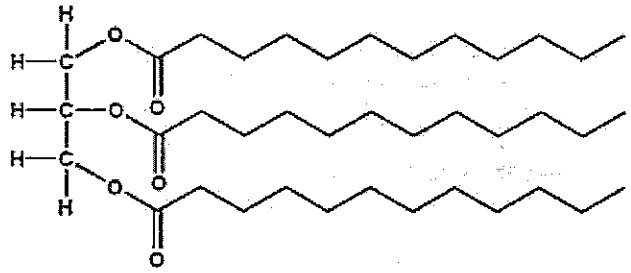
Answers

4.1.2 & 4.1.3
Carbonyl Compounds, Carboxylic acids & Esters



1) Alcohols Review
2) Aldehydes and Ketones
3) Carboxylic acids, naming, properties and reactions
4) Esters
5) Fats and Oils
6) Exam questions

gChemistry

Name

4.1.2 Carbonyl Compounds

Reactions of carbonyl compounds

Candidates should be able to:

(a) describe the oxidation of alcohols (see also unit F322: 2.2.1.f) using $Cr_2O_7^{2-}/H^+$ (ie $K_2Cr_2O_7/H_2SO_4$), including:

(i) the oxidation of primary alcohols to form aldehydes and carboxylic acids; the control of the oxidation product using different reaction conditions,

(ii) the oxidation of secondary alcohols to form ketones;

(b) describe the oxidation of aldehydes using $Cr_2O_7^{2-}/H^+$ to form carboxylic acids;

(c) describe the reduction of carbonyl compounds using $NaBH_4$ to form alcohols;

(d) outline the mechanism for nucleophilic addition reactions of aldehydes and ketones with hydrides, such as $NaBH_4$ (see also unit F322: 2.1.1.h–j);

Characteristic tests for carbonyl compounds

(e) describe the use of 2,4-dinitrophenylhydrazine to:

(i) detect the presence of a carbonyl group in an organic compound,

(ii) identify a carbonyl compound from the melting point of the derivative;

(f) describe the use of Tollens' reagent (ammoniacal silver nitrate) to:

(i) detect the presence of an aldehyde group,

(ii) distinguish between aldehydes and ketones, explained in terms of the oxidation of aldehydes to carboxylic acids with reduction of silver ions to silver.

4.1.3 Carboxylic Acids and Esters

Properties of carboxylic acids

Candidates should be able to:

(a) explain the water solubility of carboxylic acids in terms of hydrogen bonding and dipole-dipole interaction;

(b) describe the reactions of carboxylic acids with metals, carbonates and bases;

Comparison of acidity of different carboxylic acids not required.

Esters, triglycerides, unsaturated and saturated fats

(c) describe esterification of carboxylic acids with alcohols, in the presence of an acid catalyst (see also 2.2.1.g); of acid anhydrides with alcohols;

(d) describe the hydrolysis of esters:

(i) in hot aqueous acid to form carboxylic acids and alcohols,

(ii) in hot aqueous alkali to form carboxylate salts and alcohols;

(e) state the uses of esters in perfumes and flavourings;

(f) describe a *triglyceride* as a triester of glycerol (propane-1,2,3-triol) and fatty acids;

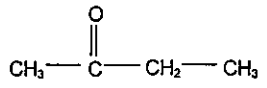
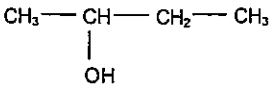
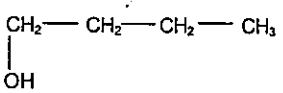
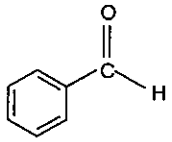
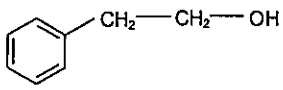
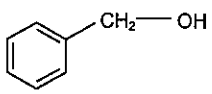
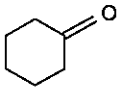
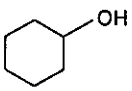
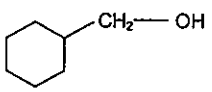
(g) compare the structures of saturated fats, unsaturated fats and fatty acids, including *cis* and *trans* isomers, from systematic names and shorthand formulae;

(h) compare the link between *trans* fatty acids, the possible increase in 'bad' cholesterol and the resultant increased risk of coronary heart disease and strokes.

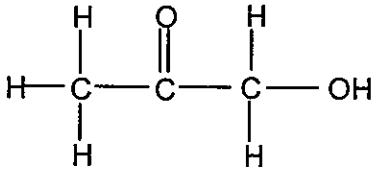
(i) describe and explain the increased use of esters of fatty acids as biodiesel.

Alcohols Review

1. Give the formulae of the alcohols that would have to be oxidised to prepare the following aldehydes and ketones.

1. 	a) 	b) 	A
2. 	a) 	b) 	B
3. 	a) 	b) 	A

2. Compound A shown below, contains two functional groups.



Compound A

a) Identify the functional groups primary alcohol + ketone

b) State the molecular formula of compound A $C_3H_6O_2$

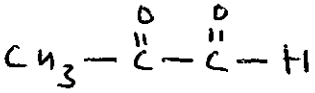
c) Compound A can be oxidised to produce a mixture of compound B, molecular formula $C_3H_4O_2$, and compound C, molecular formula $C_3H_4O_3$.

i) Identify which of the functional groups could be oxidised.
primary alcohol

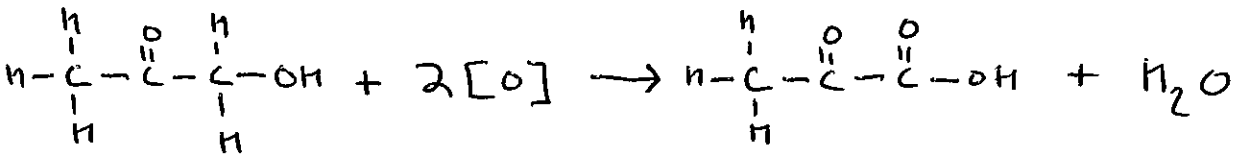
ii) Suggest a suitable oxidising mixture.
Acidified potassium dichromate

iii) State what you would observe during the reaction.
orange to green colour change

iv) Identify compound B.

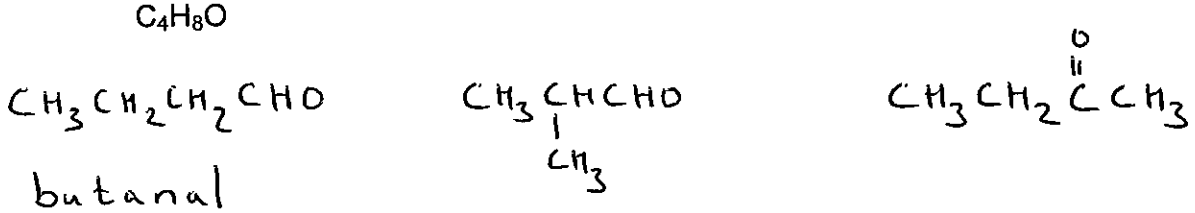


v) Write a balanced equation for the formation of compound C from compound A. Use [O] to represent the oxidising agent.



Aldehydes and Ketones

1. a) Draw the structures of the three carbonyl isomers with the molecular formula C_4H_8O



butanal

2-methylpropanal

butanone

b) 2,4-dinitrophenylhydrazine (DNPH) reacts with all three isomers. Describe what you would observe when DNPH is added to these compounds.

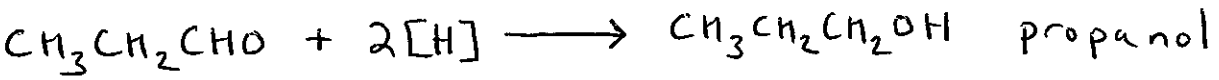
orange/yellow ppt

c) How could this reaction be used to distinguish between the three isomers?

filter off ppt, wash and dry. Determine their melting points and compare with databook values

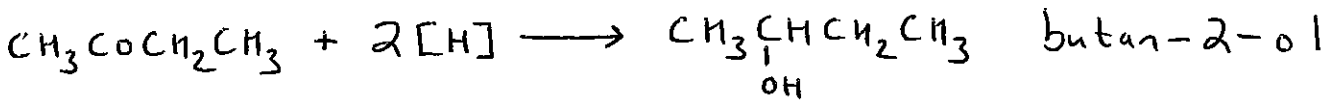
2. Write an equation for the reaction, and name the alcohol formed when the following compounds are reduced using $NaBH_4$

a) CH_3CH_2CHO



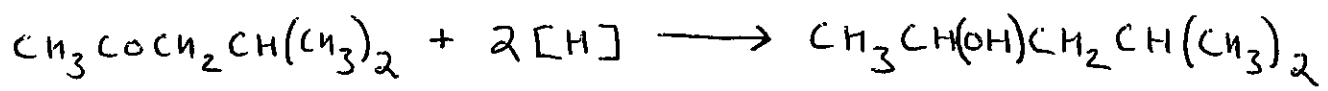
propanol

b) $CH_3COCH_2CH_3$



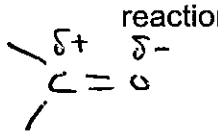
butan-2-ol

c) $CH_3COCH_2CH(CH_3)_2$



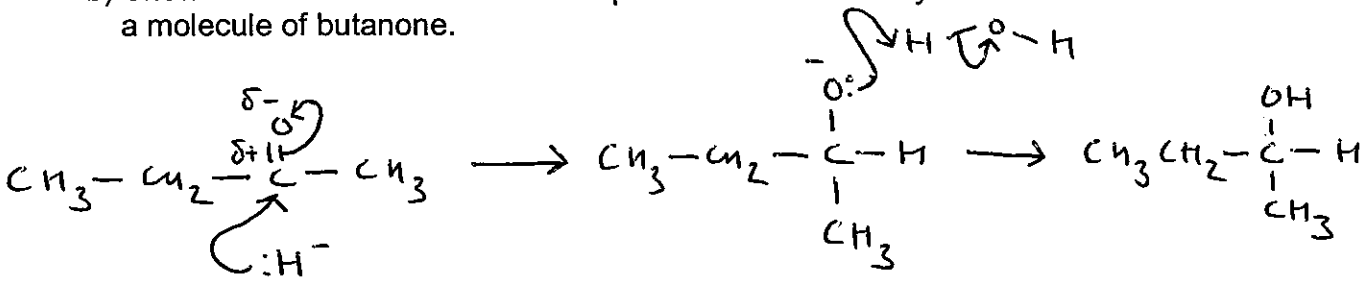
4-methyl pentan-2-ol

3. a) Explain why aldehydes and ketones undergo nucleophilic addition reactions.



carbon on C=O is electron deficient ∴ attacked by nucleophiles which are electron pair donors.

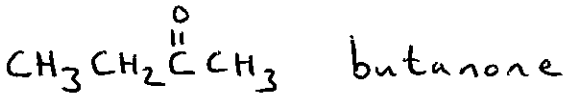
b) Show the mechanism of the nucleophilic addition of the hydride ion to a molecule of butanone.



4. An alcohol, A, undergoes the following reaction:

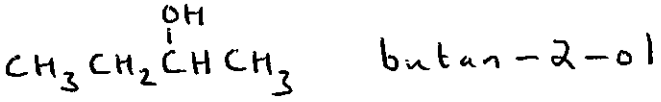
$$\underset{A}{C_4H_{10}O} \rightarrow \underset{B}{C_4H_8O}$$

a) Substance B is a ketone. Give its name and structure



butanone

b) Identify alcohol A by name or formula and justify your answer.



butan-2-ol

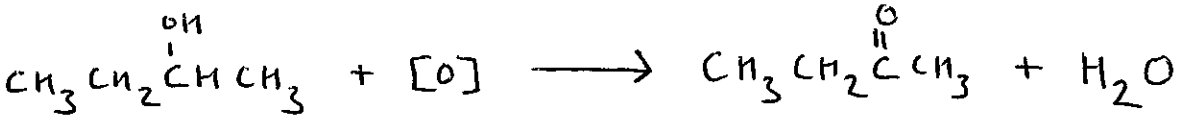
c) i) What type of reaction is involved in the conversion of A to B?

oxidation

ii) Give the reagent and conditions necessary for this conversion.

Acidified potassium dichromate

iii) Write a balanced equation for the reaction.



5. The carbonyl compounds CH_3COCH_3 and CH_3CH_2CHO are structural isomers.

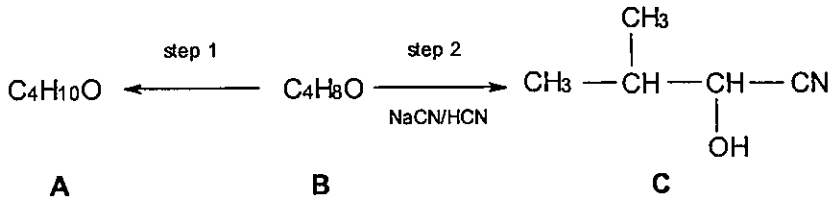
a) Name the compounds.

CH_3COCH_3 propanone $\qquad$ CH_3CH_2CHO propanal

b) State the reagents you would use and the observations you would make using a chemical test in which the two compounds give different results.

Tollens reagent – gives a silver mirror with an aldehyde but not with a ketone

6. Consider the following reaction scheme:



a) i) B gives a positive result with Tollens' reagent. Use this information and the reaction scheme to identify A –B by writing out their structures.

B = $CH_3CH(CH_3)C(=O)H$ $\qquad$ A = $CH_3CH(CH_3)CH_2OH$

ii) What would you observe when B is tested with Tollens' reagent?

Silver mirror

iii) Name one isomer of B which would also give a positive result with Tollens' reagent and one isomer which does not react with Tollens' reagent.

+ve test $CH_3CH_2CH_2C(=O)H$ $\qquad$ –ve test $CH_3CH_2C(=O)CH_3$

b) Name the type of reaction occurring at steps 1 and 2.

B ⟶ A : reduction / nucleophilic addition

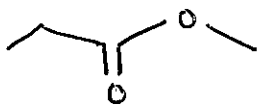
B → C : nucleophilic addition.

Esters

1. Name the following esters and draw the skeletal formula:

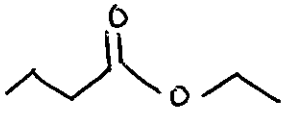
a) $CH_3CH_2COOCH_3$

methyl propanoate



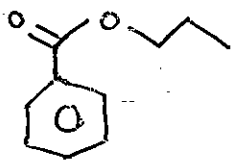
b) $CH_3(CH_2)_2COOCH_2CH_3$

ethyl butanoate



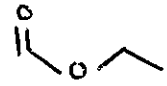
c) $C_6H_5COOCH_2CH_2CH_3$

propyl benzoate



d) $HCOOCH_2CH_3$

ethyl methanoate



2. a) Write an equation to show the acid hydrolysis of :

- $CH_3CH_2COOCH_3$

$$CH_3CH_2COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CH_2COOH + CH_3OH$$

- $CH_3(CH_2)_2COOCH_2CH_3$

$$CH_3(CH_2)_2COOCH_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3(CH_2)_2COOH + CH_3CH_2OH$$

b) Write equations to show the base hydrolysis (using sodium hydroxide as the base) of the following esters. Name the two products in each case.

- $C_6H_5COOCH_3$

$$C_6H_5COOCH_3 + NaOH \longrightarrow C_6H_5COO^-Na^+ + CH_3OH$$

sodium benzoate — methanol

- $CH_3COOCH_2CH_2CH_3$

$$CH_3COOCH_2CH_2CH_3 + NaOH \longrightarrow CH_3COO^-Na^+ + CH_3CH_2CH_2OH$$

sodium ethanoate — propan-1-ol

3. a) Describe a simple chemical test to distinguish between a carboxylic acid and an ester

Add $NaHCO_3$

carboxylic acid : effervescence (CO_2 given off)

ester : no effervescence

b) How could infra-red spectroscopy be used distinguish between a carboxylic acid and an ester?

carboxylic acid : broad peak at $\sim 3200 cm^{-1}$

$\therefore$ O-H bond

ester no peak at $3200 cm^{-1}$

$\therefore$ no O-H bond.

Carboxylic acids

1. Name each of the following acids:

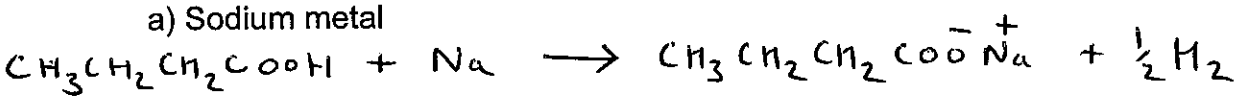
   a) CH_3CH_2COOH propanoic acid

   b) $CH_3CH_2CH_2COOH$ butanoic acid

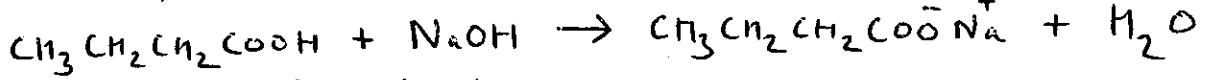
   c) $(CH_3)_2CHCOOH$ 2-methyl propanoic acid

2. Write fully balanced equations for the reactions of butanoic acid with:

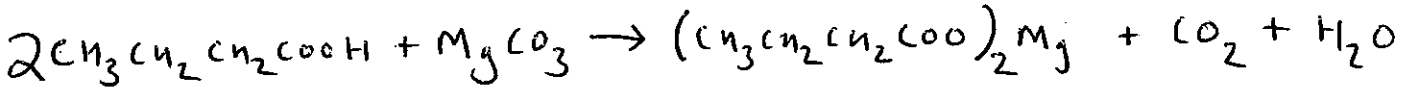
   a) Sodium metal



   b) Sodium hydroxide

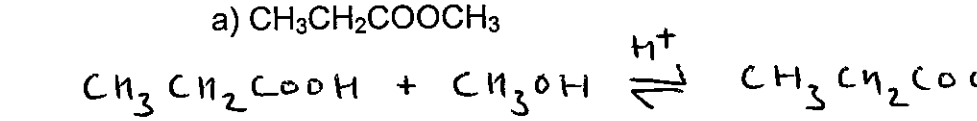


   c) Magnesium carbonate



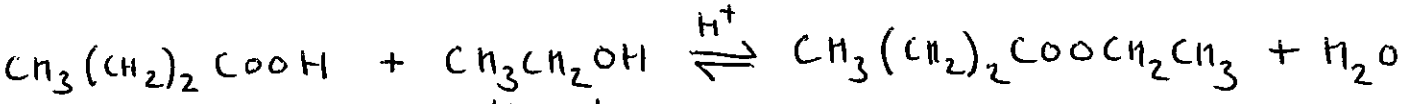
3. Write equations to show the formation of the following esters from the parent carboxylic acid and alcohol. In each case, name the two reactants.

   a) $CH_3CH_2COOCH_3$



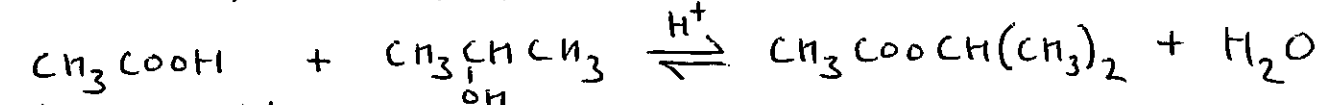
propanoic acid methanol

   b) $CH_3(CH_2)_2COOCH_2CH_3$



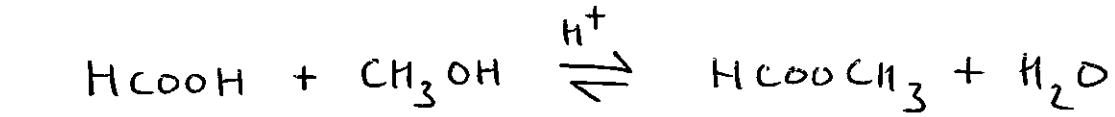
butanoic acid ethanol

   c) $CH_3COOCH(CH_3)_2$



ethanoic acid propan-2-ol

   d) $HCOOCH_3$



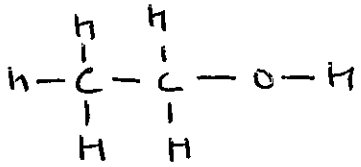
methanoic acid methanol

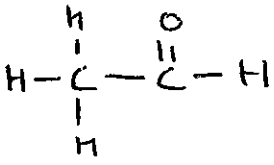
4. a) Explain why carboxylic acids are usually soluble in water.

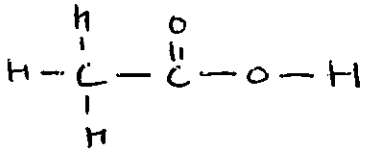
The highly polar C=O and O-H bonds allow carboxylic acid molecules to form hydrogen bonds with water molecules.

b) Draw the displayed formula for the following compounds;

i) CH_3CH_2OH ii) CH_3CHO iii) CH_3COOH



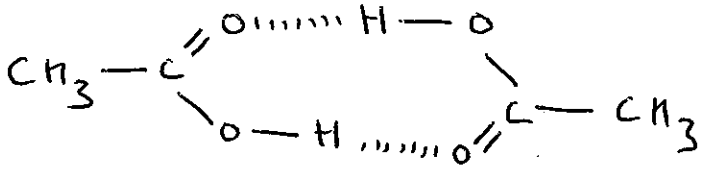




Which would have the highest boiling point, explain your answer?

iii)

2 - hydrogen bonds per molecule makes their boiling points higher than those of corresponding alcohols



Fats and Oils

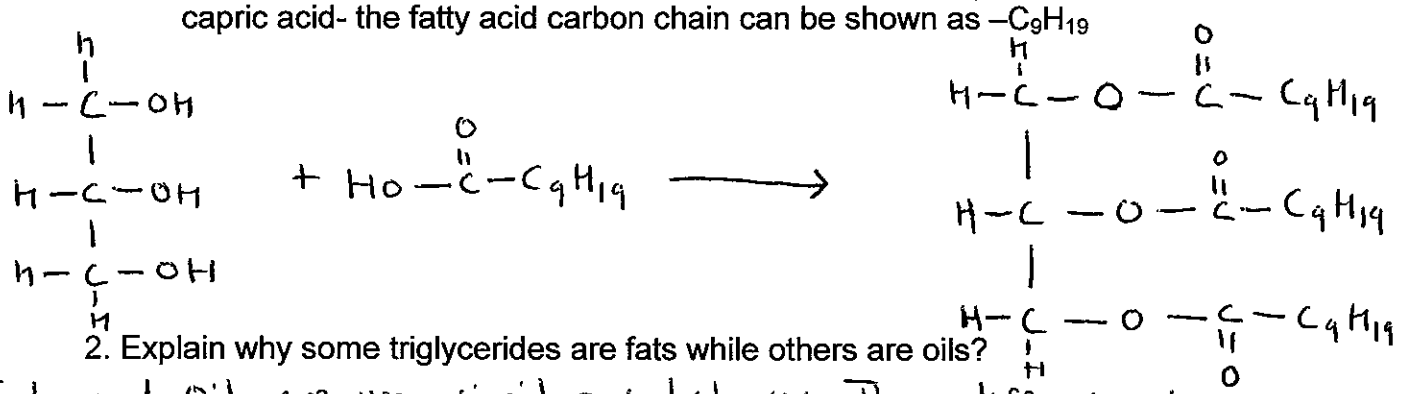
1. Capric acid (10:0) is a saturated fatty acid

   a. Draw the skeletal formula of the acid

   b. Name the functional group present in the acid

Carboxylic acid

   c. Draw the structure of the triglyceride formed between glycerol and capric acid- the fatty acid carbon chain can be shown as $-C_9H_{19}$



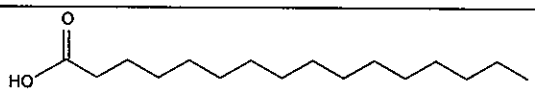
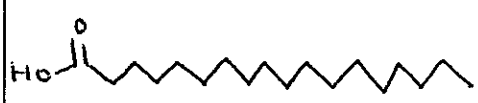
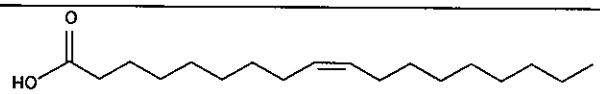
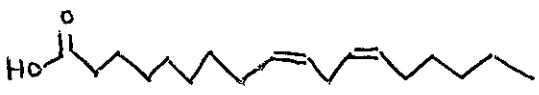
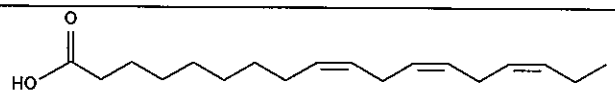
2. Explain why some triglycerides are fats while others are oils?

Fats and Oils are very similar substances. They differ in their physical states because of their melting points. When the m.p. of the ester is above room temperature the substance exists as a solid and is called a fat; when the m.p. is below room temp. the substance exists as an oil.

3. What is the difference between a simple triglyceride and a mixed triglyceride?

Simple triglycerides contain 3 molecules of the same fatty acid and mixed triglycerides have 2 or 3 different fatty acids in their structure.

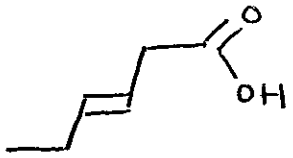
4. Complete the table below

Traditional name	Systematic name	Structure	Shorthand notation
Palmitic acid	Hexadecanoic acid		16:0
Stearic acid	Octadecanoic acid		18:0
Oleic acid	Octadec-9-enoic acid		18:1 (9)
Linoleic acid	Octadeca-9,12-dienoic acid		18:2 (9,12)
Linolenic acid	Octadeca-9,12,15-trienoic acid		18:3(9,12,15)

5. Explain the difference between saturated fats and unsaturated fats.

A saturated fat contains no double bonds; an unsaturated fat contains at least one double C=C bond.

6. Draw the skeletal formulae of cis- and trans-hex-3-enoic acid.



trans

Cis

7. Name three foods high in saturated fats.

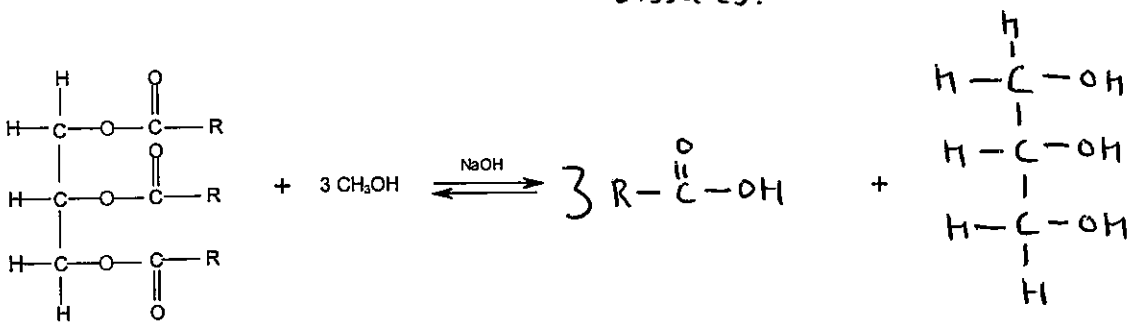
Meat products, meat pies, sausages, butter, lard, pastry, cakes, biscuits

8. Define and explain the roles of HDLs and LDLs.

HDLs - High-density lipoproteins can remove cholesterol from the arteries and transport it back to the liver for excretion or re-utilisation.

LDLs - Low density lipoproteins are responsible for carrying cholesterol and triglycerides from the liver to the tissues.

9. Complete the following reaction scheme



Triglyceride

Biodiesel

Glycerol

R= fatty acid carbon chain

10. What do you understand by the term carbon neutral?

A crop that is used to produce a carbon-neutral fuel absorbs the same amount of CO_2 when it grows as is released when the fuel is combusted.

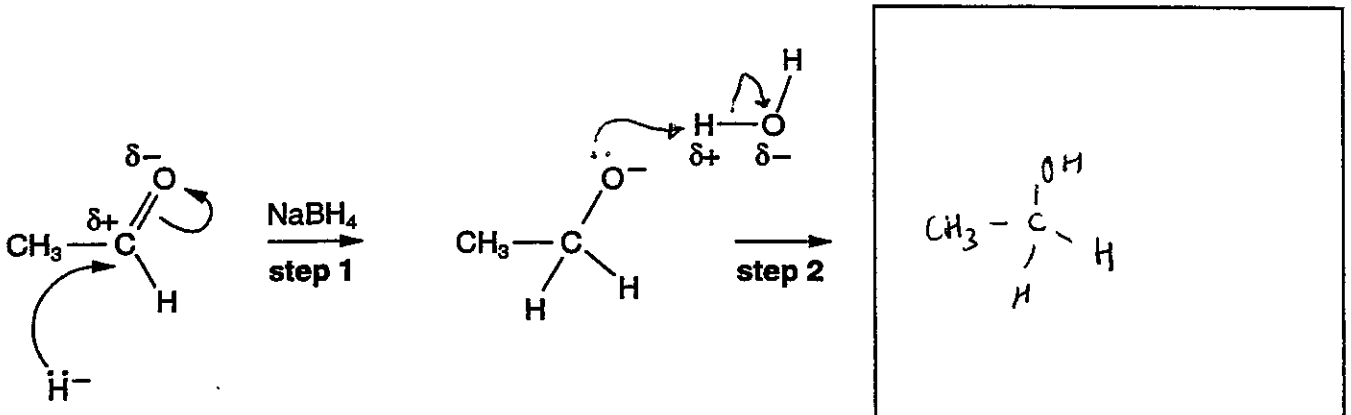
1. Ethanal, CH_3CHO, can be reduced using an aqueous solution of sodium borohydride, $NaBH_4$, as the reducing agent.

(a) Write a balanced equation for this reaction using the symbol [H] to represent the reducing agent.

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$ [2]

(b) This is a nucleophilic addition reaction in which the nucleophile can be represented as a hydride ion, $\dot{H}^-$.

A mechanism for the reaction is shown below.



ethanal **intermediate** **organic product**

(i) Add 'curly arrows' to the mechanism to show how the intermediate reacts with the water molecule in **step 2.** [2]

(ii) Draw the structure of the organic product of this reaction in the box above. [1]

(iii) What is meant by the term *nucleophile*?

an electron pair donor [1]

(iv) Describe in words exactly what is happening to the electron pairs and bonds in **step 1** of the mechanism above.

* carbon on C=O bond is electron deficient
* lone pair on H^- forms a covalent bond with this carbon
* one of the pairs of e^- in the C=O goes to the O, forming a C-O single bond

[3]

For Examiner's Use

(c) It is also possible to reduce ethanal to the same product using hydrogen gas, H_2, in the presence of a catalyst. This reaction does **not** go by a nucleophilic mechanism.

Explain why hydrogen gas cannot act as a nucleophile.

H_2 does not have a lone pair of electrons

.....[1]

[Total: 10]

For Examiner's Use

2. Like esters, carbonyl compounds can contribute to the smell of plants and food. The carbonyl compounds **D** and **E** are structural isomers.

D CH_3COCH_3 **E** CH_3CH_2CHO

(a) Name compounds **D** and **E**.

(i) **D** propanone

(ii) **E** propanal

[2]

(b) State the reagents you would use and the observations you would make for a simple chemical test

(i) in which **D** and **E** behave in the same way;

reagent(s) 2-4-dinitrophenylhydrazine

observation yellow / orange precipitate [2]

(ii) which can be used to distinguish between **D** and **E**.

reagent(s) Tollens reagent

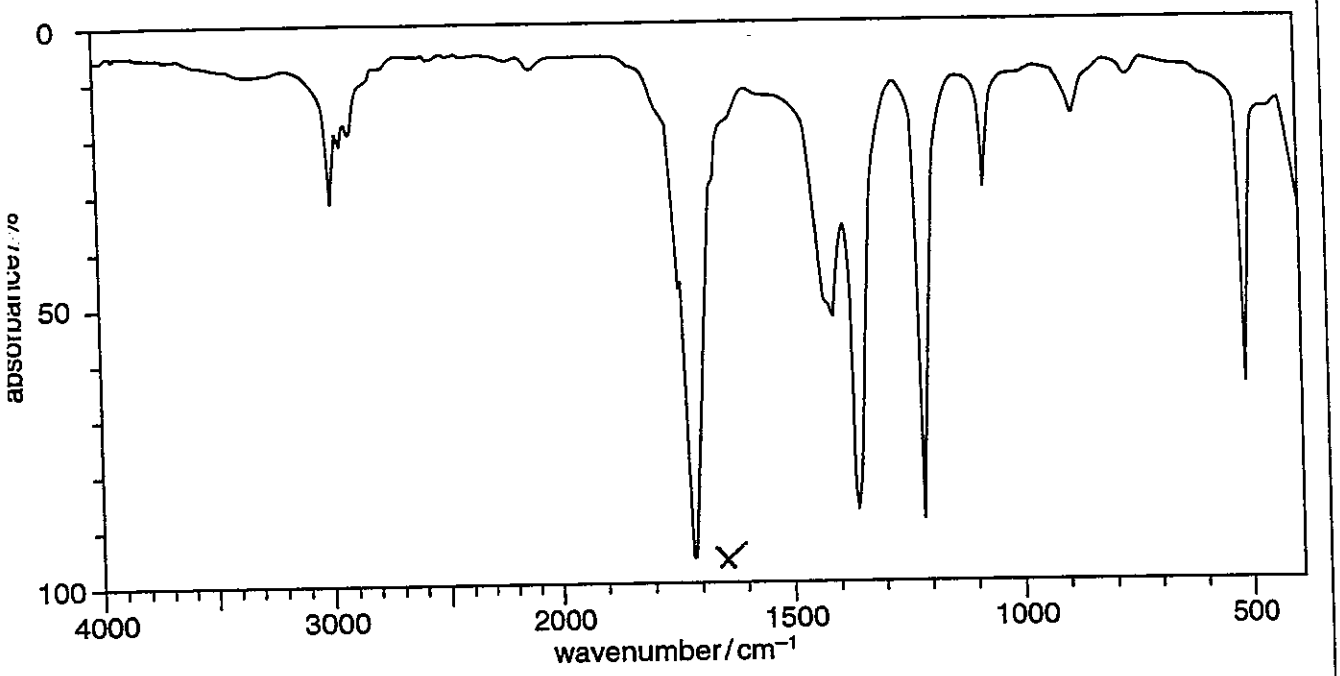
observation for **D** no change

observation for **E** silver mirror [3]

(or Fehlings, or $H^+ / Cr_2O_7^{2-}$)

For Examiner's Use

(c) The infrared spectrum of **D** is shown below.



(i) On the spectrum above, mark with a cross the absorption peak that identifies the functional group. Explain how you made your choice. (Use the *Data Sheet* provided to answer this question.)

D has a C=O bond

[2]

(ii) Reduction of compound **D** with $NaBH_4$ produces a compound with the molecular formula C_3H_8O.

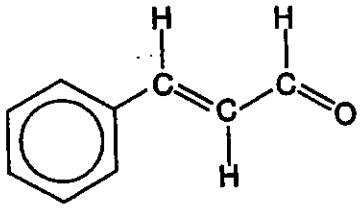
How would the infrared spectrum of this product be different from that of **D**?

* New broad peak at 3350 cm⁻¹

* no peak at 1700 cm⁻¹ [2]

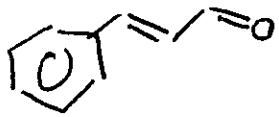
For Examiner's Use

3. Cinnamaldehyde is the compound that gives cinnamon its distinctive flavour.



cinnamaldehyde

(a) Draw the skeletal formula of cinnamaldehyde.



[1]

(b) Cinnamaldehyde shows *cis-trans* isomerism.

(i) Explain how *cis-trans* isomerism arises in cinnamaldehyde.

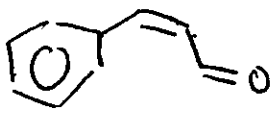
* C=C bond can't rotate about its axis

* 2 different groups on both double bond carbons [2]

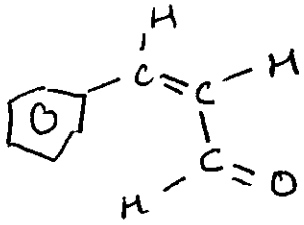
(ii) State and explain whether cinnamaldehyde is a *cis* or a *trans* isomer.

trans the H atoms are on opposite sides of the double bond [1]

(iii) Draw a skeletal or displayed formula to show the structure of the other *cis-trans* isomer of cinnamaldehyde.



or



[1]

(c) Cinnamaldehyde can be reduced using sodium borohydride, $NaBH_4$.

(i) State which functional group reacts with the sodium borohydride.

aldehyde [1]

(ii) Complete and balance the equation for this reaction.

$C_6H_5CH{=}CHCHO + 2[H] \rightarrow C_6H_5CH{=}CHCH_2OH$

[1]

For Examiner's Use

(d) In this question, one mark is available for spelling, punctuation and grammar.

Tollens' reagent can be used to identify the aldehyde group in cinnamaldehyde.

- Describe how you would make Tollens' reagent and carry out this test in the laboratory.
- Explain what happens to both the Tollens' reagent and the cinnamaldehyde in this reaction. Identify the organic product.

* add ammonia to silver nitrate solution
* warm with the aldehyde in a water bath
* Silver mirror indicates an aldehyde is present
* Ag^+ is reduced to Ag
* aldehyde is oxidised to the carboxylic acid $C_6H_5CH=CHCOOH$

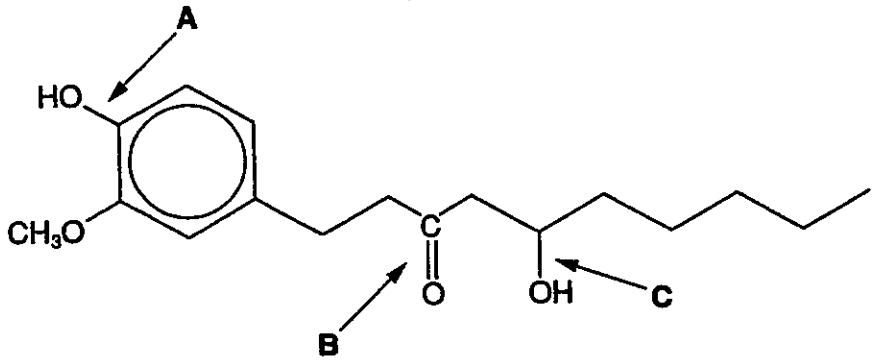
.....[7]

Quality of Written Communication. [1]

[Total: 15]

4. Gingerol is a compound extracted from root ginger. It has a distinctive smell and creates a hot taste when put into the mouth. The structure of gingerol is shown below.

For Examiner's Use



gingerol

(a) Name the **three** functional groups in gingerol labelled **A**, **B** and **C**.

A phenol **B** ketone

C (2°) alcohol [3]

(b) A solution of 2,4-dinitrophenylhydrazine can be used as a chemical test to identify one of these functional groups.

(i) Which of the functional groups, **A**, **B** or **C**, does this test identify?

B: the ketone [1]

(ii) State what you would expect to see when gingerol was added to this test solution.

yellow / orange ppt ✓ [2]

(iii) State whether or not gingerol would react with Tollens' Reagent (ammoniacal silver nitrate). Explain your reasoning.

No: it is a ketone not an aldehyde ✓

cannot be oxidised by Tollens reagent [1]

(c) Gingerol is thought to be produced by the plant to help protect it against attack from micro-organisms such as bacteria.

Suggest which part of the molecule is most likely to be responsible for the anti-bacterial properties.

the phenol group [1]

1

5. An ester, **D**, is used as a solvent for paints and varnishes.

For Examiner's Use

(a) Ester **D** can be manufactured by heating an alcohol under reflux with ethanoic acid and a catalyst.

(i) State a suitable catalyst for this reaction.

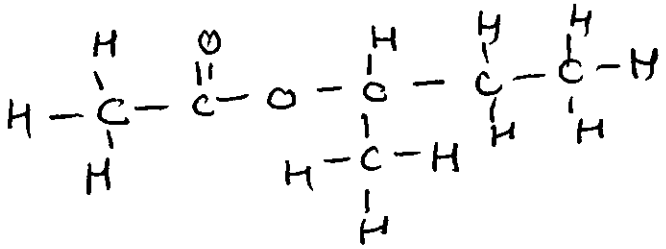
(conc) H_2SO_4 [1]

(ii) Explain why the reaction is carried out under reflux.

to prevent reactants & products being lost by evaporation [1]

(b) Ester **D** has a structural formula, $CH_3COOCH(CH_3)CH_2CH_3$.

(i) Draw the displayed formula of ester **D**.



[2]

(ii) State the name of the alcohol used to make ester **D**.

..... [1]

(c) Apart from being a good solvent, suggest another use for ester **D**.

food flavouring or perfumes [1]

[Total: 6]

6 (a) Compound **G**, shown below, is a tri-ester.

$$CH_3(CH_2)_{16}COOCH_2$$
$$|$$
$$CH_3(CH_2)_{16}COOCH$$
$$|$$
$$CH_3(CH_2)_{16}COOCH_2$$

(i) Deduce the physical state of **G** at room temperature.

Solid (because its saturated)

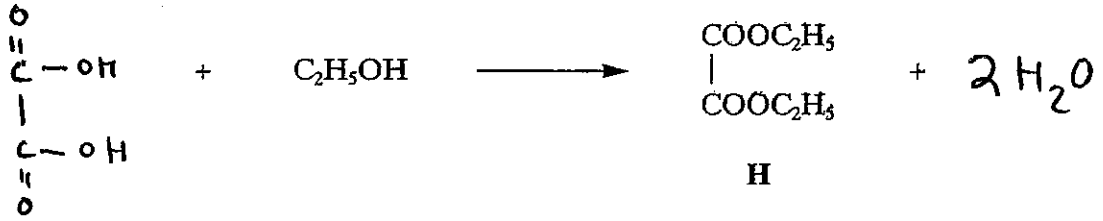
(ii) When completely hydrolysed by heating with aqueous sodium hydroxide, **G** forms an alcohol and the sodium salt of a carboxylic acid. Give the structural formula of the alcohol formed, write a formula for the sodium salt formed and state a use for this salt.

Structural formula of alcohol $HOCH_2CH(OH)CH_2OH$

Formula of sodium salt $CH_3(CH_2)_{16}COO^-Na^+$

Use for salt Soap (4)

(b) (i) Complete and balance the equation below for the formation of di-ester **H**.

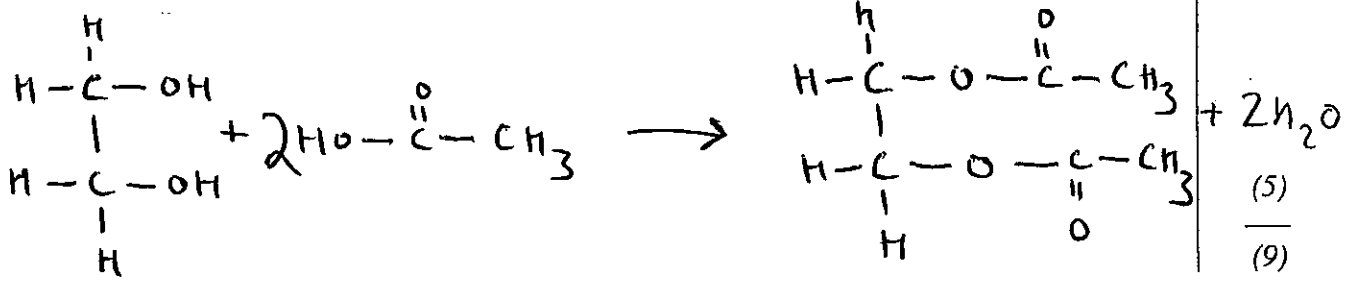


H

(ii) Identify a substance which could catalyse this reaction to form **H**.

Conc H_2SO_4

(iii) Draw a structural isomer of **H**, also a di-ester, which is formed by the reaction of ethane-1,2-diol with one other compound.



(5)

(9)