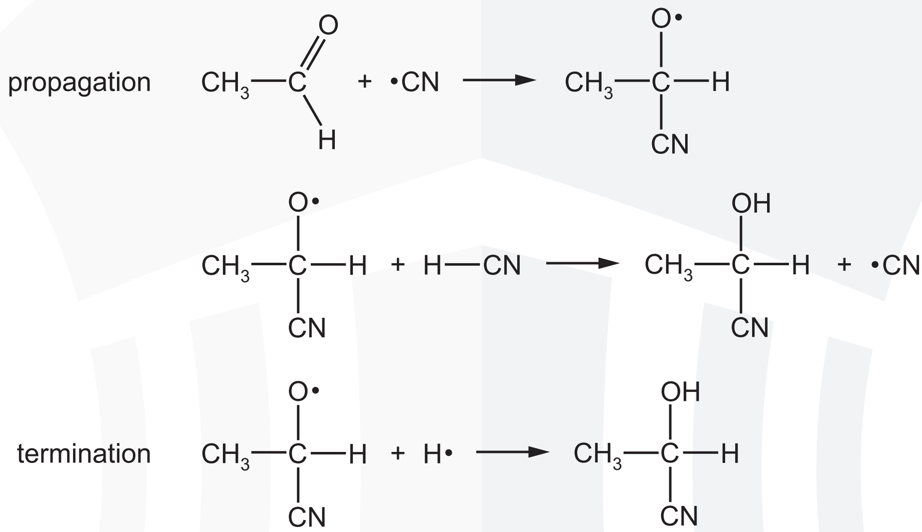
B



C

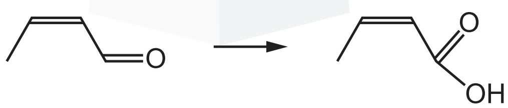


D



[J'18 P11 Q26]

41 Which reagent could be used to carry out the following reaction?



A a solution containing acidified dichromate(VI) ions

B a solution containing dilute, acidified manganate(VII) ions

C a solution containing hot, concentrated, acidified manganate(VII) ions

D concentrated sulfuric acid

42 Which statement about butanone is correct?

A Butanone can be dehydrated by concentrated sulfuric acid to give $CH_2{=}CHCH{=}CH_2$.

B Butanone gives a positive result with Tollens' reagent.

C Butanone reacts with HCN by an electrophilic addition mechanism.

D Butanone reacts with $NaBH_4$ to give a chiral product.

43 Which compound shows optical isomerism and gives a positive test with alkaline aqueous iodine?

A $CH_3COCH(OH)CH_3$

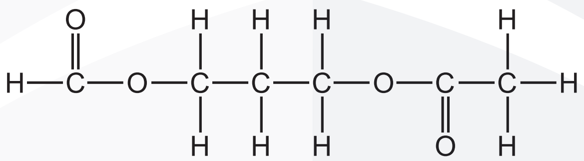
B $CH_3COCH_2CH_2OH$

C $HOCH_2CH(CH_3)CHO$

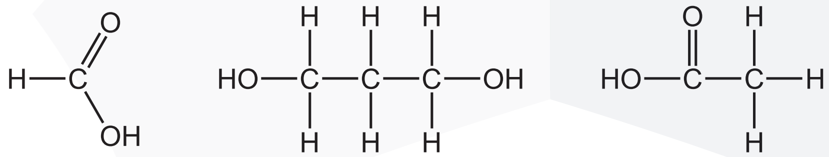
D $(CH_3)_2C(OH)CHO$

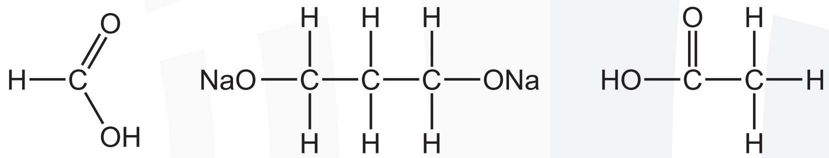
[N'18 P11 Q28]

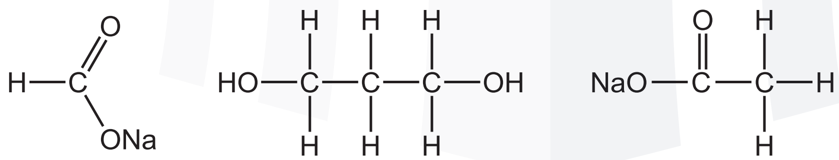
44 The diester shown can be hydrolysed by heating with an excess of aqueous sodium hydroxide.

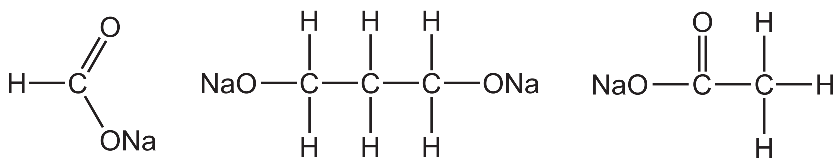


What would the products of this reaction be?

A 

B 

C 

D 

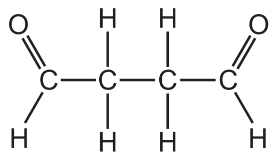
[N'18 P11 Q29]

45 Compound X has the empirical formula C_2H_3O.

Compound X reacts with 2,4-dinitrophenylhydrazine reagent to give an orange precipitate and also decolourises warmed acidified potassium manganate(VII) solution.

What could be the identity of X?

A



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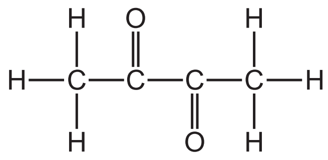

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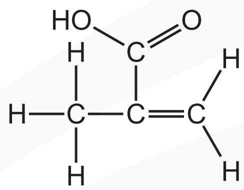

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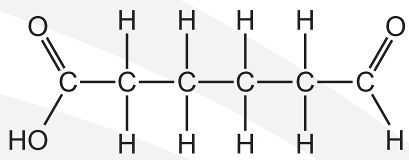


[N'18 P12 Q27]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which pairs of reagents will take part in a redox reaction?

1 CH_3COCH_3 + Tollens' reagent

2 CH_3CH_2CHO + Fehling's reagent

3 $CH_3CH{=}CH_2$ + Br_2

2 Which pairs of reagents will take part in a redox reaction under suitable conditions?

1 $CH_3(CH_2)_4CHO$ + Tollens' reagent

2 $CH_3(CH_2)_4CH_3$ + Br_2

3 $CH_3CO(CH_2)_4CH_3$ + Fehling's reagent

3 Which reactions must be warmed to form a solid product?

1 CH_3CH_2CHO + 2,4-dinitrophenylhydrazine reagent

2 CH_3CH_2CHO + Fehling's reagent

3 CH_3CH_2CHO + Tollens' reagent

4 Propanal will react with hydrogen cyanide to form 2-hydroxybutanenitrile. A suitable catalyst for this reaction is sodium cyanide.

$$CH_3CH_2CHO + HCN \overset{NaCN}{\rightleftharpoons} CH_3CH_2CH(OH)CN$$

Which statements about the reaction of propanal with hydrogen cyanide are correct?

1 The CN^- ion attacks the propanal molecule to form an intermediate ion.

2 The product of the reaction has a chiral carbon atom.

3 The CN^- ion is a stronger electrophile than the HCN molecule.

5 Propanal will react with hydrogen cyanide to form 2-hydroxybutanenitrile. A suitable catalyst for this reaction is sodium cyanide.

$$CH_3CH_2CHO + HCN \overset{NaCN}{\rightleftharpoons} CH_3CH_2CH(OH)CN$$

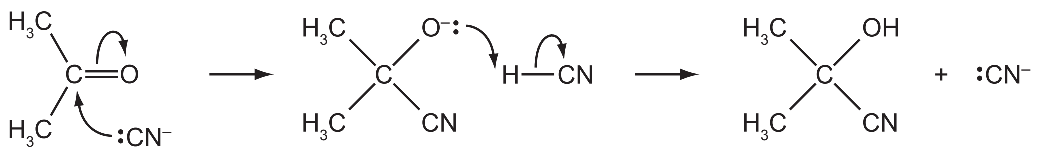
Which statements about the reaction of propanal with hydrogen cyanide are correct?

1 The sodium cyanide provides a stronger nucleophile than HCN.

2 The reaction mechanism involves two steps.

3 The product of the reaction has a chiral carbon atom.

6 Propanone and hydrogen cyanide react together by this mechanism.



Which statements about this mechanism are correct?

1 CN^- is an electrophile.

2 It is an addition reaction.

3 Heterolytic bond breaking is involved.

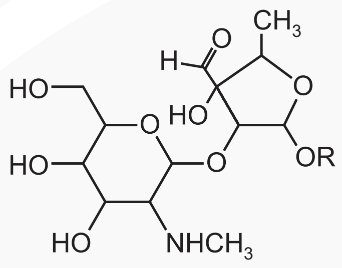
7 Which changes in bonding occur during the reaction of propanal and hydrogen cyanide?

1 A carbon-hydrogen bond is broken.

2 An oxygen-hydrogen bond is formed.

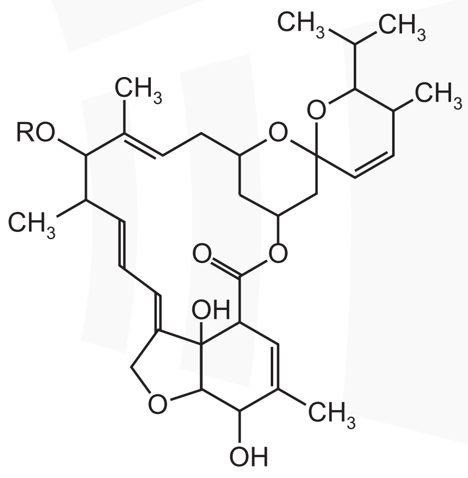
3 A carbon-carbon bond is formed.

8 Which compounds will give an orange precipitate with 2,4-dinitrophenylhydrazine reagent?

1 

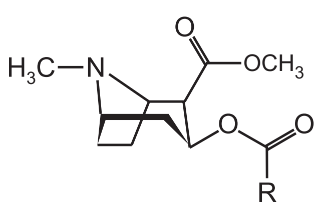
streptomycin

[R is an inert group]

2 

avermectin B_{1b}

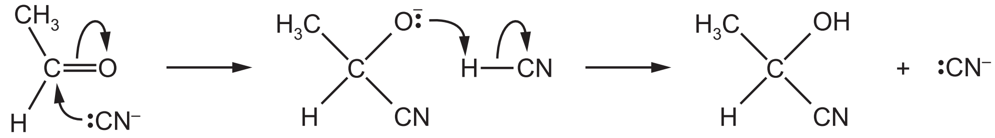
[R is an inert group]

3 

cocaine

[R is an inert group]

9 Ethanal and hydrogen cyanide react together to form a compound used in the production of acrylic fibres. The reaction mechanism involves cyanide ions.



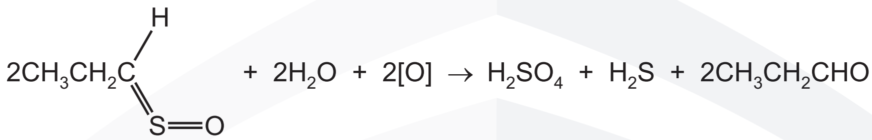
Which statements about this mechanism are correct?

1 CN^- acts as a catalyst.

2 CN^- is a nucleophile.

3 It is an addition reaction.

10 When onions are peeled in air, the reaction shown is thought to occur.



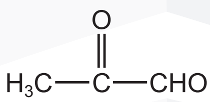
Which tests would give a positive reaction with the organic product?

1 warming with Tollens' reagent

2 warming with acidified potassium manganate(VII)

3 warming with alkaline aqueous iodine

11 The compound shown is produced when sugar burns.



Which reagents would give a positive result with this compound?

1 alkaline aqueous iodine

2 2,4-dinitrophenylhydrazine

3 Fehling's solution

12 2,2,4-trimethylpentanal is used in the manufacture of adhesives.

Which reagents would 2,2,4-trimethylpentanal react with?

1 2,4-dinitrophenylhydrazine reagent

2 Tollens' reagent

3 alkaline aqueous iodine

13 For which reactions are the colour changes described correctly?

	reagents	colour change
1	pentanal + hot, acidified potassium dichromate(VI)	orange to green
2	pentan-2-one + warm Fehling's reagent	no change
3	cyclohexane + cold, acidified potassium manganate(VII)	purple to colourless

14 For which reactions are the colour changes described correctly?

	reagents	colour change
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2	pentan-2-one + warm Fehling's reagent	no change
3	cyclohexane + cold, acidified potassium manganate(VII)	purple to colourless

15 Propanal will react with hydrogen cyanide to form 2-hydroxybutanenitrile. A suitable catalyst for this reaction is sodium cyanide.

$$CH_3CH_2CHO + HCN \xrightleftharpoons{NaCN} CH_3CH_2CH(OH)CN$$

Which statements about this reaction of propanal with hydrogen cyanide are correct?

1 The CN^- ion attacks the propanal molecule to form an intermediate ion.

2 The product of the reaction has a chiral carbon atom.

3 The CN^- ion is a stronger electrophile than the HCN molecule.

16 Substance M is refluxed with aqueous sodium hydroxide. One of the products of this reaction reacts with alkaline aqueous iodine to give a pale yellow precipitate.

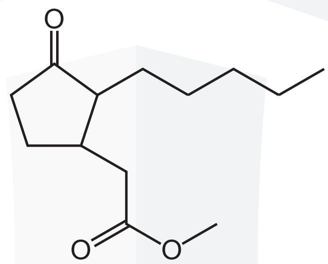
Which compounds could be substance M?

1 $CH_3CO_2CH_3$

2 $CH_3CO_2CH_2CH_3$

3 $HCO_2CH(CH_3)_2$

17 Compound M is an important ingredient in perfume.



compound M

M reacts with HCN.

Which statements about this reaction are correct?

1 A small amount of NaOH will speed up the reaction.

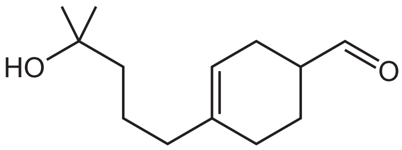
2 The reaction is initiated by the transfer of a proton to one of the C=O groups.

3 Both of the C=O groups react with HCN.

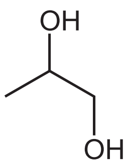
18 The compounds below are used to make perfumes.

Which compounds will produce a yellow precipitate with alkaline aqueous iodine?

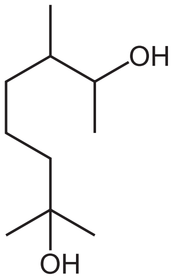
1



2



3



[N'17 P13 Q39]

19 Propanal reacts with hydrogen cyanide to form 2-hydroxybutanenitrile. A suitable catalyst for this reaction is sodium cyanide.

$$CH_3CH_2CHO + HCN \xrightleftharpoons{NaCN} CH_3CH_2CH(OH)CN$$

Which statements about the reaction of propanal with hydrogen cyanide are correct?

1 HCN is a weaker nucleophile than the nucleophile provided by NaCN.

2 The reaction mechanism involves two steps.

3 The product of the reaction has a chiral carbon atom.

[M'18 P12 Q39]

20 The M_r of compound X is 72. The composition by mass of X is 66.7% carbon, 11.1% hydrogen and 22.2% oxygen. X gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent. X does not react with Fehling's reagent.

What can be deduced from this information?

1 X is a carbonyl compound.

2 X is a ketone.

3 X is butanone.

[S'18 P11 Q40]

21 Which compounds, on reaction with $NaBH_4$, form a compound with a chiral carbon atom?

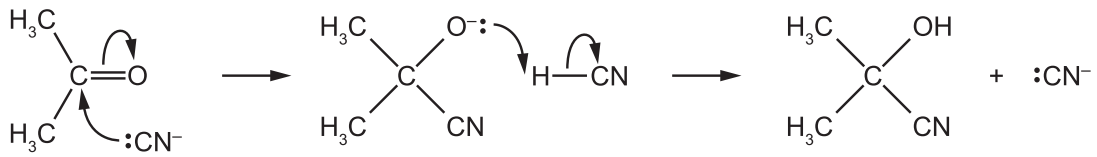
1 $CH_3CH_2CH_2COCH_3$

2 $CH_2CHCOCH_2CH_3$

3 $CH_3CH_2COCH_2CH_3$

[J'18 P13 Q37]

22 Propanone and hydrogen cyanide react together by the mechanism shown.



Which statements about this mechanism are correct?

1 CN^- is an electrophile.

2 It is an addition reaction.

3 Heterolytic bond breaking is involved.

[J'18 P13 Q39]

23 Acrolein is an organic compound with the molecular formula C_3H_4O. It is used in water treatment and as a herbicide. When acrolein reacts with 2,4-dinitrophenylhydrazine an orange precipitate is obtained. Reaction of acrolein with Tollens' reagent produces a silver mirror.

Which statements are correct?

1 Acrolein reacts with alkaline aqueous iodine to produce a yellow precipitate.

2 Acrolein can be reduced to a primary alcohol.

3 Acrolein decolourises bromine water.

[J'18 P13 Q40]

24 Ethanal reacts with HCN in the presence of KCN.

Which changes in bonding occur during this reaction?

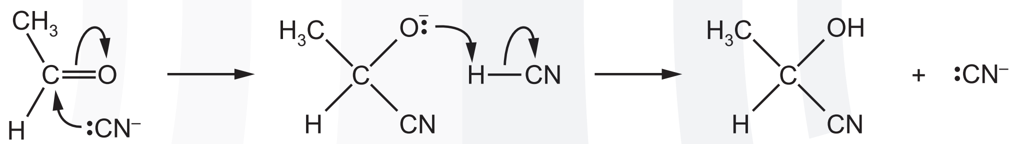
1 A carbon-carbon bond is formed.

2 A carbon-hydrogen bond is broken.

3 A carbon-nitrogen bond is broken.

[N'18 P11 Q40]

25 Ethanal and hydrogen cyanide react together to form a compound used in the production of acrylic fibres. The reaction mechanism involves cyanide ions.



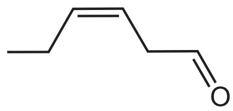
Which statements about this mechanism are correct?

1 CN^- acts as a catalyst.

2 CN^- is a nucleophile.

3 It is an addition reaction.

26 The compound cis-hex-3-enal is responsible for the characteristic smell of cut grass.



cis-hex-3-enal

Which reagents will react with cis-hex-3-enal?

1 sodium

2 sodium borohydride

3 Fehling's reagent

[N'18 P12 Q40]

27 The reaction of ethanal, CH_3CHO, with HCN to form 2-hydroxypropanenitrile is catalysed by NaCN.

What are features of the intermediate of this reaction?

1 It is chiral.

2 It has a single negative charge on one of its atoms.

3 It is a nucleophile.

[N'17 P13 Q40]

CARBONYLS WS 2

1 A hydrocarbon, **P**, with the formula C_6H_{12} readily decolourises bromine.

On reaction with hot, concentrated, acidified potassium manganate(VII) solution a single organic product, **Q**, is obtained.

Q gives an orange precipitate when reacted with 2,4-dinitrophenylhydrazine, 2,4-DNPH reagent, but has no reaction with Tollens' reagent.

(a) **(i)** Explain these observations.

....

....

....

....

....

....

....

.... [4]

(ii) Draw the skeletal formula of **P** and give its name.

name of **P** ....
[2]

(iii) Draw the skeletal formula of **Q** and give its name.

name of **Q** ....
[2]

(b) There are several structural isomers of **P** that also decolourise bromine, but only four of these structural isomers exhibit geometrical (cis-trans) isomerism.

Give the structures of any **three** structural isomers of **P** that exhibit geometrical (cis-trans) isomerism.

[3]

2 Ethanal reacts with hydrogen cyanide, in the presence of a small amount of NaCN, as shown.

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

(a) Use bond energies from the *Data Booklet* to calculate the enthalpy change for this reaction. Include a sign with your answer.

enthalpy change = ... kJ mol^{-1} [3]

(b) The product of this reaction shows stereoisomerism as it contains a chiral centre. This reaction produces an equimolar mixture of two optical isomers.

(i) Explain the meanings of the terms *stereoisomerism* and *chiral centre*.

stereoisomerism ....

....

....

chiral centre ....

....

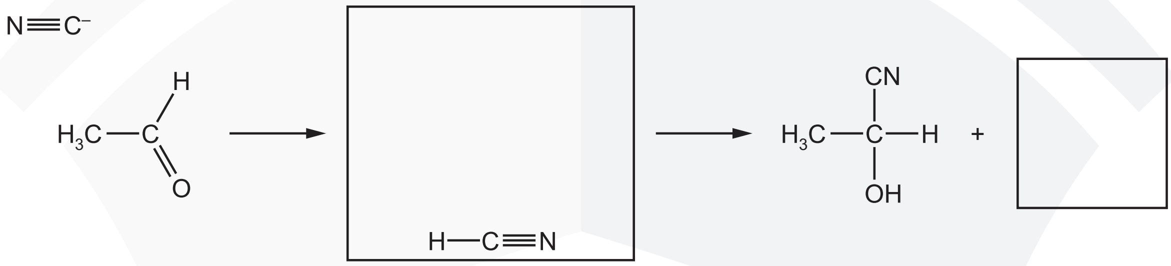
[2]

(ii) Suggest why the two optical isomers are produced in equal amounts by this reaction.

....

.... [1]

(c) **(i)** Complete the diagram to show the mechanism of this reaction. Include all necessary charges, partial charges, lone pairs and curly arrows and show the structure of the intermediate.



[5]

(ii) With reference to your mechanism in **(i)**, explain the role of the NaCN in this reaction.

....

.... [1]

3 There are seven structural isomers with the molecular formula $C_5H_{10}O$ that are carbonyl compounds. Four of these are aldehydes.

These four aldehydes, **A**, **B**, **C** and **D**, have the following properties.

- Aldehyde **A** has a straight chain while **B**, **C** and **D** are branched.
- Aldehyde **B** is the only one of the four isomers with a chiral centre and it exists as a pair of optical isomers.
- Aldehyde **C** has two methyl groups in its structure but **D** has three.

(a) **(i)** Give the structure of each of the four isomers.

A	B
C	**D**

[4]

(ii) Draw the three-dimensional structures of the two optical isomers of **B**.

[2]

(b) **(i)** Describe a chemical test that would allow you to distinguish between any of the four isomers **A** to **D** and any of the other three structural isomers of $C_5H_{10}O$, that are carbonyl compounds.

In your answer you should describe any necessary reagents and conditions as well as explaining what you would **see** in each case.

....

....

....

....

.... [3]

(ii) Describe a test that would give the same result with all seven carbonyl isomers of $C_5H_{10}O$.

....

....

.... [2]

4 **A**, **B**, **C**, **D**, **E** and **F** are all structural isomers with the molecular formula C_4H_8O.

(a) **A**, **B** and **C** all give an orange precipitate when treated with 2,4-DNPH but only **A** and **B** give a brick-red precipitate when warmed with Fehling's solution.

(i) Draw the **skeletal** formulae of **A**, **B** and **C**.

A	B	C

[3]

(ii) Name the type of structural isomerism shown by **A** and **B**.

.... [1]

(iii) State what you would **see** when a sample of **A** is warmed with Tollens' reagent.

.... [1]

(b) **D**, **E** and **F** all decolourise bromine and effervesce slowly with sodium metal.

E shows geometrical isomerism. Only **D** has a branched chain.

None of these isomers contains an oxygen atom bonded to a carbon atom involved in π bonding.

None of these isomers contains a chiral centre.

(i) Give the structures of **D**, **E** and **F**. Show the two stereoisomers of **E** and label the stereoisomerism shown.

D	
E	**E** ....
F	

[5]

(ii) Identify the gas produced during the reaction of each of these isomers with sodium metal.

.... [1]

(c) Another compound, **G**, C_3H_6O, contains the same functional group as **A**.

Give equations for the reactions of **G** with each of acidified potassium dichromate(VI) and sodium tetrahydridoborate, $NaBH_4$, using [O] or [H] as appropriate.

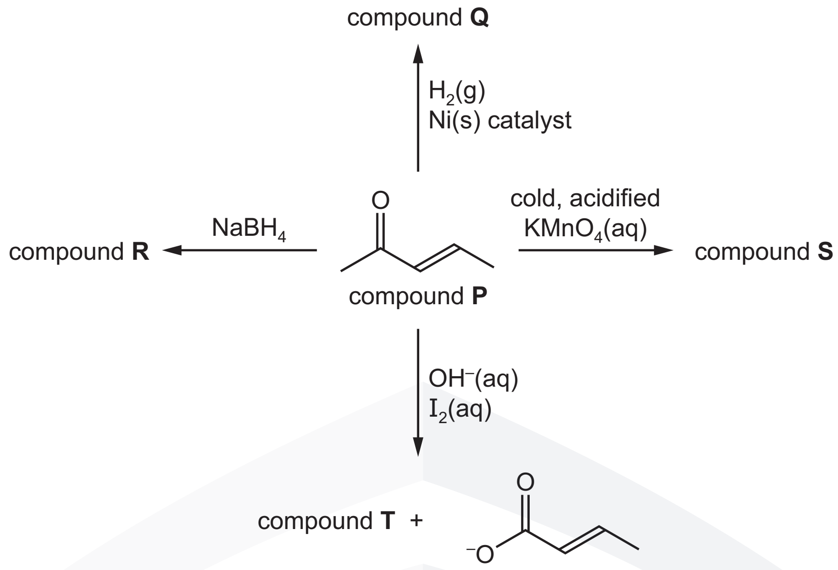
(i) reaction with acidified potassium dichromate(VI)

C_3H_6O + ... $\rightarrow$ .... [1]

(ii) reaction with $NaBH_4$

C_3H_6O + ... $\rightarrow$ .... [1]

5 Some reactions of compound **P**, C_5H_8O, are shown.



(a) **(i)** Give the structures for organic compounds **Q**, **R**, **S** and **T**.

Q

R

S

T

[4]

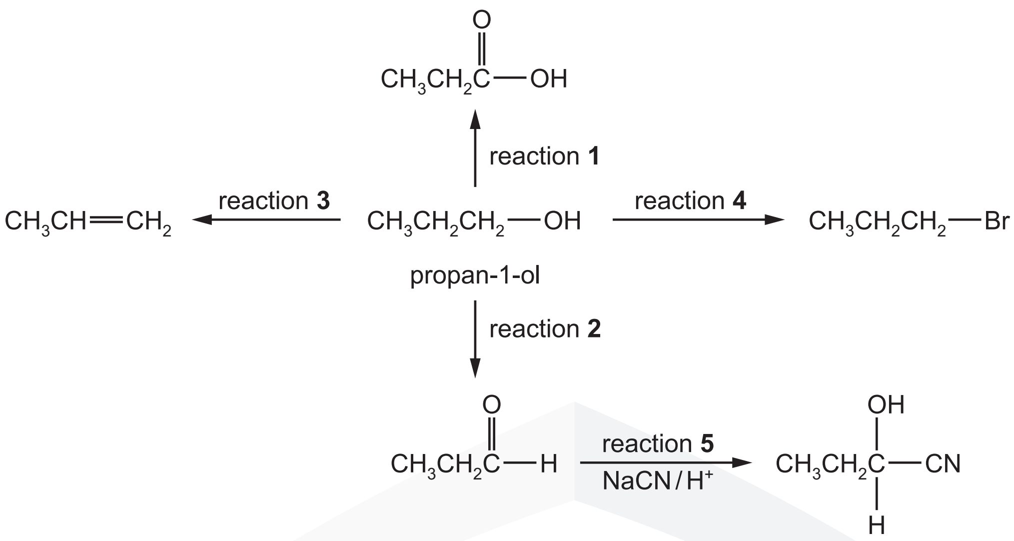
(ii) Give the systematic name of compound **P**.

.... [1]

(iii) What would you observe when compound **P** is reacted with 2,4-dinitrophenylhydrazine (2,4-DNPH)?

.... [1]

6 A reaction sequence based on propan-1-ol is shown.



(a) Reactions **1** and **2** can both be carried out using the same reagents.

(i) Identify suitable reagents for reactions **1** and **2**.

....

.... [1]

(ii) State and explain how the reaction should be carried out to ensure that reaction **2** rather than reaction **1** occurs.

....

....

....

.... [2]

(b) Identify the necessary reagents and conditions for each of reactions **3** and **4**.

reaction **3** ....

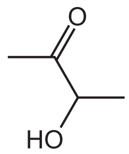
....

reaction **4** ....

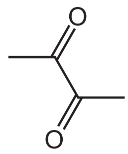
....

[2]

7 Acetoin, $CH_3COCH(OH)CH_3$, and diacetyl, $CH_3COCOCH_3$, are two of the compounds that give butter its characteristic flavour. Their skeletal formulae are shown.



acetoin



diacetyl

(a) Give the systematic name for acetoin.

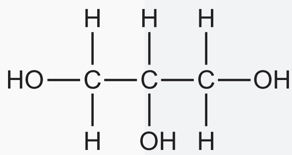
.... [1]

(b) Identify the reagents and conditions necessary for the conversion of acetoin into diacetyl.

....

.... [2]

8 **(b)** **R** contains two different functional groups, one of which is an alkene group.
R reacts with cold, dilute, acidified manganate(VII) ions to form propane-1,2,3-triol.



propane-1,2,3-triol

(i) Give the displayed formula of **R**.

(ii) State the type of reaction and what you would observe when **R** reacts with bromine water.

....

.... [2]

(iii) Draw the structure of the product formed when **R** reacts with bromine water.

[1]

(iv) Identify the gaseous product formed when **R** reacts with hot, concentrated, acidified manganate(VII) ions.

.... [1]

(c) **P** and **Q** (C_3H_6O) both form an orange precipitate when reacted with 2,4-DNPH. Only **Q** produces a yellow precipitate when reacted with alkaline aqueous iodine.

(i) Name **P** and **Q**.

P ....

Q ....
[2]

(ii) Identify the yellow precipitate formed by the reaction of **Q** with alkaline aqueous iodine.

.... [1]

(d) **P** and **Q** each react with hydrogen cyanide to form a single product.
The product formed from **P** exists as a pair of optical isomers.
The product formed from **Q** does not exhibit optical isomerism.

(i) Explain the meaning of the term *optical isomers*.

....

....

....

.... [2]

(ii) Ethanal, CH_3CHO, also reacts with hydrogen cyanide. The product of this reaction is $CH_3CH(OH)CN$.

Draw the mechanism of this reaction.
Include all necessary charges, dipoles, lone pairs and curly arrows.

[3]

9 In each section of this question choose the answer or answers from the options listed.

(a) Six particles are listed.

H• H^+ Cl• Cl^- •CH_3 $^+CH_3$

(i) Identify **two** particles produced during the reaction of methane and chlorine in the presence of UV light.

.... [1]

(ii) Identify the **two** particles produced by the heterolytic fission of a bond in chloromethane.

.... [1]

(b) Seven reaction types are listed.

addition substitution oxidation elimination

hydrolysis condensation reduction

(i) Name the type of reaction involved when Tollens' reagent is used to identify an aldehyde.

.... [1]

(ii) Name the type of reaction involved in the test for a carbonyl group using 2,4-DNPH.

.... [1]

(iii) Name the type of reaction involved in the reaction of a ketone with $NaBH_4$.

.... [1]

(iv) Name the type of reaction involved in the reaction of an aldehyde with HCN.

.... [1]

10 **(b)** The alcohols **C** and **D** are isomers of each other with molecular formula $C_4H_{10}O$. Both isomers are branched.

When **C** is heated under reflux with acidified potassium dichromate(VI) no colour change is observed.

When **D** is heated under reflux with acidified potassium dichromate(VI) the colour of the mixture changes from orange to green and **E**, $C_4H_8O_2$, is produced.

E reacts with aqueous sodium carbonate to form carbon dioxide gas.

(i) Identify **C**, **D** and **E**.

C	D	E

[3]

(ii) Write the equation for the reaction between **E** and aqueous sodium carbonate.

.... [1]

(c) The isomers **F** and **G**, $C_5H_{10}O$, both form an orange precipitate when reacted with 2,4-DNPH.

F is unbranched and reacts with alkaline aqueous iodine to produce a yellow precipitate.

G does not react with alkaline aqueous iodine. It contains a chiral centre and produces a silver mirror when warmed with Tollens' reagent.

(i) Name the yellow precipitate produced by the reaction between **F** and alkaline aqueous iodine.

.... [1]

(ii) Give the structural formula of **F** and of **G**.

F ....

G ....

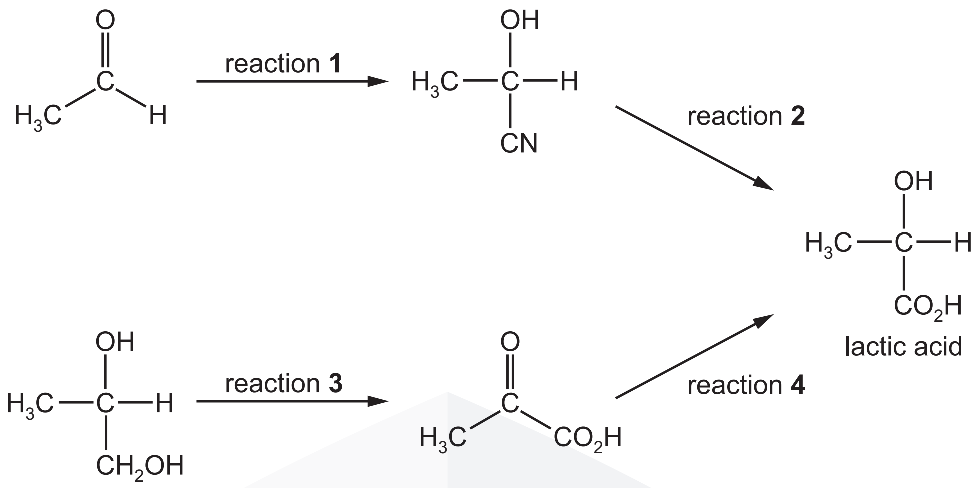
[2]

(iii) Explain the meaning of the term *chiral centre*.

....

.... [1]

11 Two possible methods of making lactic acid are shown.



(ii) State suitable reagents and conditions for reactions **1** and **3**.

reaction	reagents and conditions
1	
3	

[4]

(iii) Name the type of reaction that occurs in reaction **2**.

.... [1]

(iv) Reaction **4** uses $NaBH_4$.

Identify the role of $NaBH_4$ in this reaction.

.... [1]

(v) Lactic acid has a chiral centre.

State what is meant by the term *chiral centre*.

....

....

.... [1]

[M'18 P22 Q3]

12 **W** is $CH_3COCH_2CH_3$.

(a) The reaction between **W** and alkaline aqueous iodine produces a yellow precipitate.

(i) Give the name of the compound formed as a yellow precipitate in this reaction.

.... [1]

(ii) Give the name of **W**.

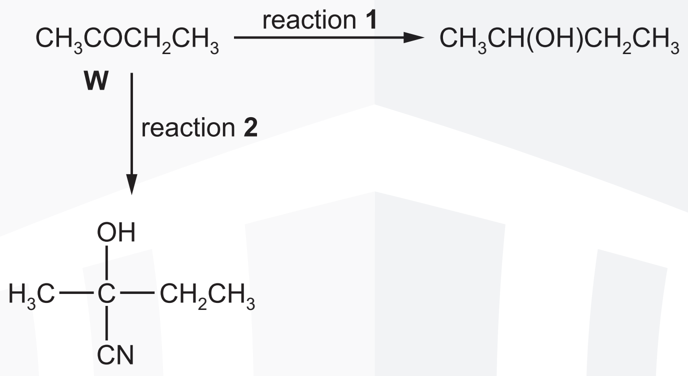
.... [1]

(b) There are two structural isomers of **W** that are also carbonyl compounds.

Draw the structures of these two isomers of **W**.

[2]

Two reactions of **W** are shown.



X

(c) **(i)** Identify the type of reaction occurring in reaction **1**.

.... [1]

(ii) Identify the reagent for reaction **1**.

.... [1]

(d) Reaction **2** is carried out by adding a mixture of HCN and NaCN to **W**.
The product, **X**, is formed as a mixture of two isomers.

(i) Complete the mechanism for this reaction.

Include the structure of the intermediate formed and all necessary charges, dipoles, lone pairs and curly arrows.

W

CN^-

X

[4]

(ii) State the name of the type of isomerism shown by **X**.

.... [1]

(iii) Explain fully why **X** shows this type of isomerism.

....

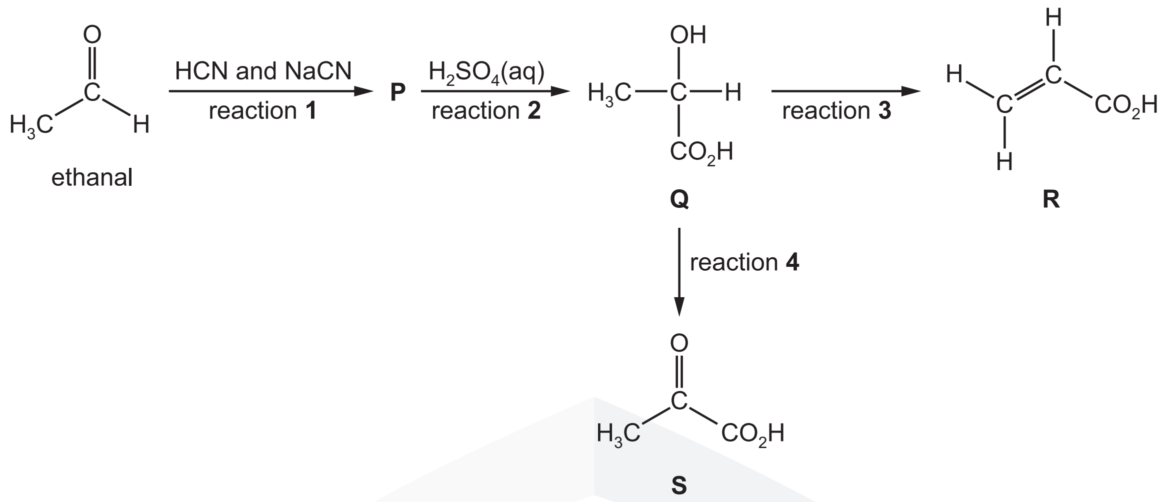
....

....

.... [2]

[J'18 P22 Q4]

13 The diagram shows a reaction sequence starting from ethanal.



(i) Draw the **displayed** formula of **P**.

[1]

(ii) Name the type of chemical reaction that occurs in reaction **3**.

.... [1]

(iii) Write an equation to represent reaction **4**.

Use [O] to represent the oxidising agent.

.... [1]

(iv) State the reagents and conditions for reaction **4**.

.... [1]

(b) Compound **Q** is formed as a mixture of two optical isomers.

(i) Explain what is meant by the term *optical isomers*.

....

....

.... [1]

(ii) Draw the **two** optical isomers of **Q**, showing clearly their three-dimensional structures.

[2]

[N'18 P22 Q4]

CARBONYLS WS 3

SECTION A

1 Which compound on reaction with hydrogen cyanide produces a compound with a chiral centre?

A CH_3CHO

B $CH_3CH_2COCH_2CH_3$

C $CH_3CO_2CH_3$

D HCHO

2 The Russian composer Borodin was also a research chemist who discovered a reaction in which two ethanal molecules combine to form a compound commonly known as aldol (reaction I). Aldol forms another compound on heating (reaction II).

I $2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$

II $CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$

Which of the following best describes reactions I and II?

	I	II
A	addition	elimination
B	addition	reduction
C	elimination	reduction
D	substitution	elimination

3 Oxidation of an alkene **Y** gives a diol; further oxidation gives a diketone.

What could be **Y**?

A $CH_3CH{=}C(CH_3)_2$

B $(CH_3)_2CHCH{=}CH_2$

C $C_6H_5CH{=}CHC_6H_5$

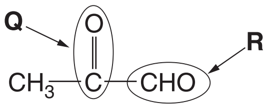
D $(C_6H_5)_2C{=}CHCH_3$

4 Ethanal may be converted into a three-carbon acid in a two-step process.

Which compound is the intermediate?

A CH_3CO_2H **B** CH_3CN **C** CH_3CH_2CN **D** $CH_3CH(OH)CN$

5 Burnt sugar has a characteristic smell caused partly by the following compound. It has two functional groups indicated by **Q** and **R**.



When this compound is tested in a laboratory with 2,4-dinitrophenylhydrazine and Fehling's reagent, which functional groups are responsible for positive tests?

	2,4-dinitrophenylhydazine	Fehling's reagent
A	**Q** and **R**	**Q** and **R**
B	**R** only	**Q** and **R**
C	**Q** and **R**	**R** only
D	**Q** only	**R** only

6 The product of the reaction between propanone and hydrogen cyanide is hydrolysed under acidic conditions.

What is the formula of the final product?

A $CH_3CH(OH)CO_2H$

B $CH_3CH_2CH_2CO_2H$

C $(CH_3)_2CHCONH_2$

D $(CH_3)_2C(OH)CO_2H$

7 $CH_3CH_2COCH_2CH_3$ reacts with hydrogen cyanide to form a cyanohydrin.

Which features apply to the product?

A It has one chiral centre.

B It is formed by electrophilic addition.

C It is formed via a C–OH intermediate.

D Its formation requires the use of cyanide ions as a catalyst.

8 For which pair of compounds can the members be distinguished by means of Tollens' test (the use of a solution containing $Ag(NH_3)_2^+$)?

A CH_3CHO and CH_3COCH_3

B CH_3COCH_3 and $C_2H_5COCH_3$

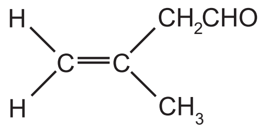
C CH_3COCH_3 and $CH_3CO_2CH_3$

D CH_3CO_2H and $CH_3CO_2CH_3$

9 Compound **P** displays *cis-trans* isomerism and gives a red-brown precipitate with Fehling's solution.

What is **P**?

A



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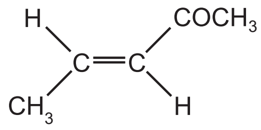

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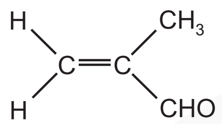

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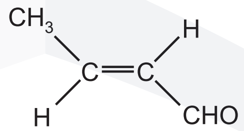


10 Compound **X** changes the colour of acidified sodium dichromate(VI) from orange to green. 1 mol of **X** reacts with 2 mol of HCN(g).

What could **X** be?

A $CH_3COCH_2COCH_3$

B $CH_3CH_2CH_2CHO$

C $H_2C{=}CHCH_2CHO$

D $OHCCH_2CH_2CHO$

11 Instead of obtaining buta-1,3-diene from fossil fuel sources, it is proposed to obtain it from ethanol, which can be obtained from non–food agricultural crops. The sequence of reactions is as follows.

$$CH_3CH_2OH \xrightarrow{\text{step I}} CH_3CHO \xrightarrow{\text{step II}} CH_3CH(OH)CH_2CHO \xrightarrow{\text{step III}} \underset{\text{buta-1,3-diene}}{CH_2{=}CHCH{=}CH_2}$$

Which term could be used to describe step I?

A condensation

B dehydration

C dehydrogenation

D hydrogenation

12 Glycol, used in anti-freeze, has the formula $HOCH_2CH_2OH$. It can be oxidised to give a number of products.

What is the molecular formula of an oxidation product of glycol that will **not** react with sodium?

A $C_2H_2O_2$ **B** $C_2H_2O_3$ **C** $C_2H_2O_4$ **D** $C_2H_4O_2$

13 Which reagent could be used to distinguish between

$CH_3CH(OH)CH_2CHO$ and $CH_3COCH_2CH_2OH$?

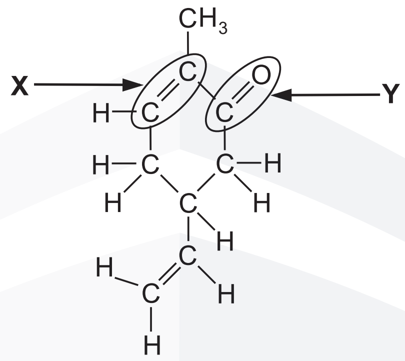
A acidified potassium dichromate(VI)

B dilute sulphuric acid

C 2,4–dinitrophenylhydrazine

D Fehling's reagent

14 This molecule is responsible for the flavour of spearmint chewing gum.



What is a true statement about the functional groups **X** or **Y**?

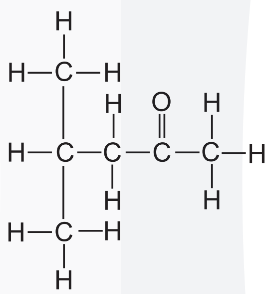
A **X** will undergo nucleophilic addition.

B **Y** will undergo nucleophilic addition.

C **X** will undergo electrophilic substitution.

D **Y** will undergo electrophilic substitution.

15 The solvent methylisobutylketone, MIBK, can be made from propanone.



Which reagent could distinguish this compound from an aldehyde?

A $Br_2(aq)$

B 2,4-dinitrophenylhydrazine

C $NaBH_4$

D Tollens' reagent

16 In 1903 Arthur Lapworth became the first chemist to investigate a reaction mechanism. The reaction he investigated was that of hydrogen cyanide with propanone.

What do we now call the mechanism of this reaction?

A electrophilic addition

B electrophilic substitution

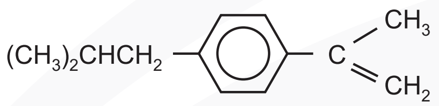
C nucleophilic addition

D nucleophilic substitution

17 Ibuprofen is an anti-inflammatory drug.

ibuprofen

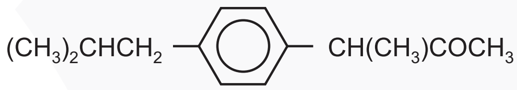
What reaction would lead to its formation?

A 

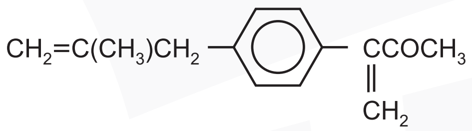
\+ hot concentrated $KMnO_4$

B 

\+ warm acidified $K_2Cr_2O_7$

C 

\+ warm $H_2SO_4(aq)$

D 

\+ H_2 / Pt catalyst

18 What is formed when propanone is refluxed with an anhydrous solution of $NaBH_4$?

A propanal

B propan-1-ol

C propan-2-ol

D propane

19 Which alcohol may be oxidised to a product which reacts with 2,4-dinitrophenylhydrazine reagent but not with Fehling's reagent?

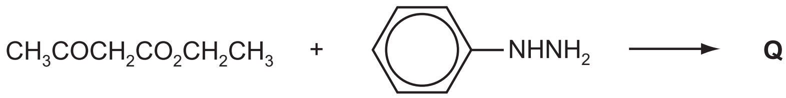
A butan-1-ol

B butan-2-ol

C 2-methylpropan-1-ol

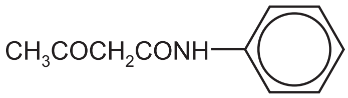
D 2-methylpropan-2-ol

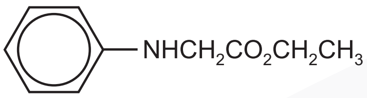
20 The first stage in the synthesis of antipyrine, a drug used in reducing fever, is the reaction between compound **P** and phenylhydrazine.

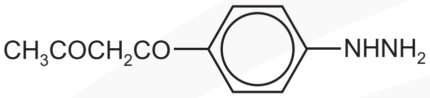


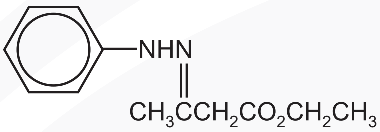
P phenylhydrazine

What is the product **Q** of this first stage?

A 

B 

C 

D 

21 Aldehydes and ketones are carbonyl compounds.

Which of them react both with $NaBH_4$ and with Tollens' reagent?

A both aldehydes and ketones

B aldehydes only

C ketones only

D neither aldehydes nor ketones

22 Apples, the fruit of trees of the genus *Malus*, are rich in malic acid. Malic acid may be synthesised in the laboratory in two steps.

$$NCCH_2CHO \xrightarrow{\text{step 1}} X \xrightarrow{\text{step 2}} HO_2CCH_2CH(OH)CO_2H$$

malic acid

Which reagents could be used for this synthesis?

	step 1	step 2
A	HCl(aq)	HCN(g)
B	HCN, NaCN(aq/alcoholic)	H_2SO_4(aq)
C	H_2SO_4(aq)	$K_2Cr_2O_7$ / H_2SO_4(aq)
D	KCN(aq/alcoholic)	HCl(aq)

23 Which reagent gives the same visible result with propanal and with propan-2-ol?

A 2,4-dinitrophenylhydrazine reagent

B acidified potassium dichromate(VI)

C sodium

D Tollens' reagent

24 Compound **X** will decolourise a warm acidified solution of manganate(VII) ions and forms orange crystals on reaction with 2,4-dinitrophenylhydrazine.

What is **X**?

A $CH_3CH{=}CHCH_2OH$

B $CH_3COCH_2CH_3$

C $CH_3CH_2CH_2CHO$

D $CH_3CH(OH)CH_2CO_2H$

25 Hydrogen bonding can occur between molecules of methanal, HCHO, and molecules of liquid **Y**.

What could liquid **Y** be?

A CH_3OH

B CH_3CHO

C CH_3COCH_3

D $CH_3CO_2CH_3$

26 Hept-4-enal is present in cow's milk.

$CH_3CH_2CH{=}CHCH_2CH_2CHO$

hept-4-enal

What is formed when hept-4-enal is reduced with **either** hydrogen and a nickel catalyst **or** sodium borohydride?

A	with H_2/Ni	$CH_3(CH_2)_5CH_2OH$
B	with H_2/Ni	$CH_3(CH_2)_5CH_3$
C	with $NaBH_4$	$CH_3(CH_2)_5CH_2OH$
D	with $NaBH_4$	$CH_3(CH_2)_5CHO$

27 Which of these reactions is shown by butanone, $CH_3COCH_2CH_3$?

A On warming with acidified potassium dichromate(VI) the solution turns green.

B On heating with Fehling's reagent a red precipitate is formed.

C With 2,4-dinitrophenylhydrazine reagent an orange precipitate is formed.

D With hydrogen cyanide an aldehyde is formed.

28 Ethanal, CH_3CHO, can be reduced using an aqueous methanolic solution of $NaBH_4$ as the reducing agent.

This is a nucleophilic addition reaction.

What could be the first step of this mechanism?

A attack of an H^+ ion at the carbon atom of the carbonyl group

B attack of an H^+ ion at the oxygen atom of the carbonyl group

C attack of an H^- ion at the carbon atom of the carbonyl group

D attack of an H^- ion at the oxygen atom of the carbonyl group

29 The product of the reaction between propanone and hydrogen cyanide is hydrolysed under acidic conditions.

What is the formula of the final product?

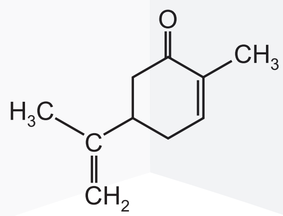
A $CH_3CH(OH)CO_2H$

B $CH_3CH_2CH_2CO_2H$

C $(CH_3)_2CHCONH_2$

D $(CH_3)_2C(OH)CO_2H$

30 Carvone gives the characteristic flavour to caraway and spearmint.



carvone

Prolonged heating of carvone with hot concentrated acidified potassium manganate(VII) produces carbon dioxide and a compound **X**.

X contains nine carbon atoms and reacts with 2,4-dinitrophenylhydrazine reagent.

What is the maximum number of molecules of 2,4-dinitrophenylhydrazine that will react with one molecule of **X**?

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

31 Which reagent will give similar results with both butanone and butanal?

A acidified aqueous potassium dichromate(VI)

B an alkaline solution containing complexed Cu^{2+} ions (Fehling's solution)

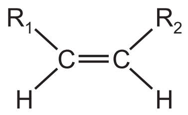
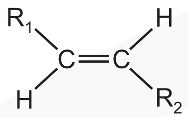
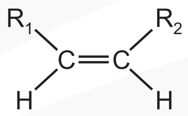
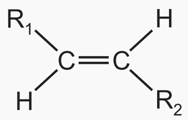
C an aqueous solution containing $[Ag(NH_3)_2]^+$ (Tollens' reagent)

D 2,4-dinitrophenylhydrazine reagent

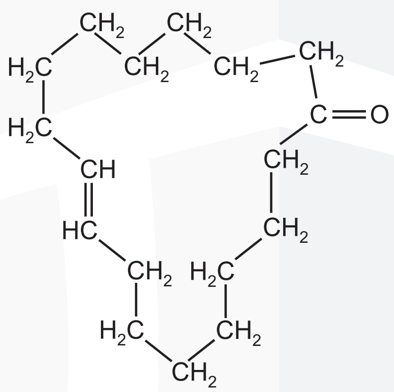
32 The presence of 11-*cis* retinal, $C_{20}H_{28}O$, in cells in the eye is important for vision.

The structure of retinal includes an aldehyde group, a cyclohexene ring and a long aliphatic side chain, in which a carbon-carbon double bond exists between carbons numbered 11 and 12.

Which pair of statements about 11-*cis* retinal could be correct?

	total number of >C=C< double bonds	arrangement around the adjacent carbons 11 and 12
A	5	
B	5	
C	6	
D	6	

33 The naturally-occurring molecule civetone is found in a gland of the African civet cat and has been used in perfumery.



civetone

With which reagent will civetone **not** react?

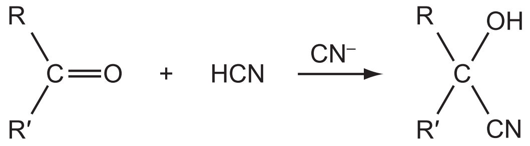
A 2,4-dinitrophenylhydrazine reagent

B Fehling's reagent

C hydrogen bromide

D sodium tetrahydridoborate(III) (sodium borohydride)

34 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2CO_2CH_3$ ions are generated from $CH_3CO_2CH_3$ by strong bases.

Which compound can be made from an aldehyde and $CH_3CO_2CH_3$ in the presence of a strong base?

A $CH_3CH(OH)CO_2CH_3$

B $CH_3CO_2CH_2CH(OH)CH_3$

C $CH_3CH_2CH(OH)CH_2CO_2CH_3$

D $(CH_3)_2C(OH)CH_2CO_2CH_3$

35 What is formed when propanone is refluxed with a solution of $NaBH_4$?

A propanal

B propan-1-ol

C propan-2-ol

D propane

36 Tartaric acid is present in some wines. It may be synthesised in the laboratory in two steps.

$$\text{OHCCHO} \xrightarrow{\text{step 1}} \text{intermediate} \xrightarrow{\text{step 2}} \underset{\text{tartaric acid}}{HO_2CCH(OH)CH(OH)CO_2H}$$

Which reagents could be used for this synthesis?

	step 1	step 2
A	HC*l*(aq)	HCN(g)
B	HCN, NaCN(aq/alcoholic)	H_2SO_4(aq)
C	H_2SO_4(aq)	$K_2Cr_2O_7$ / H_2SO_4(aq)
D	KCN(aq/alcoholic)	$K_2Cr_2O_7$ / H_2SO_4(aq)

37 Which compound would undergo nucleophilic addition?

A bromoethane, C_2H_5Br

B ethanal, CH_3CHO

C ethane, C_2H_6

D ethene, C_2H_4

38 When ethanal, CH_3CHO, reacts with HCN and the organic product is hydrolysed by aqueous acid, organic compound Y is formed.

When propanal, C_2H_5CHO, is heated under reflux with acidified potassium dichromate(VI), organic compound Z is formed.

What is the difference in relative molecular mass of compounds Y and Z?

A 12 **B** 14 **C** 16 **D** 17

39 Many, but not all, organic reactions need to be heated before reaction occurs.

Which reaction occurs at a good rate at room temperature (20 °C)?

A $C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$

B $CH_3CH_2CH_2Br + NH_3 \rightarrow CH_3CH_2CH_2NH_2 + HBr$

C $CH_3CH_2OH + KBr \rightarrow CH_3CH_2Br + KOH$

D $(CH_3)_2CO + H_2NNHC_6H_3(NO_2)_2 \rightarrow (CH_3)_2C{=}NNHC_6H_3(NO_2)_2 + H_2O$

40 $CH_3CH_2COCH_2CH_3$ reacts with hydrogen cyanide to form a cyanohydrin.

Which feature applies to the product?

A It has one chiral centre.

B It is formed by electrophilic addition.

C It is formed via a C–OH intermediate.

D Its formation requires the use of cyanide ions as a catalyst.

41 Compound X changes the colour of warm acidified sodium dichromate(VI) from orange to green. 1 mol of X reacts with 2 mol of HCN in the presence of KCN.

What could X be?

A $CH_3CH_2CH_2CHO$

B $CH_3COCH_2COCH_3$

C $H_2C{=}CHCH_2CHO$

D $OHCCH_2CH_2CHO$

42 A compound Y is treated with warm acidified potassium dichromate(VI). The resulting organic product gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent but does not give a silver mirror with Tollens' reagent.

What is Y?

A butan-1-ol

B butan-2-ol

C butanal

D 2-methylpropan-2-ol

43 Which formulae show propanone and propanal as different compounds?

A empirical, molecular, structural **and** displayed formulae

B molecular, structural and displayed formulae **only**

C structural and displayed formulae **only**

D displayed formulae **only**

44 In a sequence of reactions, ethanal is converted into a compound **H**.

$$CH_3CHO \xrightarrow{\text{HCN, NaCN}} \mathbf{F} \xrightarrow{\text{hot dilute } H_2SO_4} \mathbf{G} \xrightarrow[\text{trace of conc. } H_2SO_4]{CH_3OH\text{, heat}} \mathbf{H}$$

What could **H** be?

A $CH_3CH_2COOCH_3$

B $CH_3CH(OH)COOCH_3$

C $CH_3CH(OH)OCOCH_3$

D $CH_3CH(OCH_3)COOH$

45 In a sequence of reactions, ethanal is converted into a compound **H**.

$$CH_3CHO \xrightarrow{\text{HCN, NaCN}} \mathbf{F} \xrightarrow{\text{hot dilute } H_2SO_4} \mathbf{G} \xrightarrow[\text{trace of conc. } H_2SO_4]{CH_3OH\text{, heat}} \mathbf{H}$$

What could **H** be?

A $CH_3CH_2COOCH_3$

B $CH_3CH(OH)COOCH_3$

C $CH_3CH(OH)OCOCH_3$

D $CH_3CH(OCH_3)COOH$

46 Which compound, on reaction with hydrogen cyanide, produces a compound with a chiral centre?

A CH_3CHO

B $CH_3CH_2COCH_2CH_3$

C $CH_3CO_2CH_3$

D HCHO

47

$CH_3COCH_2CH_2OH$	CH_3COCH_2CHO	$CH_3CH(OH)CH_2CH_3$	$CH_3CH_2CH_2CHO$
W	*X*	*Y*	*Z*

Which of these compounds can be oxidised by acidified dichromate(VI) solution and also gives a positive response to Tollens' reagent?

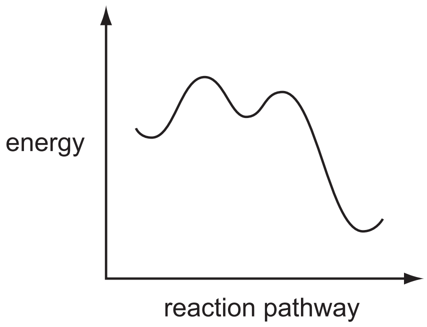
A *W* and *X* only

B *W* and *Y* only

C *X* and *Z* only

D *Y* and *Z* only

48 A reaction pathway diagram is shown.

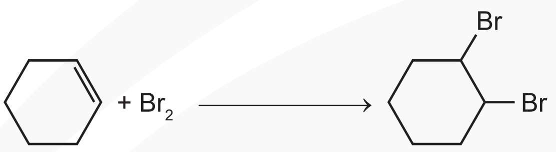


Which reaction does **not** have such a profile?

A $CH_3CHO + HCN \xrightarrow{NaCN} CH_3CH(OH)CN$

B $C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$

C $(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$

D 

49 Burnt sugar has a characteristic smell caused partly by the following compound.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CHO$$

This compound contains two functional groups.

Which reagent will react with **only one** of the functional groups?

A acidified potassium dichromate(VI)

B 2,4-dinitrophenylhydrazine

C hydrogen cyanide

D sodium hydroxide

50 Which carbonyl compound reacts with hydrogen cyanide to form a product that has **no** chiral carbon atom?

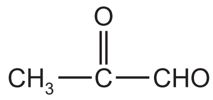
A butanone

B ethanal

C propanal

D propanone

51 Burnt sugar has a characteristic smell caused partly by the following compound.



This compound contains two functional groups.

Which reagent will react with **both** functional groups?

A acidified potassium dichromate(VI)

B Fehling's solution

C hydrogen cyanide

D sodium hydroxide

52 How many hydrogen atoms are added to each molecule of ethanal when it is reacted with $NaBH_4$ in water?

A 1 **B** 2 **C** 4 **D** 6

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

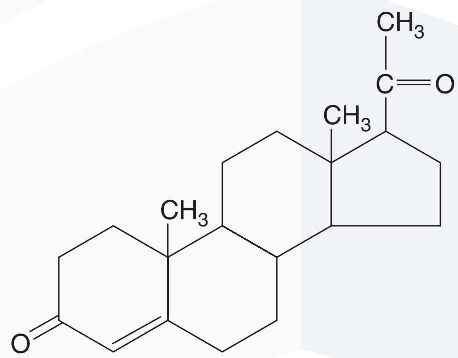
1 In the reaction between an aldehyde and HCN catalysed by NaCN, which statements about the reaction mechanism are true?

1 A new carbon-carbon bond is formed.

2 In the intermediate, the oxygen carried a negative charge.

3 The last stage involves the formation of a hydrogen-oxygen bond.

2 The compound shown is a hormone produced during pregnancy to suppress ovulation.



Which reagents would give positive results with this compound?

1 aqueous bromine

2 2,4-dinitrophenylhydrazine

3 Fehling's reagent

3 Ethanoic acid, CH_3CO_2H, is an important chemical which is used in the industrial manufacture of rayon and aspirin.

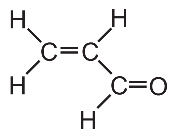
Which processes can be used to make ethanoic acid?

1 hydrolysis of ethanenitrile

2 oxidation of ethanol

3 oxidation of ethanal

4 Acrolein is produced in photochemical smog. It has a strong smell, irritates eyes and mucous membranes and is carcinogenic.



acrolein

What can be deduced from this structure?

1 All bond angles are approximately 120°.

2 It will undergo electrophilic addition reactions.

3 It will undergo nucleophilic addition reactions.

5 Lactic acid builds up in muscles when oxygen is in short supply. It can cause muscular pain. Part of the reaction sequence is shown.

$$CH_2OHCH(OH)CHO \rightarrow CH_3COCO_2H \rightarrow CH_3CH(OH)CO_2H$$

glyceraldehyde pyruvic acid lactic acid

Which statements about the reaction sequence are correct?

1 An aldehyde is oxidised to a carboxylic acid.

2 A ketone is reduced to a secondary alcohol.

3 A secondary alcohol is oxidised to a ketone.

6 A liquid **X** is known to be either a single organic compound or a mixture of organic compounds. When treated with sodium, **X** gives off hydrogen gas.

When treated with 2,4-dinitrophenylhydrazine reagent, **X** gives orange crystals.

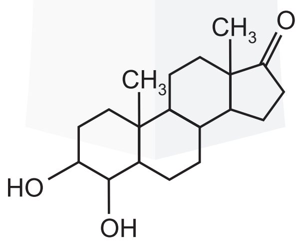
Which deductions about **X** can definitely be made?

1 At least one component of **X** is a carbonyl compound.

2 Only one of the components of **X** is a carbonyl compound.

3 At least one component of **X** is an alcohol.

7 The steroid shown is an intermediate compound obtained during the synthesis of *Formestane* which is used in the treatment of breast cancer.



Which statements about this compound are correct?

1 It reacts with hydrogen cyanide in a nucleophilic addition reaction.

2 It can be oxidised by warm acidified potassium dichromate(VI) to a carboxylic acid.

3 It will react with Fehling's solution.

8 How can the rate of reaction between ethanal and aqueous hydrogen cyanide be increased?

1 by irradiation with ultraviolet light

2 by a rise in temperature

3 by the addition of a small quantity of aqueous sodium cyanide

9 In the reaction between an aldehyde and HCN catalysed by NaCN, which statements about the reaction mechanism are true?

1 A new carbon-carbon bond is formed.

2 In the intermediate, the oxygen carries a negative charge.

3 The last stage involves the formation of a hydrogen-oxygen bond.

10 Glyceraldehyde, $HOCH_2CH(OH)CHO$, is formed during photosynthesis, and contains a chiral carbon atom.

Which reagents will react with glyceraldehyde to produce an organic product **without** a chiral carbon atom?

1 warmed acidified $K_2Cr_2O_7$

2 $NaBH_4$

3 Tollens' reagent

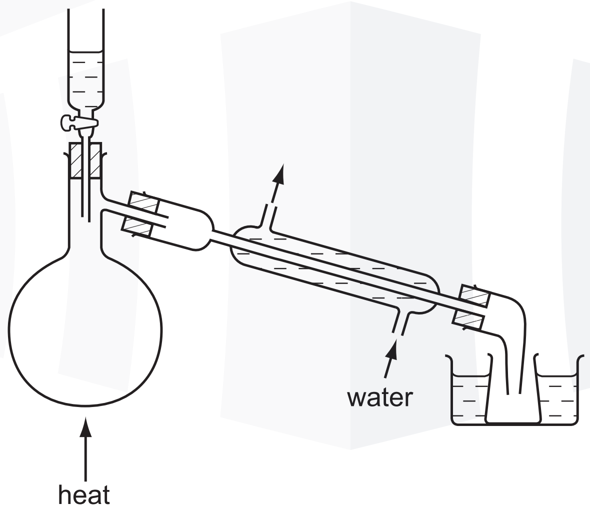
11 Which pairs of reagents will react together in a redox reaction?

1 CH_3CHO + Fehling's reagent

2 $CH_4 + Cl_2$

3 CH_3COCH_3 + Tollens' reagent

12 The diagram shows some laboratory apparatus.



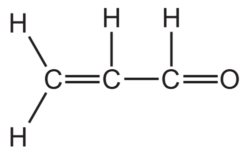
Which preparations could this apparatus be used for?

1 bromoethane, from ethanol, sodium bromide and concentrated sulfuric acid

2 ethanal, from ethanol, sodium dichromate(VI) and sulfuric acid

3 1,2-dibromoethane, from bromine and ethene

13 The diagram shows a compound present in smoke from burning garden waste.



Which reagents would undergo a colour change on reaction with this compound?

1 aqueous bromine

2 Fehling's reagent

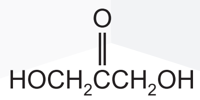
3 warm acidified $K_2Cr_2O_7$

14 Compound **X** has molecular formula $C_4H_{10}O$. Separate samples of **X** are tested with three different reagents.

Which results could **not** be obtained?

	Tollens' reagent	2,4-dinitrophenylhydrazine reagent	warm acidified potassium dichromate(VI) solution
1	silver mirror forms	orange precipitate forms	colour changes from orange to green
2	no change	no change	no change
3	no change	no change	colour changes from orange to green

15 DHA is a colourless liquid which reacts with protein in skin to cause it to darken. It has the structure shown.



DHA

Which observations would be made when testing this substance?

1 Hydrogen is produced when sodium is added.

2 A coloured precipitate is produced when 2,4-dinitrophenylhydrazine reagent is added.

3 A silver precipitate is produced when Tollens' reagent is added.

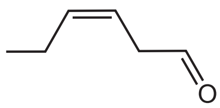
16 Which reagents react with butanone, $C_2H_5COCH_3$?

1 Tollens' reagent

2 sodium borohydride

3 2,4-dinitrophenylhydrazine reagent

17 The compound *cis*-hex-3-enal is responsible for the characteristic smell of cut grass. The human nose is particularly sensitive to this compound, being able to detect 0.25 parts per billion in air.



cis-hex-3-enal

Which reagents will react with *cis*-hex-3-enal?

1 sodium

2 sodium borohydride

3 Fehling's reagent

18 Which changes in bonding occur during the reaction of ethanal and hydrogen cyanide?

1 A carbon-carbon bond is formed.

2 A carbon-hydrogen bond is broken.

3 A carbon-nitrogen bond is broken.

19 In which reactions is the organic compound oxidised by the given reagent?

1 CH_3CH_2CHO + Fehling's reagent

2 $CH_3CH_2CH_2CHO$ + Tollens' reagent

3 CH_3CHO + 2,4-dinitrophenylhydrazine reagent

20 The M_r of compound X is 72. The composition by mass of X is 66.7 % carbon, 11.1 % hydrogen and 22.2 % oxygen. X gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent. X does **not** react with Fehling's reagent.

What can be deduced from this information?

1 X is a carbonyl compound.

2 X is a ketone.

3 X is butanone.

21 Which reactions can be used to make an alcohol in the laboratory?

1 hydrolysis of a bromoalkane with NaOH(aq)

2 reduction of a ketone with $NaBH_4$

3 reduction of an aldehyde with $NaBH_4$

22 The compounds below are treated with hydrogen cyanide.

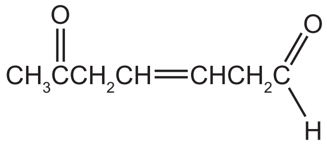
Which compounds react and produce a molecule containing a chiral centre?

1 butanal

2 pentan-3-one

3 2-chlorobutane

23 A series of tests was carried out on the compound shown below.



Which pairs of reagents would **both** give a positive result for this compound?

1 Tollens' reagent and a solution containing acidified dichromate(VI) ions

2 aqueous bromine and Fehling's reagent

3 2,4-dinitrophenylhydrazine reagent and sodium carbonate

24 The reaction of ethanal, CH_3CHO, with HCN to form a cyanohydrin is catalysed by NaCN.

What are features of the intermediate of this reaction?

1 It is chiral.

2 It has a single negative charge on one of its atoms.

3 It is a nucleophile.

CARBONYLS WS 4

1 Samples of the following compounds were labelled **A** to **E** as shown.

A $CH_3CH_2CH_2OH$

B $CH_3CH_2CH(OH)CH_3$

C CH_3CHO

D CH_3COCH_3

E $CH_3CH{=}CHCH_3$

Complete the table below by inserting the letter (or letters) of the compounds that correspond to each test.

reagent	observation	letter(s)
acidified potassium dichromate(VI)	green colour obtained on boiling	
acidified potassium manganate(VII)	ethanoic acid obtained on boiling	
hydrogen in the presence of a platinum catalyst	hydrogen absorbed	
Fehling's reagent	brown-red precipitate obtained on boiling	
2,4-dinitrophenylhydrazine	orange precipitate	
bromine in an inert solvent	solution decolourised	

[9]

2 A compound, **A**, has the following composition by mass.

C, 66.7%; H, 11.1%; O, 22.2%.

It has an M_r of 72.

(a) Calculate the molecular formula of **A**.

[2]

(b) **A** reacts with 2,4-dinitrophenylhydrazine but not with Fehling's or Tollens' reagents.

(i) State what you would see when **A** reacts with the 2,4-dinitrophenylhydrazine reagent.

....

(ii) State what functional group is present in **A**. ....

(iii) Identify **A** either by name or by its structural formula.

....[3]

(c) **A** can be reduced to compound **B**.

For this reaction

(i) state a suitable reducing agent, ...

(ii) name the functional group in **B** (two words are required),

....

(iii) give the structural formula of **B.**

[3]

3 2-Hydroxypropanoic acid (lactic acid), $CH_3CH(OH)CO_2H$, can be prepared in a two-stage synthesis from ethanal, CH_3CHO.

(a) In the first stage, ethanal reacts with hydrogen cyanide, HCN, in the presence of an NaCN catalyst to produce a cyanohydrin.

(i) Write an equation for the reaction of ethanal and HCN, giving the displayed formula of the product.

(ii) State what type of reaction this is.

....

(iii) Describe the mechanism of this reaction.

[5]

(b) In the second stage, the product from **(a)** is converted into lactic acid.

(i) Write the equation for this stage.

....

(ii) State what type of reaction this is.

....[2]

(c) In this synthesis 4.40 g of ethanal were used and at the end 5.40 g of lactic acid were obtained.

Calculate the percentage yield of lactic acid.

[3]

4 A student obtained the following results when analysing an organic compound, **H**.

test		observation
test 1	relative molecular mass	72
test 2	% composition by mass	C, 66.7%; H, 11.1%; O, 22.2%
test 3	reactions with $Br_2(aq)$	Br_2 decolourised
test 4	reaction with Na(s)	$H_2(g)$ evolved
test 5	reaction with warm $Cr_2O_7^{2-}/H^+$	green colour observed

The student allowed test 5 to go to completion and then investigated the **product** of test 5 with the following result.

test 6	reaction with 2,4-dinitrophenylhydrazine	no reaction

(a) Calculate the molecular formula of **H**.

[2]

(b) What can be deduced about the nature of **H** by the following tests?

(i) test 3 ....

(ii) test 4 ....
[2]

(c) **(i)** What functional group would have given a positive result in test 6?

....

(ii) What functional group is shown to be present in **H** by tests 5 and 6?

....
[2]

(d) On testing a sample of **H**, the student found that it was not chiral.

H did, however, show *cis-trans* isomerism.

How does *cis-trans* isomerism arise in an organic molecule?

....

....

.... [2]

(e) Use all of the information above to draw labelled, displayed formulae of the stereoisomers of compound **H**.

[2]

5 Compound **Z**, an organic compound with **three** functional groups, has the molecular formula $C_4H_6O_2$. The functional groups can be confirmed by the following tests.

(a) Test for the first functional group.

Z decolourises aqueous bromine.

What functional group is shown to be present in **Z** by this test?

.... [1]

(b) Tests for the second functional group.

Z reacts with sodium to give hydrogen and a solid compound of formula $C_4H_5O_2Na$.

When **Z** is heated with ethanoic acid and a few drops of concentrated sulphuric acid, a sweet smelling liquid of molecular formula $C_6H_8O_3$ is formed.

What functional group is shown to be present in **Z** by these tests?

.... [1]

(c) Tests for the third functional group.

A few drops of **Z** form a yellow/orange precipitate when added to 2,4-dinitrophenylhydrazine reagent.

When a few drops of **Z** are warmed with Tollens' reagent, a silver mirror is formed.

What functional group is shown to be present in **Z** by these tests?

.... [1]

(d) **Z** does **not** show *cis-trans* isomerism.

Draw the displayed formula of **Z**.

[2]

In parts **(e)** and **(f)** you may use R– to represent the part of the molecule that does not react.

(e) What is the organic compound formed by the reactions of **Z** in **each** of the tests in **(b)**?

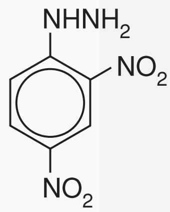
with sodium

with ethanoic acid

[2]

(f) Draw the structure of the organic compound formed by **Z** in **each** of the tests in **(c)**.

with Tollens' reagent

with 2,4-dinitrophenylhydrazine, 

[2]

(g) But-2-enoic acid is an isomer of **Z** which shows *cis-trans* isomerism.

Draw a displayed formula of the *cis* isomer of this acid.

[2]

6 Commercial paint and varnish removers contain a mixture of dichloromethane, CH_2Cl_2, and methanol, CH_3OH.

(a) What would be observed when the following reactions are carried out?
In each case, give the name or formula of the reaction product which is responsible for the observation you have made.

(i) CH_2Cl_2 is reacted with NaOH(aq) and $AgNO_3$(aq) and the mixture left to stand.

observation ....

product responsible ....

(ii) CH_3OH is mixed with PCl_5.

observation ....

product responsible ....

(iii) CH_3OH is reacted with sodium.

observation ....

product responsible ....

[6]

(b) When CH_2Cl_2 is heated under reflux with an excess of NaOH(aq), a compound **W** is formed.

W has the following composition by mass: C, 40.0%; H, 6.7%; O, 53.3%.

Use this information and the *Data Booklet* to show that the empirical formula of **W** is CH_2O.

[2]

(c) Compounds with the empirical formula CH_2O can have the molecular formula $C_2H_4O_2$.

Two possible structural formulae for compounds with molecular formula $C_2H_4O_2$ are HCO_2CH_3 and $H_2C{=}C(OH)_2$.

In the boxes below, draw displayed formulae for **three further** structural isomers with the molecular formula $C_2H_4O_2$.

Do **not** attempt to draw any structures containing rings or O–O bonds.

X	**Y**	**Z**

[3]

(d) Identify which of your compounds, **X**, **Y**, or **Z**, will react with the following reagents.

In **each** case, state what you would observe.

(i) solid $NaHCO_3$

compound ....

observation ....

(ii) Tollens' reagent

compound ....

observation ....

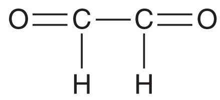
[4]

(e) **One** of the three compounds, **X**, **Y**, or **Z**, shows stereoisomerism.

Draw displayed, labelled structures of the stereoisomers of this compound.

[2]

7 Ethanedial (glyoxal) is used in the production of fabrics which have permanent creases.



ethanedial

Ethanedial undergoes many of the reactions of aldehydes.

(a) Ethanedial reacts with Tollens' reagent.

(i) What would you see if you carried out this reaction?

....

(ii) What is the structural formula of the organic compound formed?

[2]

(b) Ethanedial reacts with hydrogen cyanide, HCN, to give compound **F**.

(i) What is the structural formula of **F**?

(ii) What type of reaction is this?

....

(iii) What is the structural formula of the compound formed when **F** is heated with an aqueous mineral acid such as dilute sulphuric acid?

[3]

(c) Ethanedial can be oxidised and reduced.

(i) What is the structural formula of the organic compound formed when ethanedial is heated under reflux with an excess of acidified potassium dichromate(VI)?

(ii) What is the structural formula of the compound formed when ethanedial is reduced?

(iii) What reagent would be used for this reduction?

....

[3]

(d) When ethanedial is reacted with NaOH and the product treated with a mineral acid such as dilute sulphuric acid, the following reaction sequence takes place.

I $CHOCHO + NaOH \rightarrow HOCH_2CO_2Na$

II $HOCH_2CO_2Na + H^+ \rightarrow HOCH_2CO_2H + Na^+$

What type of reaction is the overall change?

.... [1]

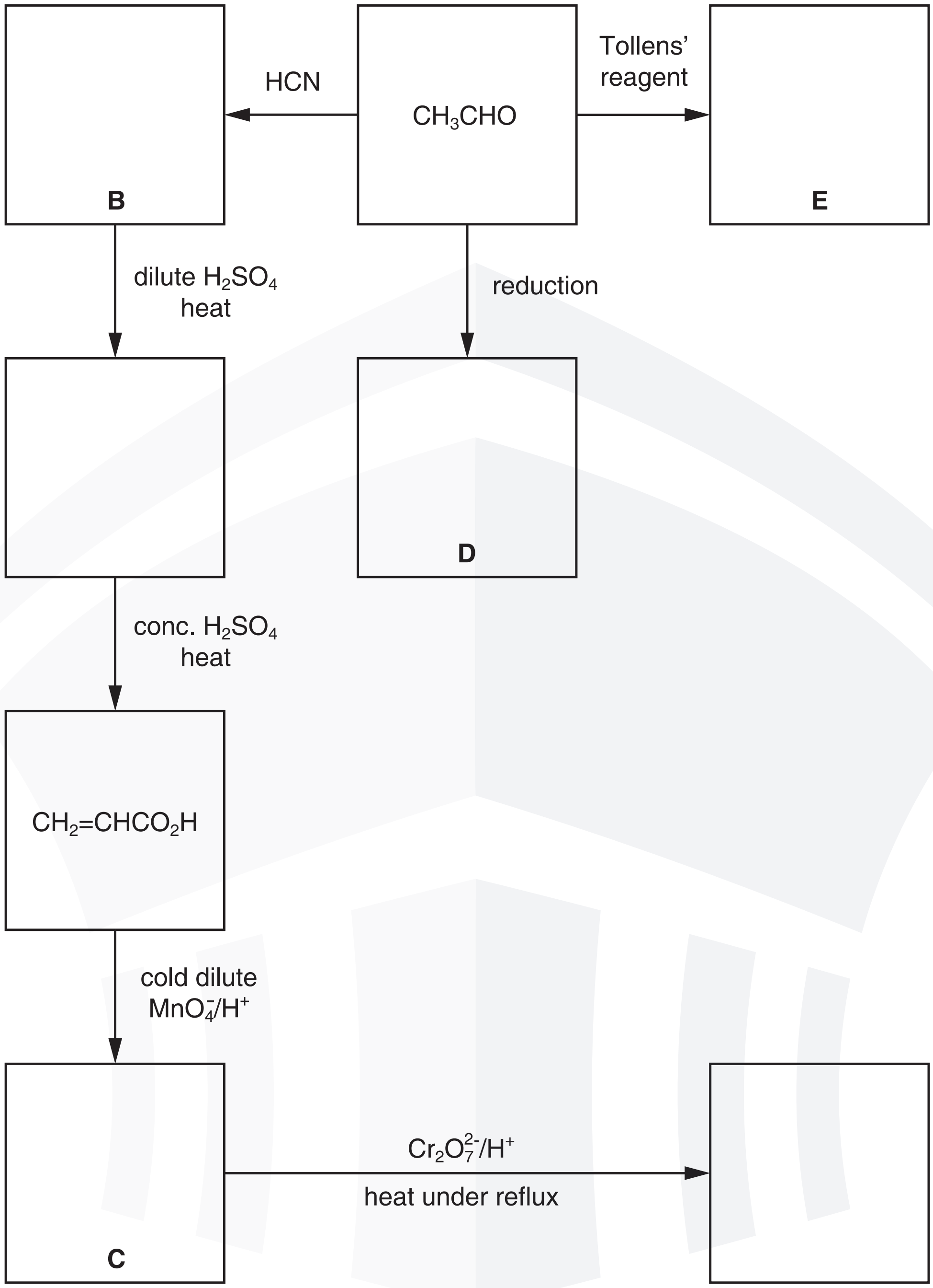
(e) An isomer of ethanedial exists which reacts with sodium metal to give hydrogen.

Suggest the displayed formula of this isomer.

[2]

8 **(a)** Complete the following reaction scheme which starts with ethanal.

In **each empty** box, write the **structural formula** of the organic compound that would be formed.



[6]

(b) Write the structural formula for the organic compound formed when, under suitable conditions,

(i) compound **C** reacts with compound **D**,

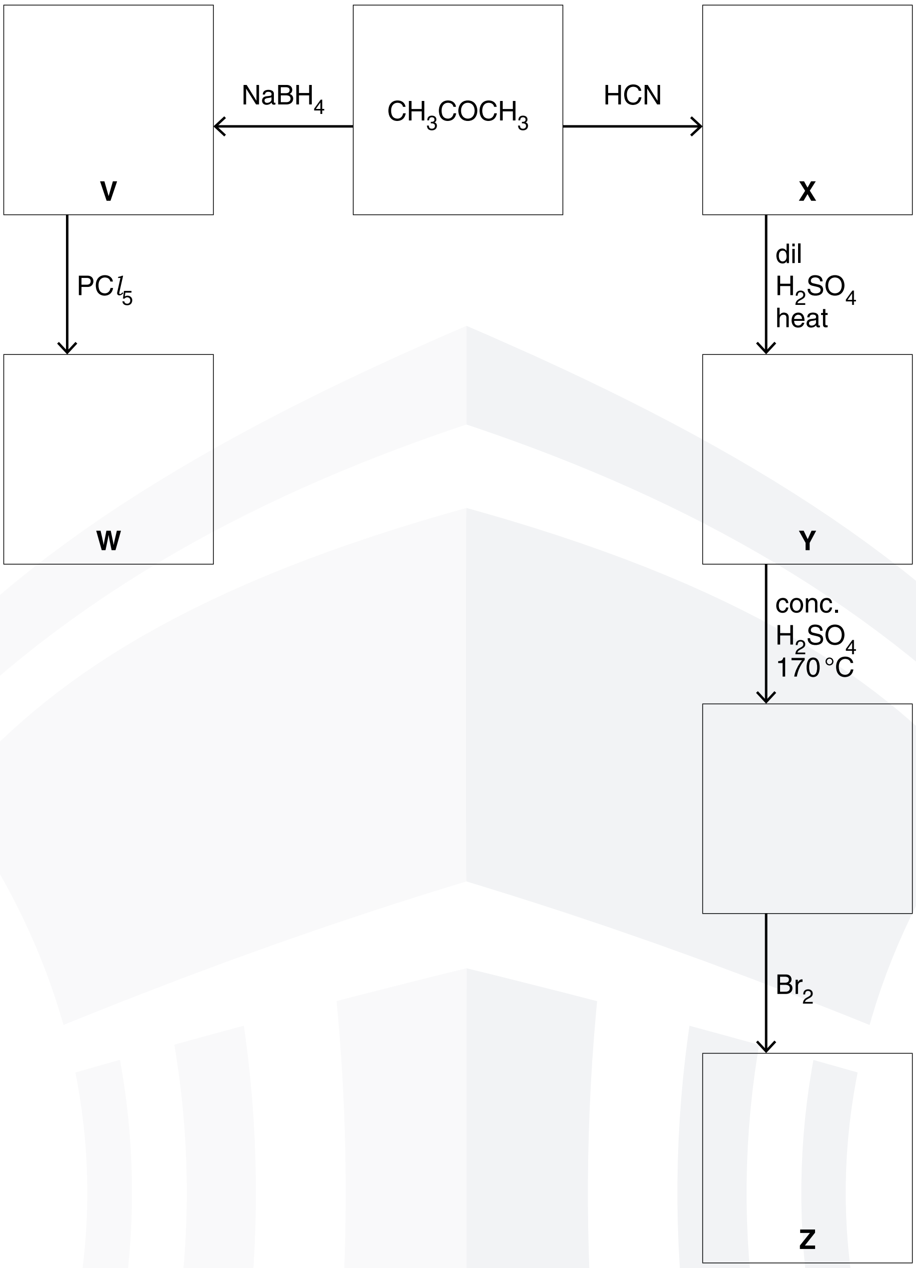
(ii) compound **C** reacts with compound **E**.

[2]

(c) Compound **B** is chiral. Draw displayed formulae of the two optical isomers of compound **B**, indicating with an asterisk (*) the chiral carbon atom.

[3]

9 **(a)** Complete the following reaction scheme which starts with propanone.
In **each empty** box, write the **structural formula** of the organic compound that would be formed.



[6]

(b) One of the compounds **V**, **W**, **X**, **Y** or **Z** is chiral.

(i) Identify this compound by its letter.

....

(ii) Draw displayed formulae of the two optical isomers of this compound.
Indicate with an asterisk (*) the chiral carbon atom.

[3]

(c) Write the structural formula for the organic compound formed when, under suitable conditions,

(i) compound **Y** reacts with compound **V**,

(ii) compound **Y** reacts with compound **Z**.

[2]

10 Lactic acid, 2-hydroxypropanoic acid, $CH_3CH(OH)CO_2H$, occurs naturally in sour milk and in our muscles when we take hard exercise.
Lactic acid is chiral and shows stereoisomerism.

(a) Draw fully displayed structures of the two optical isomers of lactic acid.
Indicate with an asterisk (*) the chiral carbon atom in the lactic acid molecule.

[3]

(b) Lactic acid may be synthesised from ethanol by the following route.

$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO \xrightarrow{\text{step 2}} CH_3CH(OH)CN \xrightarrow{\text{step 3}} CH_3CH(OH)CO_2H$$

Give the reagent(s) and essential condition(s) for **each** step.

	reagent(s)	condition(s)
step 1		
step 2		
step 3		

[6]

During exercise, lactic acid is produced in our muscles from pyruvic acid, CH_3COCO_2H.
This reaction occurs in the presence of the enzyme lactic acid dehydrogenase.

(c) (i) What type of chemical compound is the enzyme lactic acid dehydrogenase?

....

(ii) How would you detect a small quantity of pyruvic acid in a sample of lactic acid?

State the reagent(s) you would use and what would be seen in your test.

reagent(s) ....

observation ....

(iii) How would you detect a small quantity of lactic acid in a sample of pyruvic acid?

State the reagent(s) you would use and what would be seen in your test.

reagent(s) ....

observation ....

(iv) What chemical reagent would be used to convert pyruvic acid into lactic acid?

$$CH_3COCO_2H \rightarrow CH_3CH(OH)CO_2H$$

....

[6]

11 Ketones are widely used as solvents and as intermediates in the chemical industry.

Ketones contain the reactive keto group, $>C=O$.

(a) Propanone, CH_3COCH_3, undergoes a reaction with hydrogen cyanide, HCN.

(i) What type of reaction is this?

....

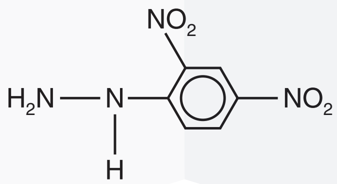
(ii) What reagents are used?

....

(iii) Draw a diagram to show the dipole present in the propanone molecule.

[3]

(b) Propanone reacts with 2,4-dinitrophenylhydrazine reagent.

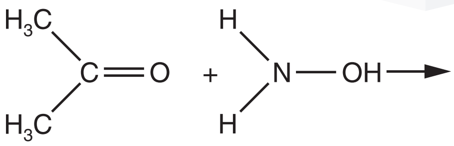


2,4-dinitrophenylhydrazine

(i) Construct a balanced equation for the reaction between propanone and 2,4-dinitrophenylhydrazine.

(ii) A similar type of reaction occurs between propanone and hydroxylamine, NH_2OH.

Draw the displayed formula of the organic product of this reaction.



[3]

HNE is a reactive compound.

(c) Give the structural formulae of all of the carbon-containing compounds formed in each case when HNE is reacted separately with the following reagents.

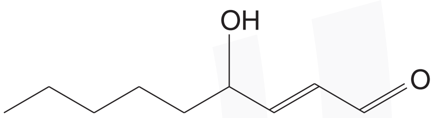
(i) hot concentrated manganate(VII) ions in acid solution

(ii) hot phosphorus trichloride, PCl_3

(iii) sodium tetrahydridoborate(III), $NaBH_4$

[4]

12 The compound *trans*-4-hydroxy-2-nonenal (HNE) is thought to lead to infections of the lung when cigarettes are smoked.



$CH_3(CH_2)_4CH(OH)CH{=}CHCHO$

***trans*-4-hydroxy-2-nonenal**

(a) What is the empirical formula of *trans*-4-hydroxy-2-nonenal?

.... [1]

(b) **(i)** HNE contains an alkene group. Name as fully as you can **two** other functional groups which are present in the HNE molecule.

....

....

(ii) How would you confirm the presence of the alkene group in HNE? State the reagent used and the observation you would make.

reagent ....

observation ....

[5]

13 Astronomers using modern telescopes of various types have found many molecules in the dust clouds in space. Many of these molecules are those of organic compounds and astronomers constantly look for evidence that amino acids such as aminoethanoic acid, $H_2NCH_2CO_2H$, are present.

One molecule that has been found in the dust clouds is hydroxyethanal, $HOCH_2CHO$.

(a) Hydroxyethanal contains two functional groups.

(i) Name, **as fully as you can**, each of the functional groups present in hydroxyethanal.

1 ....

2 ....

(ii) For **each** functional group, identify a reagent that will react with this group and **not** react with the other functional group present.
In each case, describe what would be observed when this reaction is carried out.

functional group 1 reagent ....

observation..

functional group 2 reagent ....

observation.. [7]

(b) Give the **skeletal** formulae of the organic compounds formed when hydroxyethanal is reacted separately with the following.

(i) $NaBH_4$

(ii) $Cr_2O_7^{2-}/H^+$ under reflux conditions

[2]

In a school or college laboratory, it is possible to convert a sample of hydroxyethanal into aminoethanoic acid in a three-step process.

$$HOCH_2CHO \xrightarrow{\text{step 1}} \mathbf{X} \xrightarrow{\text{step 2}} \mathbf{Y} \xrightarrow{\text{step 3}} H_2NCH_2CO_2H$$

By considering the possible reactions of the functional groups present in hydroxyethanal, you are to deduce a possible route for this conversion.

(c) **(i)** In the boxes below, draw the structural formulae of your suggested intermediates **X** and **Y**.

X	**Y**

(ii) State the reagents for **each** of the three steps you have chosen.

step 1..

step 2..

step 3.. [5]

14 Many organic compounds, including alcohols, carbonyl compounds, carboxylic acids and esters, contain oxygen.

(a) The table below lists some oxygen-containing organic compounds and some common laboratory reagents.

(i) Complete the table as fully as you can.
If you think no reaction occurs, write 'no reaction' in the box for the structural formula(e).

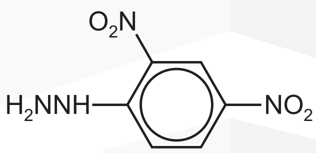
reaction	organic compound	reagent	structural formula(e) of organic product(s)
A	$(CH_3)_3COH$	$Cr_2O_7^{2-}/H^+$ heat under reflux	
B	CH_3CH_2CHO	Fehling's reagent warm	
C	$HCO_2CH(CH_3)_2$	NaOH(aq) warm	
D	$CH_2{=}CHCHO$	$NaBH_4$	
E	$(CH_3)_3COH$	$NaBH_4$	
F	$CH_3CH_2COCH_3$	MnO_4^-/H^+ heat under reflux	

(ii) During some of the reactions in **(i)** a colour change occurs.
Complete the table below for any such reactions, stating the letter of the reaction and what the colour change is.

reaction	colour at the beginning of the reaction	colour at the end of the reaction

[10]

(b) Some oxygen-containing compounds react with 2,4-dinitrophenylhydrazine.



2,4-dinitrophenylhydrazine

(i) Draw the structural formula of the organic compound formed when $HOCH_2CH_2CHO$ reacts with 2,4-dinitrophenylhydrazine reagent.

(ii) Suggest the colour of the organic product.

....

[2]

15 The molecular formula C_4H_8O can represent a number of compounds which have different functional groups and which show different types of isomerism.
Compounds **H**, **J** and **K** each have the molecular formula C_4H_8O.
In **each** of the molecules of **H**, **J** and **K**,

- the carbon chain is unbranched and the molecule is not cyclic,
- no oxygen atom is attached to any carbon atom which is involved in π bonding.

When compound **H** is reacted with sodium metal, a colourless flammable gas is produced.

Both **J** and **K** give an orange-red precipitate when reacted with 2,4-dinitrophenylhydrazine reagent but only **K** reacts with Fehling's solution.

(a) **(i)** Suggest possible structural formulae for **H**, **J** and **K**.
Three structural formulae are possible for **H** but only one for **J** and one for **K**.

H	J	K

In addition to being structural isomers of each other, some of the possible structures for **H**, **J** or **K** show *cis-trans* isomerism or are chiral.

(ii) Draw the displayed formulae of those isomers which show *cis-trans* isomerism.

(iii) Draw the displayed formulae of those isomers which are chiral, indicating in each case the chiral carbon atom with an asterisk (*).

[8]

16 Crotonaldehyde, $CH_3CH{=}CHCHO$, occurs in soybean oils.

(a) In the boxes below, write the **structural formula** of the organic compound formed when crotonaldehyde is reacted separately with each reagent under suitable conditions.
If you think no reaction occurs, write 'NO REACTION' in the box.

reaction	reagent	product
A	Br_2 in an inert organic solvent	
B	PCl_3	
C	H_2 and Ni catalyst	
D	$NaBH_4$	
E	$K_2Cr_2O_7$ / H^+	

[5]

(b) Crotonaldehyde exists in more than one stereoisomeric form.
Draw the **displayed formulae** of the **stereoisomers** of crotonaldehyde.
Label **each** isomer.

[3]

(c) Draw the **skeletal formula** of crotonaldehyde.

[1]

(d) The product of reaction E in the table opposite will react with a solution containing acidified manganate(VII) ions.
Draw the **structural formulae** of the organic products when the reagent is

(i) cold, dilute;

(ii) hot, concentrated.

[3]

17 Compound **Q**, heptan-2-one, is found in some blue cheeses.

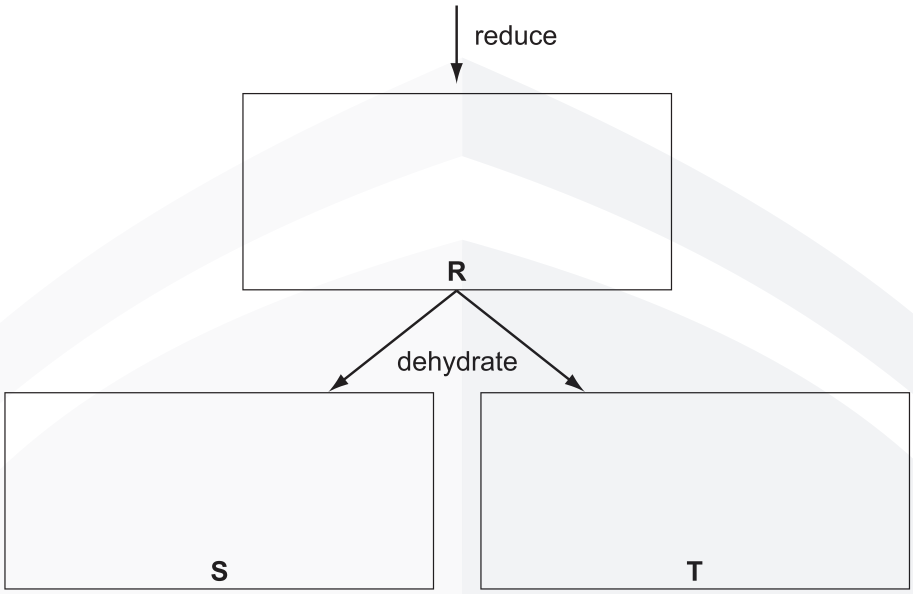
$$CH_3(CH_2)_4COCH_3$$

compound **Q**

(a) Compound **Q** may be reduced to **R**.
Compound **R** may be dehydrated to give two different products, **S** and **T**.

(i) In the boxes below, draw the **structural formulae** of **R**, **S**, and **T**.

$$CH_3(CH_2)_4COCH_3$$



(ii) State the reagents that would be used for **each** of these reactions in a school or college laboratory.

reduction ....

dehydration ....

[5]

(b) In the boxes below, write the **structural formula** of the organic compound formed when **Q** is reacted separately with each reagent under suitable conditions.
If you think no reaction occurs, write 'NO REACTION' in the box.

Tollens' reagent	
HCN	
$K_2Cr_2O_7 / H^+$	

[3]

(c) The first stage of cheese making is to produce 2-hydroxypropanoic acid (lactic acid) from milk.

$CH_3CH(OH)CO_2H$

lactic acid

Other than the use of a pH indicator, what reagent could you use to confirm the presence of some lactic acid in a sample of heptan-2-one?
State what observation you would make.

reagent ....

observation .... [2]

IODOFORM WS

1 Compounds **D** and **E** are both ketones.

$CH_3CH_2COCH_2CH_3$	$CH_3CH_2CH_2COCH_3$
D	**E**

(a) State which one of these compound reacts with alkaline aqueous iodine, and draw the structural formulae of the products formed during this reactions.

(i) compound (**D** or **E**) ....

(ii) products

.... [3]

(b) The reduction of **D** with $NaBH_4$ produces just one alcohol, but a similar reduction of **E** produces two isomers in equal amounts. Explain these observations, drawing structures where appropriate.

....

....

[3]

2 The two compounds **V** and **W** are isomers with the molecular formula C_4H_8O, and show the following properties and reactions.

- Both compounds react with sodium metal, and both decolourise bromine water.
- Compound **V** forms a yellow precipitate with alkaline aqueous iodine, whereas compound **W** does not.
- When reacted with cold $KMnO_4(aq)$, both **V** and **W** produce the same neutral compound **X**, $C_4H_{10}O_3$.
- Both **V** and **W** exist as pairs of stereoisomers.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

....

(ii) bromine water,

....

(iii) alkaline aqueous iodine.

....

[3]

(b) Suggest structures for **V** and **W**.

V	W

[2]

(c) State the type of stereoisomerism shown by compound **V** and draw the structures of the stereoisomers.

type of stereoisomerism ....

structures of stereoisomers

isomer 1	isomer 2

[2]

(d) Suggest the structure of the neutral compound **X**.

X

[1]

3 Although now remembered for his music, the Russian composer Alexander Borodin was a chemist. He is credited with the discovery of the *aldol reaction*, a product of which is compound **J**. **J** shows the following properties:

- its molecular formula is $C_4H_8O_2$,
- it is neutral,
- it reacts with sodium metal,
- it reacts with Fehling's solution,
- it does not react with aqueous bromine.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

....

(ii) Fehling's solution.

....

[2]

(b) The result of the bromine test shows a functional group is absent from compound **J**. Suggest the identity of this functional group.

.... [1]

(c) In the boxes below, draw three possible **straight-chain** structures for **J** that fit the above results, and that are structural isomers of each other.

K	**L**
M	

[3]

(d) Compound **J** reacts with alkaline aqueous iodine to give a pale yellow precipitate.

(i) Which functional group does this reaction show that **J** contains?

....

(ii) Which of your three structures **K**, **L** or **M** contains this group and is therefore **J**?

....

[2]

(e) Compound **J** exists as stereoisomers.

(i) Name the type of stereoisomerism shown by **J**.

....

(ii) Draw two structures of **J** to illustrate this stereoisomerism.

[2]

Carboxylic acids

a describe the formation of carboxylic acids from alcohols, aldehydes and nitriles ☐

b describe the reactions of carboxylic acids in the formation of:

(i) salts, by the use of reactive metals, alkalis or carbonates ☐

(ii) alkyl esters ☐

(iii) alcohols, by use of $LiAlH_4$ ☐

(iv) acyl chlorides ☐

c recognise that some carboxylic acids can be further oxidised:

(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents ☐

(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm acidified manganate(VII) ☐

d explain the relative acidities of carboxylic acids, phenols and alcohols ☐

e use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids ☐

Esters

a describe the acid and base hydrolysis of esters ☐

b state the major commercial uses of esters, e.g. solvents, perfumes, flavourings ☐

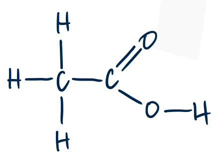
CARBOXYLIC ACIDS

19.1 Carboxylic acids	a)	describe the formation of carboxylic acids from alcohols, aldehydes and nitriles
	b)	describe the reactions of carboxylic acids in the formation of:
		(i) salts, by the use of reactive metals, alkalis or carbonates
		(ii) alkyl esters
		(iii) alcohols, by use of $LiAlH_4$
		(iv) acyl chlorides
	c)	**recognise that some carboxylic acids can be further oxidised:**
		(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents
		(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm acidified manganate(VII)
	d)	**explain the relative acidities of carboxylic acids, phenols and alcohols**
	e)	**use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids**
19.2 Acyl chlorides	**a)**	**describe the hydrolysis of acyl chlorides**
	b)	**describe the reactions of acyl chlorides with alcohols, phenols, ammonia and primary amines**
	c)	**explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides including the condensation (addition-elimination) mechanism for the hydrolysis of acyl chlorides**
19.3 Esters	a)	describe the acid and base hydrolysis of esters
	b)	state the major commercial uses of esters, e.g. solvents, perfumes, flavourings

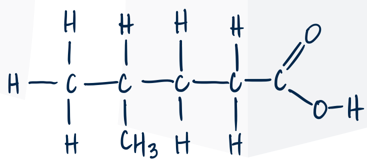
CARBOXYLIC ACIDS AND ESTERS

CARBOXYLIC ACIDS

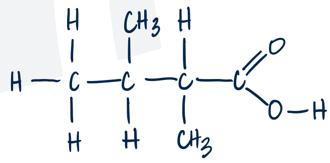
When the carbonyl group is directly joined to an oxygen atom, the carboxyl group is formed. This occurs in carboxylic acids and esters.



ethanoic acid



4-methyl pentanoic acid



2,3-dimethylbutanoic acid

CARBOXYLIC ACIDS

The reactions of the carbonyl group are drastically changed by the presence of the electronegative oxygen atom.

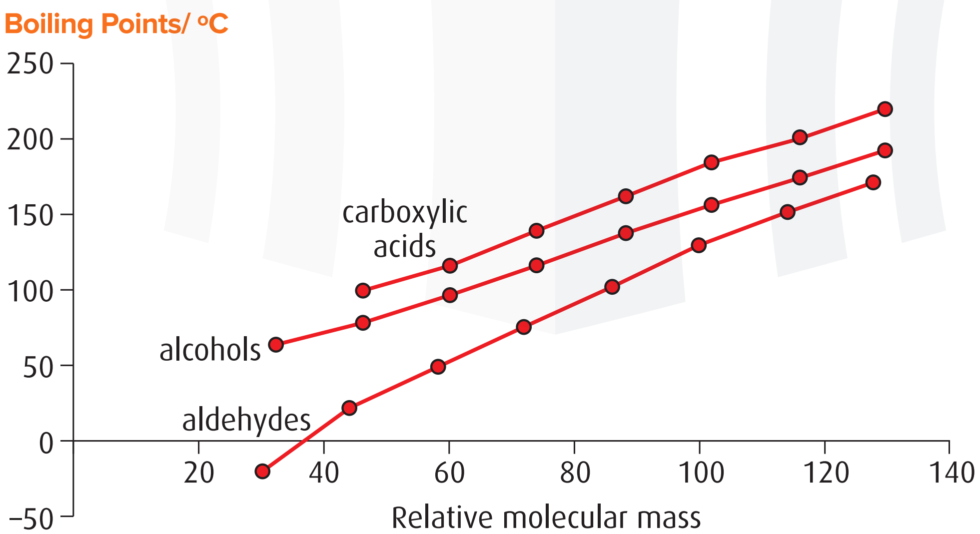
These compounds have virtually none of the reactions of carbonyl compounds.

The reactivity of carboxylic acids is dominated by the tendency of the O—H bond to ionise to give hydrogen ions, hence the incorporation of the word ‘acid’ in their name.

The extent of ionisation is small, however.

3

BOILING POINT



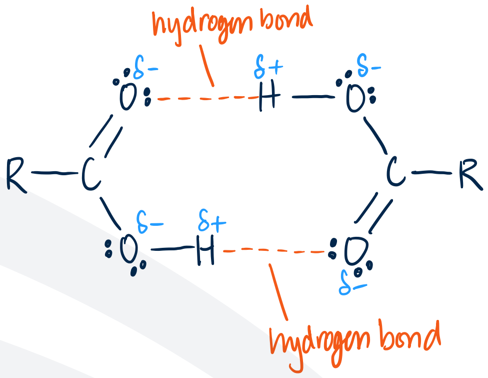
4

BOILING POINT

Carboxylic acids have hydrogen bonding between molecules and therefore have higher boiling points than aldehydes of similar relative molecular mass.

Carboxylic acids have hydrogen bonding between molecules and therefore have higher boiling points than aldehydes of similar relative molecular mass.

They also have higher boiling points than alcohols of the same relative molecular mass, as they have two O atoms per molecule and therefore have stronger hydrogen bonding than alcohols, which have only one O atom per molecule.

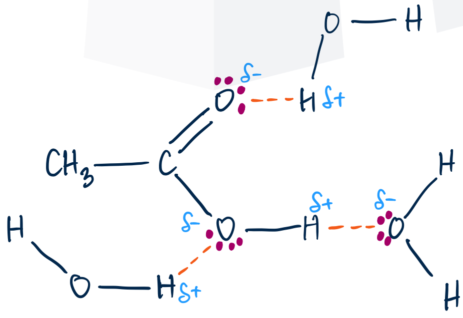


5

SOLUBILITY

Carboxylic acids with lower relative molecular mass are generally soluble in water, owing to the ability to hydrogen bond to water.

However, the solubility decreases as the length of the hydrocarbon chain (non-polar) increases, so octanoic acid is essentially insoluble in water.



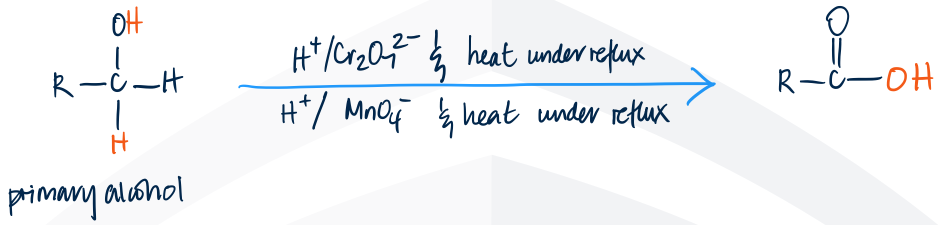
6

FROM OXIDATION OF PRIMARY ALCOHOLS

Reagent acidified potassium dichromate, $K_2Cr_2O_7$ (OR acidified potassium manganate(VII), $KMnO_4$)

Condition heat under reflux

Type oxidation



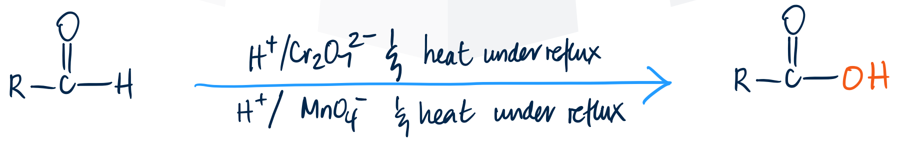
7

FROM OXIDATION OF ALDEHYDES

Reagent acidified potassium dichromate, $K_2Cr_2O_7$ (OR acidified potassium manganate(VII), $KMnO_4$) OR Fehling;s reagent OR Tollen's solution

Condition heat under reflux

Type oxidation



8

FROM HYDROLYSIS OF CYANIDES

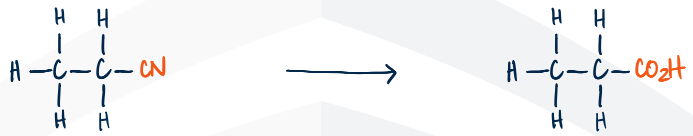
Hydrolysis of nitriles formed after the reaction of halogenoalkanes with CN^- produces carboxylic acids.

Reagent dilute HCl or NaOH (aq)

Condition heat under reflux

Type hydrolysis

$$CH_3CH_2CN + 2H_2O \longrightarrow CH_3CH_2CO_2H + NH_3$$



with acids $CH_3CH_2CN + 2H_2O + H^+ \longrightarrow CH_3CH_2CO_2H + NH_4^+$

with alkalis $CH_3CH_2CN + H_2O \quad OH^- \longrightarrow CH_3CH_2CO_2^- + NH_3$

9

ACID REACTIONS

Carboxylic acids are weak acids.

Equation $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$

Carboxylic acids neutralised alkalis to form salts

Equation $CH_3CO_2H + NaOH \longrightarrow CH_3CO_2^-Na^+ + H_2O$

Carboxylic acids neutralised carbonates to form salts, carbon dioxide and water

Equation $2\,CH_3CO_2H + Na_2CO_3 \longrightarrow 2CH_3CO_2^-Na^+ + CO_2 + H_2O$

Carboxylic acids react with most metals (e.g. Na) to form salt and hydrogen gas

Equation $CH_3CO_2H + Na \longrightarrow CH_3CO_2^-Na^+ + \frac{1}{2}H_2$

10

ESTERIFICATION

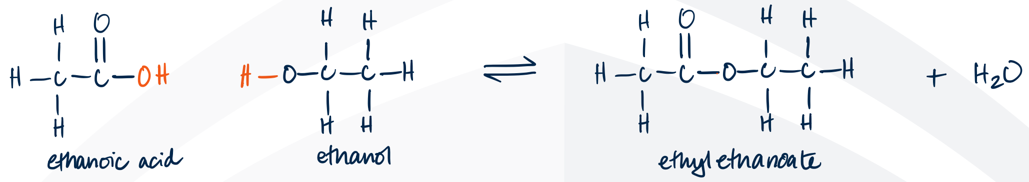
When an alcohol is heated with a carboxylic acid in the presence of a small amount of concentrated sulfuric acid as a catalyst, an ester is formed.

Reagent carboxylic acid and conc. sulfuric acid, H_2SO_4

Condition 60°C / heat

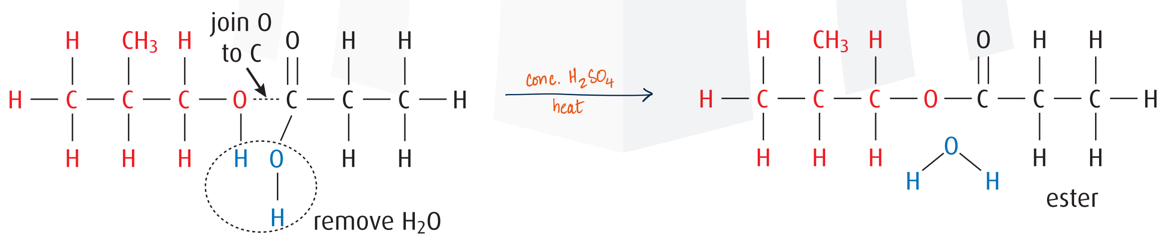
Type of reaction esterification / condensation / nucleophilic substitution

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

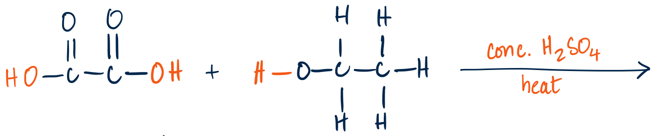


ESTERIFICATION

The alcohol and the carboxylic acid have been joined together and water has been eliminated (one H atom from the alcohol and –OH from the carboxylic acid molecule).

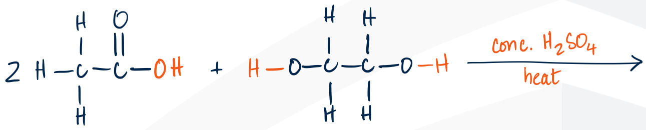


ESTERIFICATION



ethandioc acid   ethanol

$(CO_2H)_2$ + $2\ CH_3CH_2OH$



ethanoic acid   ethane-1,2-diol

13

HYDROLYSIS OF ESTERS

The most common type of reaction that esters undergo is nucleophilic substitution, illustrated by their hydrolysis.

The hydrolysis of an ester is a slow process, taking several hours of heating under reflux with dilute aqueous acids. Acid catalysed hydrolysis does not go completion.

Ester hydrolysis can also be carried out in alkaline solution. The reaction is quicker than in acid solution: OH^- is a stronger nucleophile than water. Additionally, it does not reach equilibrium, but goes to completion.

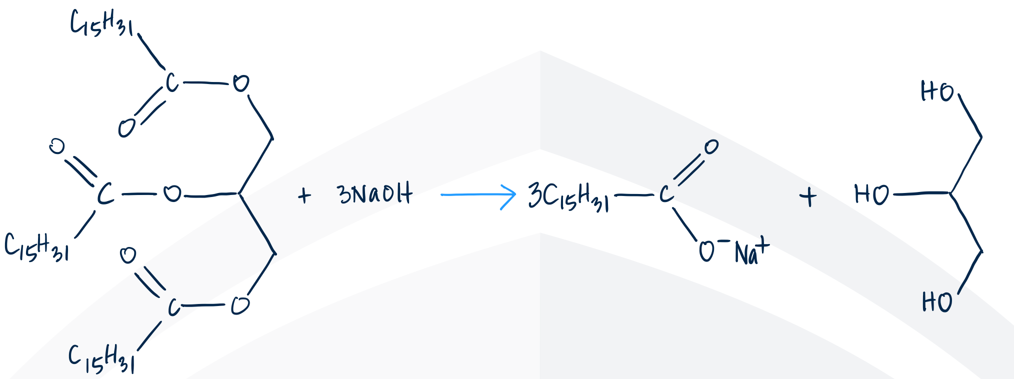
This is because the carboxylic acid produced reacts with an excess of the alkali to form the carboxylate salt.

14

HYDROLYSIS OF ESTERS

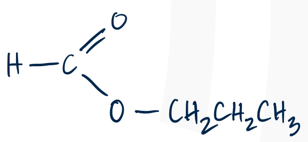
with HCl $CH_3CH_2CO_2CH_3 + H_2O \longrightarrow CH_3CH_2CO_2H + CH_3OH$

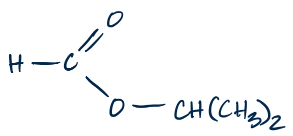
with NaOH $CH_3CH_2CO_2CH_3 + H_2O \longrightarrow CH_3CH_2CO_2^- + CH_3OH$



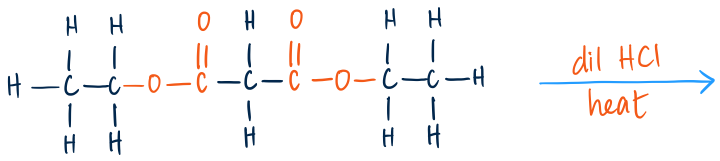
HYDROLYSIS OF ESTERS

Hydrolyse the following esters using dil HCl.





HYDROLYSIS OF ESTERS

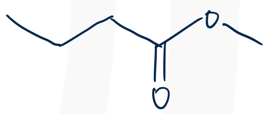


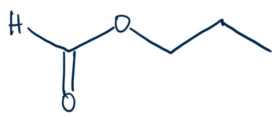
$CH_3CH_2OCOCH_2CO_2CH_2CH_3$

17

HYDROLYSIS OF ESTERS

Hydrolyse the following esters using NaOH (aq).

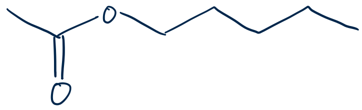


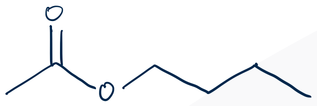


18

HYDROLYSIS OF ESTERS

Hydrolyse the following esters using dil HCl.





19

ESTERS

Esters often have a sweet, fruity smell and are used as artificial flavours and odours. Esters are good organic solvents.

Fats and oils are esters of propane-1,2,3-triol (glycerol) and long-chain carboxylic acids (fatty acids).

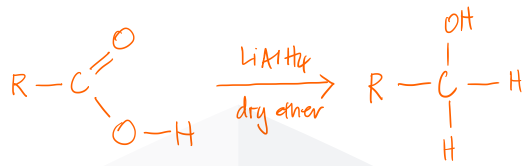
Despite containing two oxygen atoms, they do not form strong hydrogen bonds with water molecules. Neither do they form hydrogen bonds with other ester molecules (because they do not contain δ+ hydrogen atoms).

Their major intermolecular bonding is van der Waals. Their boiling points are therefore a few degrees higher than those of the alkanes of similar molecular mass lower than those of corresponding carboxylic acids.

20

REDUCTION OF THE –CO_2H GROUP

Carboxylic acids can be reduced to alcohols by reacting with lithium tetrahydridoaluminate(III) (lithium aluminium hydride), $LiAlH_4$, in dry ether.



The reaction requires the powerful reducing agent $LiAlH_4$: neither $NaBH_4$ nor H_2 + Ni are strong enough to reduce carboxylic acids.

REDUCTION OF CARBOXYLIC ACIDS

Carboxylic acids can be reduced to their corresponding primary alcohol by using the reducing agent lithium tetrahydridoaluminate, $LiAlH_4$, in dry ether at room temperature. Dry ether is used because $LiAlH_4$ reacts violently with water.

In the simplified reduction equation, the symbol [H] can be used to represent the hydrogen atoms from the reducing agent (remember that in organic chemistry, reduction can be thought of as the addition of hydrogen atoms). So for ethanoic acid being reduced to ethanol, we can show the reaction as:

$$CH_3CO_2H + 4[H] \longrightarrow CH_3CH_2OH + H_2O$$

CARBOXYLIC ACIDS WS 1

SECTION A

1 An ester with an odour of banana has the following formula.

$$CH_3CO_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

Which pair of reactants, under suitable conditions, will produce this ester?

A $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CO_2H + CH_3OH$

B $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCO_2H + CH_3CH_2OH$

C $CH_3CO_2H + CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

D $CH_3CO_2H + CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2OH$

2 An ester of structural formula $CH_3CO_2CH_3$ is heated with an aqueous solution of sodium hydroxide.

What are the two organic products of this reaction?

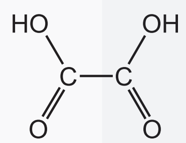
A ethanoic acid and methanol

B methanoic acid and ethanol

C sodium ethanoate and methanol

D sodium methanoate and ethanol

3 The diagram shows the structure of ethanedioic acid.



Ethanedioic acid reacts with ethanol in the presence of a few drops of concentrated sulfuric acid to form a diester. The molecular formula of the diester is $C_6H_{10}O_4$.

What is the structural formula of the diester?

A $CH_3CH_2CO_2CO_2CH_2CH_3$

B $CH_3CH_2OCOCO_2CH_2CH_3$

C $CH_3CH_2O_2CO_2CCH_2CH_3$

D $CH_3CO_2CH_2CH_2OCOCH_3$

4 Diesters can be made from diacids such as propane-1,3-dioic acid, $HO_2CCH_2CO_2H$.

Which combination of reactants would form the diester $CH_3CH_2OCOCH_2CH_2CO_2CH_2CH_3$?

A butane-1,4-dioic acid and ethanol

B ethanedioic acid and propan-1-ol

C ethanedioic acid, ethanol and butan-1-ol

D propane-1,3-dioic acid, ethanol and propan-1-ol

5 The compound cetyl palmitate, $C_{15}H_{31}CO_2C_{16}H_{33}$, is a waxy solid.

When 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 $C_{16}H_{33}OH$

6 Lactic acid, $CH_3CH(OH)CO_2H$, causes pain when it builds up in muscles.

Which reagent reacts with **both** of the –OH groups in lactic acid?

A acidified potassium dichromate(VI)

B ethanol

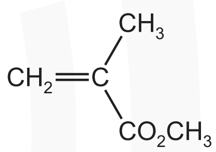
C sodium

D sodium hydroxide

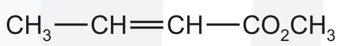
7 Methyl methylpropenoate is the monomer used to make *Perspex*.

Which diagram correctly shows methyl methylpropenoate?

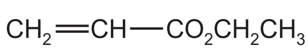
A



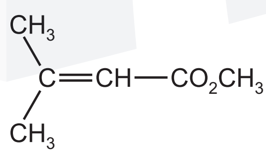
B



C



D

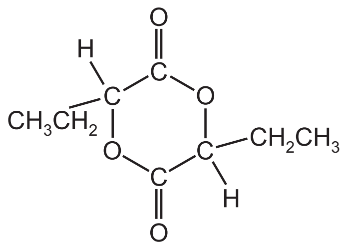


8 The ester $CH_3CH_2CH_2CO_2CH_3$ is responsible for the aroma of apples.

When this ester is hydrolysed by acid in the stomach, what is the empirical formula of the organic acid produced?

A CH_2O **B** CH_4O **C** C_2H_4O **D** $C_3H_6O_2$

9 Compound **X** can be made from 2-hydroxybutanoic acid.



compound **X**

What should be heated with 2-hydroxybutanoic acid in order to make compound **X**?

A acidified potassium dichromate(VI)

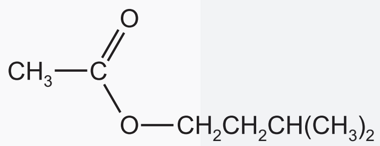
B aluminium oxide

C concentrated sulfuric acid

D dilute sodium hydroxide

10 Pheromones are used by insects and other animals as a means of communication.

The pheromone in a bee sting is 3-methylbutyl ethanoate.



3-methylbutyl ethanoate

What are the organic products when 3-methylbutyl ethanoate is heated under reflux with aqueous sodium hydroxide?

A CH_3CO_2H and $(CH_3)_2CHCH_2CH_2OH$

B CH_3CO_2H and $(CH_3)_2CHCH_2CH_2O^-Na^+$

C $CH_3CO_2^-Na^+$ and $(CH_3)_2CHCH_2CH_2OH$

D $CH_3CO_2^-Na^+$ and $(CH_3)_2CHCH_2CH_2O^-Na^+$

11 Citric acid is found in lemon juice.

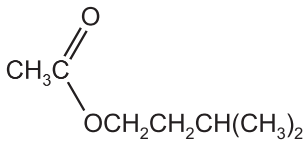
$$HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$$

citric acid

What is the volume of 0.4 mol dm^{-3} sodium hydroxide solution required to neutralise a solution containing 0.005 mol of citric acid?

A 12.5 cm^3 **B** 25.0 cm^3 **C** 37.5 cm^3 **D** 50.0 cm^3

12 An ester P with a fruity odour has the following structural formula.



Which compounds are produced when P is hydrolysed using hydrochloric acid?

A CH_3COCl and $(CH_3)_2CHCH_2CH_2OH$

B CH_3CHO and $(CH_3)_2CHCH_2CH_2OH$

C CH_3CO_2H and $(CH_3)_2CHCH_2CH_2CHO$

D CH_3CO_2H and $(CH_3)_2CHCH_2CH_2OH$

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

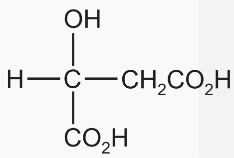
A $CH_3CO_2CH(CH_3)_2$

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 Malic acid occurs in apples.



malic acid

Under suitable conditions, which substance will react with only one of the –OH groups in the malic acid molecule?

A $Cr_2O_7^{2-}$ / H^+(aq)

B Na(s)

C NaOH(aq)

D PCl_5(s)

15 Compound **X**, $C_5H_{12}O$, is oxidised by acidified sodium dichromate(VI) to compound **Y**.

Compound **Y** reacts with butan-2-ol in the presence of a little concentrated sulfuric acid to give liquid **Z**.

What could be the formula of **Z**?

A $CH_3(CH_2)_3CO_2CH(CH_3)CH_2CH_3$

B $CH_3(CH_2)_3CO_2(CH_2)_3CH_3$

C $CH_3(CH_2)_2CO_2CH(CH_3)CH_2CH_3$

D $(CH_3)_2CHCH_2CO_2C(CH_3)_3$

16 Which ester is formed when the alcohol CH_3CH_2OH is reacted with $CH_3CH_2CH_2CO_2H$?

A butyl ethanoate

B ethyl butanoate

C ethyl propanoate

D propyl ethanoate

17 Methanoic acid, HCO_2H, has acidic properties similar to those of other carboxylic acids. In addition it can be oxidised by the same oxidising agents that are capable of oxidising aldehydes.

Which pair consists of two compounds that will give the same observations with Fehling's reagent?

A HCO_2H and CH_3CO_2H

B HCO_2H and $CH_3CO_2CH_3$

C HCO_2H and $CH_3CH_2COCH_3$

D HCO_2H and CH_3CH_2CHO

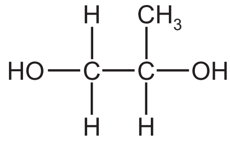
18 But-2-ene-1,4-diol is converted in two steps through an intermediate **X** into oxobutanedioic acid.

$$\underset{\text{but-2-ene-1,4-diol}}{HOCH_2CH{=}CHCH_2OH} \xrightarrow{\text{step 1}} \mathbf{X} \xrightarrow[\text{hot, acidified } KMnO_4]{\text{step 2}} \underset{\text{oxobutanedioic acid}}{HO_2CCOCH_2CO_2H}$$

What could be the reagent for step 1 and what is the intermediate **X**?

	reagent for step 1	**X**
A	cold, acidified $KMnO_4$	$HOCH_2CH_2CH(OH)CH_2OH$
B	hot, acidified $K_2Cr_2O_7$	$HO_2CCH{=}CHCO_2H$
C	steam and concentrated H_2SO_4	$HOCH_2CH(OH)CH_2CH_2OH$
D	warm, acidified $K_2Cr_2O_7$	$OHCCH(OH)CH_2CHO$

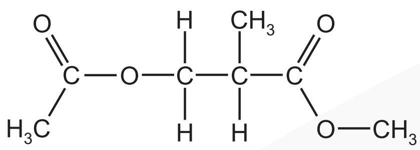
19 The fragrance compounds of perfumes are often dissolved in solvent **Y**, which has a molecular formula $C_7H_{12}O_4$. It is made by reacting propane-1,2-diol with ethanoic acid in the presence of an acid catalyst.



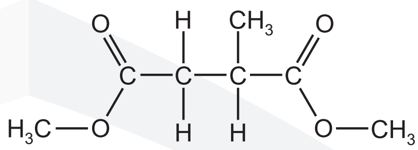
propane-1,2-diol

What is the structure of solvent **Y**?

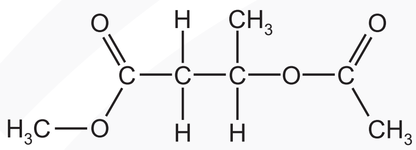
A



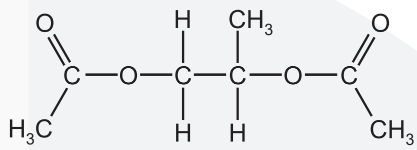
B



C



D



20 Which mixture could be used to produce propyl methanoate?

A $CH_3CH_2CO_2H$ and CH_3OH

B $CH_3CH_2CH_2CH_2OH$ and HCO_2H

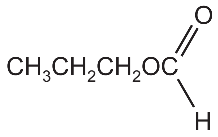
C $CH_3CH_2CH_2OH$ and HCO_2H

D $CH_3CH_2CH_2CO_2H$ and CH_3OH

21 Which row of the table is correct?

	increasing number of carbon atoms →			
A	ethyl methanoate	methyl propanoate	pentyl pentanoate	propyl butanoate
B	ethyl methanoate	methyl propanoate	propyl butanoate	pentyl pentanoate
C	methyl propanoate	propyl butanoate	ethyl methanoate	pentyl pentanoate
D	propyl butanoate	ethyl methanoate	pentyl pentanoate	methyl propanoate

22 The structural formula of compound **X** is shown below.



compound **X**

What is the name of compound **X** and how does its boiling point compare with that of butanoic acid?

	name of **X**	boiling point of **X**
A	methyl propanoate	higher than butanoic acid
B	methyl propanoate	lower than butanoic acid
C	propyl methanoate	higher than butanoic acid
D	propyl methanoate	lower than butanoic acid

23 How many of the following compounds produce a carboxylic acid on heating under reflux with an excess of hot acidified $K_2Cr_2O_7$?

CH_3CH_2CHO

CH_3COCH_3

$CH_3CH_2CH_2OH$

$CH_3CH(OH)CH_3$

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

24 How many isomeric esters, including structural isomers and stereoisomers, can be made with the molecular formula $C_5H_{10}O_2$, if methanoic acid is one of the two reactants used?

A 2 **B** 3 **C** 4 **D** 5

25 Compound X, $C_4H_8O_2$, has an unbranched carbon chain. An aqueous solution of X has an approximate pH of 3.

Compound Y, C_3H_8O, is a secondary alcohol.

X and Y are reacted together in the presence of a little concentrated sulfuric acid to form Z as the major organic product.

What is the structural formula of Z?

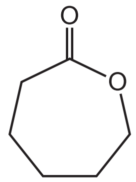
A $(CH_3)_2CHCO_2CH_2CH_2CH_3$

B $CH_3(CH_2)_2CO_2CH(CH_3)_2$

C $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$

D $(CH_3)_2CHCO_2CH(CH_3)_2$

26 Caprolactone is a cyclic ester. It is being used increasingly for the manufacture of specialist polymers.



caprolactone

From which compound could caprolactone be made by a single reaction?

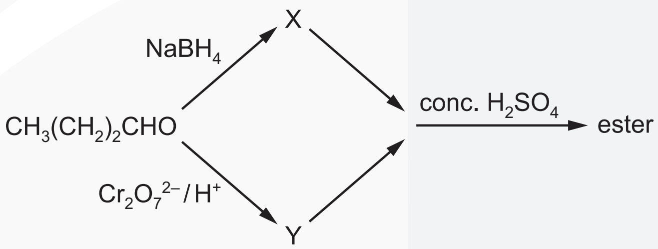
A $OHCCH_2CH_2CH_2CH_2CHO$

B $HOCH_2CH_2CH_2CH_2CH_2CH_2OH$

C $HOCH_2CH_2CH_2CH_2CH_2CO_2H$

D $HO_2CCH_2CH_2CH_2CH_2CO_2H$

27 An ester with an aroma of pineapples can be synthesised in the laboratory from butanal using this reaction scheme.



What is the structural formula of the **ester**?

A $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$

B $CH_3(CH_2)_2CO_2(CH_2)_3CH_3$

C $CH_3(CH_2)_3CO_2(CH_2)_2CH_3$

D $CH_3(CH_2)_3CO_2(CH_2)_3CH_3$

28 The ester, $CH_3CH_2CO_2CH_3$, is hydrolysed by boiling with aqueous sodium hydroxide.

Which compound is one of the products?

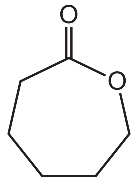
A ethanol

B propan-1-ol

C sodium methanoate

D sodium propanoate

29 Caprolactone is a cyclic ester. It is being used increasingly for the manufacture of specialist polymers.



caprolactone

From which compound could caprolactone be made by a single reaction?

A $OHCCH_2CH_2CH_2CH_2CHO$

B $HOCH_2CH_2CH_2CH_2CH_2CH_2OH$

C $HOCH_2CH_2CH_2CH_2CH_2CO_2H$

D $HO_2CCH_2CH_2CH_2CH_2CO_2H$

30 The ester $CH_3CH_2CH_2CO_2CH_2CH(CH_3)_2$ was hydrolysed under acidic conditions.

What are the organic products of this hydrolysis?

A butanoic acid and 2-methylpropan-1-ol

B butanoic acid and 2-methylpropan-2-ol

C butan-1-ol and 2-methylpropanoic acid

D propanoic acid and 2-methylpropan-1-ol

31 The ester, $CH_3CH_2CO_2CH_3$, is hydrolysed by boiling with aqueous sodium hydroxide.

Which compound is one of the products?

A ethanol

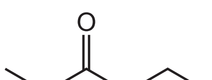
B propan-1-ol

C sodium methanoate

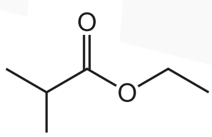
D sodium propanoate

32 Which formula represents an ester that will form propanoic acid on hydrolysis with dilute sulfuric acid?

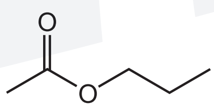
A



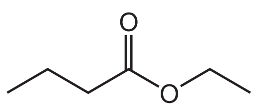
B



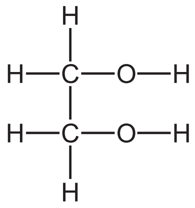
C



D



33 Ethane-1,2-diol has the following structure.



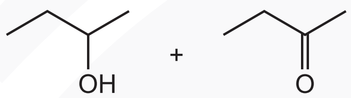
Without breaking the C–C bond, there are five possible oxidation products.

What is the **total** number of aldehyde groups and carboxylic acid groups in these five products?

	–CHO	–COOH
A	3	3
B	3	4
C	4	3
D	4	4

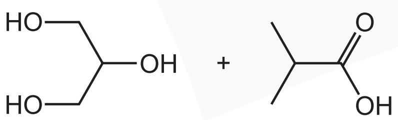
34 Which two compounds can react together to produce an ester?

A



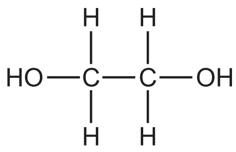
B

C



D

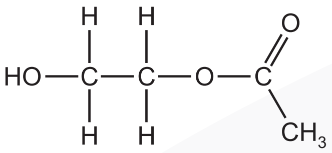
35 A solvent, **X**, used in printing inks has a molecular formula $C_6H_{10}O_4$. It may be made by reacting ethane-1,2-diol with ethanoic acid in the presence of an acid catalyst.



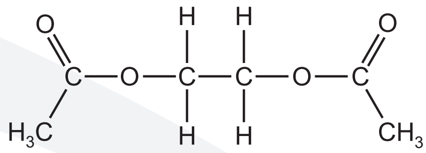
ethane-1,2-diol

What is the structure of solvent **X**?

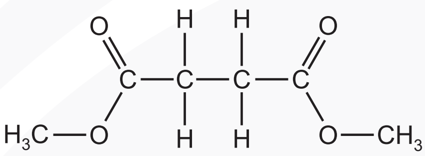
A



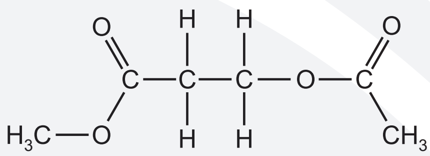
B



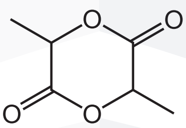
C



D



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



lactide

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

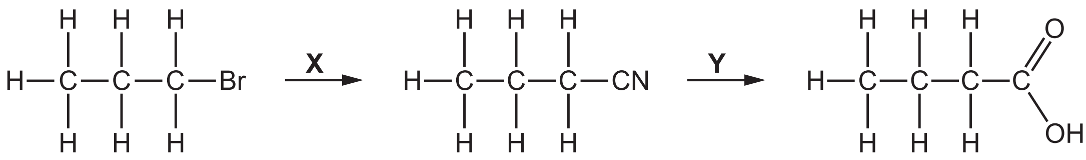
A hydroxyethanoic acid

B 2-hydroxybutanoic acid

C 2-hydroxypropanoic acid

D 3-hydroxypropanoic acid

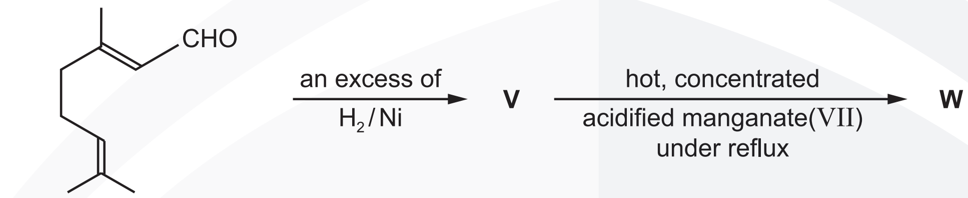
37 **X** and **Y** are the reagents required to convert 1-bromopropane into butanoic acid.



What are the correct identities of **X** and **Y**?

	X	Y
A	NH_3	$HCl(aq)$
B	KCN in C_2H_5OH	NaOH(aq)
C	KCN in C_2H_5OH	$HCl(aq)$
D	HCN	NaOH(aq)

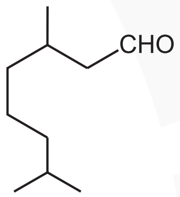
38 Citral is found in lemongrass oil. It can react to give compound **W**.



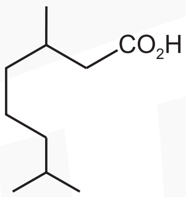
citral

What could compound **W** be?

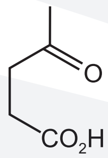
A



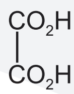
B



C



D



39 Carboxylic acids may be prepared by several different methods.

In which reaction would propanoic acid be formed?

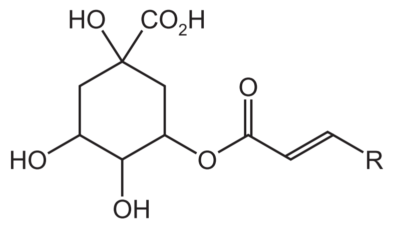
A adding ammonium propanoate to dilute sulfuric acid

B heating ethyl propanoate with aqueous sodium hydroxide

C heating propan-2-ol with acidified potassium manganate(VII) under reflux

D heating propyl ethanoate with dilute sulfuric acid

40 Chlorogenic acid is found in green coffee beans and is used in treatments for weight loss.

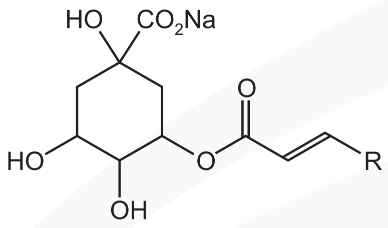


R = $C_6H_5O_2$ and takes no part in the reaction with sodium carbonate.

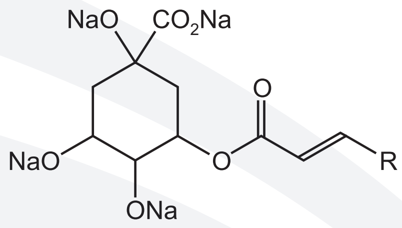
chlorogenic acid

What is produced in good yield when chlorogenic acid is treated with an excess of sodium carbonate solution at room temperature?

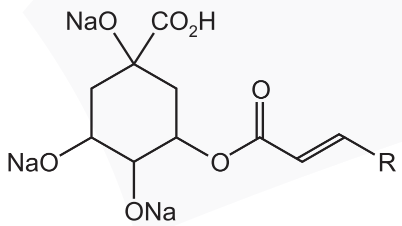
A



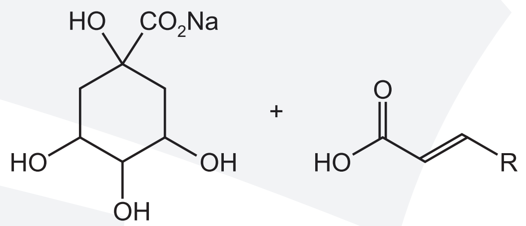
B



C



D



41 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

42 Butanoic acid can be produced from 1-bromopropane using reagents X and Y as shown.

$$\text{1-bromopropane} \xrightarrow{\text{reagent X}} \text{compound Q} \xrightarrow{\text{reagent Y}} \text{butanoic acid}$$

What could be reagents X and Y?

	X	Y
A	KCN in ethanol	HCl(aq)
B	KCN in ethanol	NaOH(aq)
C	NH_3 in ethanol	HCl(aq)
D	NaOH(aq)	$H^+ / Cr_2O_7^{2-}$(aq)

43 Carboxylic acids may be prepared by several different methods.

In which reaction would propanoic acid be formed?

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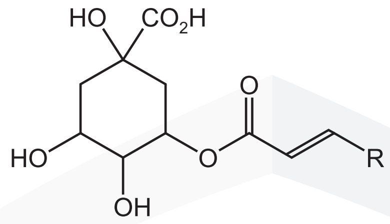

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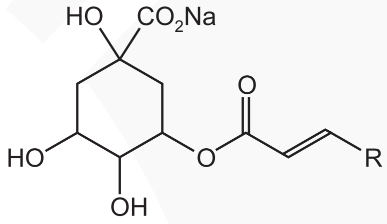
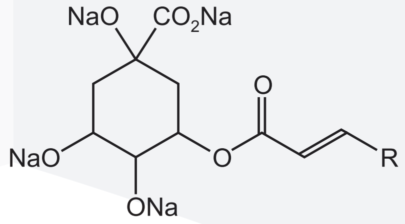
chlorogenic acid

What is produced in good yield when chlorogenic acid is treated with an excess of sodium carbonate solution at room temperature?

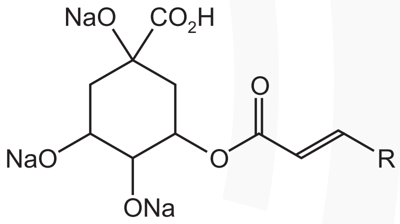
A



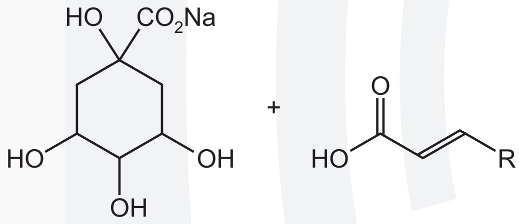
B



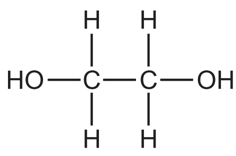
C



D

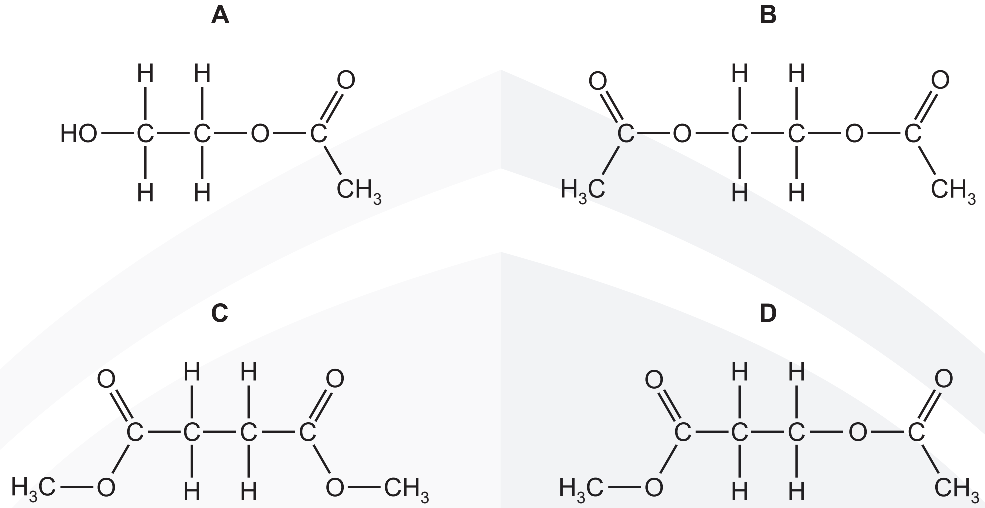


45 A solvent, **X**, used in printing inks has a molecular formula $C_6H_{10}O_4$. It may be made by reacting ethane-1,2-diol with ethanoic acid in the presence of an acid catalyst.



ethane-1,2-diol

What is the structure of solvent **X**?



46 Ethane-1,2-diol, $HOCH_2CH_2OH$, reacts with an excess of ethanoic acid, CH_3CO_2H, in the presence of an acid catalyst. A compound is formed with the molecular formula $C_6H_{10}O_4$.

What is the structure of this compound?

A $CH_3OCOCH_2CH_2CO_2CH_3$

B $CH_3CO_2CH_2CH_2CO_2CH_3$

C $CH_3CO_2CH_2CH_2OCOCH_3$

D $HOCH_2CH_2COCH_2OCOCH_3$

47 Which reaction would **not** give ethanoic acid?

A heating ethanenitrile under reflux with dilute sodium hydroxide

B heating ethanenitrile under reflux with dilute sulfuric acid

C heating ethanal under reflux with acidified sodium dichromate(VI)

D heating ethanol under reflux with acidified sodium dichromate(VI)

48 A carboxylic acid, P, has no possible 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

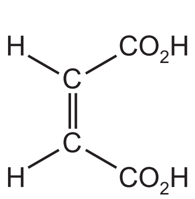
B ethyl butanoate

C pentyl ethanoate

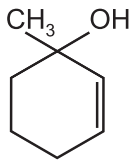
D propyl pentanoate

49 Which compound is chiral and reacts with Na_2CO_3 to give CO_2?

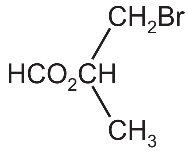
A



B



C



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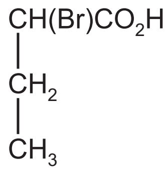


50 At room temperature, propanoic acid was reacted to produce sodium propanoate. No gas was produced during the reaction.

What could the propanoic acid have reacted with?

A $NaHCO_3(aq)$ **B** $NaOH(aq)$ **C** $Na_2CO_3(aq)$ **D** $Na_2SO_4(aq)$

[N'17 P13 Q28]

51 A sample of the ester $CH_3CH_2CH_2CO_2CH_2CH_3$ is hydrolysed. The product mixture is then treated with hot, acidified $KMnO_4$.

What are the final carbon-containing products?

A $CH_3CH_2CO_2H$ only

B $CH_3CO_2H + CH_3CH_2CO_2H$

C $CH_3CO_2H + CH_3CH_2CH_2CO_2H$

D $CH_3CH_2OH + CH_3CH_2CH_2CO_2H$

[N'17 P13 Q30]

52 Ethanedioic acid has the formula HO_2CCO_2H.

What is the formula of aluminium ethanedioate?

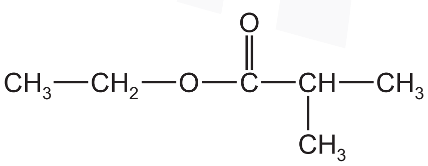
A AlC_2O_4 **B** $Al(C_2O_4)_3$ **C** $Al_2C_2O_4$ **D** $Al_2(C_2O_4)_3$

[M'18 P12 Q28]

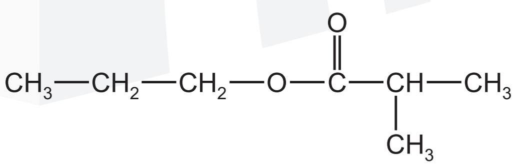
53 Ethyl propanoate is refluxed with aqueous sodium hydroxide. The alcohol produced is then reacted with methyl propanoic acid to make a second ester.

What is the structural formula of this second ester?

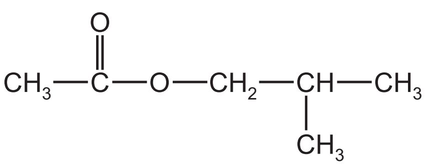
A



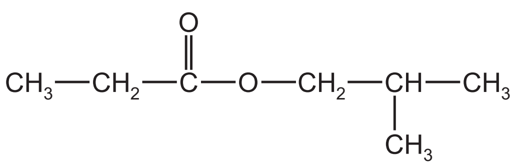
B



C



D



[S'18 P11 Q27]

54 Four reactions of propanoic acid to form salts and other products are shown.

Which reaction does **not** show the formulae of **all** the correct products?

$CH_3CH_2CO_2H(aq)$ propanoic acid

A $CH_3CH_2CO_2H(aq) \xrightarrow{KOH} CH_3CH_2CO_2^-K^+(aq) + H_2O(l)$

B $CH_3CH_2CO_2H(aq) \xrightarrow{Mg(s)} (CH_3CH_2CO_2^-)_2Mg^{2+}(aq) + H_2(g)$

C $CH_3CH_2CO_2H(aq) \xrightarrow{Na_2CO_3} CH_3CH_2CO_2^-Na^+(aq) + CO_2(g)$

D $CH_3CH_2CO_2H(aq) \xrightarrow{Ca(OH)_2} (CH_3CH_2CO_2^-)_2Ca^{2+}(aq) + H_2O(l)$

55 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

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which reagents, when used in an excess, can be used to make sodium lactate, $CH_3CH(OH)CO_2Na$, from lactic acid, $CH_3CH(OH)CO_2H$?

1 Na

2 $NaHCO_3$

3 NaOH

2 The molecule responsible for the pineapple flavour used in sweets is $CH_3CH_2CH_2CO_2CH_2CH_3$.

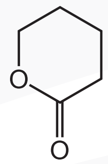
Which statements about this molecule are correct?

1 The name of this compound is ethyl butanoate.

2 This compound is a structural isomer of hexanoic acid.

3 When this compound is heated with aqueous sodium hydroxide, the products are butan-1-ol and sodium ethanoate.

3 5-hydroxypentanoic acid is readily converted into the cyclic compound L.



L

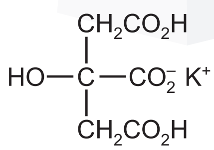
Which statements about this reaction are correct?

1 Acidified sodium dichromate(VI) is used as a reagent.

2 A water molecule is produced in the reaction.

3 The reaction is catalysed by concentrated H_2SO_4.

4 Monopotassium citrate is used as an emulsifying agent in powdered milk and in powdered soups. It may be represented by the formula shown.



monopotassium citrate

Which statements about monopotassium citrate are correct?

1 It does **not** have a chiral carbon atom.

2 It can act as a dibasic acid.

3 It reacts with $NaHCO_3$ to give CO_2.

5 An oxidising agent that can oxidise ethanal to ethanoic acid, or to ethanoate ions, will also oxidise methanoic acid, HCO_2H, to carbon dioxide and water.

Which reagents, on heating, will react differently with HCO_2H and CH_3CO_2H?

1 Na_2CO_3(aq)

2 Fehling's reagent

3 dilute acidified $KMnO_4$

6 Compound **X** has the molecular formula $C_3H_6O_3$.

Heating **X** under reflux with acidified $K_2Cr_2O_7$ forms HO_2CCOCO_2H.

Reacting **X** with $NaBH_4$ forms $HOCH_2CH(OH)CH_2OH$.

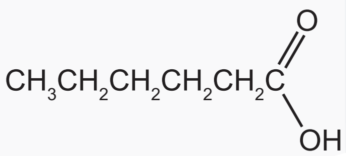
What is a possible structural formula for **X**?

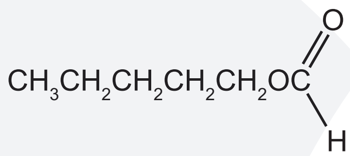
1 $HOCH_2CH_2CO_2H$

2 $HOCH_2CH(OH)CHO$

3 $HOCH_2COCH_2OH$

7 The structural formulae of two compounds are shown below.





Which statements about these compounds are correct?

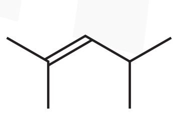
1 The two compounds are structural isomers of each other.

2 The empirical formula of both compounds is C_3H_6O.

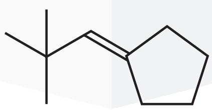
3 Both compounds are carboxylic acids.

8 Which compounds would produce a carboxylic acid and a ketone when treated with hot, concentrated, acidified $KMnO_4$?

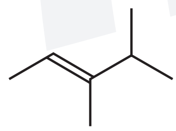
1



2



3



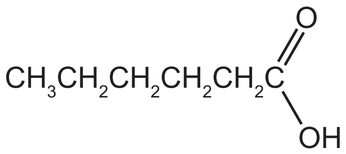
9 Which statements about the formation of a carboxylic acid are correct?

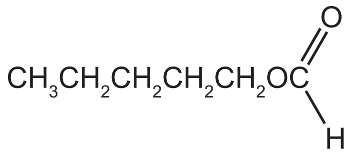
1 A carboxylic acid can be produced by hydrolysis of a nitrile.

2 A carboxylic acid can be produced by oxidation of a primary alcohol.

3 A carboxylic acid can be produced by reduction of an aldehyde.

10 The structural formulae of two compounds are shown below.





Which statements about these compounds are correct?

1 The two compounds are structural isomers of each other.

2 The empirical formula of both compounds is C_3H_6O.

3 Both compounds are carboxylic acids.

11 Which statements about ethanol and ethanoic acid are correct?

1 Both react with a suitable reagent to form an ester.

2 Both react with sodium.

3 Both are soluble in water.

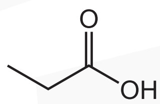
12 Which compounds, on heating with ethanolic NaOH, produce more than one product with molecular formula C_4H_8?

1 2-bromobutane

2 2-bromo-2-methylpropane

3 1-bromo-2-methylpropane

13 Propanoic acid occurs naturally as a result of the bacterial fermentation of milk and is partly responsible for the flavour of Swiss cheese.



propanoic acid

Which starting materials can be used to produce propanoic acid?

1 $CH_3CH_2CH_2OH$

2 CH_3CH_2CHO

3 CH_3CH_2CN

14 Carboxylic acids can be converted into their salts by a number of reactions at room temperature.

Which reactions would produce sodium butanoate and a gas?

1 sodium carbonate + butanoic acid

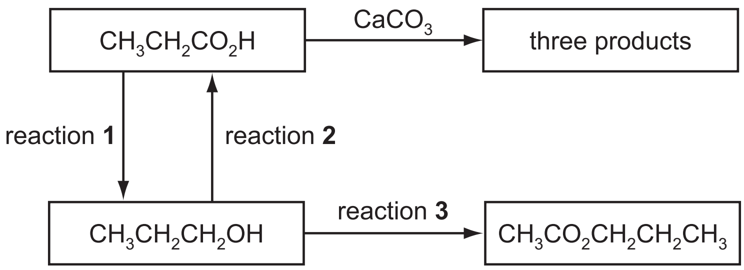
2 sodium + butanoic acid

3 sodium hydroxide + butanoic acid

[N'17 12 Q40]

CARBOXYLIC ACIDS WS 2

1 A series of reactions based on propanoic acid is shown.



(a) Write an equation for reaction **1**, using [H] to represent the reducing agent.

.... [2]

(b) **(i)** What type of reaction is reaction **2**?

.... [1]

(ii) Suggest a suitable reagent and conditions for reaction **2.**

.... [2]

(c) Write an equation for the reaction of propanoic acid with calcium carbonate, $CaCO_3$.

.... [2]

(d) **(i)** Suggest a suitable reagent and conditions for reaction **3.**

....

.... [2]

(ii) Identify the **other** product of reaction **3.**

.... [1]

[W'14 P21 Q4]

2 This question is about molecules with molecular formula $C_4H_8O_2$.

(a) Give the structural formulae of the pair of **chain** isomers with the formula $C_4H_8O_2$ that are carboxylic acids.

[2]

(b) **(i)** Give the structural formulae of a pair of **positional** isomers with the formula $C_4H_8O_2$ that are esters.

[2]

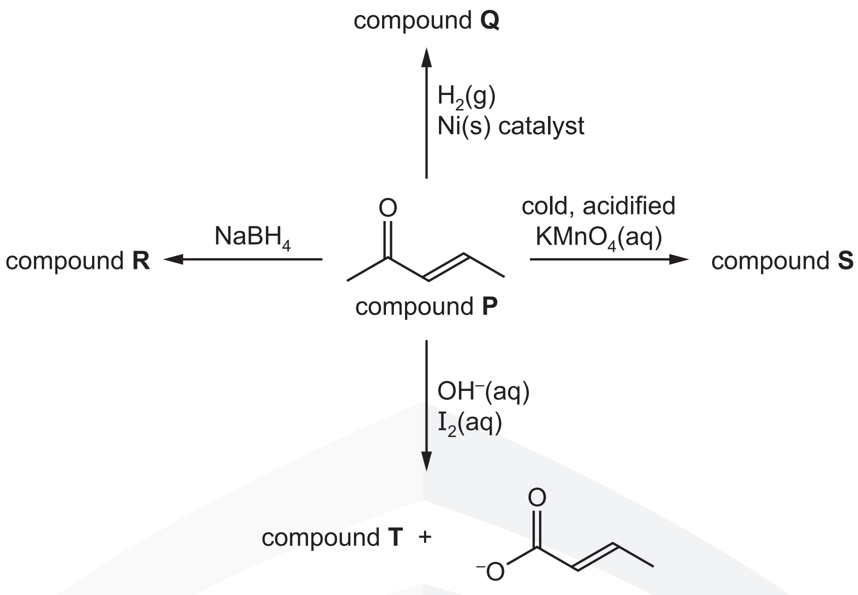
(ii) Give the reagents and conditions needed to produce one of your esters in **(i)**.

....

.... [2]

[S'16 P22 Q4]

3 Some reactions of compound **P**, C_5H_8O, are shown.



(a) (i) Give the structures for organic compounds **Q**, **R**, **S** and **T**.

Q

R

S

T

[M'16 P22 Q5]

4 This question is about molecules with molecular formula $C_4H_8O_2$.

(a) Give the structural formulae of the pair of **chain** isomers with the formula $C_4H_8O_2$ that are carboxylic acids.

[2]

(b) (i) Give the structural formulae of a pair of **positional** isomers with the formula $C_4H_8O_2$ that are esters.

[2]

(ii) Give the reagents and conditions needed to produce one of your esters in **(i)**.

....

.... [2]

[S'16 P22 Q4]

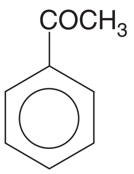
CARBOXYLIC ACIDS WS 3

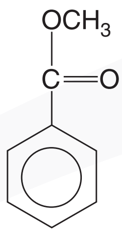
SECTION A

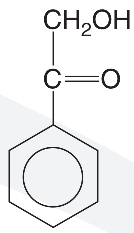
1 A compound **R** has all of the following properties:

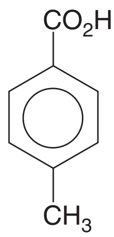
it is neutral;
it gives an orange precipitate with 2,4-dinitrophenylhydrazine;
it evolves hydrogen chloride when treated with PCl_5 in the cold.

What could **R** be?

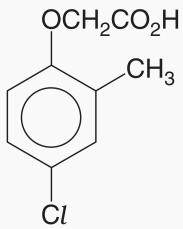
A 

B 

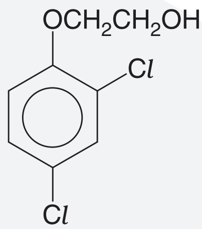
C 

D 

2 MCPA and 2,4-D are two widely-used selective weedkillers.



MCPA



2,4-D

Which reagent will distinguish MCPA from 2,4-D?

A acidified $AgNO_3(aq)$

B Fehling's solution

C Na

D $Na_2CO_3(aq)$

3 The acarid mite releases *lardolure* to attract other mites to a host: this chemical can be destroyed by hydrolysis with acid.

$$\mathrm{CH_3CH_2CH_2[CH(CH_3)CH_2]_3CH(CH_3)O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H}$$

A simplified formula for *lardolure* may be written as $\mathrm{RCH(CH_3)O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H}$.

What are the products of its hydrolysis?

A $RCH(CH_3)CO_2H + CH_3OH$

B $RCH(CH_3)CO_2H + HCO_2H$

C $RCH(CH_3)OH + CO_2$

D $RCH(CH_3)OH + HCO_2H$

4 An ester with an odour of banana has the following formula.

$$CH_3CO_2CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$$

In which of the following do the substances react together, under suitable conditions, to produce this ester?

A $CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CO_2H + CH_3OH$

B $CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCO_2H + CH_3CH_2OH$

C $CH_3CO_2H + CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2OH$

D $CH_3CO_2H + CH_3\underset{\substack{|\\ CH_3}}{C}H_2CHCH_2OH$

5 In its reaction with sodium, 1 mol of a compound **X** gives 1 mol of H_2(g).

Which compound might **X** be?

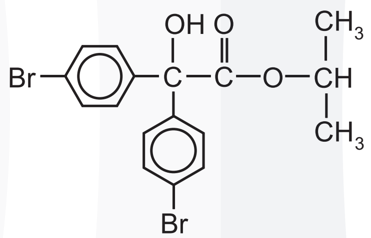
A $CH_3CH_2CH_2CH_2OH$

B $(CH_3)_3COH$

C $CH_3CH_2CH_2CO_2H$

D $CH_3CH(OH)CO_2H$

6 *Acarol* is sold as an insecticide for use on fruit and vegetables.



Acarol

The final stage of its manufacture is an esterification.

Which alcohol is used to form the ester?

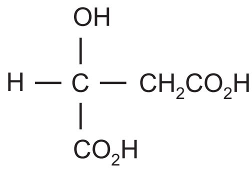
A di(4-bromophenyl)methanol

B methanol

C propan-1-ol

D propan-2-ol

7 Malic acid occurs in apples.



malic acid

Which substance will react with all three –OH groups present in the malic acid molecule?

A ethanol in the presence of concentrated sulphuric acid

B potassium hydroxide

C sodium

D sodium carbonate

8 Which compound has a boiling point which is influenced by hydrogen bonding?

A CH_3CHO

B CH_3OCH_3

C HCO_2H

D HCO_2CH_3

9 Which compound is a product of the hydrolysis of $CH_3CO_2C_3H_7$ by boiling aqueous sodium hydroxide?

A CH_3OH **B** C_3H_7OH **C** $C_3H_7CO_2H$ **D** $C_3H_7CO_2^-Na^+$

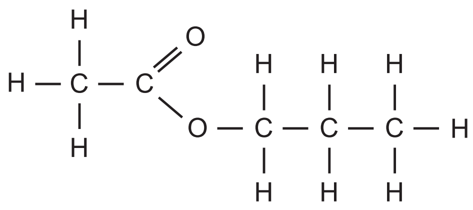
10 Compounds *X*, *Y* and *Z* all react with PCl_5 to release hydrogen chloride, but only one of them reacts with 2,4-dinitrophenylhydrazine reagent.

Which one of the following combinations could be *X*, *Y* and *Z*?

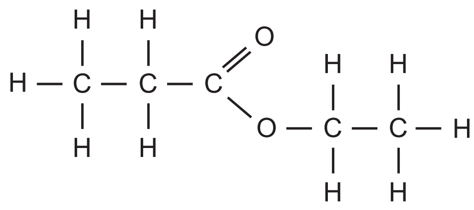
	X	*Y*	*Z*
A	CH_2OH–CH_2OH	CHO–CHO	CO_2H–CO_2H
B	CH_2OH–CH_2OH	CH_2OH–CHO	CHO–CO_2H
C	CH_2OH–CHO	CH_2OH–CO_2H	CHO–CO_2H
D	CH_2OH–CO_2H	CHO–CO_2H	CO_2H–CO_2H

11 What is the structure of the ester formed from propanoic acid and ethanol?

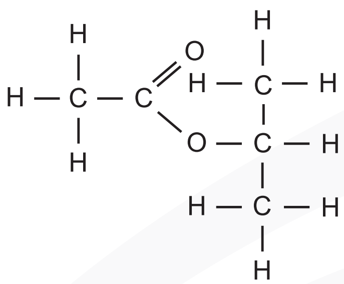
A



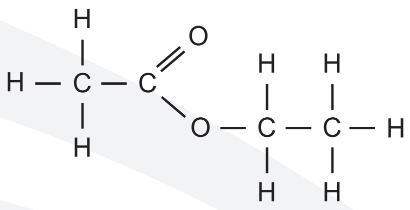
B



C



D



12 A common industrial solvent is a mixture of propanone, CH_3COCH_3, and pentyl ethanoate $CH_3CO_2(CH_2)_4CH_3$.

Which reagent would have no effect on this solvent?

A Na(s)

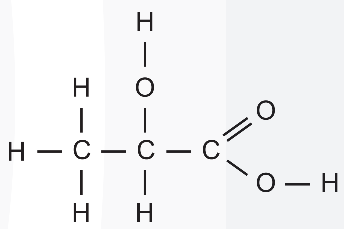
B $NaBH_4$

C NaOH(aq)

D 2,4-dinitrophenylhydrazine reagent

13 Lactic acid occurs naturally, for example in sour milk.

Its displayed formula is shown.



Which reaction occurs with lactic acid?

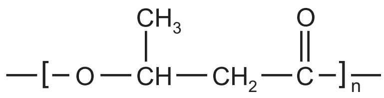
A It decolourises aqueous bromine rapidly.

B It is insoluble in water.

C It reduces Fehling's reagent.

D Two molecules react with each other in the presence of a strong acid.

14 PHB (polyhydroxybutyric acid) is a natural polymer produced by a range of micro-organisms. It can also be manufactured from sugar. PHB is readily biodegradable.



PHB (polyhydroxybutyric acid)

What type of reaction will cause PHB to break down?

A addition

B hydrolysis

C reduction

D substitution

15 Which pair of compounds is formed when the ester $C_2H_5CO_2CH_3$ is boiled with aqueous sodium hydroxide?

A	$C_2H_5CO_2H$	CH_3OH
B	$C_2H_5CO_2Na$	CH_3ONa
C	$C_2H_5CO_2Na$	CH_3OH
D	C_2H_5OH	CH_3CO_2Na

16 Which formula represents the organic compound formed by the reaction of propanoic acid with methanol in the presence of concentrated sulphuric acid as a catalyst?

A $CH_3CH_2COCH_3$

B $CH_3CH_2CO_2CH_3$

C $CH_3CO_2CH_2CH_3$

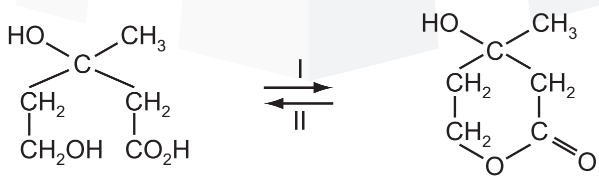
D $CH_3CH_2CH_2CO_2CH_3$

17 The ester $CH_3CH_2CH_2CO_2CH_3$ is responsible for the aroma of apples.

When this ester is hydrolysed by acid in the stomach, what is the empirical formula of the organic acid produced?

A CH_4O **B** C_2H_4O **C** $C_2H_4O_2$ **D** $C_3H_7O_2$

18 Mevalonic acid, 3,5-dihydroxy-3-methylpentanoic acid, is involved in cholesterol formation in the body. It is an oil that occurs as a mixture of the two interchanging molecules shown in the diagram.



What names are used to describe the pair of interchanging reactions I and II?

A condensation and addition

B dehydrogenation and hydrogenation

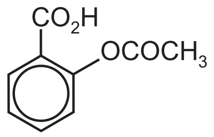
C esterification and hydrolysis

D neutralisation and acidification

19 The stomach wall can become sensitive to acidic compounds.

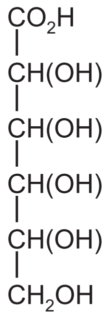
Which is the most acidic compound?

A



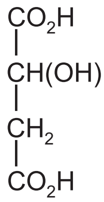
aspirin

B



gluconic acid

C



malic acid

D

$CH_3CH(OH)CO_2H$

lactic acid

20 Ethyl ethanoate can be obtained from ethanoic acid and ethanol by the following reaction.

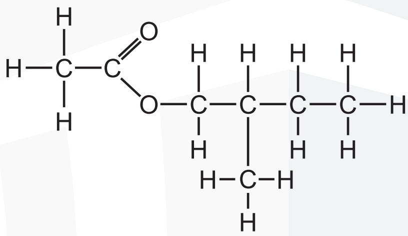
$$CH_3CH_2OH + CH_3CO_2H \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

Ethanol (30 g) and ethanoic acid (30 g) are heated under reflux together, and 22 g of ethyl ethanoate are obtained.

What is the yield of the ester?

A 25 % **B** 38 % **C** 50 % **D** 77 %

21 Bees use 2-methylbutyl ethanoate as an ‘alarm’ pheromone. When disturbed, individual bees on guard will raise their abdomen and emit the alarm pheromone, fanning their wings to aid its dispersal. This alerts other bees to a danger and makes them ready to sting when required.



2-methylbutyl ethanoate

Which starting materials would be required to synthesise 2-methylbutyl ethanoate?

A CH_3CH_2OH and $CH_3CH_2CH(CH_3)CO_2H$

B CH_3CO_2H and $CH_3CH_2CH(CH_3)CH_2OH$

C CH_3CH_2OH and $CH_3CH_2CH(CH_3)CH_2CO_2H$

D CH_3CO_2H and $CH_3CH_2CH(CH_3)CH_2CO_2H$

22 Trichloroethanoic acid, CCl_3CO_2H, is used in cosmetic surgery to perform a 'chemical peel' to remove dead skin.

Trichloroethanoic acid can be made by reacting chlorine with ethanoic acid.

What is the mechanism of this reaction?

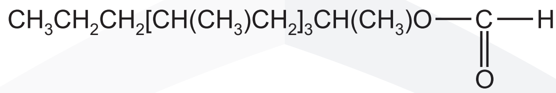
A electrophilic addition

B electrophilic substitution

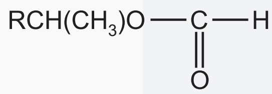
C free radical addition

D free radical substitution

23 The acarid mite releases *lardolure* to attract other mites to a host. This chemical can be destroyed by hydrolysis with acid.



A simplified formula for *lardolure* may be written as follows.



What are the products of its hydrolysis?

A $RCH(CH_3)CO_2H + CH_3OH$

B $RCH(CH_3)CO_2H + HCO_2H$

C $RCH(CH_3)OH + CO_2$

D $RCH(CH_3)OH + HCO_2H$

24 Esters are frequently used as solvents and as flavouring agents in fruit drinks and confectionery.

An ester $C_8H_{12}Br_2O_4$ can be prepared in low yield by the reaction shown.

$$CH_3C(Br)(CH_2Br)CO_2H + (CH_3)_2C(OH)CO_2H \rightleftharpoons C_8H_{12}Br_2O_4 + H_2O$$

What is the structural formula of the ester $C_8H_{12}Br_2O_4$?

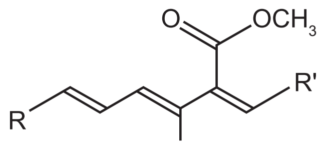
A $CH_3C(Br)(CH_2Br)CO_2C(CH_3)_2CO_2H$

B $CH_3C(Br)(CH_2Br)CO_2C(OH)(CH_3)CO_2CH_3$

C $CH_3C(Br)(CH_3)CO_2C(CH_3)_2CO_2CH_2Br$

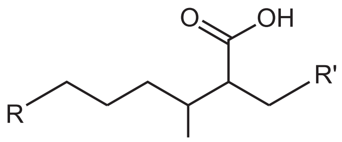
D $(CH_3)_2C(Br)C(CO_2H)(CH_2Br)CO_2CH_3$

25 Part of the structure of strobilurin, a fungicide, is shown. R and R' are inert groups.

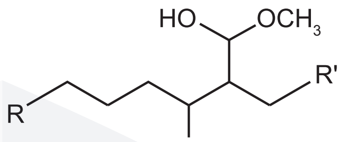


If strobilurin is first warmed with aqueous sulfuric acid, and its product then treated with hydrogen in the presence of a palladium catalyst, what could be the structure of the final product?

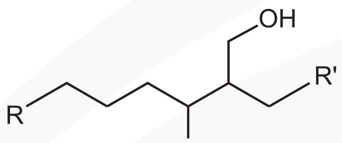
A



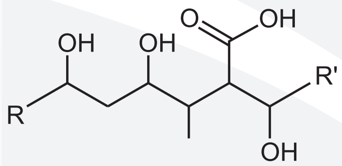
B



C



D



26 Which formula represents an ester which will form sodium ethanoate on hydrolysis with aqueous sodium hydroxide?

A $H_3C-CH_2-C(=O)-O-CH_2-CH_3$

B $H_3C-CH_2-C(=O)-O-CH_3$

C $H-C(=O)-O-CH_2-CH_3$

D $H_3C-C(=O)-O-CH_2-CH_2-CH_3$

27 The ester $CH_3CH_2CH_2CO_2CH_3$ is responsible for the aroma of apples.

When this ester is hydrolysed by acid in the stomach, what is the empirical formula of the organic acid produced?

A CH_2O **B** CH_4O **C** C_2H_4O **D** $C_3H_6O_2$

28 Which pair of substances could react to give the ester $CH_3CH_2CO_2CH_3$?

A ethanol and ethanoic acid

B methanol and ethanoic acid

C methanol and propanoic acid

D propan-1-ol and methanoic acid

29 An organic compound **J** reacts with sodium to produce an organic ion with a charge of –3. **J** reacts with NaOH(aq) to produce an organic ion with a charge of –1.

What could be the structural formula of **J**?

A $HO_2CCH(OH)CH_2CO_2H$

B $HO_2CCH(OH)CH_2CHO$

C $HOCH_2CH(OH)CH_2CO_2H$

D $HOCH_2COCH_2CHO$

30 A sample of ethyl propanoate is hydrolysed by heating under reflux with aqueous sodium hydroxide. 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?

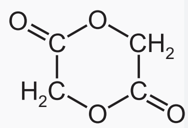
A 32.4 % and 67.6 %

B 38.3 % and 61.7 %

C 42.3 % and 57.7 %

D 50.0 % and 50.0 %

31 Compound C is used in textile and leather processing.



compound C

Which starting material(s), on gentle heating with a few drops of concentrated sulfuric acid, generates compound C?

A CH_3COOH only

B $HOCH_2COOH$ only

C CH_3COOCH_2COOH only

D CH_3COOH mixed with $HOCH_2COOH$

32 How many isomeric esters have the molecular formula $C_4H_8O_2$?

A 2 **B** 3 **C** 4 **D** 5

33 A sample of propyl ethanoate is hydrolysed by heating under reflux with aqueous sodium hydroxide. 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 %

34 A common industrial solvent is a mixture of propanone, CH_3COCH_3, and pentyl ethanoate $CH_3CO_2(CH_2)_4CH_3$.

Which reagent would have **no** reaction with this industrial solvent?

A $HCl(aq)$

B HCN(aq) with a little KCN

C Na(s)

D $NaBH_4$

35 Which reagent reacts with ethanol and also reacts with ethanoic acid?

A acidified potassium dichromate(VI)

B sodium

C sodium carbonate

D sodium hydroxide

36 Compound **X**, $C_6H_{12}O$, is oxidised by acidified sodium dichromate(VI) to compound **Y**.

Compound **Y** reacts with ethanol in the presence of a little concentrated sulfuric acid to give liquid **Z**.

What is the formula of **Z**?

A $CH_3(CH_2)_4COCH_2CH_3$

B $CH_3(CH_2)_4CO_2CH_2CH_3$

C $CH_3CH_2CO_2(CH_2)_4CH_3$

D $CH_3CO_2(CH_2)_5CH_3$

37 Lactic acid (2-hydroxypropanoic acid), $CH_3CH(OH)CO_2H$, is found in sour milk.

Which reaction could occur with lactic acid?

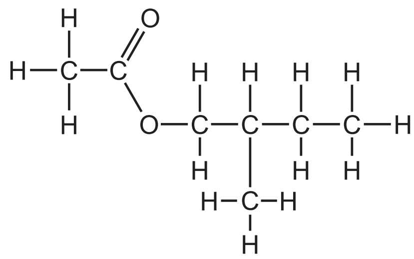
A $CH_3CH(OH)CO_2H + CH_3OH \rightarrow CH_3CH(OCH_3)CO_2H + H_2O$

B $CH_3CH(OH)CO_2H + HCO_2H \rightarrow CH_3CH(O_2CH)CO_2H + H_2O$

C $CH_3CH(OH)CO_2H + NaHCO_3 \rightarrow CH_3CH(ONa)CO_2H + H_2O + CO_2$

D $CH_3CH(OH)CO_2H + Cl_2 \rightarrow CH_3CH(Cl)CO_2H + HOCl$

38 Bees use 2-methylbutyl ethanoate as an 'alarm' pheromone to alert other bees.



2-methylbutyl ethanoate

Which starting materials would be required to synthesise 2-methylbutyl ethanoate?

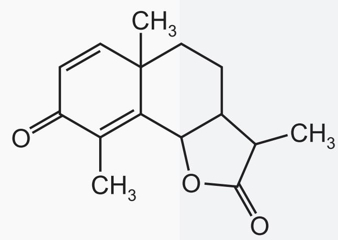
A CH_3CH_2OH and $CH_3CH_2CH(CH_3)CO_2H$

B CH_3CO_2H and $CH_3CH_2CH(CH_3)CH_2OH$

C CH_3CH_2OH and $CH_3CH_2CH(CH_3)CH_2CO_2H$

D CH_3CO_2H and $CH_3CH_2CH(CH_3)CH_2CO_2H$

39 Santonin is a drug that was once widely used to expel parasitic worms from the body.



santonin

When santonin is first treated with warm dilute H_2SO_4, and then the product of this reaction is treated with cold acidified $KMnO_4$, a final product **X** is obtained.

How many atoms of hydrogen in each molecule of product **X** can be displaced with sodium metal?

A 2 **B** 4 **C** 5 **D** 6

40 Compound **Y** has M_r of 88. It does not fizz when added to a solution of sodium hydrogencarbonate. It can be hydrolysed by dilute sulfuric acid to produce two organic products with M_r values of 46 and 60.

What is the identity of compound **Y**?

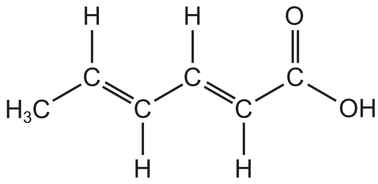
A butanoic acid

B ethyl ethanoate

C 3-hydroxybutanal

D butyl methanoate

41 Sorbic acid is used as a food preservative because it kills fungi and moulds.



sorbic acid

Sorbic acid will react with

- hydrogen in the presence of a nickel catalyst,
- bromine in an organic solvent.

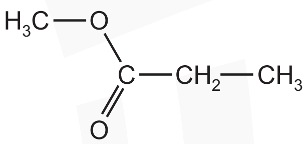
How many moles of hydrogen and of bromine will be incorporated into one mole of sorbic acid by these reactions?

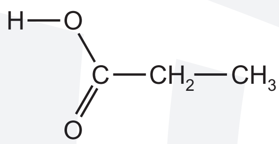
	moles of hydrogen	moles of bromine
A	2	2
B	2	$2\frac{1}{2}$
C	3	2
D	3	$2\frac{1}{2}$

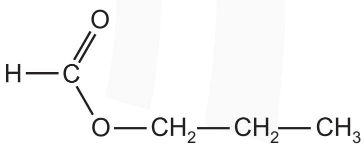
42 How many isomeric esters, including structural isomers and stereoisomers, can be made with the molecular formula $C_5H_{10}O_2$, if methanoic acid is one of the two reactants used?

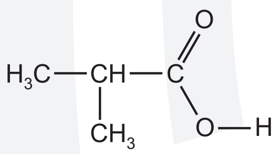
A 2 **B** 3 **C** 4 **D** 5

43 How many of the compounds shown will react with aqueous sodium hydroxide to form the sodium salt of a carboxylic acid?



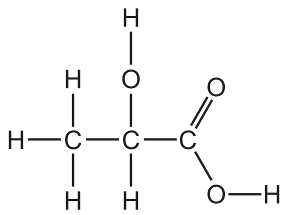






A 1 **B** 2 **C** 3 **D** 4

44 Lactic acid occurs naturally, for example in sour milk.



lactic acid

What is a property of lactic acid?

A It decolourises aqueous bromine rapidly.

B It is insoluble in water.

C It reduces Fehling's reagent.

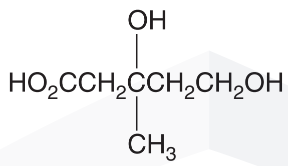
D Two molecules react with each other in the presence of a strong acid.

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Mevalonic acid is an intermediate in the biosynthesis of cholesterol, and is shown below.



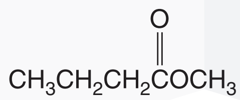
Which properties does mevalonic acid have?

1 It has only one chiral carbon atom.

2 It can be esterified both by ethanoic acid and by ethanol, in the presence of H^+ ions.

3 It contains both primary and secondary alcohol groups.

2 The flavour of pineapples is partly due to the compound **Q**.



Q

When **Q** is heated under reflux with NaOH(aq) and the mixture distilled, what compounds will be found in the distillate?

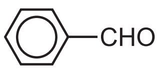
1 CH_3OH

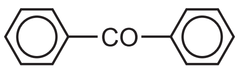
2 $CH_3CH_2CH_2CO_2Na$

3 $CH_3CH_2CH_2OH$

3 Which carbonyl compounds could be easily oxidised to carboxylic acids that are readily soluble in cold water?

1 CH_3CH_2CHO

2 

3 

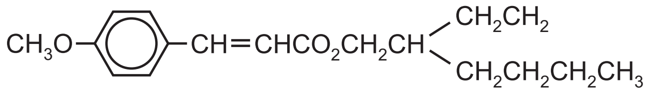
4 Which statements about lactic acid, $CH_3CH(OH)CO_2H$, are correct?

1 Lactic acid forms optical isomers.

2 Two hydrogen atoms per lactic acid molecule can be involved in hydrogen bonding.

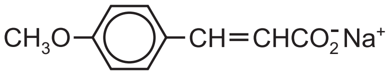
3 Lactic acid would form an aldehyde when oxidised by acidified potassium dichromate(VI).

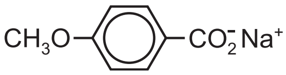
5 A sun protection cream contains the following ester as its active ingredient.



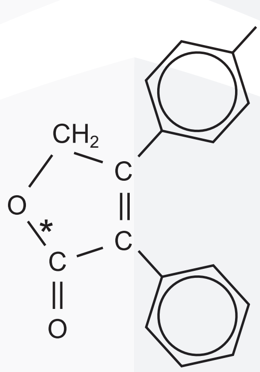
What are the products of its partial or total hydrolysis by aqueous sodium hydroxide?

1 $CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OH$

2 

3 

6 Rofecoxib, an efficient drug against arthritis, has the following structure. R is an inert group.



Which reactions are possible with this structure?

1 The bond marked * is hydrolysed by heating with aqueous sodium hydroxide.

2 Aqueous bromine is decolourised.

3 An orange precipitate is formed with 2,4-dinitrophenylhydrazine reagent.

7 Fats and grease that build up on pans used in cooking are esters. Pans which are dirty from fats or grease may be cleaned by heating them with a reagent that will react with the ester group.

What may be used to clean such pans by this reaction?

1 vinegar - aqueous ethanoic acid, CH_3CO_2H

2 alcohol - ethanol, C_2H_5OH

3 baking powder - sodium hydrogencarbonate, $NaHCO_3$

8 Monopotassium citrate is used as an emulsifying agent in powdered milk and in powdered soups. It may be represented by the formula shown.

$$\begin{array}{c} CH_2CO_2H \\ | \\ HO—C—CO_2^-\,K^+ \\ | \\ CH_2CO_2H \end{array}$$

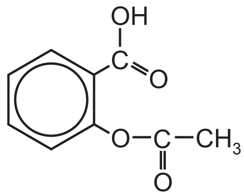
Which statements about monopotassium citrate are correct?

1 It can form optical isomers.

2 It can act as a dibasic acid.

3 It can form esters with both acids and alcohols.

9 Aspirin is a widely-available pain-killer, whose properties have been known for centuries. The structure of aspirin is shown.



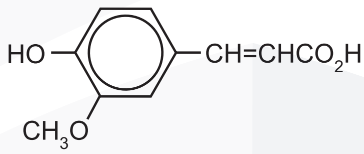
Which functional groups are present in aspirin?

1 alcohol

2 carboxylic acid

3 ester

10 Ferulic acid is an antioxidant that occurs widely in plants.



ferulic acid

Which reagents can react with the –CH=CHCO$_2$H part of the molecule?

1 NaOH(aq)

2 acidified $KMnO_4$

3 HBr

11 An organic compound, **X**, will react with calcium metal to produce a salt with the empirical formula $CaC_4H_4O_4$.

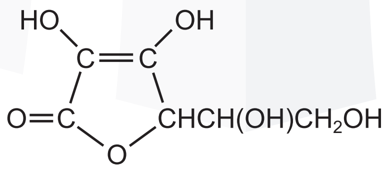
What could be the identity of **X**?

1 ethanoic acid

2 butanedioic acid

3 2-methylpropanedioic acid

12 The structure of the antioxidant vitamin C is shown in the diagram.



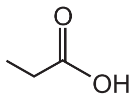
On the basis of this structure, which properties is vitamin C likely to have?

1 It is soluble in water.

2 It decolourises aqueous bromine rapidly.

3 It reduces Fehling's reagent.

13 Propanoic acid occurs naturally as a result of the bacterial fermentation of milk, and is partly responsible for the flavour of Swiss cheese.



propanoic acid

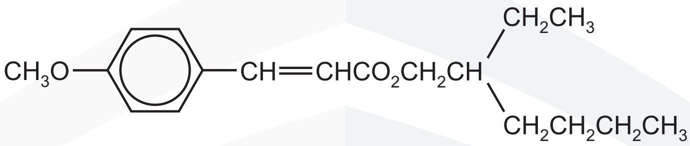
Which starting materials could be used to synthesise propanoic acid?

1 $CH_3CH_2CH_2OH$

2 CH_3CH_2CN

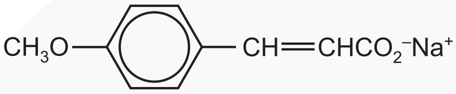
3 CH_3CH_2CHO

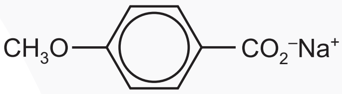
14 A sun protection cream contains the following ester as its active ingredient.



Which substances are present in the products of its hydrolysis by aqueous sodium hydroxide?

1 $CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OH$

2 

3 

15 Organic acids and alcohols react together to form esters.

Which pairs of compounds could produce a product of molecular formula $C_4H_6O_4$?

1 CH_3CO_2H and C_2H_5OH

2 HCO_2H and $HOCH_2CH_2OH$

3 HO_2CCO_2H and CH_3OH

16 An organic compound, **X**, will react with an excess of calcium metal to produce a salt with the empirical formula $CaC_4H_6O_4$.

What could be the identity of **X**?

1 ethanoic acid

2 butanedioic acid

3 methylpropanedioic acid

17 On acid hydrolysis, which compounds produce propanoic acid?

1 $CH_3CH_2CO_2CH_3$

2 $CH_3CH_2CH_2CN$

3 $CH_3CH_2CH_2Cl$

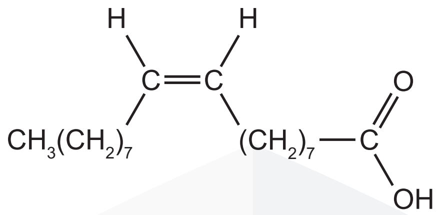
18 Which compounds will produce ethanoic acid when boiled under reflux with dilute alkali followed by acidification?

1 CH_3CH_2Cl

2 $CH_3CO_2CH_3$

3 CH_3CN

19 Oleic acid is found in olive oil. It has the following formula.



Which reagents will give a positive result with oleic acid?

1 aqueous bromine

2 acidified potassium dichromate(VI)

3 Fehling's reagent

20 The ester $C_2H_5CO_2CH_2CH_2CH_3$ can be made in a school or college laboratory by a sequence of reactions using compound **X** as the **only** organic material.

What might be the identity of compound **X**?

1 $CH_3CH_2CH_2OH$

2 CH_3CH_2CHO

3 CH_3COCH_3

21 In an organic synthesis, a 62% yield of product is achieved.

Which conversions are consistent with this information?

1 74.00 g of butan-2-ol $\rightarrow$ 44.64 g of butanone

2 74.00 g of butan-1-ol $\rightarrow$ 54.56 g of butanoic acid

3 74.00 g of 2-methylpropan-1-ol $\rightarrow$ 54.56 g of 2-methylpropanoic acid

22 An organic compound, **X**, will react with calcium metal to produce a salt with the empirical formula $CaC_4H_4O_4$.

What could be the identity of **X**?

1 ethanoic acid

2 butanedioic acid

3 2-methylpropanedioic acid

23 Which reagents, when used in an excess, can be used to make sodium lactate, $CH_3CH(OH)CO_2Na$, from lactic acid, $CH_3CH(OH)CO_2H$?

1 Na

2 $NaHCO_3$

3 NaOH

CARBOXYLIC ACIDS WS 4

1 **(a)** **(i)** This question is about esters; esters occur naturally and are widely used.
In the boxes below, draw the structural formulae of any **three** different esters that have the molecular formula $C_5H_{10}O_2$.

(ii) Write an equation for the hydrolysis of **one** of these esters by hot, aqueous sodium hydroxide.

....[4]

(b) State **two** general physical properties of esters.

(i) ....

(ii) ....[2]

(c) State **two** commercial uses of esters.

(i) ....

(ii) ....[2]

[S'03 Q7]

2 Esters are compounds which provide the flavour of many fruits and the perfumes of many flowers.

(a) The ester $CH_3(CH_2)_2CO_2CH_3$ contributes to the aroma of apples.

(i) State the reagents and conditions needed for the hydrolysis of this ester.

....

(ii) Write the equation for the hydrolysis of this ester.

....

(iii) Apart from their use as perfumes and food flavourings, state **one** major commercial use of esters.

....[3]

[S'04 Q4]

3 Although there are many different types of food eaten around the world, animal fats and/or vegetable oils are commonly used in cooking.

Animal fats and vegetable oils are usually glyceryl esters, that is esters of glycerol, propane-1,2,3-triol.

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Many animal fats contain esters of stearic acid, $CH_3(CH_2)_{16}CO_2H$.

Vegetable oils often contain esters of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$.

(a) Draw the structural formula of the glyceryl ester formed when one molecule of glycerol is completely esterified with stearic acid.

[1]

(b) What reagent(s) would you use, in a school or college laboratory, to obtain a small sample of oleic acid, $C_{17}H_{33}CO_2H$, from the glyceryl ester present in a vegetable oil?

.... [1]

Oleic acid is the *cis* isomer and elaidic acid the *trans* isomer of

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H.$$

(c) By using this formula, draw the structural formula of elaidic acid, clearly showing the stereochemistry.

[1]

Oleic and elaidic acids are examples of mono-unsaturated acids.
Many vegetable oils contain esters of polyunsaturated fatty acids. Such oils are often hydrogenated to form esters containing saturated or mono-unsaturated fatty acids.

(d) **(i)** Suggest the meaning of the term *polyunsaturated fatty acid*.

....

....

(ii) What reagent and condition(s) are used for the hydrogenation of an unsaturated fatty acid?

reagent ....

condition(s) .... [3]

In cooking, unsaturated fats are often oxidised to give aldehydes or ketones.

(e) **(i)** Give the structural formulae of the two aldehydes formed by the partial oxidation of the unsaturated fat below.
In the structure, *X*, represents the rest of the fat molecule.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7X$$
$$\downarrow$$

(ii) Name the reagent you would use to show that the product contained **either** an aldehyde **or** a ketone. What change would be seen?

reagent ....

observation ....

(iii) What reagent would you use to **confirm** the presence of an aldehyde?
What change would be seen?

reagent ....

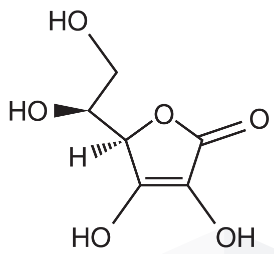
observation ....

[6]

Animal fats and vegetable oils can become rancid because of oxidation. The rancid fat or oil has an unpleasant smell and taste.

Antioxidants are used to prevent the spoilage of many foodstuffs by oxidation.

One antioxidant that is widely used is vitamin C, ascorbic acid.



ascorbic acid

(f) (i) How many chiral carbon atoms are present in one molecule of ascorbic acid? If none, write 'none'.

....

(ii) The ascorbic acid molecule contains three functional groups.

Two of these are alcohol (primary and secondary) and alkene.

What is the name of the third functional group?

.... [2]

[S'11 P22 Q5]

4 Each of the three organic compounds, **V**, **W**, and **X**, has the empirical formula CH_2O.
The number of carbon atoms in each of their molecules is shown in the table.

compound	number of C atoms
V	1
W	2
X	3

V gives a brick red precipitate when warmed with Fehling's reagent; **W** and **X** do not.

W is a fruity smelling liquid.

In **X**, the carbon atoms are bonded directly to one another.

X gives an effervescence when shaken with Na_2CO_3(aq); **V** and **W** do not.

(a) Give the structural formula of **V**.

[1]

(b) **(i)** What functional group is present in **W**?

....

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

[2]

(c) When **X** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **Y**, gives no reaction with 2,4-dinitrophenylhydrazine reagent.

(i) Give the structural formula of **X**.

(ii) Give the structural formula of **Y**, the compound formed from **X**.

[2]

(d) When **X** is warmed with a little concentrated sulfuric acid, a small amount of a cyclic compound, **Z**, is formed.

Z has the molecular formula $C_6H_8O_4$.

(i) Suggest a displayed formula for **Z**.

(ii) What type of reaction occurs when **Z** is formed from **X**?

.... [2]

[W'11 P23 Q5]

5 Compound **X** has the molecular formula $C_4H_8O_2$.

(a) (i) Treatment of **X** with sodium metal produces a colourless flammable gas.
What does this result tell you about the functional groups that could be present in **X**?

....

....

(ii) There is no reaction when **X** is treated with sodium hydrogencarbonate, $NaHCO_3$.
What does this result tell you about the functional groups that could be present in **X**?

....

....

(iii) When **X** is shaken with aqueous bromine the orange colour disappears.
What does this result tell you about the functional groups that could be present in **X**?

....

....
[3]

(b) The molecule of **X** has the following features.

- The carbon chain is unbranched and the molecule is not cyclic.
- No oxygen atom is attached to any carbon atom which is involved in π bonding.
- No carbon atom has more than one oxygen atom joined to it.

There are five possible isomers of **X** which fit these data. Four of these isomers exist as two pairs of stereoisomers.

(i) Draw displayed formulae of **each** of these two pairs.

pair 1		
pair 2		

(ii) These four isomers of **X** show two types of stereoisomerism.

State which type of isomerism each pair shows.

pair 1 ....

pair 2 ....

[6]

[W'12 P21 Q21]

6 A student reacted together an alcohol and a carboxylic acid under appropriate conditions to produce an ester.
A sweet smelling organic liquid, **Q**, with the empirical formula C_2H_4O was produced.
The M_r of **Q** was found by experiment to be 87.5.

(a) What is the molecular formula of **Q**?

.... [1]

(b) In the boxes below, draw the structural formulae of **four** isomers with this formula that are esters.

W	**X**
Y	**Z**

[4]

A sample of **Q** was hydrolysed by heating with aqueous sulfuric acid.
The resulting mixture was heated under reflux with acidified potassium dichromate(VI) to give a **single** organic product, **R**.
The product, **R**, was collected and subjected to the following tests.

A sample of **R** gave no reaction with Tollens' reagent.

A second sample of **R** gave no reaction with 2,4-dinitrophenylhydrazine reagent.

A third sample of **R** gave an effervescence with sodium carbonate.

(c) **(i)** What does the result of the test with Tollens' reagent show about **R**?

....

(ii) What does the result of the test with 2,4-dinitrophenylhydrazine reagent show about **R**?

....

(iii) What functional group does the result of the test with sodium carbonate show to be present in **R**?

....

[3]

(d) **(i)** What is the identity of the single organic compound, **R**?

....

(ii) Which of your structures, **W**, **X**, **Y** or **Z**, represents the ester, **Q**?

....

[2]

(e) Which, if any, of your esters, **W**, **X**, **Y** or **Z**, is chiral?

....

.... [1]

[S'13 P22 Q5]

7 Compound **R** is a weak diprotic (dibasic) acid which is very soluble in water.

(a) A solution of **R** was prepared which contained 1.25 g of **R** in 250 cm^3 of solution. When 25.0 cm^3 of this solution was titrated with 0.100 mol dm^{-3} NaOH, 21.6 cm^3 of the alkali were needed for complete reaction.

(i) Using the formula H_2X to represent **R**, construct a balanced equation for the reaction between H_2X and NaOH.

....

(ii) Use the data above to calculate the amount, in moles, of OH^- ions used in the titration.

(iii) Use your answers to **(i)** and **(ii)** to calculate the amount, in moles, of **R** present in 25.0 cm^3 of solution.

(iv) Calculate the amount, in moles, of **R** present in 250 cm^3 of solution.

(v) Calculate M_r of **R**.

[5]

(b) Three possible structures for **R** are shown below.

S	**T**	**U**
$HO_2CCH{=}CHCO_2H$	$HO_2CCH(OH)CH_2CO_2H$	$HO_2CCH(OH)CH(OH)CO_2H$

(i) Calculate the M_r of each of these acids.

M_r of **S** = ... M_r of **T** = ... M_r of **U** = ...

(ii) Deduce which of the structures, **S**, **T** or **U**, correctly represents the structure of the acid, **R**.

R is represented by ....

[2]

It is possible to convert **S**, **T**, or **U** into one another.

(c) State the reagent(s) and essential conditions that would be used for the following conversions.

S into **T**

....

S into **U**

....

T into **S**

.... [5]

(d) Give the structural formula of the organic product formed in **each** of the following reactions.

T reacting with an excess of Na

U reacting with an excess of Na_2CO_3

[2]

(e) The acid **S** shows stereoisomerism. Draw structures to show this isomerism.
Label each isomer.

[2]

(f) When one of the isomers of **S** is heated at 110 °C in the absence of air, a cyclic compound **V**, with molecular formula $C_4H_2O_3$, is formed.
The other isomer of **S** does not react at this temperature.

Suggest the displayed formula of **V**.

[2]

[W'13 P21 Q4]

8 Compound **Q** is a viscous liquid which is very soluble in water.
The M_r of **Q** is 90.0.

Three possible structures for **Q** are shown below.

R	S	T
$HOCH_2CH_2CO_2H$	$HOCH_2CO_2CH_3$	$HCO_2CH_2CH_2OH$

(a) **(i)** What type of isomerism do **R**, **S** and **T** show?

....

(ii) What oxygen-containing functional groups are present in **R**, **S** and **T**?
Give their **full names**.

R .... and ....

S .... and ....

T .... and ....

(iii) Which functional group(s) in **(ii)** will react with sodium carbonate?

....

(iv) Which functional group(s) in **(ii)** will react with sodium metal?

....

[6]

(b) When 0.002 mol of **Q** is reacted with an excess of solid sodium carbonate, Na_2CO_3, 24 cm^3 of carbon dioxide, measured at room temperature and pressure, is produced.

(i) Calculate the amount, in moles, of carbon dioxide produced in this reaction.

(ii) Hence calculate the amount, in moles, of carbon dioxide produced by 1 mol of **Q**.

[2]

When 0.002 mol of **Q** is reacted with an excess of metallic sodium, 48 cm^3 of hydrogen, measured at room temperature and pressure, is produced.

(c) **(i)** Calculate the amount, in moles, of hydrogen molecules produced in this reaction.

(ii) Hence calculate the amount, in moles, of hydrogen molecules produced by 1 mol of **Q**.

[2]

(d) Use your answers to **(b)** and **(c)** to deduce which structure, **R**, **S** or **T**, corresponds to the structure of **Q** and write balanced equations for the reactions that occurred.

identity of **Q** is ....

equation for reaction with sodium carbonate

....

equation for reaction with sodium metal

.... [5]

[W'13 P23 Q4]

IR SPECTROSCOPY

a analyse an infra-red spectrum of a simple molecule to identify functional groups (see the Data Booklet for functional groups required in the syllabus) ☐

IR SPECTROSCOPY

22 Analytical techniques

Analytical techniques are important tools for investigating organic compounds.

	Learning outcomes Candidates should be able to:
22.2 Infra-red spectroscopy	a) analyse an infra-red spectrum of a simple molecule to identify functional groups (see the *Data Booklet* for functional groups required in the syllabus)

INFRA-RED (IR) SPECTROSCOPY

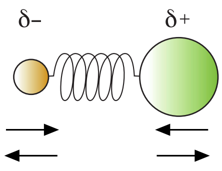
IR ABSORPTION

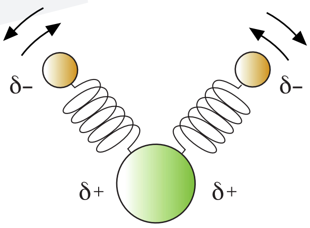
Infrared spectroscopy is used to identify functional groups in organic molecules.

Most compounds absorb infrared radiation.

The wavelengths of the radiation they absorb correspond to the natural frequencies at which vibrating bonds in the molecules bend and stretch.

However, it is only molecules that change their polarity as they vibrate that interact with infrared radiation.





2

IR ABSORPTION

Bonds vibrate in particular ways and absorb radiation at specific wavelengths. This means that it is possible to look at an infrared spectrum and identify functional groups.

As a result, the infrared spectrum gives valuable clues to the presence of functional groups in organic molecules.

An 'IR spectrum' can be read to analyze the structure of an organic molecule - most importantly the functional groups present. These are analysed in an instrument called the spectrophotometer.

Only molecules that are polar (and hence have dipole moments) can absorb IR radiation.

3

SKILL CHECK

Which of these molecules will absorb IR radiation?

A. O_2

B. HCN

C. H_2S

D. N_2

E. CCl_4

F. CO_2

4

IR ABSORPTION

The major use of infrared spectroscopy is in determining the structures of organic compounds. In an infrared spectrometer, infrared radiation in the range 400–4000cm^{-1} is passed through a sample.

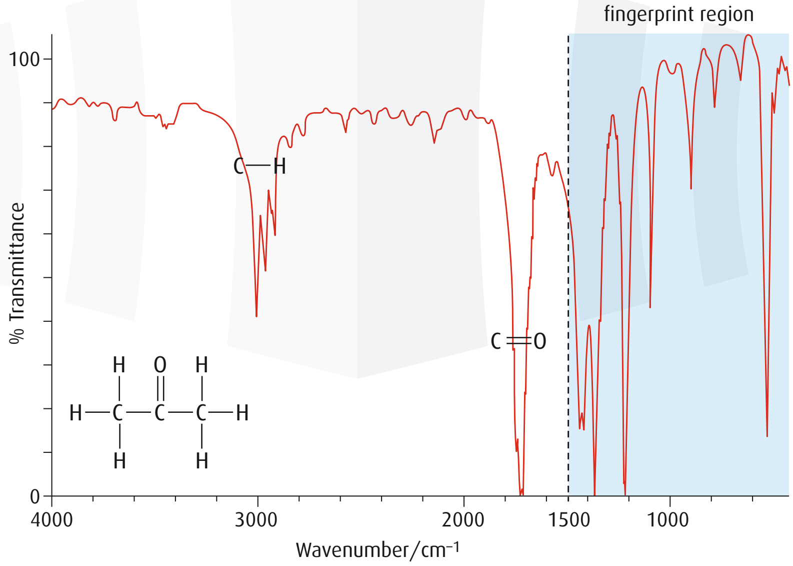
The printout of the spectrum then shows which frequencies (wavenumbers) are absorbed.

Infrared spectra are always looked at with the baseline (representing 100% transmittance, i.e. zero absorbance) at the top.

The troughs (usually called 'bands') thus represent wavenumbers at which radiation is absorbed.

5

IR SPECTRUM OF PROPANONE



6

IR SPECTRUM OF PROPANONE

The infrared spectrum can be used to determine the bonds present in a molecule.

Thus, in the region above 1500 cm^{-1} in the infrared spectrum of propanone there are two bands, corresponding to the C–H stretch and the C=O stretch.

The region below 1500 cm^{-1} is called the 'fingerprint region' and is characteristic of the molecule as a whole. Comparison of the spectrum in the fingerprint region with spectra in databases of infrared spectra can be used to identify the molecule.

For example, the infrared spectra of butanone and propanone can be distinguished using the fingerprint region. They both show very similar bands in the region above 1500cm^{-1} because they have the same functional group, but they have different fingerprint regions.

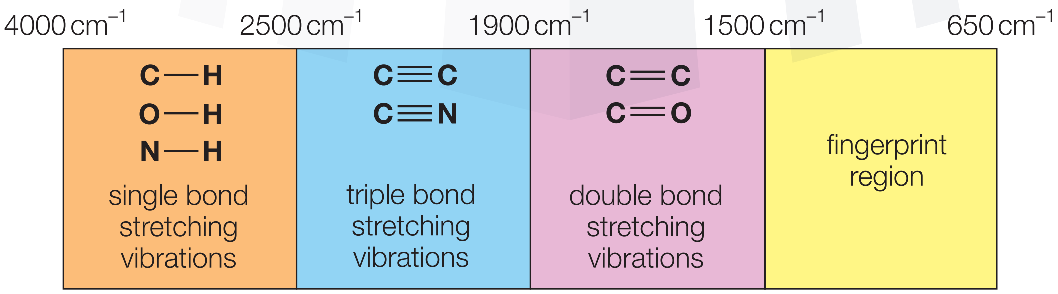
7

IR SPECTRUM OF PROPANONE

We are interested in identifying the bonds/functional groups in an organic molecule.

To a good approximation the various bonds in a molecule can be considered to vibrate independently of each other.

The wavenumbers at which some bonds vibrate are shown below.



8

WAVENUMBERS

So how do we connect molecular features to wavenumbers absorbed? **Take a look at this table:**

Bond	Functional group	Characteristic range of wavenumber / cm^{-1}
C–Cl	chloroalkane	600–800
C–O	alcohol, ether, ester, carboxylic acid	1000–1300
C=C	alkene	1610–1680
C=O	aldehyde, ketone, carboxylic acids, ester	1700–1750
C≡C	alkyne	2100–2260
O–H	hydrogen bonded in carboxylic acids	2400–3400
C–H	alkane, alkene, arene	2840–3100
O–H	hydrogen bonded in alcohols, phenols	3200–3600
N–H	primary amine	3300–3500

9

WAVENUMBERS

Note: These values are a very close approximation to the actual wavenumbers absorbed by different parts of the molecule. The surrounding environment of each type of bond determines the exact wavenumber absorbed.

We can use an infrared spectrum to identify the bonds present in a molecule but cannot always distinguish between functional groups. For example, we could identify the presence of C=O in a molecule but would not be able to distinguish between an aldehyde and a ketone.

10

SKILL CHECK

Which of the following molecules will have an infrared band in the 1700 to 1750cm^{-1} region?

A. but-2-ene

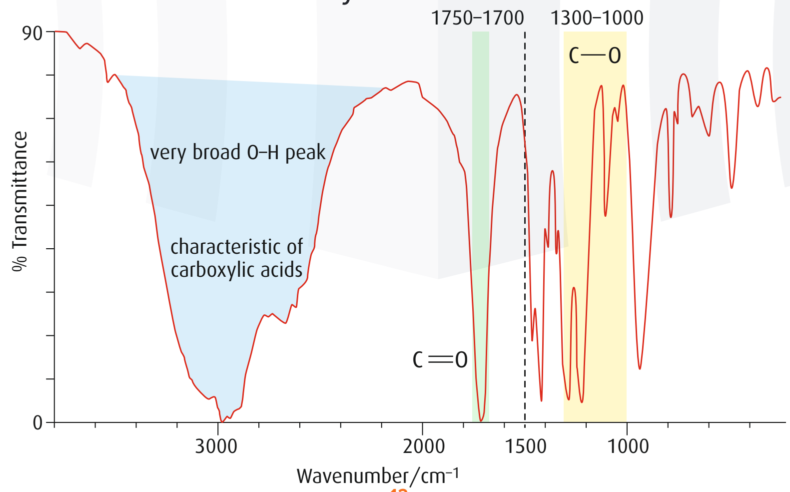
B. propanal

C. $CH_3CH_2CH(OH)CH_3$

11

BUTANOIC ACID

This is the IR spectrum for butanoic acid. The 'broad band' absorption around 3000 cm^{-1} is characteristic of carboxylic acids:



12

BUTANOIC ACID

We first of all look at the region above 1500 cm^{-1}.

We can identify the C=O stretch, as this absorption band occurs in the 1700–1750 cm^{-1} region.

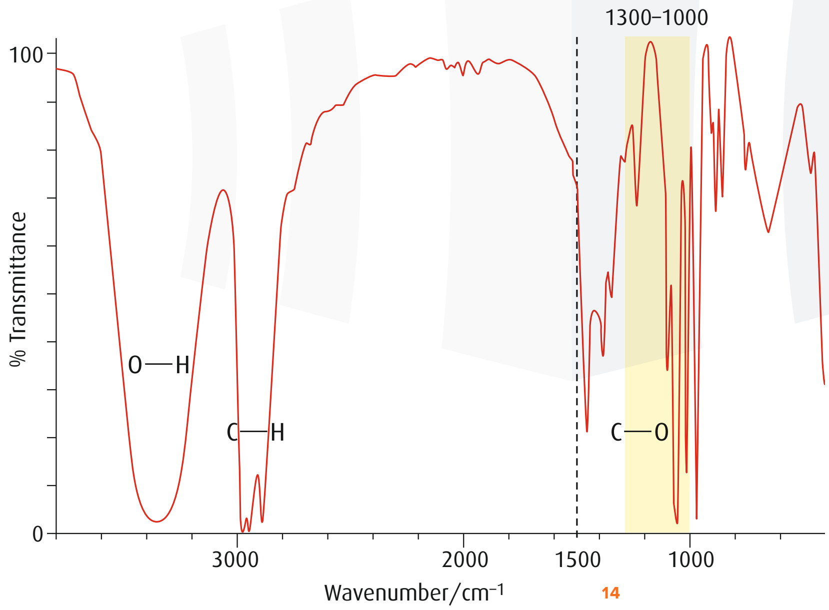
The very broad absorption band between about 2400 and 3400cm^{-1} is due to the O–H stretch in carboxylic acids and is very characteristic of those molecules.

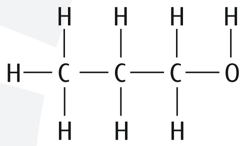
The functional group of a carboxylic acid contains a C–O bond, and therefore we should now look in the ngerprint region to con rm the presence of an absorption in the region 1000–1300cm^{-1} which is, indeed, the case.

If there were no band in this region, we would have to review our hypothesis that the molecule is a carboxylic acid.

13

PROPAN-1-OL





propan-1-ol

We can identify

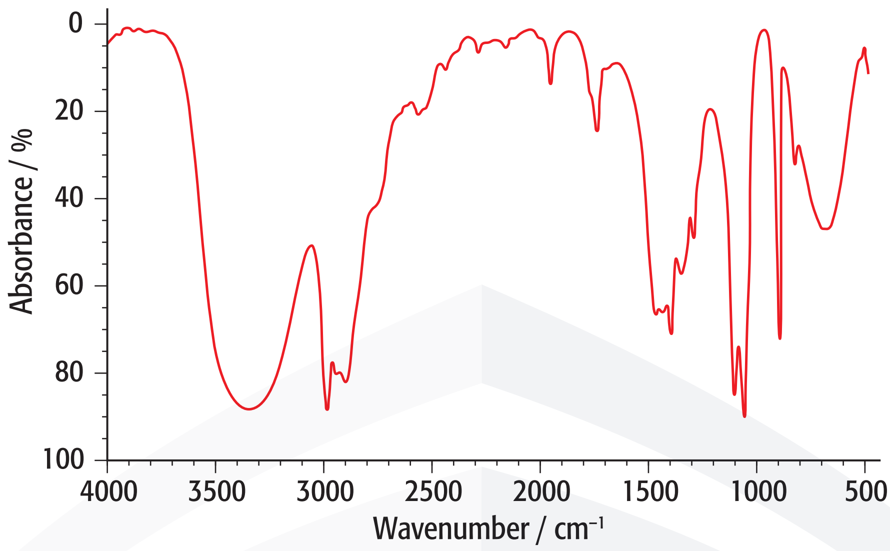
O–H (about 3350cm^{-1}) and

C–H (about 2900–3000cm^{-1}) bonds.

A C–O bond should also be present, and we can see that there is a band in the region 1000–1300cm^{-1}.

14

ETHANOL



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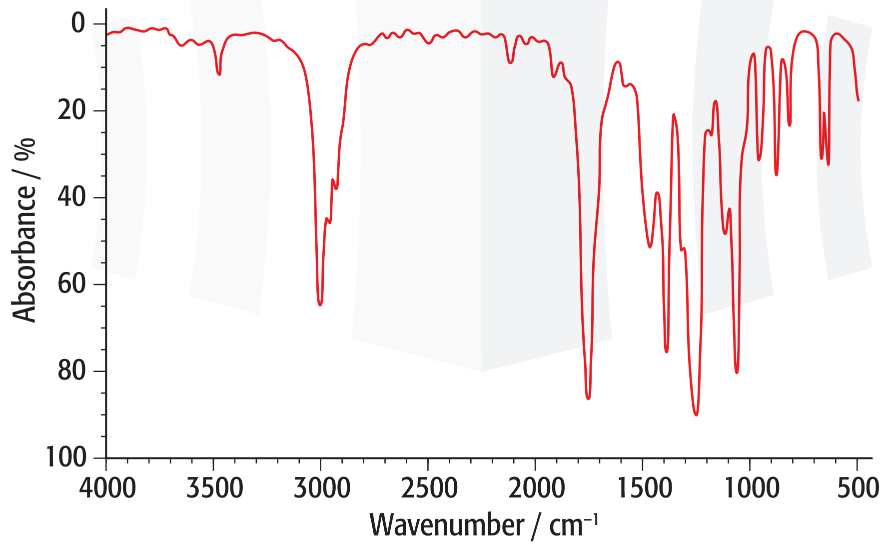
ETHYL ETHANOATE



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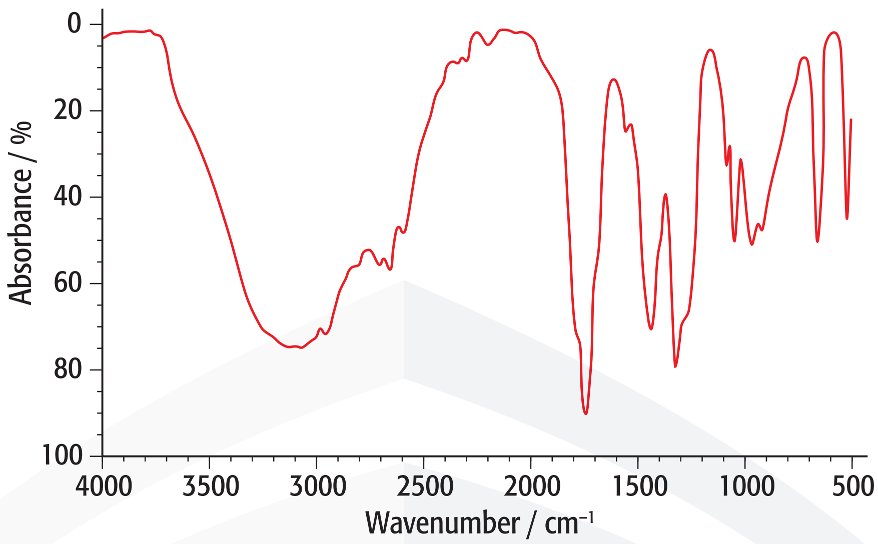
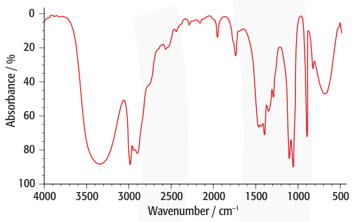
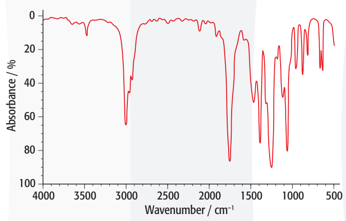
ETHANOIC ACID

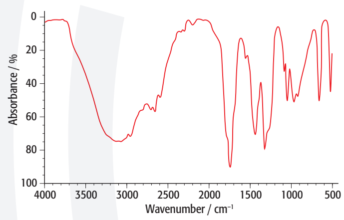


17

COMPARING IR SPECTRUMS







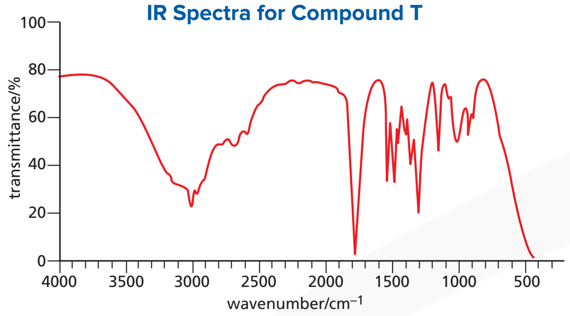
18

SKILL CHECK

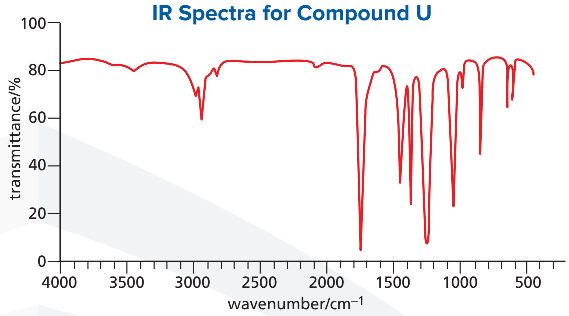
Compounds T and U are isomers with the molecular formula $C_3H_6O_2$.

Suggest their structures based on the spectra shown below:

IR Spectra for Compound T



IR Spectra for Compound U



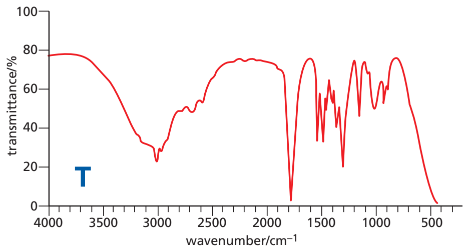
19

SKILL CHECK

Both T and U show a C=O absorption in their spectrum at 1700-1800 cm^{-1}, and a C—O absorption at about 1250cm^{-1}.

T shows 'broad band' absorption around 3000 cm^{-1}, indicating the presence of an O-H bond, while U shows no O-H band.

So, T is **$CH_3CH_2CO_2H$** (propanoic acid) and U could either be the ester **$CH_3CO_2CH_3$** (methyl ethanoate) or the ester **$HCO_2CH_2CH_3$** (ethyl ethanoate).



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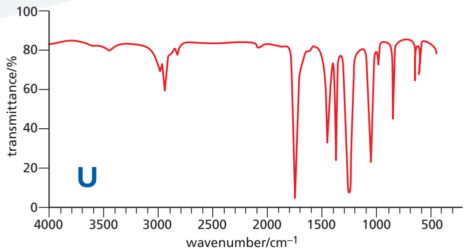
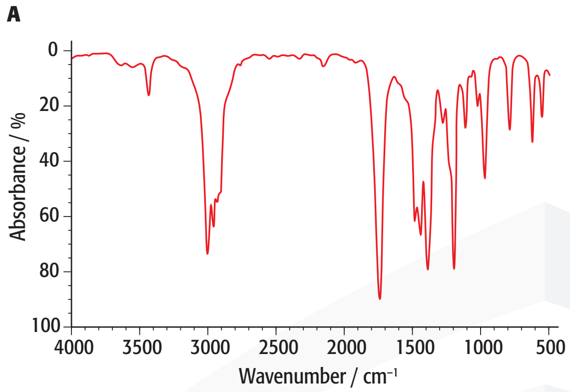
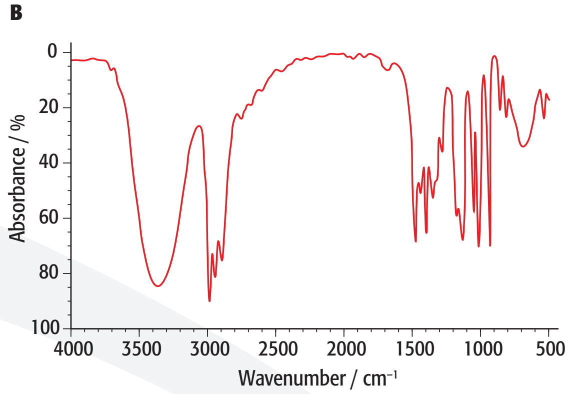


SKILL CHECK

Which one of the infra-red spectra is that of butanone and which one is of butan-2-ol?

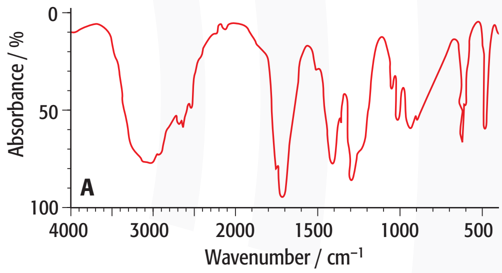


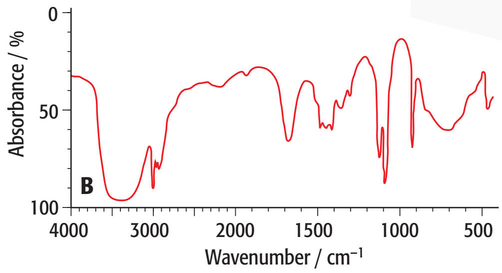


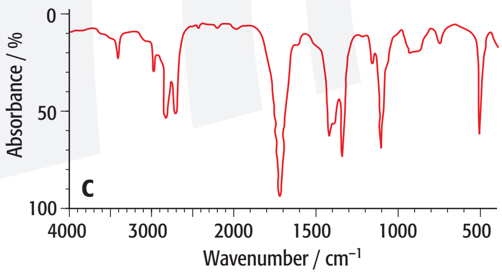
21

SKILL CHECK

Which one of the infra-red spectra is that of ethanal? Give three reasons.



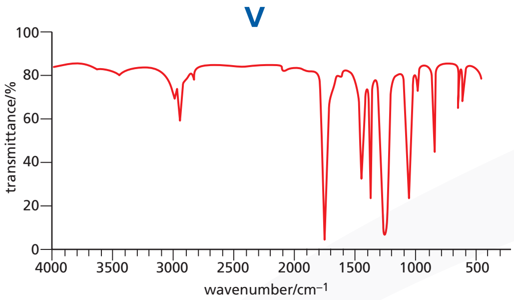


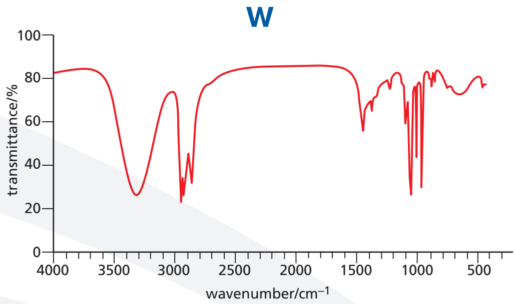


22

SKILL CHECK

Compound **V** (C_3H_6O) gives a silver mirror when warmed with Tollens' reagent. It can be converted to compound **W** by reagent **X**. Use the spectra below to identify the functional groups present in **V** and **W**, and suggest the identity of reagent **X.**

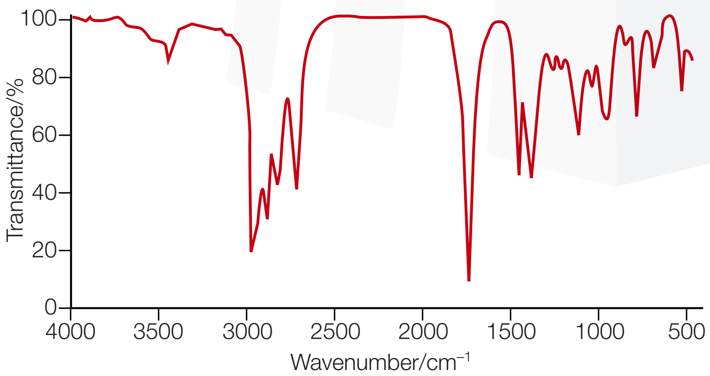




23

SKILL CHECK

Oxidation of butan-1-ol gives a product with the infrared spectrum shown below. Use the data sheet to interpret the spectrum. State the reagents and conditions that were used to carry out the oxidation of the alcohol and give your reasons.



24

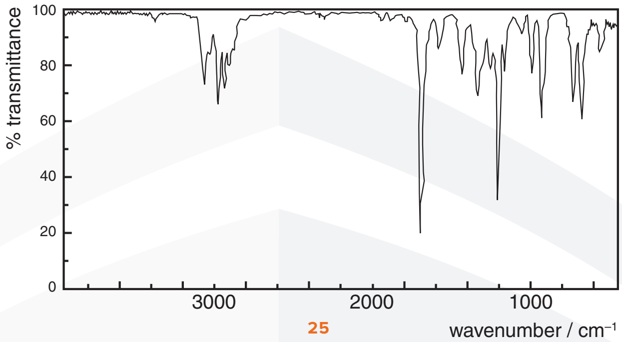
SKILL CHECK

The infra-red spectrum of compound A is shown below.

(a) What information does the absorption at 1690 cm^{-1} give about compound A?

(b) There is a sharp absorption at 2950 cm^{-1}. What could this be due to?

(c) The infra-red spectrum of compound A does not show a broad absorption at about 3300 cm^{-1}. What information does give about compound A?



25

SKILL CHECK

Q. Infrared spectroscopy is a powerful tool for identifying organic compounds. List the absorption regions expected for:

(i) ethanoic acid.

(ii)methylmethanoate.

26

SKILL CHECK

Q. Identify the absorption listed in (a) which could be used to distinguish between these two compounds. Explain why the other absorptions could not be used.

27

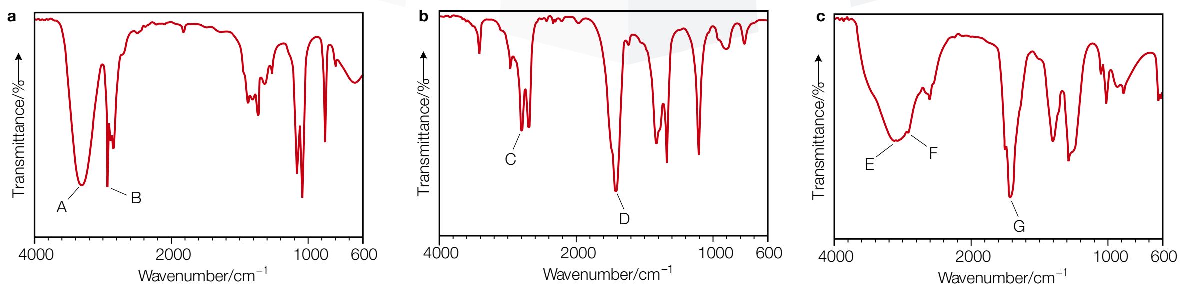
SKILL CHECK

The following are the infrared spectra of ethanol, ethanal and ethanoic acid.

(a) Which spectrum belongs to which compound?

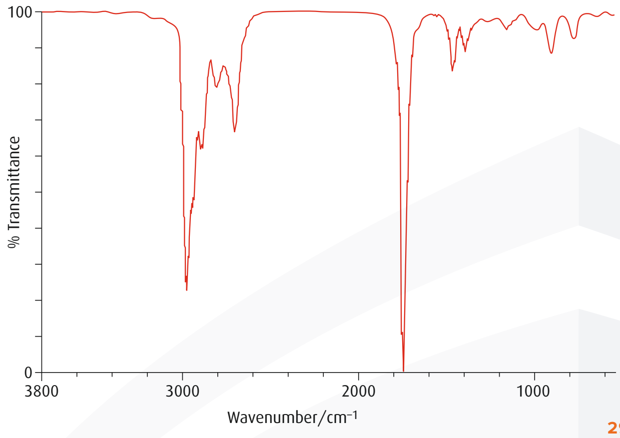
(b) Why do all three spectra have a peak at around 3000 cm^{-1}?

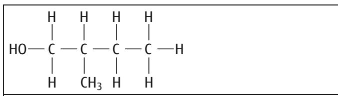
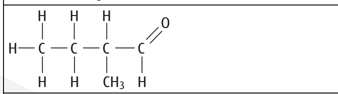
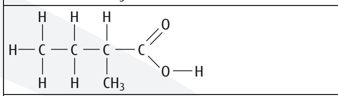
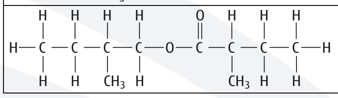
(c) Why do two of the spectra have broad peaks at wavenumbers between 3000 and 3500cm^{-1}?



SKILL CHECK

A student recorded the IR spectrum of a compound, X. He knew that X was one of the following compounds. Deduce which of the molecules is X and explain your choice by reference to the spectrum.



	I
	II
	III
	IV

ENVIRONMENTAL CONCERNS

Small molecules in the atmosphere (especially CO_2, CH_4, H_2O and CFCs) are responsible for the **greenhouse effect**: they absorb infrared radiation that is emitted from the surface of the Earth, preventing it from being lost to space.

Consequently, the amount of heat lost is less than that gained from solar radiation, and the Earth warms up.

ENVIRONMENTAL CONCERNS

- IR spectroscopy works quickly and accurately to monitor pollutants, including nitrogen dioxide, sulfur dioxide, carbon monoxide and carbon dioxide, as well as more than a hundred VOCs (volatile organic compounds) and low-level ozone.
- Scientists can use the characteristic wavelengths of infrared radiation absorbed by the molecules of the pollutants to identify them. They can also analyse the intensity of the absorptions to find the concentration of each pollutant present in a sample.
- Monitored over a period of time, this data provides useful information on the effectiveness of pollution control measures introduced locally and on a global level.

31

IR SPECTROSCOPY WS 1

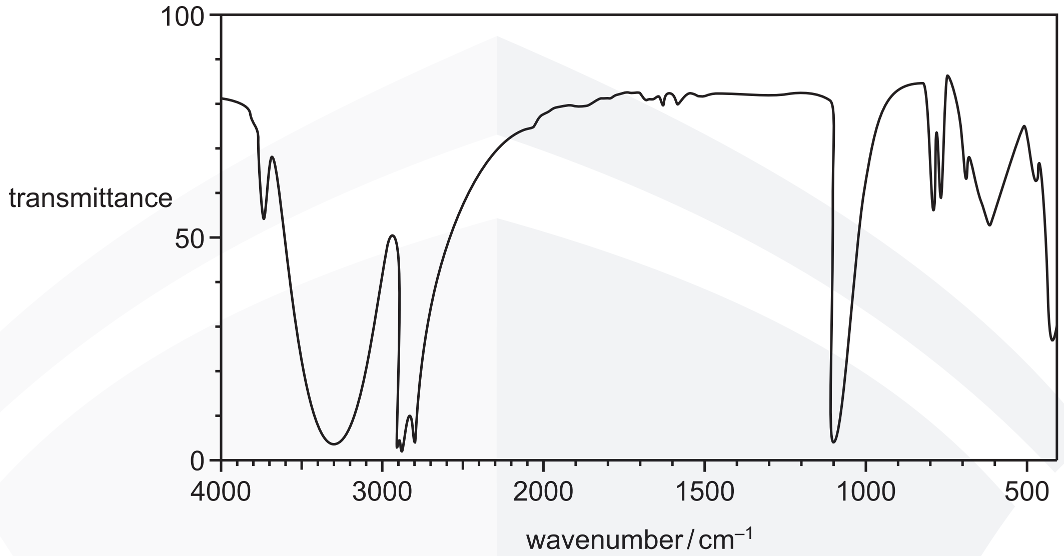
SECTION A

1 How many **structural** isomers with the molecular formula $C_4H_{10}O$ give infra-red absorptions both at approximately 1200 cm^{-1} and at approximately 3400 cm^{-1}?

A 2 **B** 4 **C** 6 **D** 7

[M'18 P12 Q30]

2 Compound X contains three carbon atoms. Part of a simplified infra-red spectrum of compound X is shown.



Which compound could be X?

A CH_3CH_2CHO

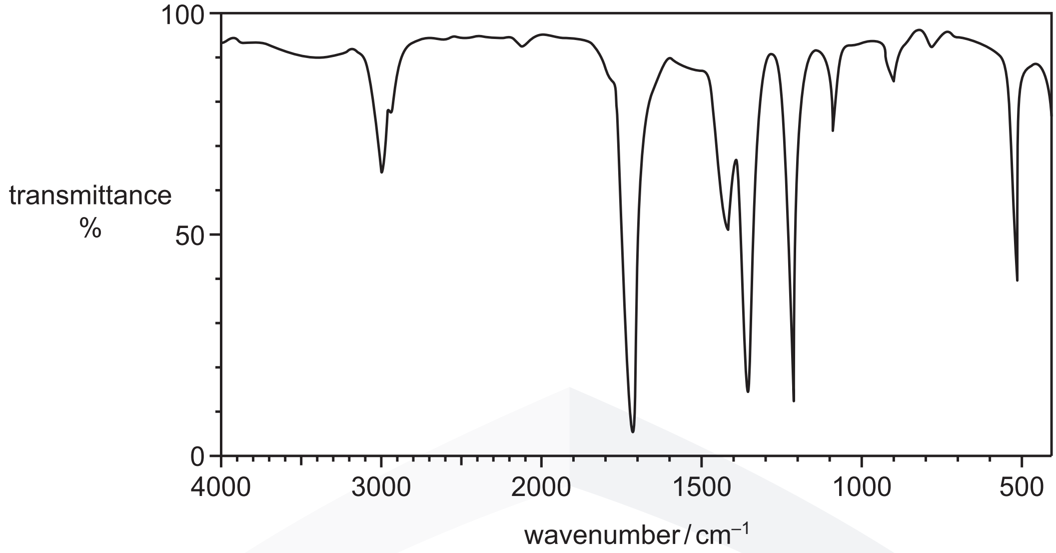
B $CH_3CH_2CO_2H$

C $CH_3CH_2CH_2OH$

D $CH_3CO_2CH_3$

[J'18 P11 Q30]

3 The infra-red spectrum of an organic compound is shown.



Which compound could give this spectrum?

A $CH_3CH_2CO_2H$

B $CH_3CH(OH)CH_3$

C CH_3COCH_3

D CH_3COCH_2OH

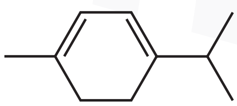
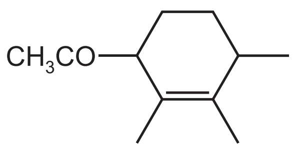
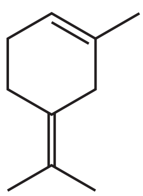
[J'18 P12 Q30]

4 Compound **S** can be extracted from natural compounds. Reacting **S** with hot, concentrated $KMnO_4$ produces the organic product, **T**. Some of the absorptions found in the infra-red spectra of **S** and **T** are described.

S has no strong absorption between 1670 and 1740 cm^{-1}.

T has a strong absorption at 1720 cm^{-1} but has **no** strong, broad absorption between 2500 and 3000 cm^{-1}.

From this information, what could be the formulae of **S** and **T**?

	S	T
A	$CH_3(CH_2)_5CH{=}CH_2$	$CH_3(CH_2)_5CO_2H$
B		$CH_3COCH_2CH_2COCH(CH_3)_2$
C		$CH_3COCH(COCH_3)CH_2CH_2CH(COCH_3)CH_3$
D		$HO_2CCH_2CH_2COCH_2COCH_3$

IR SPECTROSCOPY WS 2

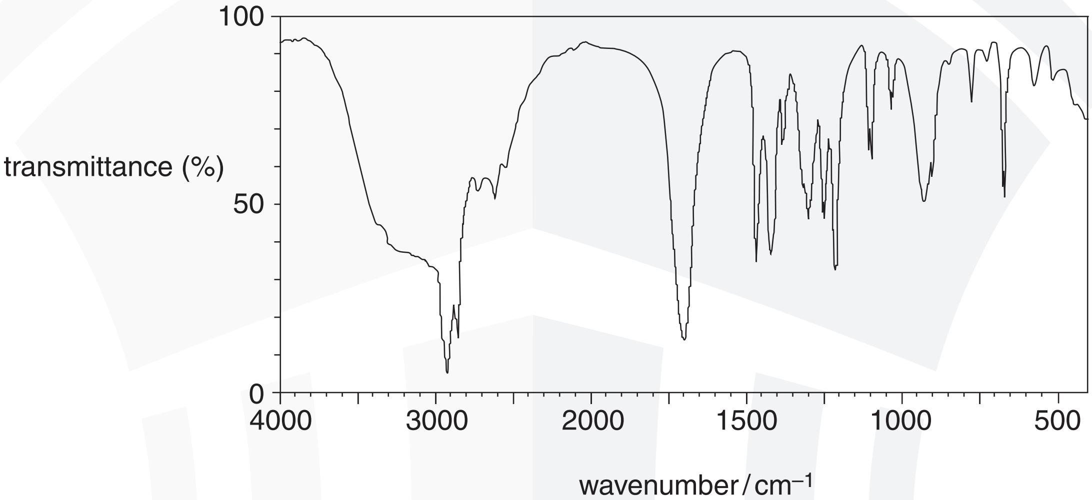
1 Compound **F** was found to be present in the smoke.
Compound **F** contains C, H and O only and contains 54.2% oxygen by mass.
The molar mass of compound **F** is 118.0 g mol^{-1}.

(i) Using the information, show that the molecular formula of compound **F** is $C_4H_6O_4$.

Show all of your working.

[2]

(ii) The infrared spectrum of compound **F** is shown below.



Using this spectrum, name the functional group present in compound **F**.

.... **[1]**

2 A student was given three compounds, an aldehyde, a ketone, and a carboxylic acid.

(a) The student carried out the same two chemical tests on each compound. This allowed her to distinguish between all three compounds.

- Describe two suitable tests that the student could have used.
- Show how the observations would allow her to distinguish between the compounds.

....

....

....

....

....

....

.... **[4]**

(b) Explain how the student could use infrared spectroscopy to confirm which compound is a carboxylic acid.

....

....

.... **[1]**

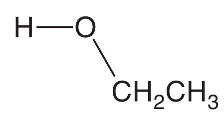
3 Ethanol, C_2H_5OH, can be produced by the fermentation of glucose, $C_6H_{12}O_6$.

(a) Write a balanced equation for the fermentation of glucose.

....[2]

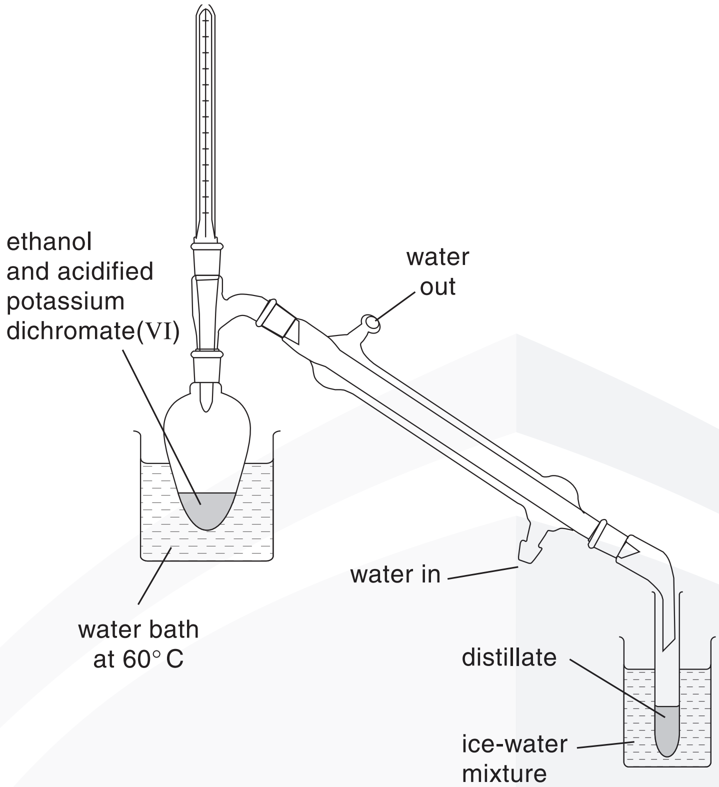
(b) Ethanol has a relatively high boiling point. This can be explained in terms of intermolecular hydrogen bonds.

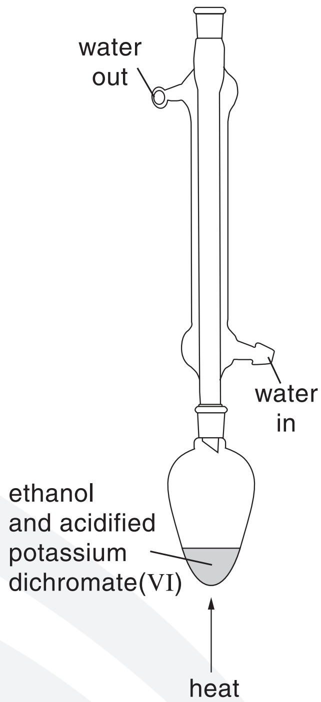
Draw a second molecule of ethanol alongside the one drawn below and show how a hydrogen bond could be formed. Clearly show any relevant dipoles and lone pairs of electrons.



[3]

(c) When ethanol is heated with acidified potassium dichromate(VI) solution, it can be oxidised to form either ethanal, CH_3CHO (Fig. 4.1), or ethanoic acid, CH_3COOH (Fig. 4.2).





The boiling points of ethanol, ethanal and ethanoic acid are given in the table below.

	CH_3CH_2OH	CH_3CHO	CH_3COOH
boiling point / °C	78	21	118

Use this table of boiling points to explain

(i) why the organic product is likely to be ethanal if the apparatus shown in Fig. 4.1 is used,

....

....[2]

(ii) why the organic product is likely to be ethanoic acid if the apparatus shown in Fig. 4.2 is used.

....

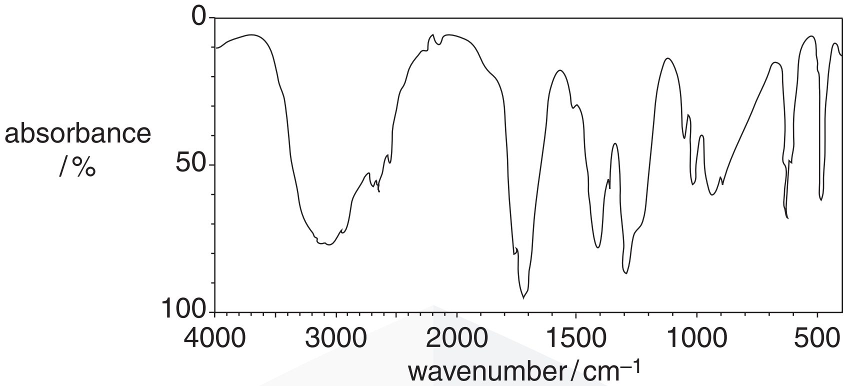
....[2]

(d) Write a balanced equation for the oxidation of ethanol to ethanoic acid. Use [O] to represent the oxidising agent.

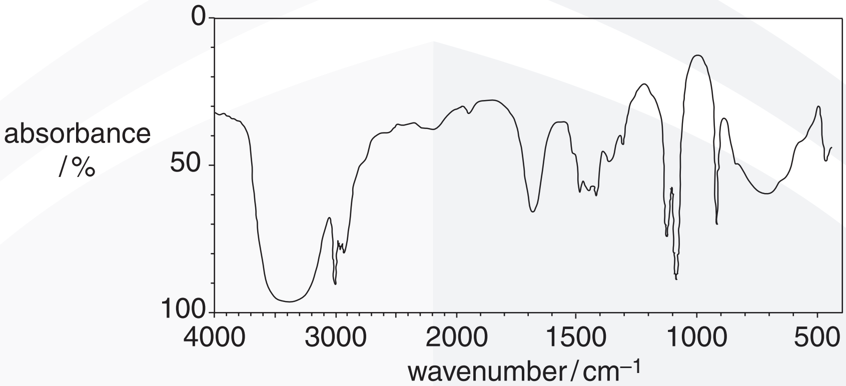
....[2]

(e) The ethanal collected using the apparatus shown in Fig. 4.1 was analysed by infra-red spectroscopy. Use your *Data Sheet* to justify which of the three spectra shown below is most likely to be that of ethanal.

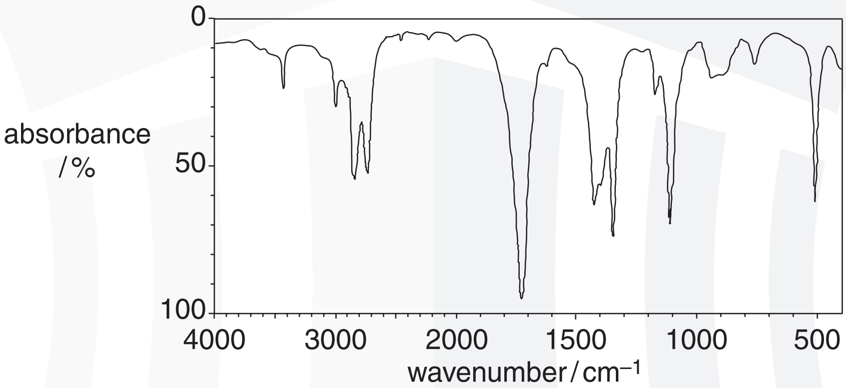
spectrum **A**



spectrum **B**



spectrum **C**



The organic product collected when using the apparatus shown in Fig. 4.1 is most likely

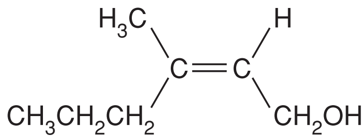
to be that shown by spectrum .... because..

....

....[3]

[Total: 14]

4 Body odour often begins with secretions from glands called apocrine glands, which are most numerous in the armpits. Bacteria, which live in the armpits, use these secretions to produce energy and many different waste products. Scientists have isolated one of these waste products, compound **E**, which is shown below.



compound **E**

(a) Compound **E** contains two functional groups, one of which is a primary alcohol.

(i) **Name** the other functional group and state how you could test for it.

name of the other functional group ....

test ....

observation .... [3]

(ii) Name compound **E**. .... [1]

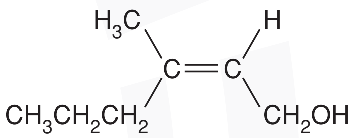
(b) Compound **E** can be oxidised to form a carboxylic acid.

(i) State a suitable oxidising mixture for this reaction.

.... [2]

(ii) Write a balanced equation for this oxidation of compound **E**.

Use [O] to represent the oxidising mixture.



compound **E**

[3]

(iii) Explain how compound **E** and the carboxylic acid could be distinguished by infra-red spectroscopy.

....

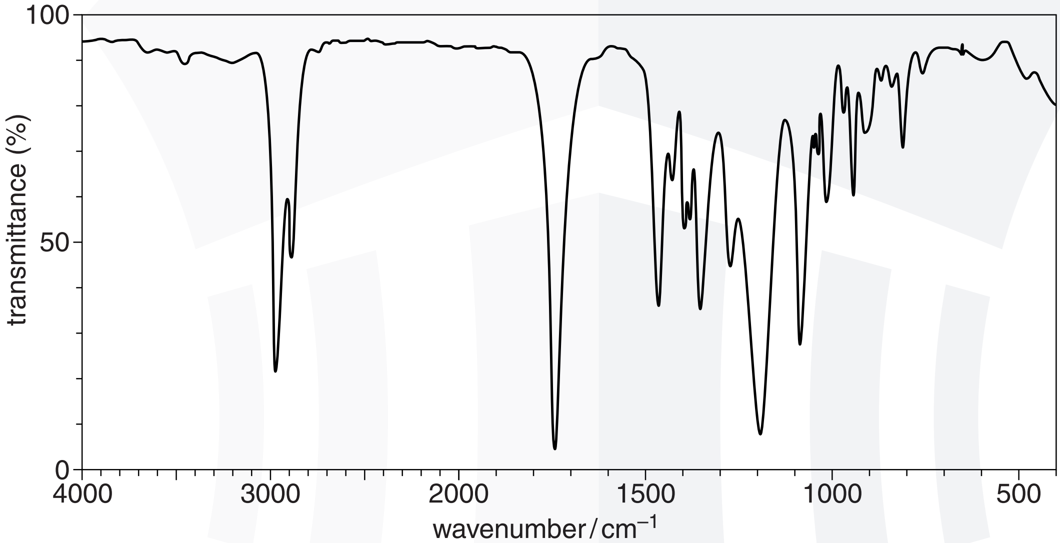
.... [1]

(c) Compound **E** reacts with an excess of HBr to produce a mixture of **two** organic compounds, each with the molecular formula $C_7H_{14}Br_2$.

Identify both organic compounds in the mixture.

[2]

5 A student carries out the oxidation of **ethanol**, which can form two different oxidation products. The infrared spectrum of the compound the student obtained is given below.



Use the spectrum to identify the compound formed.

.... **[1]**

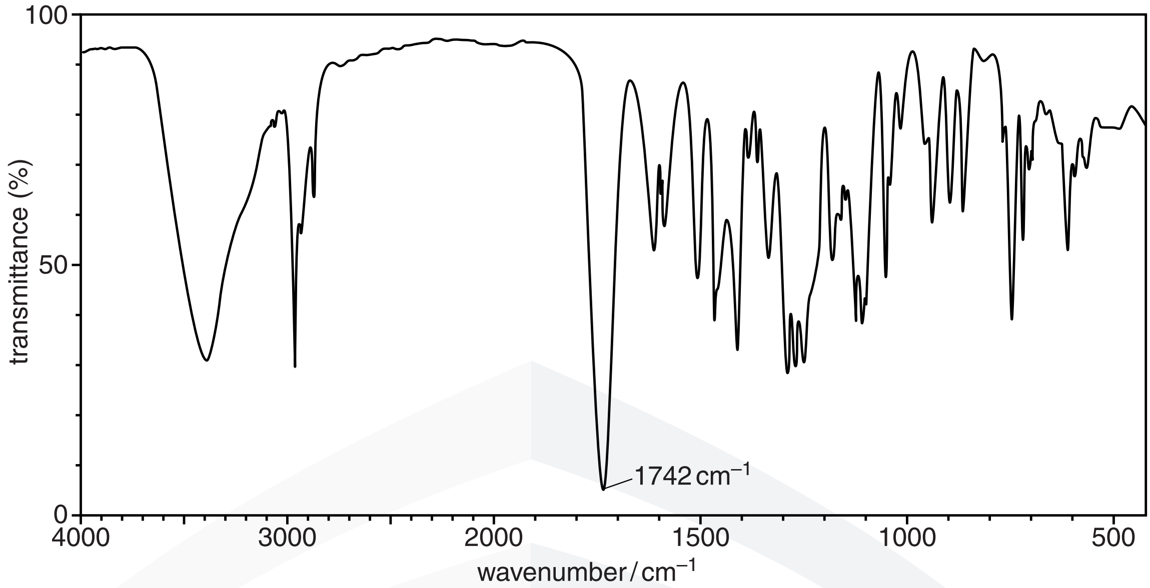
(iii) Explain how the spectrum in **(ii)** shows that no ethanol remains.

....

....

.... **[2]**

6 The infrared spectrum of indicator **B** is shown below.



(i) Use the spectrum to identify **two** functional groups present in indicator **B**.

Give your reasoning.

....

....

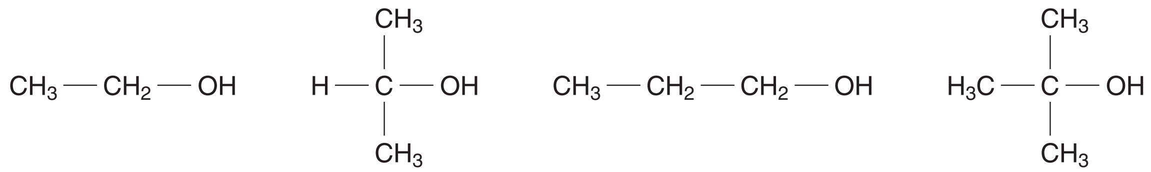
.... **[3]**

7 An analytical chemist was provided with a compound **J** which has an unbranched carbon skeleton. After analysis, the chemist obtained the following results.

type of analysis	**evidence**
infrared spectroscopy	broad absorption at 3350 cm^{-1}
percentage composition by mass	C, 70.59%; H, 13.72%; O, 15.69%

The Mr of J was found to be 102. Use this information to suggest all the possible structures for the unbranched compound J.

8 Alcohols **A**, **B**, **C** and **D** are shown below.



A **B** **C** **D**

(a) Compound **A** is ethanol, a very useful alcohol.

Identify the two main methods used in the industrial production of ethanol.
Write an equation for each method.

method 1 ....

....

equation ....

method 2 ....

....

equation .... **[4]**

(b) A student heated each alcohol, **A**–**D**, with acidified potassium dichromate(VI) as the oxidising agent. With alcohols **A**, **B** and **C**, the colour turned from orange to green.

(i) Identify the organic product and write a balanced equation for the reaction of alcohol **B** with acidified potassium dichromate(VI).

Use [O] to represent the oxidising agent, acidified potassium dichromate(VI).

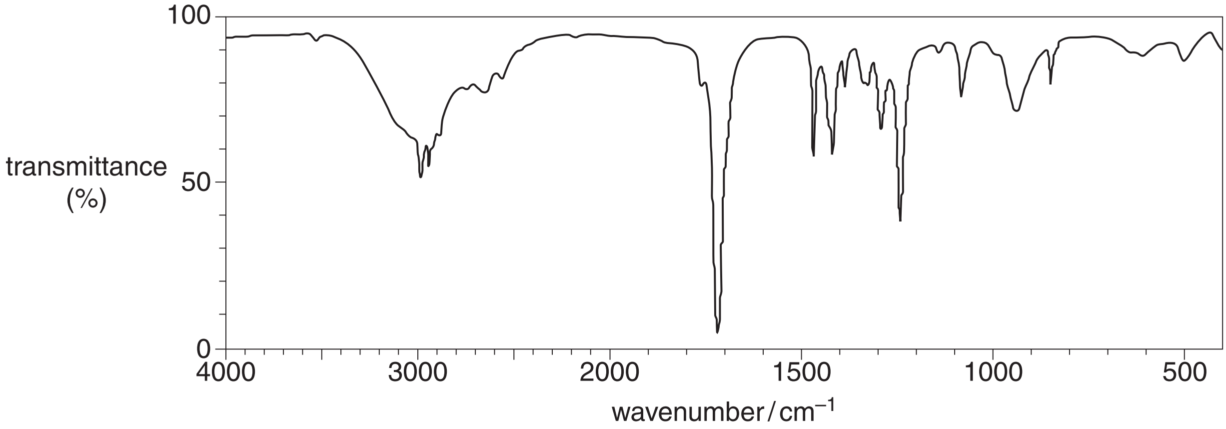
organic product:

balanced equation:

[2]

(ii) The organic product obtained from **C** was analysed by infrared (IR) spectroscopy.

The IR spectrum of the product is shown below.



Use your *Data Sheet* to identify the organic product. Explain your reasoning.

organic product:

reasoning ....

....

.... **[3]**

(c) The student heated alcohol **D** with ethanoic acid in the presence of an acid catalyst. An organic product **E** was formed with a fruity smell.

(i) Name alcohol **D**.

.... **[1]**

(ii) Name the functional group in the organic product **E**.

.... **[1]**

(iii) Draw the structure of the organic product **E**.

[2]

9 Infrared spectroscopy and mass spectrometry are used to identify substances.

(a) Police use breathalysers to detect ethanol in the breath of drivers.

(i) Some modern breathalysers use infrared spectroscopy.

Suggest **two** characteristic infrared absorptions that could be used to identify the presence of ethanol vapour.

1 ……………………. cm^{-1}

2 ……………………. cm^{-1} **[2]**

(ii) Some older breathalysers used the redox reaction between acidified dichromate(VI) ions and ethanol. A colour change was seen which indicated the presence of ethanol in the breath.

What is the colour change that would be seen in this breathalyser if ethanol was present in the breath?

……………………………….. to ……………………………….. **[1]**

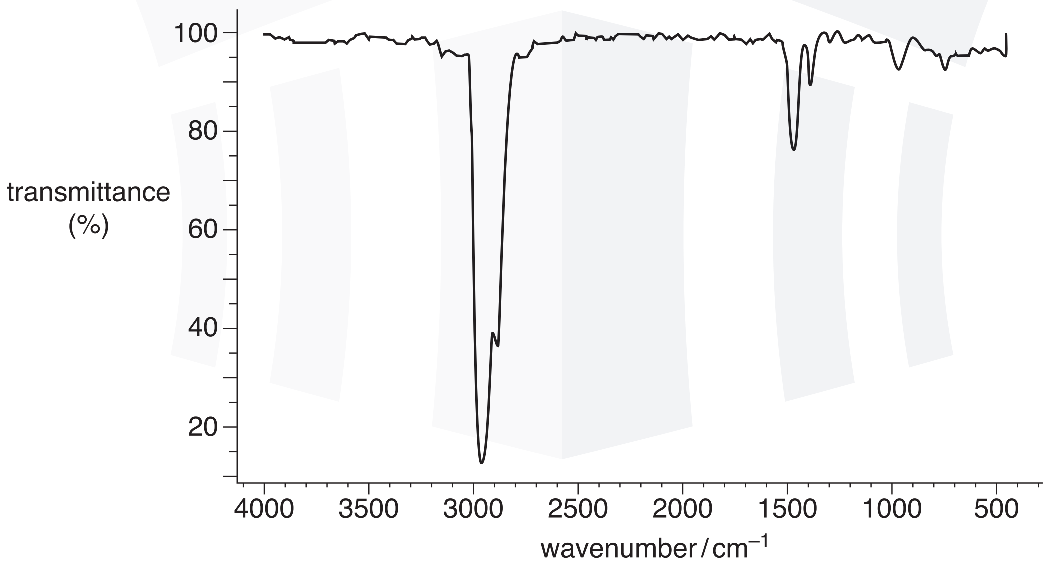
(iii) Give an equation to show the reaction between acidified dichromate(VI) ions and ethanol.

Use [O] to represent the acidified dichromate(VI) ions, the oxidising agent.

.... **[2]**

(b) Infrared spectroscopy and mass spectrometry are used in the search for organic molecules in outer space.

Compound **A** has been analysed by infrared spectroscopy.



(i) A research chemist concludes that compound **A** is a hydrocarbon.

What evidence is there to support this conclusion?

....

....

....

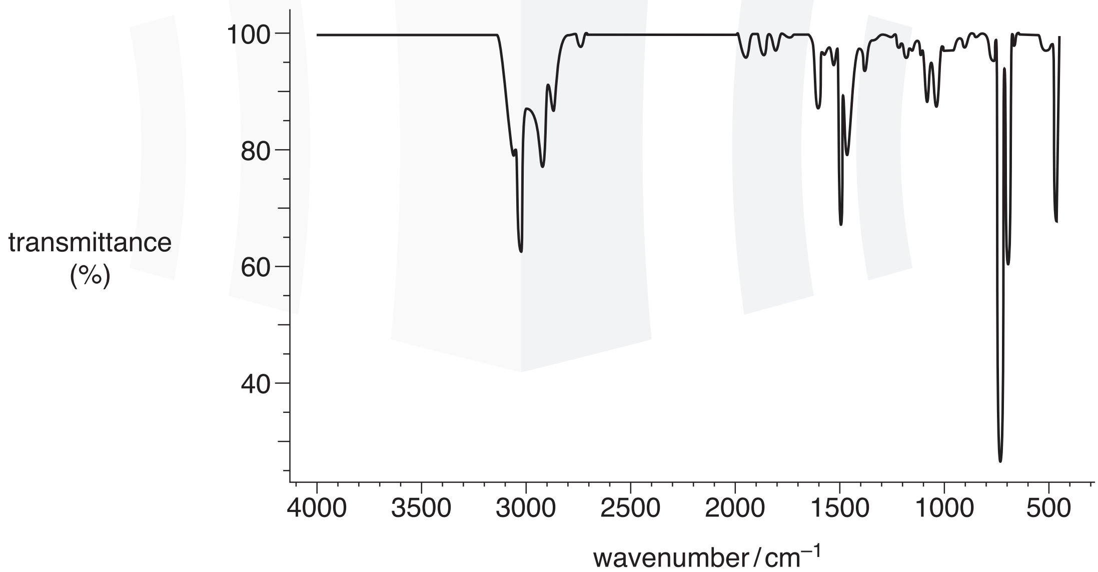
.... **[2]**

10 Compound **G** was extracted from the leaves of a plant. A sample of **G** was analysed by a research chemist. A summary of the chemist's results is shown in the table.

type of analysis	**evidence**
infrared spectroscopy	absorptions at 1080, 1720 and a very broad absorption at 2900 cm^{-1}
percentage composition by mass	C, 26.7%; H, 2.22%; O, 71.1%
volumetric analysis	0.00105 mol of **G** has a mass of 0.0945 g

Use this information to suggest a possible structure for compound **G**.

11 An environmental chemist used infrared spectroscopy to monitor air pollution outside a petrol station. The infrared spectrum below was obtained from one of these pollutants.



What evidence is there in the spectrum that the pollutant may be a hydrocarbon rather than an alcohol or a carbonyl compound?

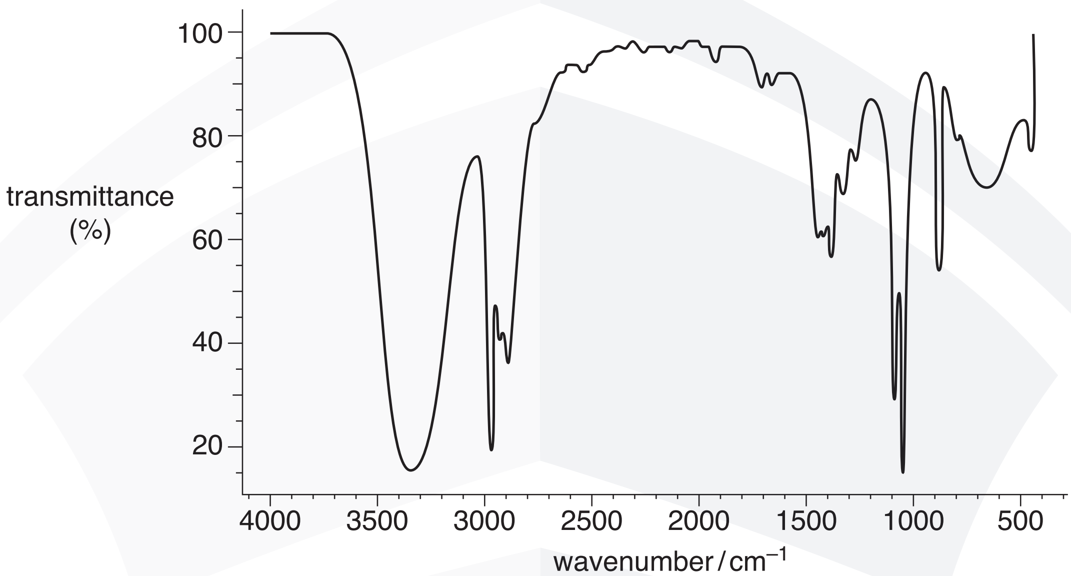
12 Compound **X** and compound **Y** react together to make an ester **Z**. Samples of **X** and **Y** were analysed by a research chemist. A summary of the chemist's results are shown below.

Analysis of compound X

type of analysis	evidence
infrared spectroscopy	absorption at 1720 cm^{-1} and a very broad absorption between 2500 and 3300 cm^{-1}
percentage composition by mass	C, 48.65%; H, 8.11%; O, 43.24%

Analysis of compound Y

infrared spectrum of **Y**



Mr of X = 74 and Mr of Y = 46

Use this information to suggest the identity of compound **X**, compound **Y** and ester **Z**.

13 **(d)** $CH_3(CH_2)_3CO_2H$ is a colourless liquid with an unpleasant odour.

It reacts with methanol in the presence of an acid catalyst to produce an organic product **V**, which has a pleasant fruity smell.

(i) Name **V**.

.... [1]

(ii) A student analysed $CH_3(CH_2)_3CO_2H$, methanol and **V** using infra-red spectroscopy. The spectra were returned to the student without labels.

Identify which of the infra-red spectra, X, Y or Z, corresponds to **V**.

compound	$CH_3(CH_2)_3CO_2H$	methanol	**V**
spectrum			

Explain your answer with reference to relevant features of the **three** spectra in the region above 1500 cm^{-1}.

....

....

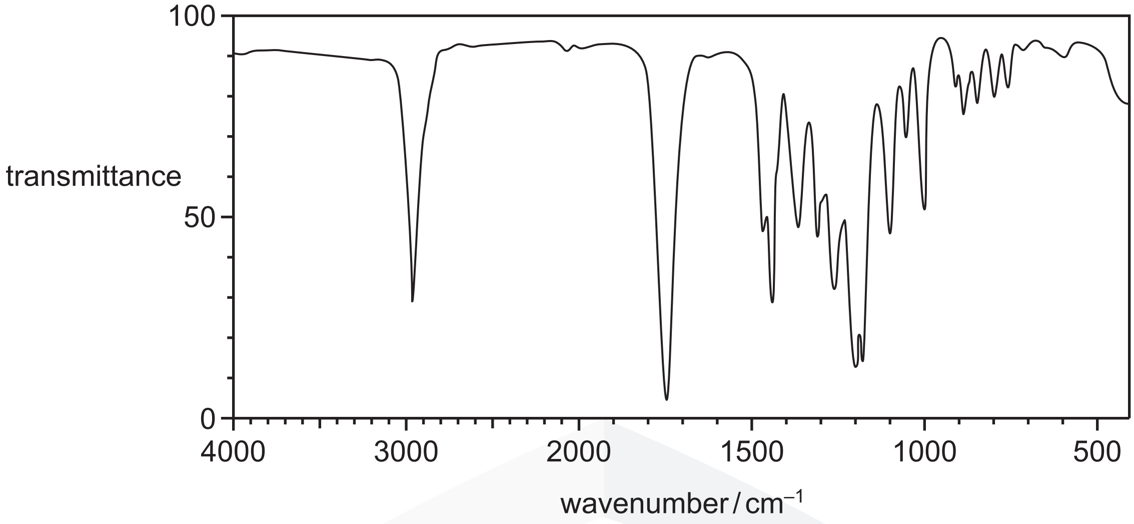
....

....

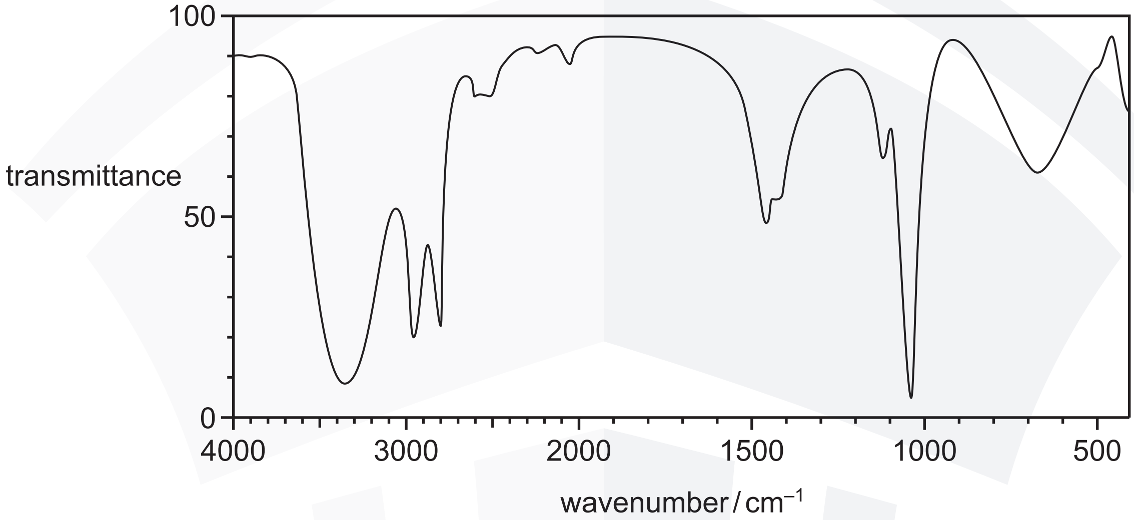
....

.... [4]

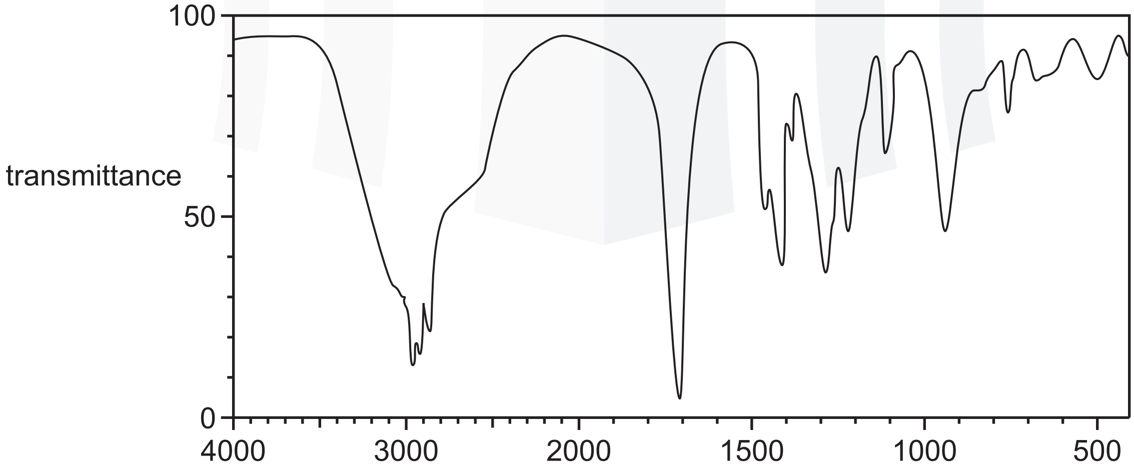
infra-red spectrum X



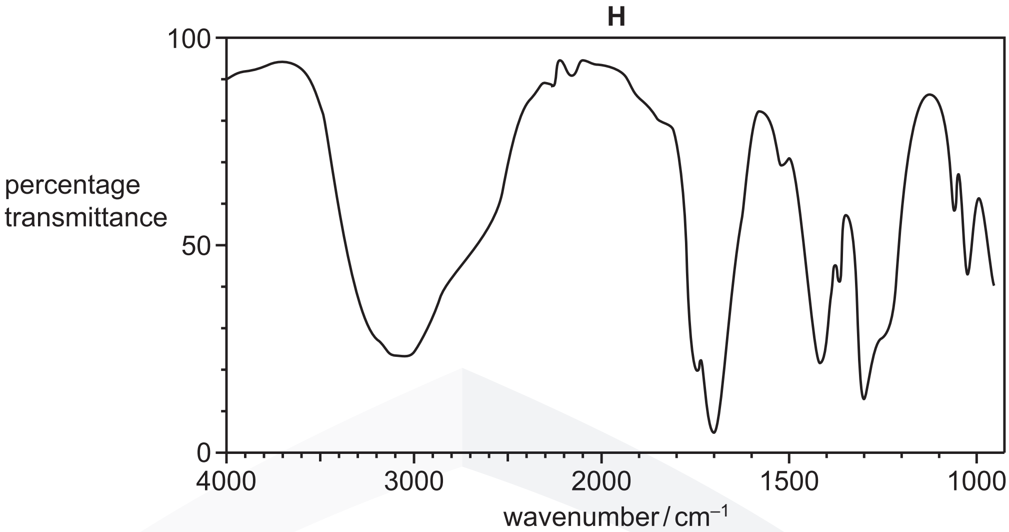
infra-red spectrum Y

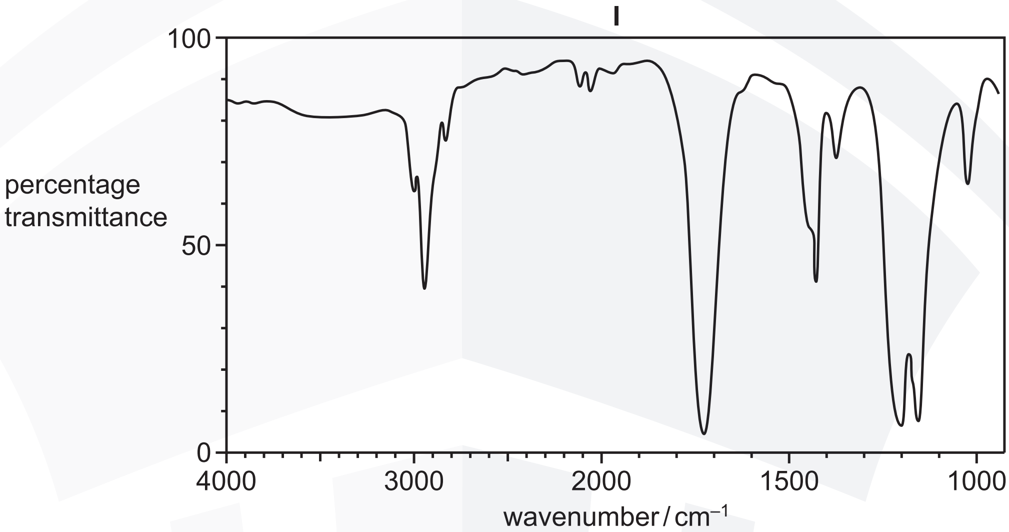


infra-red spectrum Z



14 **(d)** **H** and **I** are isomers with molecular formula $C_2H_4O_2$. The infra-red spectra of isomers **H** and **I** are shown.





(i) Identify the bonds responsible for the principal peaks above 1500 cm^{-1} in each spectrum.

spectrum of **H** ....

....

spectrum of **I** ....

....

[2]

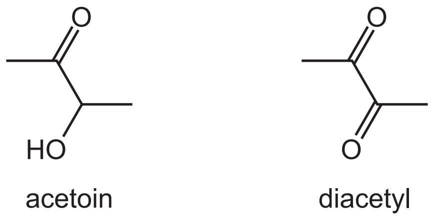
(ii) Name **H** and **I**.

H ....

I ....

[2]

15 Acetoin, $CH_3COCH(OH)CH_3$, and diacetyl, $CH_3COCOCH_3$, are two of the compounds that give butter its characteristic flavour. Their skeletal formulae are shown.



(a) Give the systematic name for acetoin.

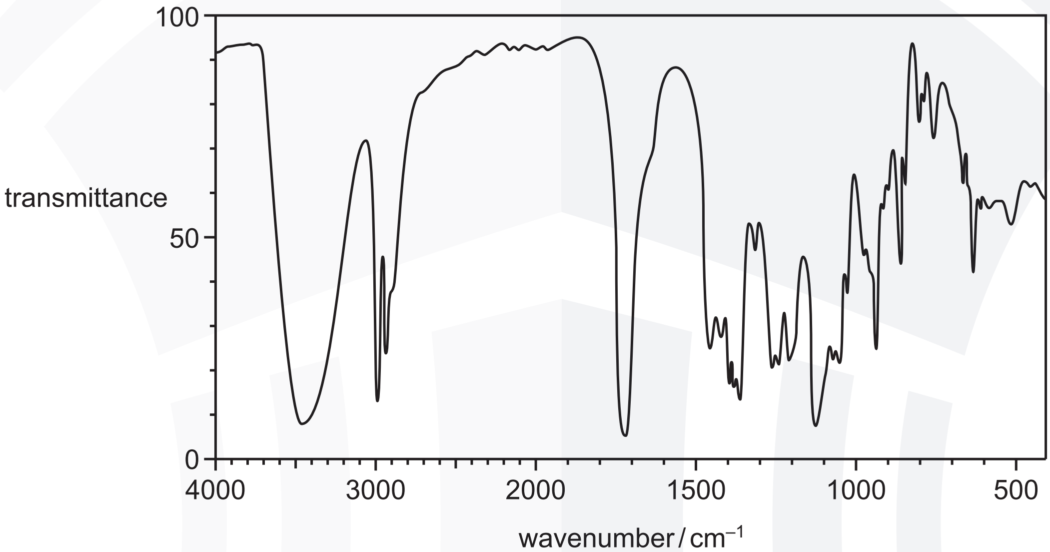
.... [1]

(b) Identify the reagents and conditions necessary for the conversion of acetoin into diacetyl.

....

.... [2]

(c) The infra-red spectrum for acetoin is shown.



(i) Explain the main features of this spectrum, with reference to the peaks with wavenumbers greater than 1500 cm^{-1}.

....

....

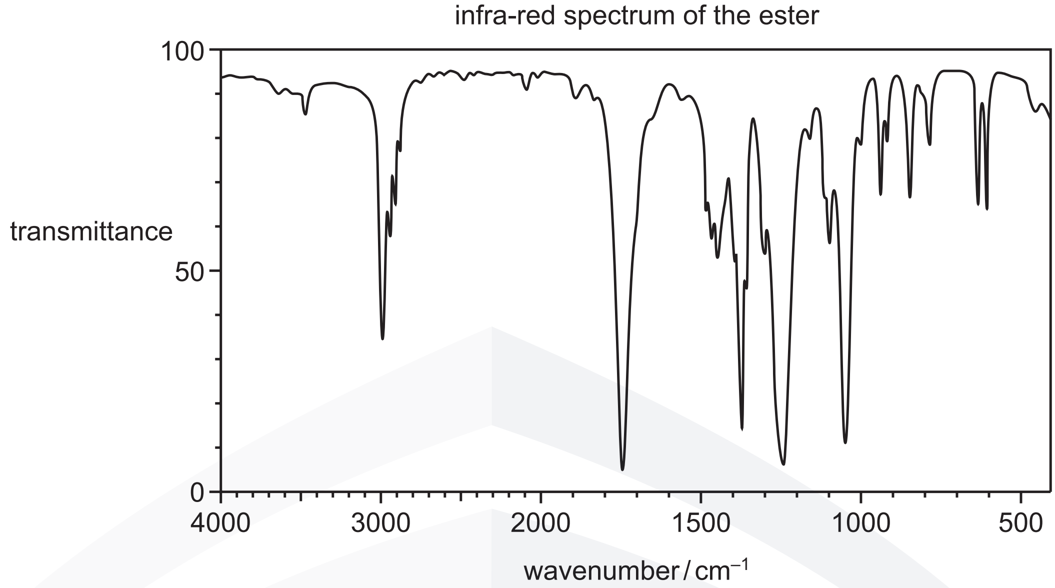
....

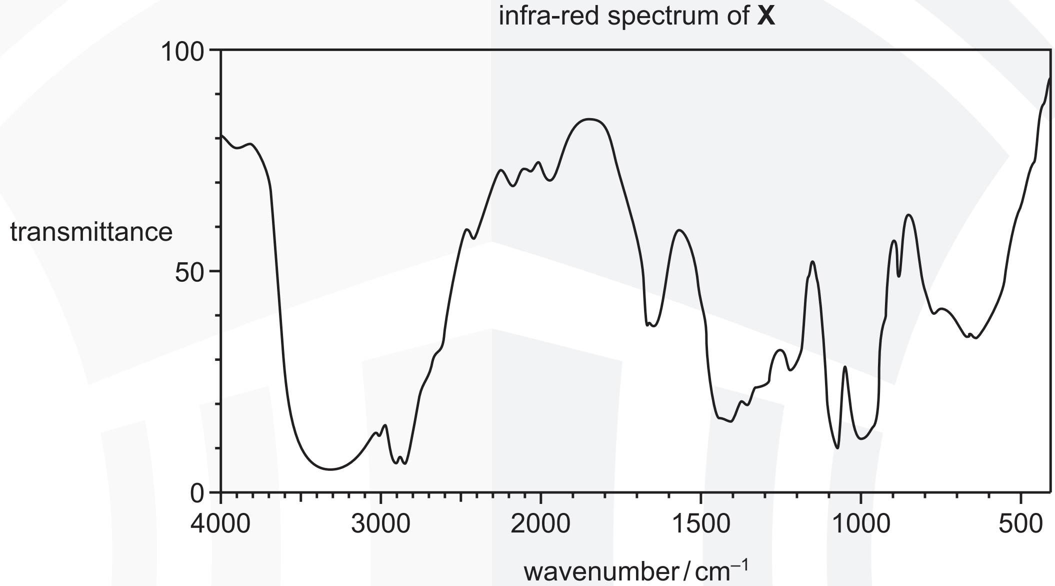
....

.... [3]

16 **(c)** The infra-red spectra of one of the esters and of another isomer, **X**, are shown.

X decolourises bromine water and is not an ester or an acid.





Explain the differences between these two spectra, with particular reference to the peaks with wavenumbers above 1500 cm^{-1}.

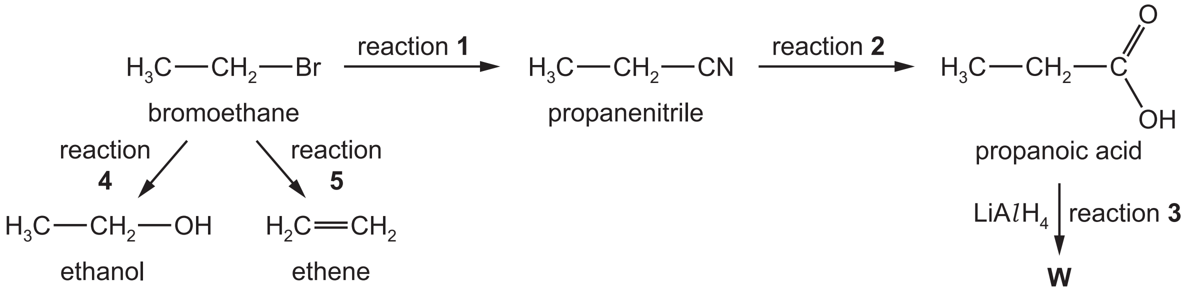
....

....

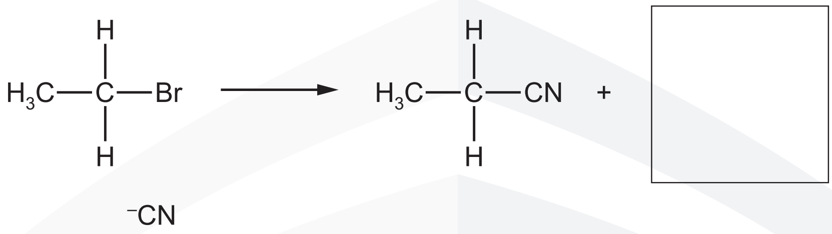
....

.... [3]

17 A reaction sequence is shown.



(a) Complete the diagram to show the mechanism of reaction **1**. Include all necessary charges, partial charges, lone pairs and curly arrows.

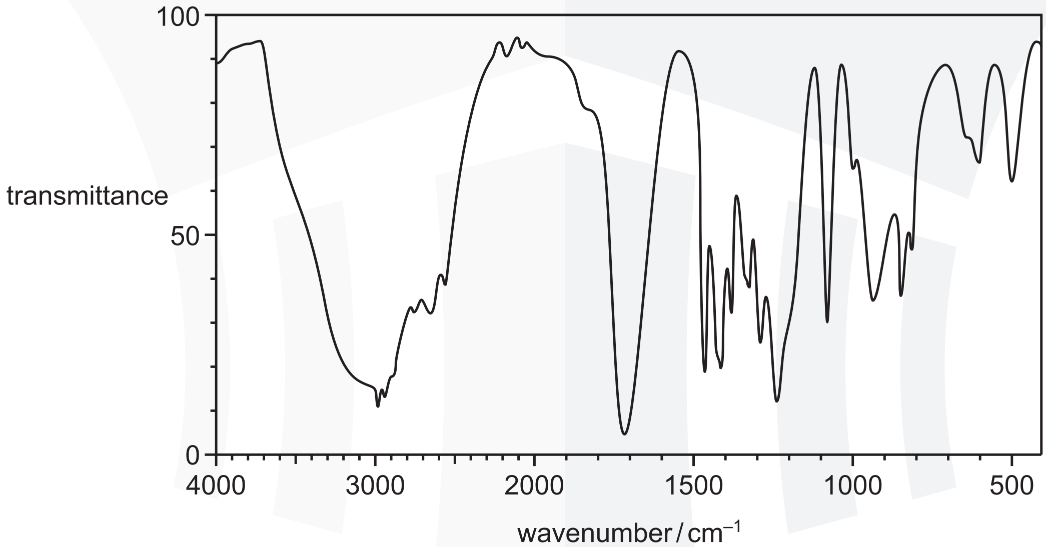


[2]

(b) **(i)** Give the name of the type of reaction involved in reaction **3**.

.... [1]

The infra-red spectrum of the propanoic acid produced by reaction **2** is shown.



(ii) Describe and explain the main difference between the infra-red spectrum of **W** and that of propanoic acid.

....

.... [2]

18 **(ii)** Give the systematic name of compound **P**.

.... [1]

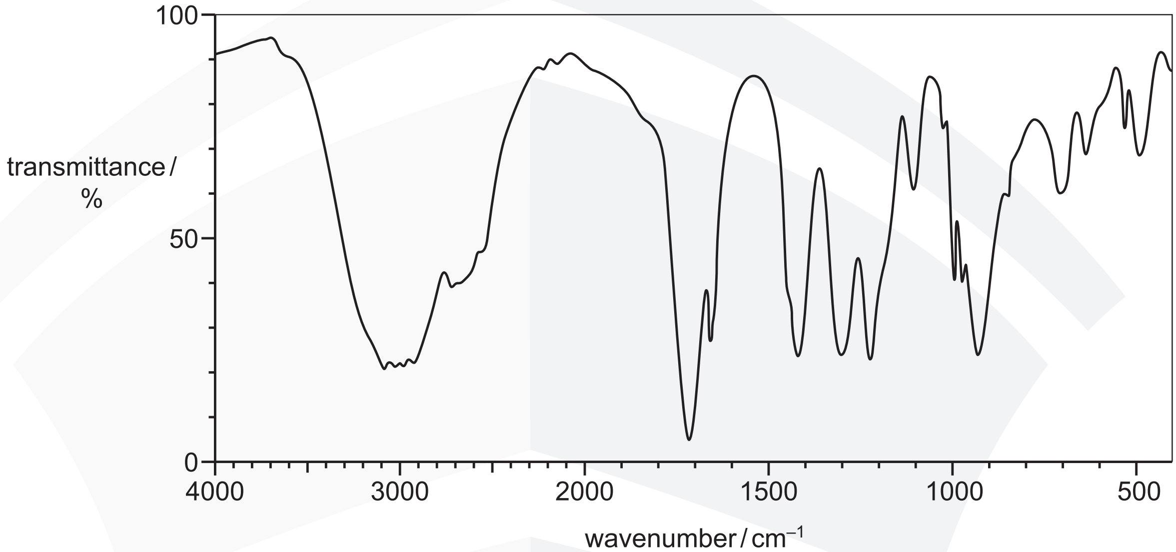
(iii) What would you observe when compound **P** is reacted with 2,4-dinitrophenylhydrazine (2,4-DNPH)?

.... [1]

(b) Compound **U** contains a chiral centre and has the same molecular formula as compound **P**, C_5H_8O.

- Compound **U** readily decolourises a sample of bromine water.
- Compound **U** does not show cis-trans isomerism.
- When compound **U** is heated under reflux in the presence of excess acidified potassium dichromate(VI), the organic product gives the infra-red spectrum shown.

infra-red spectrum of **product**



Use the information given to suggest a structure for compound **U**.
Explain your answer.

[4]

19 **(c)** The product of reaction **2** is cyclohexene.

Cyclohexene can be converted into adipic acid (hexanedioic acid), $HO_2C(CH_2)_4CO_2H$.

(i) Identify the reagents and conditions for the conversion of cyclohexene into adipic acid.

....

.... [2]

(ii) Suggest **three** main differences between the infra-red spectra of cyclohexene and adipic acid.

In each case, identify the bond responsible and its characteristic absorption range (in wavenumbers).

1 ....

....

....

2 ....

....

....

3 ....

....

....

[3]

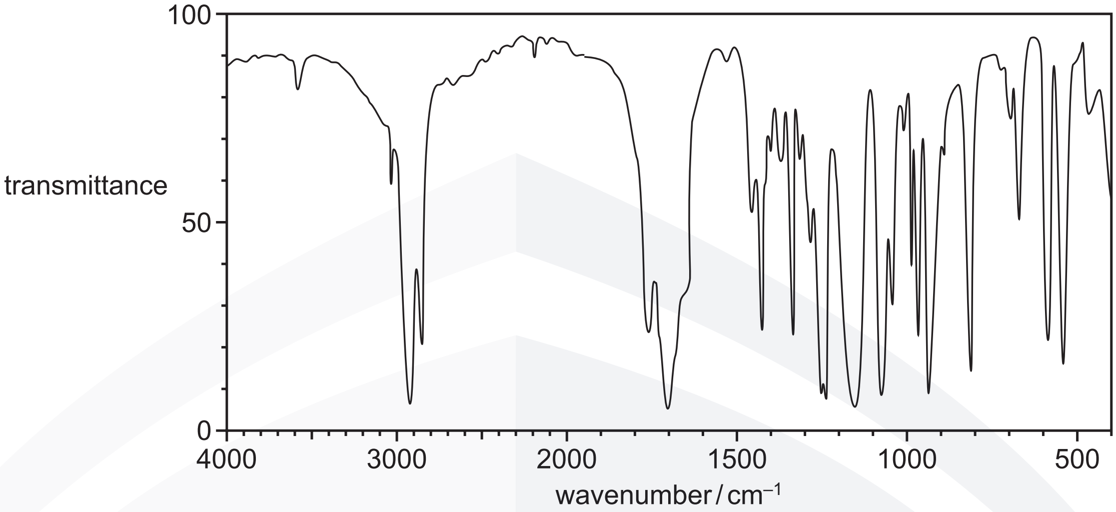
[M‘18 P22 Q4]

20 **(d)** When glycolic acid is heated in the presence of a sulfuric acid catalyst, a new compound, **Y**, $C_4H_4O_4$, is formed.
The equation for the reaction is given.

$$2CH_2(OH)CO_2H \rightarrow C_4H_4O_4 + 2H_2O$$

glycolic acid **Y**

(i) The infra-red spectrum of **Y** is shown.



State how this spectrum differs from an infra-red spectrum of glycolic acid. Explain your answer with particular reference to the peaks within the range 1500 – 4000 cm^{-1}.

....

....

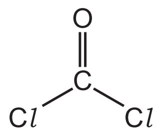
.... [2]

(ii) Suggest a structure for **Y**.

[2]

[N'18 P21 Q4]

21 **(c)** A different trihalomethane, $CHCl_3$, reacts with O_2 to produce carbonyl dichloride. $HCl(g)$ is also released as a product of this reaction.

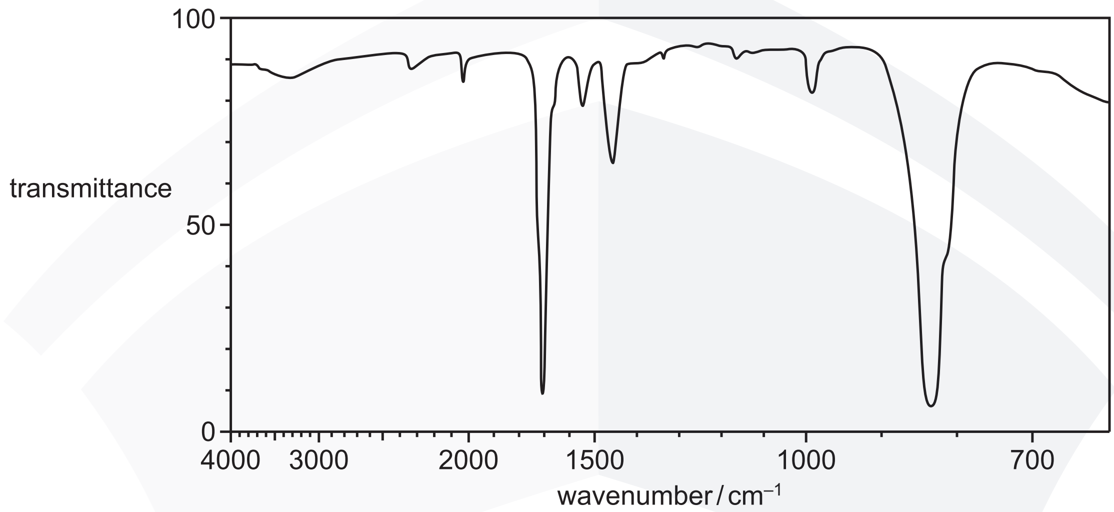


carbonyl dichloride

(i) Write an equation for this reaction of $CHCl_3$ with O_2.

.... [1]

(ii) The conversion of $CHCl_3$ to carbonyl dichloride can be monitored by infra-red spectroscopy. The infra-red spectrum of carbonyl dichloride is shown.



On the infra-red spectrum of carbonyl dichloride identify with an **X** the absorption that would **not** be present in an infra-red spectrum of $CHCl_3$.

Explain your answer.

....

.... [2]

(iii) Suggest another difference between the infra-red spectra of $CHCl_3$ and carbonyl dichloride.

....

.... [1]

[N'18 P22 Q3]

OVERALL ORGANIC WS 1

SECTION A

1 Ethene reacts with aqueous bromine to give two products, CH_2BrCH_2Br and CH_2BrCH_2OH.

Which statement about these products is correct?

A Both products are obtained in this reaction by electrophilic substitution.

B Both products are obtained in this reaction by nucleophilic addition.

C Both products can be hydrolysed to form the same organic compound.

D Both products can form hydrogen bonds with water.

2 A student investigates four different fuels. Each fuel is used separately to raise the temperature of 1 dm^3 of water from 20 °C to 100 °C. Each fuel undergoes complete combustion. All other conditions are the same in each experiment.

Which fuel would produce the **smallest** amount of carbon dioxide in these experiments?

	fuel	energy released per mole of fuel
A	ethanol	1367 kJ mol^{-1}
B	methane	890 kJ mol^{-1}
C	methanol	715 kJ mol^{-1}
D	propane	2220 kJ mol^{-1}

3 One reaction in the Krebs cycle, in which energy is released to the human body, is the conversion of fumaric acid into malic acid.

$$\underset{\text{fumaric acid}}{HO_2CCH{=}CHCO_2H} \rightarrow \underset{\text{malic acid}}{HO_2CCH(OH)CH_2CO_2H}$$

Which reagent(s) could achieve this conversion in the laboratory?

A acidified $KMnO_4(aq)$

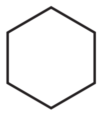
B $Br_2(aq)$ followed by hot $NaOH(aq)$

C $H_2O(l)$ with Pt catalyst

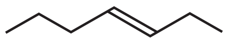
D $H_2O(g)$ with H_2SO_4

4 Which compound has an M_r of 84 and will react with HBr to give a product with an M_r of 164.9?

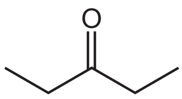
A



B



C



D

5 1,1-dichloropropane reacts with aqueous sodium hydroxide in a series of steps to give propanal.

$$CH_3CH_2CHCl_2 \xrightarrow{NaOH(aq)} CH_3CH_2CHO$$

Which term describes the first step of this reaction?

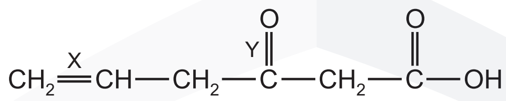
A addition

B elimination

C oxidation

D substitution

Compound Q contains three double bonds per molecule.

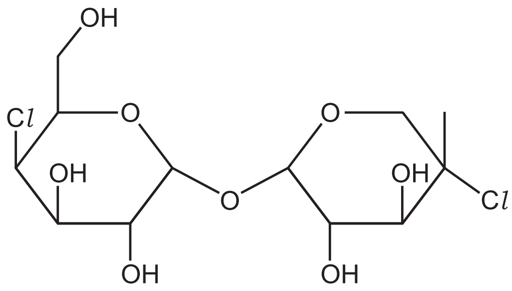


Q

Which bond, X or Y, will be ruptured by hot, concentrated acidified $KMnO_4$ and how many lone pairs of electrons are present in one molecule of Q?

	bond ruptured by hot, concentrated acidified $KMnO_4$	number of lone pairs
A	X	5
B	X	6
C	Y	5
D	Y	6

6 Compound X has been investigated for use as an artificial sweetener.



X

The two C–Cl bonds can be hydrolysed by hot NaOH(aq). The C-O-C bonds **cannot** be hydrolysed by hot NaOH(aq).

What are the numbers of specified types of –OH groups before and after hydrolysing the two C–Cl bonds?

	before hydrolysis	after hydrolysis		
	secondary	primary	secondary	tertiary
A	0	1	2	4
B	0	2	1	4
C	4	1	5	1
D	4	2	4	1

7 Which pair of reagents will take part in a redox reaction?

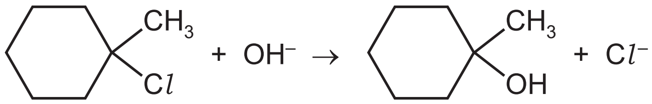
A CH_3CHCH_2 + Br_2

B $CH_3CH_2CH_2OH$ + concentrated H_3PO_4

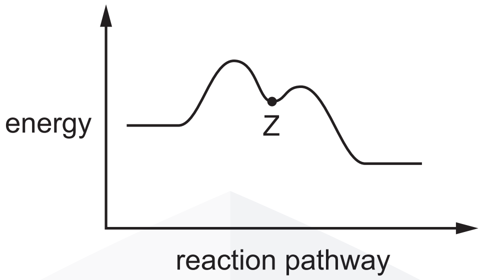
C CH_3COCH_3 + HCN

D $HCO_2C_2H_5$ + dilute H_2SO_4

8 1-chloro-1-methylcyclohexane is hydrolysed by heating with NaOH(aq).



The reaction pathway is shown.



One carbon atom in 1-chloro-1-methylcyclohexane is bonded to three other carbon atoms.

What is the charge on this carbon atom at point Z?

A $\delta+$ **B** $+$ **C** $\delta-$ **D** $-$

9 Which organic compound would **not** give **either** a yellow precipitate when treated with alkaline aqueous iodine **or** an orange precipitate when treated with 2,4-dinitrophenylhydrazine reagent?

A propanal

B propan-1-ol

C propan-2-ol

D propanone

10 In which reaction is the organic compound oxidised?

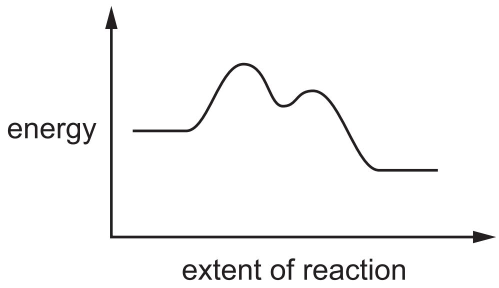
A $CH_3CH_2CH_2CHO$ + Tollens' reagent

B $CH_3CH_2CH_2CHO$ + $LiAlH_4$

C $CH_3CH_2CH_2OH$ + concentrated H_3PO_4

D $CH_3CO_2C_2H_5$ + dilute H_2SO_4

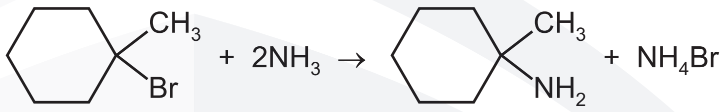
11 A reaction pathway diagram is shown.

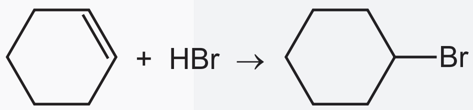


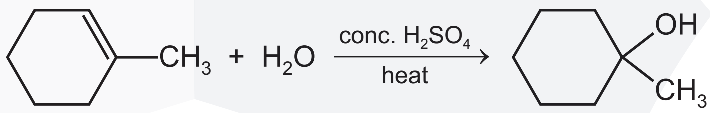
The four reactions that follow are all exothermic.

Which reaction would **not** have such a pathway?

A $CH_3I + NaCN \rightarrow CH_3CN + NaI$

B 

C 

D 

12 Many, but not all, organic reactions need to be heated before a reaction occurs.

Which reaction occurs quickly at room temperature, 20 °C?

A $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

B $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$

C $CH_3CH_2OH \rightarrow C_2H_4 + H_2O$

D $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

[N'17 P13 Q22]

13 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

[N'17 P13 Q25]

14 Which reagent could detect the presence of alcohol in a mixture consisting mainly of alkanes and alkenes?

A Na

B Br_2 (in CCl_4)

C $KMnO_4$(aq)

D 2,4-dinitrophenylhydrazine

[J'18 P11 Q24]

15 Ethanal, CH_3CHO, is used to make product R in a three-stage synthesis.

$$CH_3CHO \xrightarrow[\text{/NaCN}]{\text{HCN}} \text{product P} \xrightarrow[\text{reflux}]{H_2SO_4\text{(aq),}} \text{product Q} \xrightarrow[\text{(a few drops)}]{\text{conc. } H_2SO_4} \text{product R}$$

Two molecules of Q react to give one molecule of R plus two molecules of water.

R has two ester functional groups in each molecule. R does not react with sodium.

What is the empirical formula of R?

A CHO **B** $C_3H_4O_2$ **C** $C_3H_5O_2$ **D** $C_6H_{10}O_5$

[J'18 P12 Q28]

16 Which compound can be used to make propanoic acid by treatment with a single reagent?

A $CH_2{=}CHCH_2CH_3$

B $CH_3CH_2CH_2CN$

C $CH_3CH(OH)CN$

D $CH_3CH(OH)CH_3$

[N'18 P12 Q29]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Several steps are involved in the synthesis of 2-hydroxypropanoic acid from ethanol.

$$C_2H_5OH \rightarrow \rightarrow \rightarrow CH_3CH(OH)CO_2H$$

Which statements concerning this synthesis are correct?

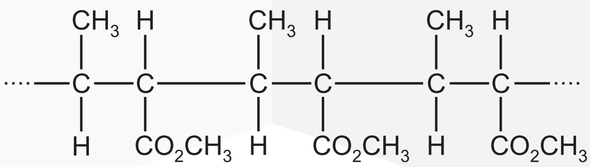
1 The chain length can be increased during a step involving reaction between HCN and an aldehyde.

2 The carboxyl group can be made by hydrolysis of a nitrile by boiling with NaOH(aq) and then acidifying.

3 The ethanol should be first oxidised by heating it under reflux with an excess of acidified potassium dichromate(VI).

[S'16 P11 Q39]

2 The diagram shows the structure of an addition polymer, X.



Which reagents react with polymer X?

1 aqueous sulfuric acid

2 aqueous sodium hydroxide

3 sodium

[S'16 P11 Q40]

3 Propanal reacts with hydrogen cyanide to form 2-hydroxybutanenitrile. A suitable catalyst for this reaction is sodium cyanide.

$$CH_3CH_2CHO + HCN \xrightarrow{NaCN} CH_3CH_2CH(OH)CN$$

Which statements about the reaction of propanal with hydrogen cyanide are correct?

1 The sodium cyanide provides a stronger nucleophile than HCN.

2 The reaction can be classified as nucleophilic substitution.

3 The hydrogen cyanide molecule attacks the propanal molecule to form an intermediate ion.

[S'16 P12 Q39]

4 Which syntheses will be successful?

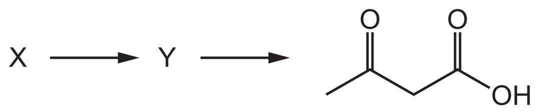
1 $CH_3CH_2CH_3$ from $CH_3CH{=}CH_2$ + $LiAlH_4$

2 $CH_3CH(OH)CH_3$ from CH_3COCH_3 + $NaBH_4$

3 $CH_3CH_2CH_2OH$ from CH_3CH_2CHO + $NaBH_4$

[S'16 P13 Q38]

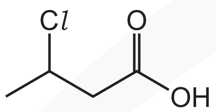
5 3-oxobutanoic acid can be synthesised in a two-step process.

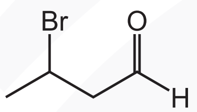


3-oxobutanoic acid

What could be the structure of X?

1 

2 

3 

[N'18 P11 Q39]

6 The ester $C_2H_5CO_2CH_2CH_2CH_3$ can be made in a school or college laboratory by a sequence of four reactions or fewer using compound Z as the **only** organic material.

What might be the identity of compound Z?

1 $CH_3CH_2CH_2OH$

2 CH_3CH_2CHO

3 CH_3COCH_3

[J'18 P12 Q40]

OVERALL ORGANIC WS 2

1 **P**, **Q** and **R** are structural isomers with the molecular formula C_4H_8.

All three compounds readily decolourise bromine in the dark.

P and **Q** do not exhibit stereoisomerism but **R** exists as a pair of geometrical (cis-trans) isomers.

All three compounds react with hot concentrated, acidified potassium manganate(VII) to produce a variety of products as shown in the table.

compound	products
P	CO_2 and **S** (C_3H_6O)
Q	CO_2 and $CH_3CH_2CO_2H$
R	CH_3CO_2H only

S reacts with 2,4-dinitrophenylhydrazine reagent, 2,4-DNPH, to form an orange crystalline product but does not react with Fehling's reagent.

(a) Give the structural formulae of **P**, **Q**, **R** and **S**.

P .... **Q** ....

R .... **S** ....
[4]

(b) **(i)** Explain what is meant by the term *stereoisomerism*.

....

....

.... [2]

(ii) Draw the **displayed** formulae of the geometrical isomers of **R** and name them both.

name .... name .... [2]

(c) State a reagent that could be used for the reduction of **S** and **name** the organic product of this reduction.

reagent .... product .... [2]

[W'14 P21 Q3]

2 **P**, **Q**, **R** and **S** are structural isomers with the molecular formula C_5H_{10}.

All four compounds readily decolourise bromine in the dark.

P, **R** and **S** do not exhibit stereoisomerism but **Q** exists as a pair of geometrical (cis-trans) isomers.

All four compounds react with hot concentrated, acidified potassium manganate(VII) to produce a variety of products as shown in the table.

compound	products
P	CO_2 and $CH_3CH_2CH_2CO_2H$
Q	CH_3CO_2H and $CH_3CH_2CO_2H$
R	CO_2 and **T** (C_4H_8O)
S	CH_3CO_2H and $(CH_3)_2CO$

T reacts with 2,4-dinitrophenylhydrazine reagent, 2,4-DNPH, to form an orange crystalline product but does not react with Fehling's reagent.

(a) Give the structural formulae of **P**, **Q**, **R**, **S** and **T**.

P .... **Q** ....

R .... **S** ....

T .... [5]

(b) **(i)** Explain what is meant by the term *stereoisomerism*.

....

....

.... [2]

(ii) Draw the **displayed** formulae of the geometrical isomers of **Q** and name them both.

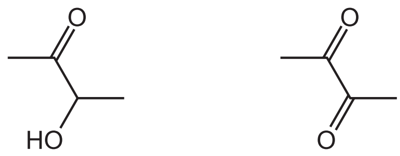
name .... name .... [2]

(c) Name the organic product of the reaction of **T** with sodium borohydride, $NaBH_4$.

.... [1]

[W'14 P23 Q3]

3 Acetoin, $CH_3COCH(OH)CH_3$, and diacetyl, $CH_3COCOCH_3$, are two of the compounds that give butter its characteristic flavour. Their skeletal formulae are shown.



acetoin diacetyl

(a) Give the systematic name for acetoin.

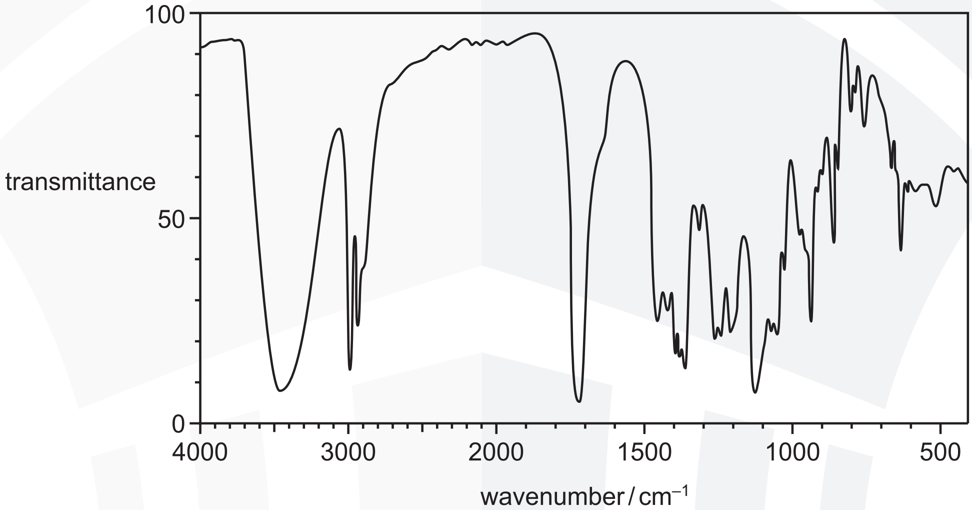
.... [1]

(b) Identify the reagents and conditions necessary for the conversion of acetoin into diacetyl.

....

.... [2]

(c) The infra-red spectrum for acetoin is shown.



(i) Explain the main features of this spectrum, with reference to the peaks with wavenumbers greater than 1500 cm^{-1}.

....

....

....

....

.... [3]

(ii) State and explain how the infra-red spectrum for diacetyl would differ from the infra-red spectrum for acetoin.

....

....

.... [2]

(d) If a sample of acetoin is reacted with concentrated sulfuric acid, a single product is formed that does **not** exhibit stereoisomerism.

However, if a sample of acetoin is reacted with HBr, a mixture of a pair of stereoisomers is produced.

(i) Give the structural formula of the product of the reaction of acetoin with concentrated sulfuric acid.

.... [1]

(ii) Explain why the product in **(i)** does **not** exhibit stereoisomerism.

....

....

.... [2]

(iii) Explain why the product of reaction of acetoin with HBr **does** exhibit stereoisomerism.

....

....

.... [1]

(iv) Draw the two stereoisomers from **(iii)** using the conventional representation.

[2]

[S'16 P23 Q4]

4 Isomerism occurs in many organic compounds. The two main forms of isomerism are structural isomerism and stereoisomerism. Many organic compounds that occur naturally have molecules that can show stereoisomerism, that is *cis-trans* or optical isomerism.

(a) **(i)** Explain what is meant by *structural isomerism*.

....

.... [1]

(ii) State **two** different features of molecules that can give rise to **stereoisomerism**.

....

.... [2]

Unripe fruit often contains polycarboxylic acids, that is acids with more than one carboxylic acid group in their molecule. One such acid is citric acid shown below.

$$\begin{array}{c} OH \\ | \\ HO_2CCH_2CCH_2CO_2H \\ | \\ CO_2H \end{array}$$

(b) **(i)** Does citric acid show optical isomerism? Explain your answer.

....

.... [1]

(ii) Dehydration of citric acid produces $HO_2CCH{=}C(CO_2H)CH_2CO_2H$. Draw the structure of the repeat unit formed by addition polymerisation of this molecule.

[2]

A second polycarboxylic acid present in unripe fruit is a colourless crystalline solid, **W**, which has the following composition by mass: C, 35.8%; H, 4.5%; O, 59.7%.

(c) Show by calculation that the empirical formula of **W** is $C_4H_6O_5$.

[2]

A sample of **W** (M_r = 134) of mass 1.97 g was dissolved in water and the resulting solution titrated with 1.00 mol dm^{-3} NaOH.
29.4 cm^3 of 1.00 mol dm^{-3} NaOH were required for complete neutralisation.

(d) Use these data to deduce the number of carboxylic acid groups present in one molecule of **W**.

[3]

[S'10 P21 Q5]

5 This question is about molecules with molecular formula C_4H_8.

(a) Give the structures of a pair of **positional** isomers with the formula C_4H_8.

[1]

(b) Give the structures of a pair of **chain** isomers with the formula C_4H_8, that do **not** exhibit stereoisomerism.

[1]

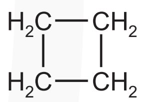
(c) Give the structures and full names of a pair of **stereoisomers** with the formula C_4H_8.

....

[2]

(d) The structure of a molecule, **A**, of formula C_4H_8 is shown.

Draw a functional group isomer of molecule **A** in box **B**. Explain how molecules **A** and **B** could be distinguished by a chemical test.



A **B**

....

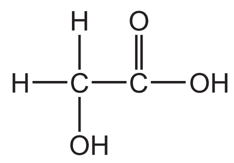
....

.... [3]

[Total: 7]

[S'16 P21 Q4]

6 The structure of glycolic acid is shown.



glycolic acid

(a) Complete the table to show what you would **observe** when an aqueous solution of glycolic acid is added separately to each of the reagents. If a reaction occurs, state the functional group of glycolic acid that is responsible for the reaction.

reagent	observation with glycolic acid	does a reaction occur? ✓/✗	functional group
$Na_2CO_3(aq)$			
2,4-DNPH			
acidified $Cr_2O_7^{2-}$			

[4]

(b) Two reaction sequences to make glycolic acid are shown.

sequence A $\quad HCHO \xrightarrow[\text{reaction } \mathbf{1}]{\text{HCN and NaCN}} \mathbf{X} \xrightarrow[\text{reaction } \mathbf{2}]{} CH_2(OH)CO_2H$

sequence B $\quad CH_3CO_2H \xrightarrow[\text{reaction } \mathbf{3}]{Br_2} CH_2BrCO_2H \xrightarrow[\text{reaction } \mathbf{4}]{} CH_2(OH)CO_2H$

(i) Draw the structure of **X**.

[1]

(ii) Name the reagent for reaction **2**.

.... [1]

(iii) Name the mechanism of reaction **3**.

.... [1]

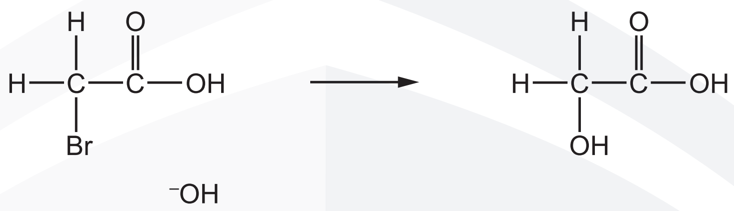
(iv) Suggest the essential condition for reaction **3**.

.... [1]

(v) Reaction **4** occurs via an S_N2 mechanism.

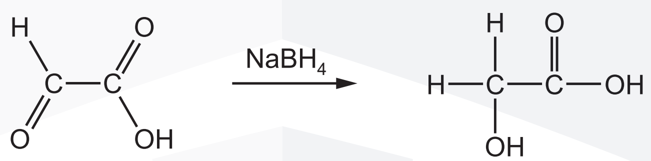
Complete the diagram for the mechanism for reaction **4**.

Include all relevant charges, partial charges, curly arrows and lone pairs.



[2]

(c) Glycolic acid can also be made by reacting glyoxylic acid with $NaBH_4$.



glyoxylic acid   glycolic acid

(i) State the role of $NaBH_4$ in this reaction.

.... [1]

(ii) Write an equation for this reaction using molecular formulae.
Use [H] to represent $NaBH_4$.

.... [2]

[N'18 P21 Q4]

OVERALL ORGANIC WS 3

SECTION A

1 A compound **X** has all of the following properties:

it is a liquid at room temperature and atmospheric pressure;

it does not mix completely with water;

it does not decolorise acidified potassium manganate(VII).

What could **X** be?

A ethane

B ethanoic acid

C ethanol

D ethyl ethanoate

2 A compound **X** has all of the properties below.

- It is a liquid at 25 °C.
- It mixes completely with water.
- It reacts with aqueous sodium hydroxide.

What could **X** be?

A ethanoic acid

B ethanol

C ethene

D ethyl ethanoate

3 Which compound

- is unaffected by hot alkaline potassium manganate(VII);
- gives hydrogen when treated with sodium?

A $(CH_3)_2CHCOCH_3$

B $(CH_3)_3COH$

C $CH_3CH_2CH(OH)CH_3$

D $CH_3CO_2CH(CH_3)_2$

4 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.

$$CH_3CH_2OH \xrightarrow[-\,H_2]{\text{Cu catalyst}} CH_3CHO \xrightarrow[+\,CH_3CH_2OH]{\text{Cu catalyst}} CH_3CH(OH)OCH_2CH_3$$

$$CH_3CH(OH)OCH_2CH_3 \xrightarrow[-\,H_2]{\text{Cu catalyst}} CH_3CO_2CH_2CH_3$$

Which process is involved at some stage in this reaction sequence?

A disproportionation

B electrophilic addition

C nucleophilic addition

D reduction

5 In which class of compound, in its general formula, is the ratio of hydrogen atoms to carbon atoms the highest?

A alcohols

B aldehydes

C carboxylic acids

D halogenoalkanes

6 Which reagent could be used to convert $CH_3CO_2CH_3$ into $ClCH_2CO_2CH_3$?

A concentrated hydrochloric acid at 100 °C

B phosphorus pentachloride at room temperature

C sulphur dichloride oxide (thionyl chloride, $SOCl_2$) at 50 °C

D chlorine in bright sunlight at 100 °C

7 Which compound would undergo nucleophilic addition?

A ethene, C_2H_4

B bromoethane, C_2H_5Br

C ethanal, CH_3CHO

D ethane, C_2H_6

8 Which compound gives an organic product with a lower boiling point when it is heated under reflux with an excess of acidified potassium dichromate(VI)?

A 2-methylbutan-1-ol

B 2-methylbutan-2-ol

C pentan-1-ol

D pentan-2-ol

9 Ethyl phenylethanoate, $C_6H_5CH_2CO_2C_2H_5$, gives a characteristic flowery aroma to honey.

Which sequence of reagents, with heating in each case, leads to the preparation of $C_6H_5CH_2CO_2C_2H_5$ from $C_6H_5CH_2Br$?

A $C_6H_5CH_2Br \xrightarrow{\text{NaOH(aq)}} \xrightarrow{C_2H_5COCl}$

B $C_6H_5CH_2Br \xrightarrow{\text{NaOH(aq)}} \xrightarrow{C_2H_5CO_2H,\ \text{conc. } H_2SO_4}$

C $C_6H_5CH_2Br \xrightarrow{\text{NaCN(alcoholic)}} \xrightarrow{H^+(aq)} \xrightarrow{C_2H_5OH,\ \text{conc. } H_2SO_4}$

D $C_6H_5CH_2Br \xrightarrow{\text{NaOH(aq)}} \xrightarrow{\text{conc. } MnO_4^-,\ H^+(aq)} \xrightarrow{C_2H_5OH,\ \text{conc. } H_2SO_4}$

10 A compound **Y** has the following properties.

- It is a liquid at room temperature and atmospheric pressure.
- It does not mix completely with water.
- It does not decolourise acidified potassium manganate(VII).

What could **Y** be?

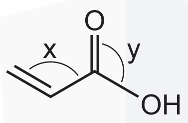
A ethane

B ethanoic acid

C ethanol

D ethyl ethanoate

11 Acrylic acid is produced from propene, a gaseous product of oil refineries.



acrylic acid

Which statement about acrylic acid is **not** correct?

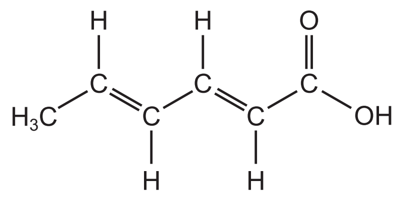
A Both bond angles x and y are approximately 120°.

B It decolourises aqueous bromine.

C It gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

D It reacts with an alcohol to give an ester.

12 Sorbic acid is used as a food preservative because it kills fungi and moulds.



sorbic acid

Sorbic acid will react with

- hydrogen in the presence of a nickel catalyst,
- bromine in an organic solvent.

How many moles of hydrogen and of bromine will be incorporated into one mole of sorbic acid by these reactions?

	moles of hydrogen	moles of bromine
A	2	2
B	2	$2\frac{1}{2}$
C	3	2
D	3	$2\frac{1}{2}$

13 In the general formula of which class of compound, is the ratio of hydrogen atoms to carbon atoms the highest?

A alcohols

B aldehydes

C carboxylic acids

D halogenoalkanes

14 Energy is released in the human body by the oxidation of glucose in a complex sequence of reactions. Part of this sequence is the Krebs cycle. One reaction in the Krebs cycle is the conversion of fumaric acid into malic acid.

$$HO_2CCH{=}CHCO_2H \rightarrow HO_2CCH(OH)CH_2CO_2H$$

fumaric acid malic acid

Which reagents could achieve this transformation in the laboratory?

A acidified $KMnO_4$

B Br_2(aq) followed by hot NaOH(aq)

C H_2O with Pt catalyst

D steam with H_2SO_4

15 Fumaric acid can be converted into oxaloacetic acid by a two-step process involving the intermediate **Q**.

$$\underset{\text{fumaric acid}}{HO_2CCH{=}CHCO_2H} \xrightarrow{\text{step 1}} \mathbf{Q} \xrightarrow{\text{step 2}} \underset{\text{oxaloacetic acid}}{HO_2CCOCH_2CO_2H}$$

Each of these steps can be achieved in the laboratory by a single reagent.

What could be the intermediate **Q** and the reagent for step 2?

	Q	reagent for step 2
A	$HO_2CCHBrCH_2CO_2H$	warm acidified $KMnO_4$
B	$HO_2CCHBrCH(OH)CO_2H$	warm NaOH(aq)
C	$HO_2CCH(OH)CH_2CO_2H$	Fehling's solution
D	$HO_2CCH(OH)CH_2CO_2H$	warm acidified $K_2Cr_2O_7$

16 Complete combustion of compound X gives carbon dioxide and water only. A sample of X is mixed with aqueous potassium(V) dichromate and boiled under reflux for one hour. The mixture is then distilled and the only organic substance present is collected.

The organic substance collected reacts with sodium to give hydrogen, but does not react with 2,4-dinitrophenylhydrazine reagent and does not react with ethanol in the presence of concentrated sulfuric acid to give an ester.

What can be deduced from this information?

A X is a carboxylic acid.

B X is a ketone.

C X is an alcohol.

D X is an alkane.

17 A compound **Y** has the following properties.

- It is a liquid at room temperature and atmospheric pressure.
- It does not mix completely with water.
- It does not give steamy fumes with PCl_5.

What could **Y** be?

A ethane

B ethanoic acid

C ethanol

D ethyl ethanoate

18 But-2-ene-1,4-diol is converted in two steps through an intermediate **X** into ketobutanedioic acid.

$$\underset{\text{but-2-ene-1,4-diol}}{HOCH_2CH{=}CHCH_2OH} \xrightarrow[\text{step 1}]{} \mathbf{X} \xrightarrow[\text{step 2}]{\text{hot acidified } KMnO_4} \underset{\text{ketobutanedioic acid}}{HO_2CCOCH_2CO_2H}$$

What could be the reagent for step 1 and the intermediate **X**?

	reagent for step 1	**X**
A	cold acidified $KMnO_4$	$HOCH_2CH_2CH(OH)CH_2OH$
B	hot acidified $KMnO_4$	$OHCCH(OH)CH_2CHO$
C	steam and concentrated H_2SO_4	$HOCH_2CH(OH)CH_2CH_2OH$
D	warm acidified $K_2Cr_2O_7$	$HO_2CCH{=}CHCO_2H$

19 Complete combustion of compound **X** produces carbon dioxide and water only. **X** produces steamy fumes with PCl_5. **X** does not give any visible product with 2,4-dinitrophenylhydrazine reagent.

What can be deduced with certainty from this information?

A **X** is a carboxylic acid.

B **X** is a hydrocarbon.

C **X** is an alcohol.

D **X** is not an aldehyde.

20 Which pair of reactions *could* have the same common intermediate?

W $CH_3CH_2CH_3 \rightarrow$ intermediate $\rightarrow (CH_3)_2CHCN$

X $CH_3CH(OH)CH_3 \rightarrow$ intermediate $\rightarrow (CH_3)_2C(OH)CN$

Y $CH_3CH{=}CH_2 \rightarrow$ intermediate $\rightarrow CH_3CH(OH)CH_3$

Z $CH_3CO_2CH_2CH_2CH_3 \rightarrow$ intermediate $\rightarrow CH_3CH_2CH_2Br$

A **W** and **X** **B** **W** and **Y** **C** **X** and **Z** **D** **Y** and **Z**

21 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.

$$CH_3CH_2OH \xrightarrow[-2[H]]{\text{Cu catalyst}} CH_3CHO \xrightarrow[+\,CH_3CH_2OH]{\text{Cu catalyst}} CH_3CH(OH)OCH_2CH_3$$

$$CH_3CH(OH)OCH_2CH_3 \xrightarrow[-2[H]]{\text{Cu catalyst}} CH_3CO_2CH_2CH_3$$

Which process is involved at some stage in this reaction sequence?

A electrophilic addition

B nucleophilic addition

C nucleophilic substitution

D reduction

22 In which reaction is the organic compound oxidised?

A CH_3CH_2OH + concentrated H_3PO_4

B $CH_3CH_2CH_2CHO$ + Tollens' reagent

C CH_3COCH_3 + 2,4-dinitrophenylhydrazine reagent

D CH_3CN + dilute H_2SO_4

23 Many organic reactions need to be heated before reaction occurs, but some do not require heating.

Which reaction occurs quickly at room temperature?

A $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

B $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$

C $CH_3CH_2OH \rightarrow C_2H_4 + H_2O$

D $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

OVERALL ORGANIC WS 4

1 Organic chemistry is the chemistry of carbon compounds. The types of organic reactions that you have studied are listed below.

addition	elimination	hydrolysis
oxidation	reduction	substitution

Addition and substitution reactions are further described as follows.

electrophilic	nucleophilic	free radical

Complete the table below.

Fill in the central column by using **only** the types of reaction given in the lists above. Use **both** lists when appropriate.

In the right hand column give the name(s) or formula(e) of the reagent(s) you would use to carry out the reaction given.

organic reaction	type of reaction	reagent(s)
$CH_3CHO \rightarrow CH_3CH(OH)CN$		
$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CHBrCH_3$		
$CH_3CH(OH)CH_3 \rightarrow CH_3CH{=}CH_2$		
$CH_3CH{=}CH_2 \rightarrow CH_3CH(OH)CH_2OH$		

[Total: 10]

[W'08 Q4]

2 The African weaver ant aggressively defends its territory by giving off alarm pheromones when threatened. Four organic compounds have been identified in the mandibular glands of these ants, and are related to this behaviour.

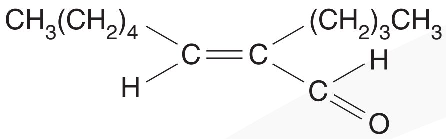
The structures of these molecules are as follows.

$CH_3CH_2CH_2CH_2CH_2CH_2OH$

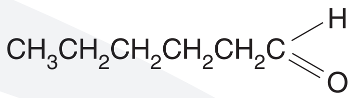
A

$CH_3(CH_2)_7C(=O)CH_2CH_3$

B



C



D

Outline a series of chemical tests, with the observations, to distinguish each compound from the others.

Positive identification is required for each compound, and this may require the use of more than one test.

A ....

....

....

B ....

....

....

C ....

....

....

D ....

....

....

[Total : 8]

[W'01 Q6]

3 Commercial paint and varnish removers contain a mixture of dichloromethane, CH_2Cl_2, and methanol, CH_3OH.

(a) What would be observed when the following reactions are carried out?
In each case, give the name or formula of the reaction product which is responsible for the observation you have made.

(i) CH_2Cl_2 is reacted with NaOH(aq) and $AgNO_3$(aq) and the mixture left to stand.

observation ....

product responsible ....

(ii) CH_3OH is mixed with PCl_5.

observation ....

product responsible ....

(iii) CH_3OH is reacted with sodium.

observation ....

product responsible ....
[6]

(b) When CH_2Cl_2 is heated under reflux with an excess of NaOH(aq), a compound **W** is formed.

W has the following composition by mass: C, 40.0%; H, 6.7%; O, 53.3%.

Use this information and the *Data Booklet* to show that the empirical formula of **W** is CH_2O.

[2]

(c) Compounds with the empirical formula CH_2O can have the molecular formula $C_2H_4O_2$.

Two possible structural formulae for compounds with molecular formula $C_2H_4O_2$ are HCO_2CH_3 and $H_2C{=}C(OH)_2$.

In the boxes below, draw displayed formulae for **three further** structural isomers with the molecular formula $C_2H_4O_2$.

Do **not** attempt to draw any structures containing rings or O–O bonds.

X	**Y**	**Z**

[3]

(d) Identify which of your compounds, **X**, **Y**, or **Z**, will react with the following reagents.

In **each** case, state what you would observe.

(i) solid $NaHCO_3$

compound ....

observation ....

(ii) Tollens' reagent

compound ....

observation ....

[4]

(e) **One** of the three compounds, **X**, **Y**, or **Z**, shows stereoisomerism.

Draw displayed, labelled structures of the stereoisomers of this compound.

[2]

[S'07 Q4]

4 Ethanoic acid, CH_3CO_2H, is formed as vinegar by the bacterial oxidation of ethanol present in wine and other solutions.

$$CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$$

Ethanoic acid can also be formed in the laboratory by the oxidation of ethanol.

(a) **(i)** What oxidising agent is used for this laboratory reaction?

....

(ii) What colour change would be observed?

from .... to ....

[2]

When ethanoic acid is prepared in this way in the laboratory, the reagents are heated under reflux for some time before the ethanoic acid is separated.

(b) **(i)** Why is the reaction carried out by heating under reflux?

....

....

(ii) What would be the main organic compound formed if, instead of heating under reflux, the reagents were heated together and the products immediately distilled off?

....

[2]

(c) Ethanoic acid is manufactured from methanol, CH_3OH, by reacting it with carbon monoxide in the presence of a catalyst containing rhodium metal and iodide ions.

$$CH_3OH + CO \rightarrow CH_3CO_2H$$

The reaction proceeds in a number of stages.

(i) One stage in this process is the reaction of methanol with hydrogen iodide.

What organic compound is formed in this reaction?

....

(ii) A later stage involves the conversion of an intermediate compound.

$$\begin{array}{ccc} CH_3C{=}O & \rightarrow & CH_3C{=}O \\ | & & | \\ I & & OH \end{array}$$

What type of reaction is this?

....

[2]

(d) Methanol can be converted into ethanoic acid in the laboratory in a three-stage process.

$$CH_3OH \xrightarrow{\text{step I}} CH_3I \xrightarrow{\text{step II}} CH_3CN \xrightarrow{\text{step III}} CH_3CO_2H$$

What reagent(s) and conditions are used in each step of the conversion?

step I

reagent(s) ....

conditions ....

step II

reagent(s) ....

conditions ....

step III

reagent(s) ....

conditions ....

[6]

[W'07 Q5]

5 An organic ester, **B**, has the empirical formula C_2H_4O. An experiment by a student in a college gave a value of 87.5 for M_r of **B**.

(a) What is the molecular formula of **B**?

.... [1]

(b) In the boxes below, draw the structural formulae of **four** isomers of **B** that are esters.

W	**X**
Y	**Z**

[4]

The student hydrolysed his sample of **B** by heating with aqueous mineral acid and then separating the alcohol, **C**, that was formed. He heated the alcohol **C** under reflux with acidified dichromate(VI) ions and collected the product **D**.

A sample of **D** gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent. A second sample of **D** gave no reaction with Tollens' reagent.

(c) **(i)** What group does the reaction with 2,4-dinitrophenylhydrazine reagent show to be present in **D**?

....

(ii) What does the result of the test with Tollens' reagent show about **D**?

....

(iii) What is the structural formula of the alcohol **C**?

(iv) Which of your esters, **W**, **X**, **Y**, or **Z** has the same structure as that of the ester **B**?

.... [4]

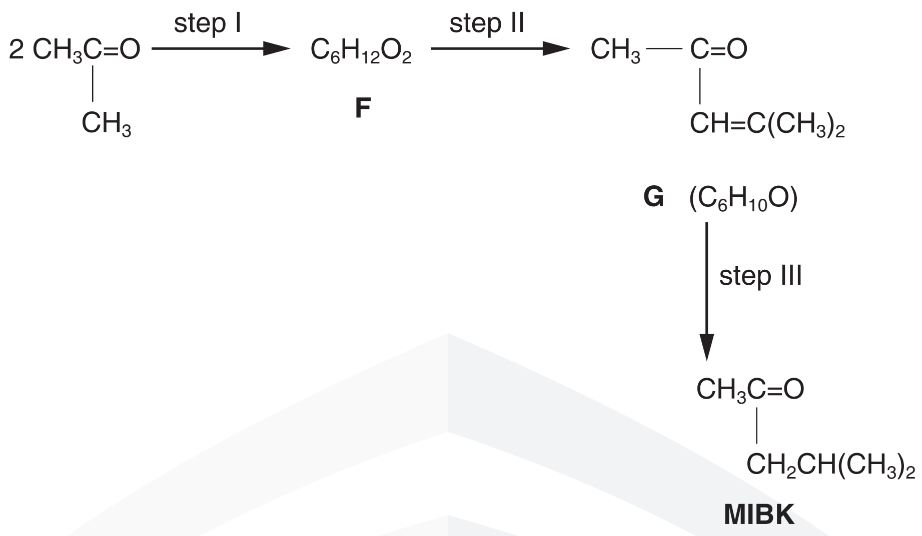
(d) Which, if any of your esters, **W**, **X**, **Y**, or **Z** is chiral? Explain your answer.

....

.... [1]

[W'08 Q5]

6 Propanone, CH_3COCH_3, an important industrial solvent, can be converted into another industrially important solvent, MIBK, by the following sequence.



(a) When **F** is formed in step **I** no other compound is produced.
Suggest a structural formula for **F**, which contains one –OH group.

[1]

(b) Compound **G** has two functional groups.

Name **one** functional group present in **G** and show how you would identify it. Put your answers in the table.

functional group in **G**	reagent used in test	what would be seen

[3]

(c) **G** is formed from **F** in step II.
Use your answers to **(a)** and **(b)** to suggest

(i) what type of reaction occurs in step II,

....

(ii) a reagent for step II.

.... [2]

(d) The production of MIBK from **G** in step **III** involves the hydrogenation of the >C=C< group and is carried out catalytically. A mixture of compounds is formed because the >C=O group is also reduced.

What reagent(s) and solvent are normally used in a laboratory to reduce a >C=O group without reducing a >C=C< group present in the same molecule?

reagent(s) ....

solvent .... [2]

G has a number of structural isomers.

(e) Draw the displayed formulae of a pair of structural isomers of **G** which contain the CH_3CO– group and which exhibit *cis-trans* isomerism.

Label each structure *cis* or *trans* and give your reasoning.

[3]

[S'09 P21 Q5]

7 Three organic compounds, **G**, **H**, and **J**, each have the empirical formula CH_2O.
The numbers of carbon atoms in their molecules are shown in the table.

compound	number of C atoms
G	1
H	2
J	3

In **H** and in **J**, the carbon atoms are bonded directly to one another.

G gives a silver mirror when treated with Tollens' reagent.

H and **J** each give a brisk effervescence with Na_2CO_3(aq).

(a) Identify **G**.

.... [1]

(b) **(i)** What functional group is common to both **H** and **J**?

....

(ii) Identify **H**.

....

(iii) Identify **J**.

.... [3]

(c) When **J** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **K**, gives a red-orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Draw the structural formula of **K**, the compound formed from **J**.

[1]

(d) When **J** is warmed with concentrated sulfuric acid, a cyclic compound, **L**, is formed. **L** has the molecular formula $C_6H_8O_4$.

(i) Suggest a displayed formula for **L**.

(ii) What type of reaction occurs when **L** is formed from **J**?

.... [2]

[W'09 P21 Q5]

8 Isomerism occurs in many organic compounds. The two main forms of isomerism are structural isomerism and stereoisomerism. Many organic compounds that occur naturally have molecules that can show stereoisomerism, that is *cis-trans* or optical isomerism.

(a) (i) Explain what is meant by *structural isomerism*.

....

....

(ii) State **two** different features of molecules that can give rise to **stereoisomerism**.

....

....

[3]

Unripe fruit often contains polycarboxylic acids, that is acids with more than one carboxylic acid group in their molecule.

One of these acids is commonly known as tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$.

(b) Give the structural formula of the organic compound produced when tartaric acid is reacted with an excess of $NaHCO_3$.

[1]

Another acid present in unripe fruit is citric acid,

$$\begin{array}{c} OH \\ | \\ HO_2CCH_2CCH_2CO_2H \\ | \\ CO_2H \end{array}$$

(c) Does citric acid show optical isomerism? Explain your answer.

....

....

.... [1]

A third polycarboxylic acid present in unripe fruit is a colourless crystalline solid, **W**, which has the following composition by mass: C, 35.8%; H, 4.5%; O, 59.7%.

(d) **(i)** Show by calculation that the empirical formula of **W** is $C_4H_6O_5$.

(ii) The M_r of **W** is 134. Use this value to determine the molecular formula of **W**.

[3]

A sample of **W** of mass 1.97 g was dissolved in water and the resulting solution titrated with 1.00 mol dm^{-3} NaOH. 29.4 cm^3 were required for complete neutralisation.

(e) **(i)** Use these data to deduce the number of carboxylic acid groups present in one molecule of **W**.

(ii) Suggest the displayed formula of **W**.

[5]

[S'10 P21 Q5]

9 **(c)** Compound **F**, is an ester with the molecular formula $C_4H_8O_2$.

F is one of four isomers, **S**, **T**, **U**, and **V**, that are all esters.

In the boxes below, the structural formula of **S** is given.

Draw the structural formulae of the other **three** isomers of **F** that are esters.

$HCO_2CH(CH_3)_2$			
S	**T**	**U**	**V**

[3]

(d) When the ester **F** is hydrolysed, an alcohol **G** is produced.

(i) What reagent can be used to hydrolyse an ester to an alcohol?

....

(ii) What other type of organic compound is produced at the same time?

....

[2]

(e) On mild oxidation, the alcohol **G** gives a compound **H** which forms a silver mirror with Tollens' reagent.

(i) What functional group does the reaction with Tollens' reagent show to be present in compound **H**? Give the name of this group.

....

(ii) What type of alcohol is **G**?

....

(iii) What could be the structural formula of the alcohol **G**?

[3]

(f) **(i)** Which of the four isomers, **S**, **T**, **U**, or **V**, could **not** be **F**?

....

(ii) Explain your answer.

....

....
[2]

[S'10 P22 Q4]

10 Organic reactions involve substances which may be

atoms, *molecules*, *ions* or *free radicals*.

We also apply the terms

electrophilic, *nucleophilic*, *addition*, *elimination* and *substitution*

to organic reactions.

Consider the following reactions.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	reaction 1
$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$	reaction 2
$CH_3I + OH^- \rightarrow CH_3OH + I^-$	reaction 3
$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$	reaction 4

(a) Using the terms mentioned above, state as clearly as you can the nature of each of the following reactions.

reaction 1 ....

reaction 2 .... [2]

(b) By considering the four reactions above, suggest a formula for **each** of the following substances.
In **each** case, state which reaction you are considering.

(i) **one** substance that is an addition product

reaction.......   addition product

(ii) **one** substance that is a leaving group

reaction.......   leaving group

(iii) **one** substance that behaves as an electrophile

reaction.......   electrophile

[3]

(c) What is meant by the term *nucleophile*?

....

.... [1]

(d) Reactions 3 and 4 involve nucleophiles.

For **each** reaction, give the formula of the nucleophile.

reaction 3

reaction 4

[2]

(e) One characteristic reaction of ethene is its ability to decolourise bromine.

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

In this reaction, ethene behaves as a nucleophile.

Suggest an explanation for how ethene can behave in this way.

....

.... [1]

[S'10 P23 Q4]

11 Astronomers using modern spectroscopic techniques of various types have found evidence of many molecules, ions and free radicals in the dust clouds in Space. Many of the species concerned have also been produced in laboratories on Earth.

Two such species are the dicarbon monoxide molecule, C_2O, and the amino free radical, NH_2.

(a) **(i)** Dicarbon monoxide can be produced in a laboratory and analysis of it shows that the sequence of atoms in this molecule is carbon-carbon-oxygen and there are no unpaired electrons, but one of the atoms is only surrounded by six electrons.

Draw a 'dot-and-cross' diagram of C_2O and suggest the shape of the molecule.

shape ....

(ii) What is meant by the term *free radical*?

....

....

(iii) Explain why NH_2 is described as a 'free radical'.

....

....[5]

Two derivatives of ethene which have been detected in dust clouds in Space are acrylonitrile (2-propenenitrile), CH_2=CHCN, and vinyl alcohol (ethenol), CH_2=CHOH.

(b) Like ethene, acrylonitrile can be polymerised. The resulting polymer can be used to make carbon fibres.

(i) Draw the structural formula of the polymer made from acrylonitrile, showing **two** repeat units.

(ii) What type of polymerisation is this reaction?

....[2]

Vinyl alcohol cannot be polymerised in the same way as acrylonitrile because it will readily isomerise into another common organic compound, **Z**.

(c) **(i)** Suggest the structural formula of the organic compound **Z**.

(ii) Suggest the structural formula of another isomer of vinyl alcohol which has a cyclic (ring) structure.

[2]

Acrolein (2-propenal), CH_2=CHCHO, has also been found in Space.

(d) Give the structural formulae of the organic compounds formed when acrolein is reacted separately with **each** of the following reagents.

reagent	product
Br_2 in an inert solvent	
NaCN + dilute H_2SO_4	
Tollens' reagent	
$NaBH_4$	

[4]

[W'10 P23 Q3]

12 Although few halogenoalkanes exist naturally, such compounds are important as intermediates in organic reactions and as solvents.

The bromoalkane **B** has the following composition by mass: C, 29.3%; H, 5.7%; Br, 65.0%. The relative molecular mass of **B** is 123.

(a) Calculate the molecular formula of **B**.

[3]

Halogenoalkanes such as bromoethane, C_2H_5Br, have two different reactions with sodium hydroxide, NaOH, depending on the conditions used.

(b) **(i)** When hot aqueous NaOH is used, the C_2H_5Br is hydrolysed to ethanol, C_2H_5OH.

Describe the mechanism of this reaction. In your answer, show any relevant charges, dipoles, lone pairs of electrons and movement of electron pairs by curly arrows.

(ii) What will be formed when C_2H_5Br is reacted with NaOH under different conditions?

....

(iii) What are the conditions used?

....

(iv) What type of reaction is this?

....[7]

When 1,4-dichlorobutane, $ClCH_2CH_2CH_2CH_2Cl$, is reacted with NaOH, two different reactions can occur, depending on the conditions used.

(c) **(i)** Draw the **displayed** formula of the product formed when 1,4-dichlorobutane is reacted with hot aqueous NaOH as in **(b)(i)**.

(ii) Draw the **skeletal** formula of the product formed when 1,4-dichlorobutane is reacted with NaOH in the way you have described in **(b)(ii)** and **(b)(iii)**.

[2]

[W'10 P23 Q4]

13 The structural formulae of six different compounds, **P – U**, are given below.

$CH_3CH{=}CHCH_2CH_3$	$CH_3CH_2COCH_2CH_3$	$CH_2{=}CHCH_2CH_2CH_3$
P	**Q**	**R**
$CH_3CH_2CH_2CH_2CH_2OH$	$HOCH_2CH_2CH(OH)CH_3$	$CH_3CH_2CH_2OCH_2CH_3$
S	**T**	**U**

(a) **(i)** What is the empirical formula of compound **T**?

....

(ii) Draw the skeletal formula of compound **S**.

[2]

(b) **(i)** Compounds **S** and **U** are isomers.

What type of isomerism do they show?

....

(ii) Two of the six formulae **P – U** can **each** be drawn in two forms which are known as stereoisomers.

Which two compounds have formulae that can be drawn in two forms?

What type of stereoisomerism does each show?

Identify each compound by its letter.

compound	type of stereoisomerism

[3]

(c) Compound **S** can be converted into compound **R**.

(i) What type of reaction is this?

....

(ii) What reagent would you use for this reaction?

....

(iii) Write the structural formula of the compound formed when **T** undergoes the same reaction using an excess of the reagent you have used in **(c)(ii)**.

.... [3]

(d) Compound **P** may be converted into compound **Q** in a two-step reaction.

$$\underset{\textbf{P}}{CH_3CH{=}CHCH_2CH_3} \xrightarrow{\text{step 1}} \text{intermediate} \xrightarrow{\text{step 2}} \underset{\textbf{Q}}{CH_3CH_2COCH_2CH_3}$$

(i) What is the structural formula of the intermediate compound formed in this sequence?

(ii) Outline how step 1 may be carried out to give this intermediate compound.

....

....

....

(iii) What reagent would be used for step 2?

.... [4]

[W'11 P23 Q4]

14 Organic compounds which contain oxygen may contain alcohol, aldehyde, carboxylic acid, ester or ketone functional groups. The functional groups may be identified by their reactions with specific reagents.

Compound **X** has the empirical formula CH_2O and M_r of 90.

(a) There is no reaction when **X** is treated with $NaHCO_3$.

What functional group does this test show to be **not** present in **X**?

.... [1]

(b) When 0.600 g of **X** is reacted with an excess of Na, 160 cm^3 of H_2, measured at room temperature and pressure, is produced.

(i) What functional group does this reaction show to be present in **X**?

....

(ii) Use the data to calculate the amount, in moles, of hydrogen **atoms** produced from 0.600 g of **X**.

(iii) Hence, show that each molecule of **X** contains **two** of the functional groups you have given in **(i)**.

[4]

(c) When **X** is warmed with Fehling's reagent, a brick red precipitate is formed. Treatment of **X** with 2,4-dinitrophenylhydrazine reagent produces an orange solid.

(i) What functional group do these reactions show to be present in **X**? Draw the displayed formula of this functional group.

(ii) Use your answers to **(b)(i)**, **(b)(ii)** and **(c)(i)** to deduce the structural formula of **X**.

(iii) What is the structural formula of the organic product of the reaction of **X** with Fehling's reagent?

[3]

(d) Compound **X** can be both oxidised and reduced.

(i) Give the structural formula of the compound formed when **X** is reacted with $NaBH_4$ under suitable conditions.

(ii) Give the structural formula of the compound formed when **X** is heated under reflux with acidified $K_2Cr_2O_7$.

[2]

[S'12 P21 Q5]

15 Oxygen-containing organic compounds may contain a number of different functional groups including alcohol, aldehyde, carboxylic acid, ester or ketone functional groups. These functional groups may be identified by their reactions with specific reagents.

(a) On treating compounds containing each of these functional groups with the reagents below, only five reactions occur. Complete the table by placing a tick (✓) in each box where you believe a reaction will occur. You should place **no more** than five ticks in the table.

reagent	alcohol R_2CHOH	aldehyde RCHO	carboxylic acid RCO_2H	ester RCO_2R'	ketone RCOR'
$NaHCO_3$					
Na					
$Cr_2O_7^{2-}/H^+$					

[5]

Compound **G** has the empirical formula CH_2O and M_r of 90.

An aqueous solution of **G** is neutral. There is no reaction when **G** is treated with $NaHCO_3$.

When 0.30 g of pure **G** is reacted with an excess of Na, 80 cm^3 of H_2, measured at room temperature and pressure, is produced.

(b) **(i)** What functional group do these two reactions show to be present in **G**?

....

(ii) Use the data to calculate the amount, in moles, of hydrogen **atoms** produced from 0.30 g of **G**.

(iii) Hence, show that each molecule of **G** contains **two** of the functional groups you have given in **(i)**.

[4]

(c) Treatment of **G** with 2,4-dinitrophenylhydrazine reagent produces an orange solid. When **G** is warmed with Fehling's reagent, no reaction occurs.

(i) What functional group do these reactions show to be present in **G**? Draw the displayed formula of this functional group.

(ii) Use your answers to **(b)(i)** and **(c)(i)** to deduce the structural formula of **G**.

[2]

(d) Compound **G** can be both oxidised and reduced.

(i) When **G** is heated under reflux with acidified $K_2Cr_2O_7$, compound **H** is formed. Give the structural formula of compound **H**.

(ii) When **G** is reacted with $NaBH_4$ under suitable conditions, compound **J** is formed. Give the structural formula of compound **J**.

[2]

[S'12 P22 Q4]

16 Many naturally occurring organic compounds contain oxygen. Such compounds may contain alcohol, aldehyde, carboxylic acid, ester or ketone functional groups. These functional groups may be identified by their reactions with specific reagents.

Compound **F** is a white solid which has the molecular formula $C_3H_6O_3$.

Compound **F** is soluble in water. Addition of $NaHCO_3$ to this solution produces a colourless gas, **G**, which turns lime water milky.

(a) **(i)** What is the identity of the gas **G**?

....

(ii) What functional group does this test show to be present in **F**?

....

[2]

(b) When **F** is heated with concentrated sulfuric acid, a colourless liquid **H** is produced. When cold dilute acidified $KMnO_4$ is shaken with **H**, the solution becomes colourless.

(i) What *type of reaction* occurs when **H** is formed from **F**?

....

(ii) Use your answers to **(a)(ii)** and **(b)(i)** to deduce the structural formula of the colourless liquid **H**.

[4]

(c) Compound **F** will react with sodium.

Calculate the volume of H_2, measured at room temperature and pressure, which will be produced when 0.600 g of **F** is reacted with an excess of Na.

[4]

(d) There are two structural isomers of **F** that give the reactions described in **(a)** and **(b)**.

(i) Suggest two structural formulae for these isomers.

J	**K**

(ii) Isomers **J** and **K** can both be oxidised.
What will be produced when **each** of the isomers **J** and **K** is heated under reflux with acidified $K_2Cr_2O_7$?

product from **J**	product from **K**

[2]

[S'12 P23 Q5]

17 Many organic compounds, including alcohols, carbonyl compounds, carboxylic acids and esters, contain oxygen.

(a) The table below lists some oxygen-containing organic compounds and some common laboratory reagents.

(i) Complete the table as fully as you can.
If you think no reaction occurs, write 'no reaction' in the box for the structural formula(e).

reaction	organic compound	reagent	structural formula(e) of organic product(s)
A	$CH_3CH(OH)CH_3$	$NaBH_4$	
B	CH_3COCH_3	Tollens' reagent warm	
C	$CH_3CO_2CH(CH_3)_2$	KOH(aq) warm	
D	$(CH_3)_3COH$	$Cr_2O_7^{2-}$ / H^+ heat under reflux	
E	CH_3COCH_3	$NaBH_4$	
F	$(CH_3)_3COH$	PCl_5	
G	$CH_3CH{=}CHCH_2OH$	MnO_4^- / H^+ heat under reflux	

(ii) During some of the reactions in **(i)** a colour change occurs.
Complete the table below for any such reactions, stating the letter of the reaction and what the colour change is.

reaction	colour at the beginning of the reaction	colour at the end of the reaction

[12]

[W'12 P23 Q4]

18 Organic chemistry is the chemistry of carbon compounds. The types of organic reactions that you have studied are listed below.

addition	elimination	hydrolysis
oxidation	reduction	substitution

Addition and substitution reactions are further described as follows.

electrophilic	nucleophilic	free radical

Complete the table below.
Fill in the central column by using **only** the types of reaction given in the lists above.
Use **both** lists when appropriate.
In the right hand column give the formula(e) of the reagent(s) you would use to carry out the reaction given.

organic reaction	type of reaction	reagent(s)
$CH_3CH_2CH_2CH_2Br \rightarrow CH_3CH_2CH_2CH_2NH_2$		
$CH_3CH_2CH_2CH_2OH \rightarrow BrCH_2CH_2CH_2CH_2OH$		
$CH_3COCH_3 \rightarrow CH_3C(OH)(CN)CH_3$		
$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3CH{=}CHCH_3$		

[Total: 11]

[S'13 P21 Q4]

19 Crotyl alcohol, $CH_3CH{=}CHCH_2OH$, is a colourless liquid which is used as a solvent.

(a) In the boxes below, write the **structural formula** of the organic compound formed when crotyl alcohol is reacted separately with each reagent under suitable conditions.
If you think no reaction occurs, write 'NO REACTION' in the box.

A	Br_2 in an inert organic solvent	
B	PCl_5	
C	H_2 and Ni catalyst	
D	$NaBH_4$	
E	$K_2Cr_2O_7 / H^+$ heat under reflux	

[5]

(b) Draw the **displayed formula** of the organic compound formed when crotyl alcohol is reacted with cold, dilute acidified potassium manganate(VII).

[1]

(c) Draw the **skeletal formula** of the compound formed in reaction E.

[2]

(d) Crotyl alcohol is obtained from crotonaldehyde, $CH_3CH{=}CHCHO$.

(i) Describe one test that would confirm the presence of a small amount of unreacted crotonaldehyde in the crotyl alcohol.
Give the name of the reagent used and state what you would see.

reagent ....

observation ....

(ii) What *type of reaction* is the conversion of crotonaldehyde into crotyl alcohol?

....

[3]

(e) Compound **P**, another unsaturated compound, is found in some blue cheeses.
The percentage composition by mass of compound **P** is C: 73.7%; H: 12.3%; O: 14.0%.

Calculate the empirical formula of compound **P**.

[2]

[S'13 P22 Q4]

DATA BOOKLET

1 Important values, constants and standards

molar gas constant	$R = 8.31\ J\,K^{-1}\,mol^{-1}$
the Faraday constant	$F = 9.65 \times 10^{4}\ C\,mol^{-1}$
the Avogadro constant	$L = 6.02 \times 10^{23}\ mol^{-1}$
the Planck constant	$h = 6.63 \times 10^{-34}\ J\,s$
speed of light in a vacuum	$c = 3.00 \times 10^{8}\ m\,s^{-1}$
rest mass of proton, $^{1}_{1}H$	$m_p = 1.67 \times 10^{-27}\ kg$
rest mass of neutron, $^{1}_{0}n$	$m_n = 1.67 \times 10^{-27}\ kg$
rest mass of electron, $^{0}_{-1}e$	$m_e = 9.11 \times 10^{-31}\ kg$
electronic charge	$e = -1.60 \times 10^{-19}\ C$
molar volume of gas	$V_m = 22.4\ dm^3\,mol^{-1}$ at s.t.p $V_m = 24.0\ dm^3\,mol^{-1}$ under room conditions (where s.t.p. is expressed as 101 kPa, approximately, and 273 K (0 °C))
ionic product of water	$K_w = 1.00 \times 10^{-14}\ mol^2\,dm^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$= 4.18\ kJ\,kg^{-1}\,K^{-1}$ ($= 4.18\ J\,g^{-1}\,K^{-1}$)

2 Ionisation energies (1st, 2nd, 3rd and 4th) of selected elements, in kJ mol^{-1}

	Proton number	First	Second	Third	Fourth
H	1	1310	–	–	–
He	2	2370	5250	–	–
Li	3	519	7300	11800	–
Be	4	900	1760	14800	21000
B	5	799	2420	3660	25000
C	6	1090	2350	4610	6220
N	7	1400	2860	4590	7480
O	8	1310	3390	5320	7450
F	9	1680	3370	6040	8410
Ne	10	2080	3950	6150	9290
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
A*l*	13	577	1820	2740	11600
Si	14	786	1580	3230	4360
P	15	1060	1900	2920	4960
S	16	1000	2260	3390	4540
C*l*	17	1260	2300	3850	5150
Ar	18	1520	2660	3950	5770
K	19	418	3070	4600	5860
Ca	20	590	1150	4940	6480
Sc	21	632	1240	2390	7110
Ti	22	661	1310	2720	4170
V	23	648	1370	2870	4600
Cr	24	653	1590	2990	4770
Mn	25	716	1510	3250	5190
Fe	26	762	1560	2960	5400
Co	27	757	1640	3230	5100
Ni	28	736	1750	3390	5400
Cu	29	745	1960	3350	5690
Zn	30	908	1730	3828	5980
Ga	31	577	1980	2960	6190

	Proton number	First	Second	Third	Fourth
Br	35	1140	2080	3460	4850
Rb	37	403	2632	3900	5080
Sr	38	548	1060	4120	5440
Ag	47	731	2074	3361	–
I	53	1010	1840	2040	4030
Cs	55	376	2420	3300	–
Ba	56	502	966	3390	–

3 Bond energies

3(a) Bond energies in diatomic molecules (these are exact values)

Homonuclear

Bond	Energy/kJ mol^{-1}
H–H	436
D–D	442
N≡N	944
O=O	496
P≡P	485
S=S	425
F–F	158
Cl–Cl	242
Br–Br	193
I–I	151

Heteronuclear

Bond	Energy/kJ mol^{-1}
H–F	562
H–Cl	431
H–Br	366
H–I	299
C≡O	1077

3(b) Bond energies in polyatomic molecules (these are average values)

Homonuclear

Bond	Energy/kJ mol^{-1}
C–C	350
C=C	610
C≡C	840
C┅C (benzene)	520
N–N	160
N=N	410
O–O	150
Si–Si	222
P–P	200
S–S	264

Heteronuclear

Bond	Energy/kJ mol^{-1}
C–H	410
C–C*l*	340
C–Br	280
C–I	240
C–N	305
C=N	610
C≡N	890
C–O	360
C=O	740
C=O in CO_2	805
N–H	390
N–C*l*	310
O–H	460
Si–C*l*	359
Si–H	320
Si–O (in $SiO_2(s)$)	460
Si=O (in $SiO_2(g)$)	640
P–H	320
P–C*l*	330
P–O	340
P=O	540
S–H	347
S–C*l*	250
S–O	360
S=O	500

4 Standard electrode potential and redox potentials, $E^\ominus$ at 298 K (25 °C)

For ease of reference, two tables are given:

(a) an extended list in alphabetical order

(b) a shorter list in decreasing order of magnitude, i.e. a redox series.

(a) $E^\ominus$ in alphabetical order

Electrode reaction	$E^\ominus$/V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$	–0.43
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Cu + 4NH_3$	–0.05
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	–0.56
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Electrode reaction			$E^{\ominus}$ / V
$K^+ + e^-$	⇌	K	–2.92
$Li^+ + e^-$	⇌	Li	–3.04
$Mg^{2+} + 2e^-$	⇌	Mg	–2.38
$Mn^{2+} + 2e^-$	⇌	Mn	–1.18
$Mn^{3+} + e^-$	⇌	Mn^{2+}	+1.49
$MnO_2 + 4H^+ + 2e^-$	⇌	$Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^-$	⇌	MnO_4^{2-}	+0.56
$MnO_4^- + 4H^+ + 3e^-$	⇌	$MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^-$	⇌	$NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^-$	⇌	$HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^-$	⇌	$NH_4^+ + 3H_2O$	+0.87
$Na^+ + e^-$	⇌	Na	–2.71
$Ni^{2+} + 2e^-$	⇌	Ni	–0.25
$[Ni(NH_3)_6]^{2+} + 2e^-$	⇌	$Ni + 6NH_3$	–0.51
$H_2O_2 + 2H^+ + 2e^-$	⇌	$2H_2O$	+1.77
$HO_2^- + H_2O + 2e^-$	⇌	$3OH^-$	+0.88
$O_2 + 4H^+ + 4e^-$	⇌	$2H_2O$	+1.23
$O_2 + 2H_2O + 4e^-$	⇌	$4OH^-$	+0.40
$O_2 + 2H^+ + 2e^-$	⇌	H_2O_2	+0.68
$O_2 + H_2O + 2e^-$	⇌	$HO_2^- + OH^-$	–0.08
$Pb^{2+} + 2e^-$	⇌	Pb	–0.13
$Pb^{4+} + 2e^-$	⇌	Pb^{2+}	+1.69
$PbO_2 + 4H^+ + 2e^-$	⇌	$Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^-$	⇌	$SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^-$	⇌	$2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^-$	⇌	$2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^-$	⇌	Sn	–0.14
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	+0.15
$V^{2+} + 2e^-$	⇌	V	–1.20
$V^{3+} + e^-$	⇌	V^{2+}	–0.26
$VO^{2+} + 2H^+ + e^-$	⇌	$V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^-$	⇌	$VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^-$	⇌	$VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^-$	⇌	Zn	–0.76

(b) $E^{\ominus}$ in decreasing order of oxidising power

(a selection only – see also the extended alphabetical list on the previous pages)

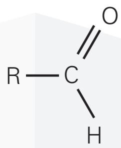
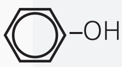
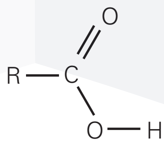
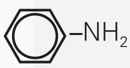
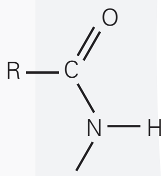
Electrode reaction			$E^{\ominus}$/V
$F_2 + 2e^-$	⇌	$2F^-$	+2.87
$S_2O_8^{2-} + 2e^-$	⇌	$2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^-$	⇌	$2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^-$	⇌	$Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^-$	⇌	$2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇌	$2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^-$	⇌	$2H_2O$	+1.23
$Br_2 + 2e^-$	⇌	$2Br^-$	+1.07
$ClO^- + H_2O + 2e^-$	⇌	$Cl^- + 2OH^-$	+0.89
$NO_3^- + 10H^+ + 8e^-$	⇌	$NH_4^+ + 3H_2O$	+0.87
$NO_3^- + 2H^+ + e^-$	⇌	$NO_2 + H_2O$	+0.81
$Ag^+ + e^-$	⇌	Ag	+0.80
$Fe^{3+} + e^-$	⇌	Fe^{2+}	+0.77
$I_2 + 2e^-$	⇌	$2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	⇌	$4OH^-$	+0.40
$Cu^{2+} + 2e^-$	⇌	Cu	+0.34
$SO_4^{2-} + 4H^+ + 2e^-$	⇌	$SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	+0.15
$S_4O_6^{2-} + 2e^-$	⇌	$2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^-$	⇌	H_2	0.00
$Pb^{2+} + 2e^-$	⇌	Pb	–0.13
$Sn^{2+} + 2e^-$	⇌	Sn	–0.14
$Fe^{2+} + 2e^-$	⇌	Fe	–0.44
$Zn^{2+} + 2e^-$	⇌	Zn	–0.76
$2H_2O + 2e^-$	⇌	$H_2 + 2OH^-$	–0.83
$V^{2+} + 2e^-$	⇌	V	–1.20
$Mg^{2+} + 2e^-$	⇌	Mg	–2.38
$Ca^{2+} + 2e^-$	⇌	Ca	–2.87
$K^+ + e^-$	⇌	K	–2.92

5 Atomic and ionic radii

(a) Period 1	**atomic/nm**		**ionic/nm**			
single covalent	H	0.037	H^{+}	0.208		
van der Waals	He	0.140				
(b) Period 2						
metallic	Li	0.152	Li^{+}	0.060		
	Be	0.112	Be^{2+}	0.031		
single covalent	B	0.080	B^{3+}	0.020		
	C	0.077	C^{4+}	0.015	C^{4-}	0.260
	N	0.074			N^{3-}	0.171
	O	0.073			O^{2-}	0.140
	F	0.072			F^{-}	0.136
van der Waals	Ne	0.160				
(c) Period 3						
metallic	Na	0.186	Na^{+}	0.095		
	Mg	0.160	Mg^{2+}	0.065		
	Al	0.143	Al^{3+}	0.050		
single covalent	Si	0.117	Si^{4+}	0.041		
	P	0.110			P^{3-}	0.212
	S	0.104			S^{2-}	0.184
	Cl	0.099			Cl^{-}	0.181
van der Waals	Ar	0.190				
(d) Group 2						
metallic	Be	0.112	Be^{2+}	0.031		
	Mg	0.160	Mg^{2+}	0.065		
	Ca	0.197	Ca^{2+}	0.099		
	Sr	0.215	Sr^{2+}	0.113		
	Ba	0.217	Ba^{2+}	0.135		
	Ra	0.220	Ra^{2+}	0.140		

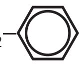
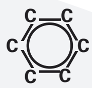
(e) Group 14	atomic/nm		ionic/nm			
single covalent	C	0.077				
	Si	0.117	Si^{4+}	0.041		
	Ge	0.122	Ge^{2+}	0.093		
metallic	Sn	0.162	Sn^{2+}	0.112		
	Pb	0.175	Pb^{2+}	0.120		
(f) Group 17						
single covalent	F	0.072	F^{-}	0.136		
	Cl	0.099	Cl^{-}	0.181		
	Br	0.114	Br^{-}	0.195		
	I	0.133	I^{-}	0.216		
	At	0.140				
(g) First row transition elements						
metallic	Sc	0.164			Sc^{3+}	0.081
	Ti	0.146	Ti^{2+}	0.090	Ti^{3+}	0.067
	V	0.135	V^{2+}	0.079	V^{3+}	0.064
	Cr	0.129	Cr^{2+}	0.073	Cr^{3+}	0.062
	Mn	0.132	Mn^{2+}	0.067	Mn^{3+}	0.062
	Fe	0.126	Fe^{2+}	0.061	Fe^{3+}	0.055
	Co	0.125	Co^{2+}	0.078	Co^{3+}	0.053
	Ni	0.124	Ni^{2+}	0.070	Ni^{3+}	0.056
	Cu	0.128	Cu^{2+}	0.073		
	Zn	0.135	Zn^{2+}	0.075		

6 Typical proton (^1H) chemical shift values (δ) relative to TMS = 0

Type of proton	Environment of proton	Example structures	Chemical shift range (δ)
C–H	alkane	$-CH_3$, $-CH_2-$, >CH–	0.9–1.7
	alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, >CH–C=O	2.2–3.0
	alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, > CH–Ar	2.3–3.0
	alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$, >CH–Br	3.2–4.0
	attached to alkyne	≡C–H	1.8–3.1
	attached to alkene	$=CH_2$, =CH–	4.5–6.0
	attached to aromatic ring		6.0–9.0
	aldehyde		9.3–10.5
O–H (see note below)	alcohol	RO–H	0.5–6.0
	phenol		4.5–7.0
	carboxylic acid		9.0–13.0
N–H (see note below)	alkyl amine	R–NH–	1.0–5.0
	aryl amine		3.0–6.0
	amide		5.0–12.0

Note: δ values for –O–H and –N–H protons can vary depending on solvent and concentration.

7 Typical carbon (^{13}C) chemical shift values (δ) relative to TMS = 0

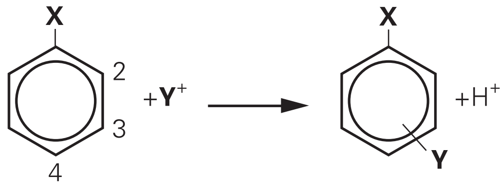
Hybridisation of the carbon atom	Environment of carbon atom	Example structures	Chemical shift range (δ)
sp^3	alkyl	$\mathbf{C}H_3$–, $\mathbf{C}H_2$–, –$\mathbf{C}$H<	0–50
sp^3	next to alkene/arene	–$\mathbf{C}H_2$–C=C, –$\mathbf{C}H_2$– 	10–40
sp^3	next to carbonyl/carboxyl	–$\mathbf{C}H_2$–COR, –$\mathbf{C}H_2$–CO_2R	25–50
sp^3	next to nitrogen	–$\mathbf{C}H_2$–NH_2, –$\mathbf{C}H_2$–NR_2, –$\mathbf{C}H_2$–NHCO	30–65
sp^3	next to chlorine (–CH_2–Br and –CH_2–I are in the same range as alkyl)	–$\mathbf{C}H_2$–Cl	30–60
sp^3	next to oxygen	–$\mathbf{C}H_2$–OH, –$\mathbf{C}H_2$–O–CO–	50–70
sp^2	alkene or arene	>$\mathbf{C}$=$\mathbf{C}$<, 	110–160
sp^2	carboxyl	R–$\mathbf{C}O_2$H, R–$\mathbf{C}O_2$R	160–185
sp^2	carbonyl	R–$\mathbf{C}$HO, R–$\mathbf{C}$O–R	190–220
sp	alkyne	R–$\mathbf{C}\equiv\mathbf{C}$–	65–85
sp	nitrile	R–$\mathbf{C}\equiv$N	100–125

8 Characteristic infra-red absorption frequencies for some selected bonds

Bond	Functional groups containing the bond	Absorption range (in wavenumbers)/cm^{-1}	Appearance of peak (*s* = strong, *w* = weak)
C–O	alcohols, ethers, esters	1040–1300	***s***
C=C	aromatic compounds, alkenes	1500–1680	***w*** unless conjugated
C=O	amides ketones and aldehydes esters	1640–1690 1670–1740 1710–1750	***s*** ***s*** ***s***
C≡C	alkynes	2150–2250	***w*** unless conjugated
C≡N	nitriles	2200–2250	***w***
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	***s*** ***w***
N–H	amines, amides	3300–3500	***w***
O–H	carboxylic acids, RCO_2–H H-bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	***s*** and very broad ***s*** ***s*** and sharp

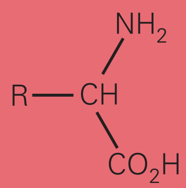
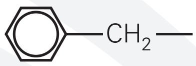
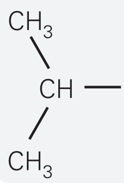
9 The orientating effect of groups in aromatic substitution reactions.

The position of the incoming group, **Y**, is determined by the nature of the group, **X**, already bonded to the ring, and not by the nature of the incoming group **Y**.



X– groups that direct the incoming Y group to the 2– or 4– positions	X– groups that direct the incoming Y group to the 3– position
$–NH_2$, –NHR or $–NR_2$	$–NO_2$
–OH or –OR	$–NH_3$
–NHCOR	–CN
$–CH_2$, –alkyl	–CHO, –COR
–C*l*	$–CO_2H$, $–CO_2R$

10 Names, structures and abbreviations of some amino acids

Name	3-letter abbreviation	1-letter symbol	structure of side chain R– in 
alanine	Ala	A	CH_3–
aspartic acid	Asp	D	HO_2CCH_2–
cysteine	Cys	C	$HSCH_2$–
glutamic acid	Glu	E	$HO_2CCH_2CH_2$–
glycine	Gly	G	H–
lysine	Lys	K	$H_2NCH_2CH_2CH_2CH_2$–
phenylalanine	Phe	F	
serine	Ser	S	$HOCH_2$–
tyrosine	Tyr	Y	
valine	Val	V	

Key

atomic number
atomic symbol
name
relative atomic mass

Group																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 T*l* thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 F*l* flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –