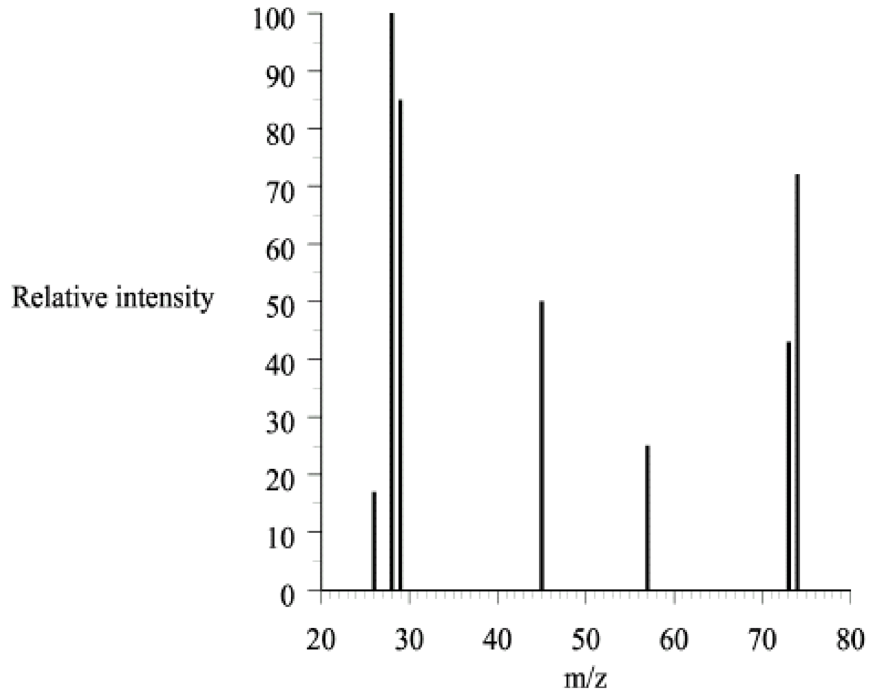
SECOND-YEAR HL CHEMISTRY

Final Review: Organic Chemistry

1. N03
2. M03/9

9. A pleasant-smelling liquid **A**, was hydrolysed in acid conditions to give two organic products, **B** and **C**. Product **B**, a carboxylic acid, was readily soluble in water. The mass spectrum of **B** is shown below.



(a) (i) Identify the M_r of **B**. *[1]*

(ii) Suggest fragment ions responsible for the peaks at m/z values of 29, 45 and 57. *[3]*

(iii) Using the information in (ii), deduce the structural formula of **B**. *[1]*

(b) Product **C** was also soluble in water and on analysis was found to contain

60.0 % C, 13.3 % H and 26.7 % O by mass.

The M_r of compound **C** is 60.

(i) Calculate the empirical and molecular formulas of **C**. *[3]*

(ii) Draw **three** possible structural formulas for the isomers with this molecular formula. *[3]*

(iii) Explain why **two** of the isomers in (ii) will show a broad absorption in their infrared spectra which will be missing in the spectrum of the third isomer. *[1]*

(iv) Explain how the two isomers showing the broad absorption in their infrared spectra could be identified from their ^{1}H NMR spectra. *[2]*

(c) Compound **C** was oxidised to compound **D** by refluxing with acidified sodium dichromate(VI). **D** was not acidic, but contained the **same** number of carbon atoms as **C**. Deduce the structural formulas of **C** and **D** and state the name of each one. *[4]*

(d) Deduce the structural formula of **A**. *[1]*

(e) An alcohol **E** does not react with acidified potassium dichromate(VI) but forms an alkene, **F**, with molecular formula C_4H_8, when heated with concentrated sulfuric acid.

(i) Deduce the structures and state the names of **E** and **F**. *[4]*

(ii) Write an equation for the conversion of **E** to **F** and state the type of reaction that occurs. *[2]*

3. N02/9

9. (a) Alkanes are often described as having low reactivity, although they do react with halogens.

(i) Explain why alkanes are unreactive. *[2]*

(ii) The first step in the reaction of propane with bromine can be represented by the equation.

$$Br_2 \rightarrow 2Br\square$$

State the type of species formed in this step and name the type of bond fission. *[2]*

(iii) Propane could be converted to 1-bromopropane or 2-bromopropane in this reaction. Deduce the peak height ratios in the ^{1}H NMR spectra of each of these three compounds. *[3]*

(b) The reaction between 1-bromopropane and warm dilute sodium hydroxide solution is described as an S_N2 nucleophilic substitution reaction.

(i) Explain each of the terms in S_N2. *[3]*

(ii) Write an equation and a mechanism for the reaction. *[5]*

(c) (i) 1-bromopropane is described as a *primary* halogenoalkane and 2-bromopropane is described as a *secondary* halogenoalkane. Explain these terms with reference to the two examples given. *[2]*

(ii) Give the structural formula of a tertiary halogenoalkane. *[1]*

(iii) State the type of substitution reaction undergone by tertiary halogenoalkanes. *[1]*

(d) Propan-1-ol, in the presence of a small amount of oxidising agent, forms compound X, and when refluxed with an excess of oxidising agent, forms compound Y.

(i) Identify a suitable oxidising agent and state the colour change. *[2]*

(ii) Draw the structural formulas of both compound X and compound Y. *[2]*

(iii) Explain why alkanoic acids are more acidic than alkanols. *[2]*

4. M02/5. This question is about four compounds **A**, **B**, **C** and **D**. **B**, **C** and **D** can be made from **A** by the following reactions. **A**, **B** and **C** are liquid at room temperature, and each compound.s molecular formula is shown.

$$\underset{\mathbf{D}}{C_4H_8} \longleftarrow \underset{\mathbf{A}}{C_4H_{10}O} \longrightarrow \underset{\mathbf{B}}{C_4H_8O} \longrightarrow \underset{\mathbf{C}}{C_4H_8O_2}$$

Sodium was added to each liquid compound. Gas bubbles formed slowly in **A** but rapidly in **C**. The infrared spectra of the compounds showed characteristic absorptions at the following wavenumbers (cm^{-1}):

A: 3400

B: 1720

C: 1720 and 3100

D: 1650

(a) Explain, by referring to the Data Booklet, how the infrared absorptions listed above can be used to identify the functional groups present in each of the compounds A, B, C and D. [4]

(b) Use the information above to identify each of the compounds A, B, C and D, giving the name and structural formula of each one. [4]

(c) (i) State the type of reaction occurring when A is converted to B and C, and state a suitable reagent and conditions for the reaction. [3]

(ii) Explain why B is much harder to obtain than C in this reaction. [1]

(d) State the type of reaction occurring when A is converted to D, and name a catalyst that is used. What other product is formed as well as D? [3]

(e) Identify the gas formed when A and C react with sodium and write an equation for each of the reactions occurring. Name the other product of the reaction between sodium and C. [4]

(f) Arrange the compounds A, B and C in increasing order of boiling point (lowest boiling point first). Explain your choice. [4]

(g) None of the compounds A, B, C and D exist as optical isomers. State the structural feature which is present in a compound that exists as optical isomers. Draw the structural formula of the isomer of A that exists as optical isomers. [2]

5. N01/7. (a) (i) Draw the structural formula of methyl methanoate. State the conditions and the starting materials for the preparation of methyl methanoate in the laboratory. Write a balanced chemical equation for the reaction. [6]

(ii) Draw the structural formula of an isomer of methyl methanoate. State two physical properties and one chemical property that would be different for the two compounds. State how each of these properties differ for the two compounds. [5]

(b) (i) Explain the term condensation and state the structural features of the monomers required to form condensation polymers. How does addition polymerisation differ from condensation polymerisation? [3]

(ii) Terylene is a polymer produced from the polymerisation of the two monomers ethane-1,2-diol and benzene-1,4-dicarboxylic acid. State what type of polymer Terylene is and draw the structural formula of its repeating unit. [3]

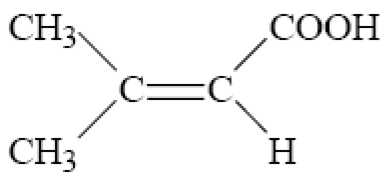
(c) (i) Draw the structures of 2-chloropropanoic acid and 2-hydroxypropanoic acid. [2]

(ii) 2-chloropropanoic acid can be converted to 2-hydroxypropanoic acid by nucleophilic substitution. Define the term nucleophile and state the nucleophile required for this reaction. [2]

(iii) 2-chloropropanoic acid and 2-hydroxypropanoic acid can both show optical activity. Identify the feature which both molecules possess that accounts for this property. When 2-hydroxypropanoic acid is formed from 2-chloropropanoic acid, the product shows no optical activity. Deduce the type of nucleophilic substitution that takes place and explain your answer. [4]

6. M01 Paper had no Organic Chemistry Questions.
7. N00/8. Molecule A contains two important functional groups and has the structural formula:

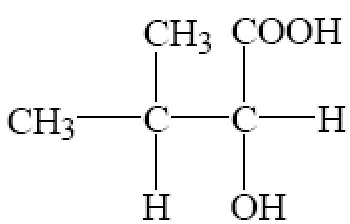
(a) For each functional group present in A, give one chemical reaction that could be carried out and the result that would indicate the presence of the group. [4]



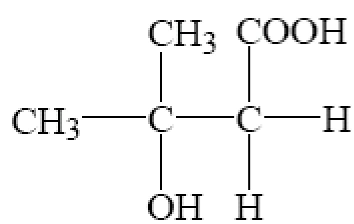
(b) (i) With the help of Table 18 in the Data Booklet, identify three characteristic infrared absorption ranges corresponding to specific bonds for compound A. [2]

(ii) With the help of Table 19 in the Data Booklet, identify three characteristic1H NMR chemical shift values for A. State the ratio of the areas of the peaks obtained for compound A. [3]

(c) When compound A reacts with water in the presence of an acid catalyst, products B and C can be obtained.



Compound **B**



Compound **C**

(i) Which of the two techniques IR or NMR spectroscopy would be more useful in determining whether the product is B or C? Explain your answer. [3]

(ii) How could B and C be distinguished by means of a chemical reaction? State the basis of the reaction, the reagent you would use, and the results expected for both B and C. [4]

(d) (i) Explain what is meant by optical activity. Describe the structural characteristic of an optically active molecule. [2]

(ii) Identify which compound, B or C, can show optical activity. Draw structures of the two enantiomers to illustrate clearly the relationship between them. How do the two enantiomers differ in their optical activity? [4]

(e) Both B and C contain two hydroxyl groups, but only one of these groups is acidic. Give two reasons why that is the case. [3]

8. M00/9. (a) A compound **C** with an empirical formula of $C_4H_{10}O$ has a mass spectrum which includes peaks at 74 and 59 and an infrared spectrum with a band at 3230-3350 cm^{-1}. Use this data to:

(i) [2] determine, with reasoning, the molecular formula of **C**;

(ii) [1] account for the peak at 59;

(iii) [1] identify the functional group giving the band at 3230-3350 cm^{-1}.

b) [2] **C** reacts with acidified dichromate(VI) to produce an organic acid. Give **two** possible structural formulae of **C**.

c) When **C** is dehydrated it gives a compound **D** which has an infrared spectrum with a band at 1620-1680 cm^{-1}. Use this data to:

(i) [1] identify the functional group present;

(ii) [2] give **two** possible structural formulae of **D**;

(iii) [3] give the **four** possible structures of the compound formed when **D** reacts with hydrogen chloride.

d) [1] **D** actually forms **E**, $CH_3C(Cl)(CH_3)CH_3$, when it reacts with hydrogen chloride. Which structural formulae of **D** produces **E**?

e) **E** is hydrolysed with OH^- ions to produce **F** by an S_N1 mechanism.

i) [3]What is meant by an S_N1 mechanism?

ii) [3] Why does an S_N1 rather than an S_N2 mechanism occur?

iii) [5] Give the stepwise mechanism for the conversion of **E** to **F**.

(f) [1] State and explain whether or not **F** reacts with acidified dichromate(VI).

9. 98/3. There are four different compounds with the formula $C_3H_6Cl_2$.

a) [3] Draw structural formulas **and** give the names of three of these.

b) [2] identify two structures in (a)that are polar. Give your reasoning

c) [4] The compounds in (a), like most halogenoalkanes, react with OH^- ions mainly by an S_N1 or an S_N2 mechanism. Identify the mechanism expected for each of the compounds in the list below and use an appropriate compound from this list to indicate the mechanism of an S_N2 reaction.

$CH_3CH_2CH_2CH_2Cl \rightarrow CH_3CH_2CHClCH_3 + (CH_3)_3CCl$

10. 95/4.Halogenoalkanes undergo hydrolysis reactions with aqueous potassium hydroxide, KOH.

(a) (i) [1 ma*rk*] Write an equation for the reaction of a halogenoalkane of formula C_4H_9Br with KOH.

(b) Hydrolysis reactions like (a)(i) may occur by either of two mechanisms: S_N1 or S_N2.

(i) [*2 marks*] Explain the meaning of the terms S_N1 and S_N2.

(ii) [4 *marks*] Predict the mechanism (S_N1 or S_N2) expected for the reaction of aqueous KOH with the following halogenoalkanes, and write an equation (using structural formulae) to illustrate each mechanism.

1bromobutane

2bromo2methylpropane

(iii) [1 mark] Account for the mechanisms in (ii) in terms of the properties of the halogenoalkanes involved.

(iv) [2 *marks*] Describe how the rate of each of the reactions in (ii) is affected when the concentration of the KOH is doubled. Explain your reasoning.

11. 94/4. a) [3 marks] A volatile organic compound, X, contains 24.7% carbon, 2.1% hydrogen and 73.2% chlorine, by mass. A 2.18 g sample of X is found to occupy 505 cm^3 at 0ºC and 101.3 kPa.

(i) Determine the empirical formula of compound X.

(ii) Determine the relative molecular mass of compound X and determine its molecular formula.

(b) [5 marks] Compound X is known to exist in three isomeric forms.

(i) Give the correct names of these three isomers, and sketch their structural formulae.

(ii) The isomers of compound X illustrate two different types of isomerism. Show how your examples illustrate the two different types of isomerism.

(c) [4 marks] (i) The addition of one mole of chlorine gas to one mole of ethyne produces one of the isomers of X. This isomer has a net dipole moment of zero. Identify the isomer produced and explain your reasoning.

(ii) The addition of one mole of hydrogen chloride gas to one mole of ethyne produces a compound which is readily polymerized. Sketch the molecular structure of the resulting polymer, and name this commercially important substance.

12. <u>93/4</u>. An organic compound was found by CHN analysis to contain 40.45% C; 7.86% H and 15.73% N. A separate experiment determined the relative molecular mass of the compound to be 89.0 g mol^{-1}.

(a) [3 marks] Determine the empirical formula of the compound.

(b) [1 mark] What is the molecular formula of the compound?

(c) [2 marks] The compound is found to react readily with both dilute hydrochloric acid, HCl, and with aqueous sodium carbonate, Na_2CO_3. On the basis of these observations, suggest two functional groups which might be present in the molecule.

(d) [2 marks] Give two possible structural formulae for the compound.

(e) [1 mark] The compound is found to be 'optically active'. What is meant by this?

(f) [1 mark] On the basis of the information given in part (e), one of the two structures drawn for part (d) can be eliminated. Identify the isomer which can be eliminated and defend your choice.

13. <u>93/11</u>. An aliphatic compound, X, is known to have the molecular formula $C_4H_{10}O$.

a) [3 marks]. It shows a very strong infra-red absorption at 3300 cm^{-1}. To what class of compounds may compound X be assigned? Write three possible structural formulae for compound X.

b) [1 mark] Dehydration of compound X by hot, concentrated sulphuric acid yields a gaseous compound, Z, of formula C_4H_8. Write a balanced equation which describes this process.

14. <u>90/4</u> A white powder consists of C_6H_5COONa, $C_6H_5NH_2{\cdot}HCl$ ($C_6H_5NH_3Cl$) and $C_6H_5NHCOCH_3$. The following reagents are available for separating the mixture: water, diethyl ether, dilute HCl(aq) and dilute NaOH(aq).

(a) [5 marks] Give an experimental procedure for separating and obtaining pure benzoic acid, C_6H_5COOH, aniline, $C_6H_5NH_2$, and acetanilide, $C_6H_5NHCOCH_3$, from the mixture.

(b) [3 marks] Give any chemical reactions that take place in the separation procedure.

(c) [2 marks] A student measured the melting point of benzoic acid after separating the three solids and obtained the value of 115-120°C. Upon recrystallizing the benzoic acid from water he obtained the value of 121-122°C. Account for these experimental results.

15. <u>90/10</u>. Pentan-2-ol and pentan-3-ol are each heated with an acidified solution of potassium dichromate.

(c) [4 marks] Draw the structural formulae of the two alcohols and the products of their reactions with potassium dichromate.

SECOND-YEAR HL CHEMISTRY

Final Review: Organic Chemistry

Solutions

1. N03 (none)
2. M03/9

9. (a) (i) 74; *[1]*

(ii) 29 = $C_2H_5^+$ / CHO^+ ;
45 = $COOH^+$;
57 = $C_2H_5CO^+$ / $C_2O_2H^+$ **not** $C_4H_9^+$; *[3]*
If no + sign shown, penalize once only.

(iii) *Omitted H atom(s) – penalize once on whole question.*

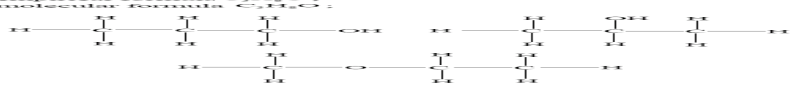
Must be fully correct
or C_2H_5COOH / $C_2H_5CO_2H$ / CH_3CH_2COOH ; *[1]*

(b) (i)

C	H	O
$\frac{60}{12}$	$\frac{13.3}{1}$	$\frac{26.7}{16}$;

empirical formula C_3H_8O ;
molecular formula C_3H_8O ; *[3]*

(ii)



[3]

[1] for each formula.
Accept $CH_3CH_2CH_2OH$, $CH_3CH(OH)CH_3$ *and* $CH_3OCH_2CH_3$.
Incorrect structure must have M_r *= 60 and all bonding complete to be considered for ECF. An alternative is isomers of ethanoic acid.* *[1]*

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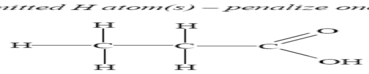

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or C_2H_5COOH / $C_2H_5CO_2H$ / CH_3CH_2COOH ; *[1]*

(b) (i) C H O $\frac{60}{12}$ $\frac{13.3}{1}$ $\frac{26.7}{16}$;

empirical formula C_3H_8O ;
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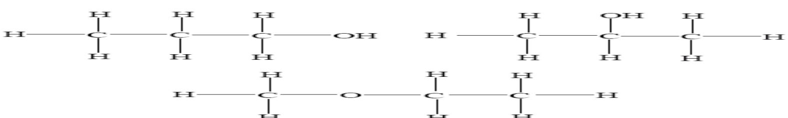

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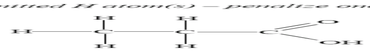
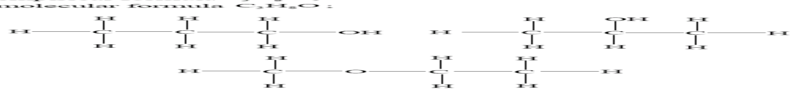


Must be fully correct
or C_2H_5COOH / $C_2H_5CO_2H$ / CH_3CH_2COOH ; *[1]*

(b) (i) C H O $\frac{60}{12}$ $\frac{13.3}{1}$ $\frac{26.7}{16}$;

empirical formula C_3H_8O ;
molecular formula C_3H_8O ; *[3]*

(ii)



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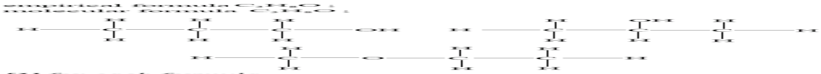

9. (a) (i) 74; *[1]*

(ii) $29 = C_2H_5^+$ / CHO^+ ;
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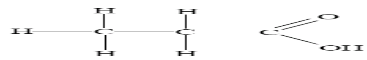

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or C_2H_5COOH / $C_2H_5CO_2H$ / CH_3CH_2COOH ; *[1]*

(b) (i)

C	H	O	
$\frac{60}{12}$	$\frac{13.3}{1}$	$\frac{26.7}{16}$	;

empirical formula C_3H_8O ;
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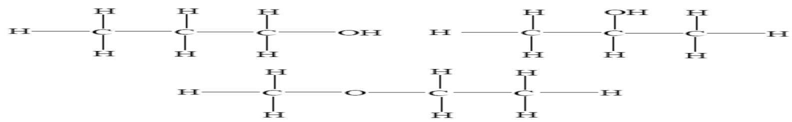
(ii)



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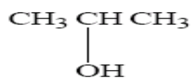
Incorrect structure must have $M_r = 60$ *and all bonding complete to be considered for ECF. An alternative is isomers of ethanoic acid.* *[1]*

(iii) two compounds contain OH / one isomer does not contain OH; *[1]*

(iv) $CH_3CH_2CH_2OH$ 4 peaks; *[2]*



3 peaks;

*Allow **[1]** for different number of peaks / different ratio of peaks.*
*Allow **[1]** for chemical shift for OH in appropriate range.*
Allow ECF from (b)(ii) for number of peaks.

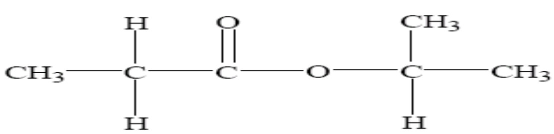
(c) C: $CH_3CH(OH)CH_3$
propan-2-ol;

D:  ; / CH_3COCH_3 *[4]*

propanone / acetone;

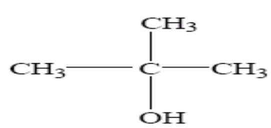
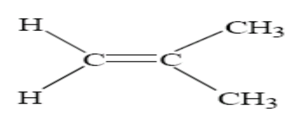
If displayed formula given, double bond must be shown from C to O.
In each case, allow ECF for name if wrong structure is given.

(d)



[1]

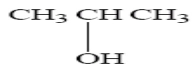
Accept $CH_3CH_2COOCH(CH_3)_2$. *Allow ECF.*

(e) (i) E:  ; F:  ;

(2)-methylpropan-2-ol (*ECF*); methylpropene; *[4]*
Accept $(CH_3)_3COH$ *and* $CH_2C(CH_3)_2$. *Must be consistent with alcohol.*
Allow ECF for names, i.e. must be consistent with structures.

(iii) two compounds contain OH / one isomer does not contain OH; *[1]*

(iv) $CH_3CH_2CH_2OH$ 4 peaks; *[2]*



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(c) C: $CH_3CH(OH)CH_3$
propan-2-ol;

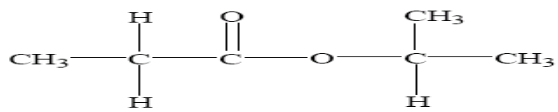
D: 

/ CH_3COCH_3 *[4]*

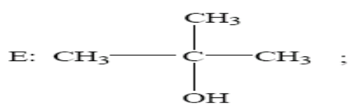
propanone / acetone;

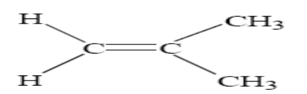
If displayed formula given, double bond must be shown from C to O.
In each case, allow ECF for name if wrong structure is given.

(d)



Accept $CH_3CH_2COOCH(CH_3)_2$. *Allow ECF.* *[1]*

(e) (i) E: 

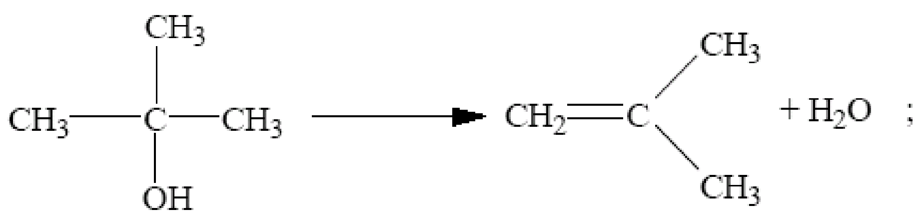
F: 

;

(2)-methylpropan-2-ol (*ECF*); methylpropene; *[4]*

Accept $(CH_3)_3COH$ *and* $CH_2C(CH_3)_2$. *Must be consistent with alcohol.*

Allow ECF for names, i.e. must be consistent with structures.

(ii) 

Previous formulas from (e)(i) + H_2O *as product.*

dehydration / elimination; *[2]*

Do not accept condensation.

3. N02/9

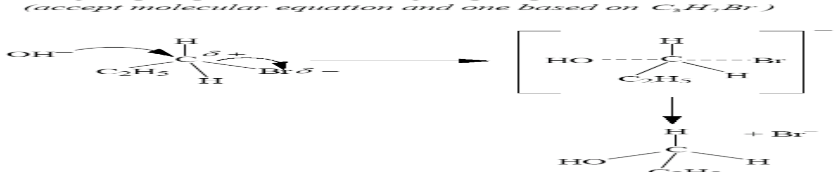
9. (a) (i) no polar bonds / little polarity in C—H bond;
high C—C and C—H bond energies; *[2]*

(ii) free radical;
homolytic; *[2]*

(iii) $CH_3CH_2CH_3 = 3:1$; *(accept 6:2)*
$CH_3CH_2CH_2Br = 3:2:2$;
$CH_3CHBrCH_3 = 6:1$ *[3]*

(b) (i) substitution means replacement of one atom / group in a molecule by another;
nucleophiles are reagents that have non-bonding pairs of electrons;
2 means bimolecular / number of particles in the rate-determining step / *OWTTE*; *[3]*

(ii) $CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + BR^-$
(accept molecular equation and one based on C_3H_7Br *)*



attack by OH^- on correct carbon;
C — Br arrow correct;
correct intermediate (--- and charge);
structure of product; *[5]*

9. (a) (i) no polar bonds / little polarity in C—H bond;
high C—C and C—H bond energies; *[2]*

(ii) free radical;
homolytic; *[2]*

(iii) $CH_3CH_2CH_3 = 3:1$; *(accept 6:2)*
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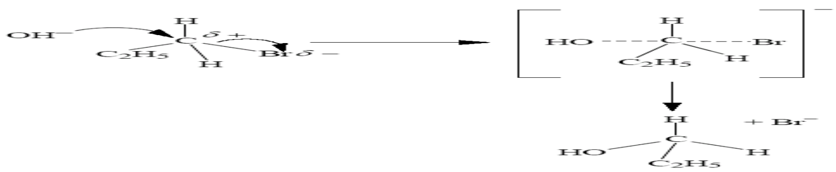

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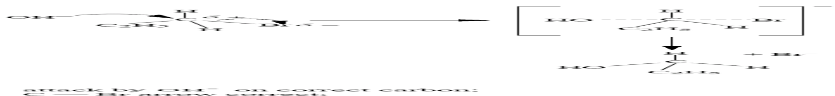

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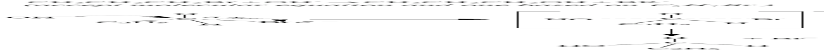

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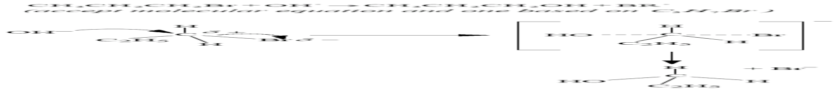


attack by OH^- on correct carbon;
C — Br arrow correct;
correct intermediate (--- and charge);
structure of product; *[5]*

(c) (i) primary = 2 × H atoms, 1 alkyl group;
secondary = 1 × H atom, 2 alkyl groups; *[2]*

(ii) *e.g.*

Accept any suitable answer. Allow R in place of specific alkyl groups. *[1]*

(iii) S_N1 *[1]*

(d) (i) **acidified** (potassium) manganate(VII) / permanganate / potassium dichromate(VI);
purple to colourless / orange to green; *[2]*

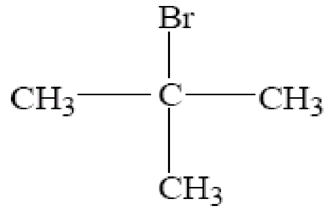
(ii)

compound X   compound Y *[2]*

(iii) O — H / hydroxyl bond in acids is more polar because of the (electron-withdrawing) C — O group / carbonyl O attracts electrons to itself;
$RCOO^-$ is more stable than RO^- (because of delocalization); *[2]*

(c) (i) primary = 2 × H atoms, 1 alkyl group;
secondary = 1 × H atom, 2 alkyl groups; ***[2]***

(ii) *e.g.*



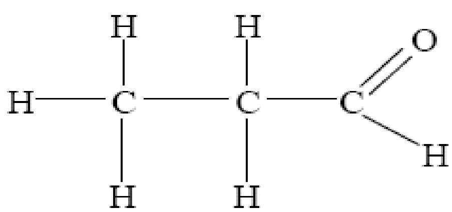
[1]

Accept any suitable answer. Allow R in place of specific alkyl groups.

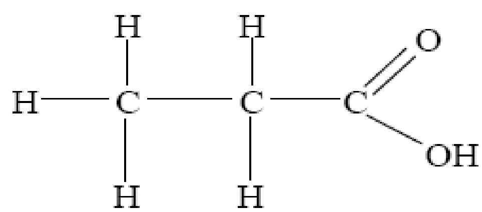
(iii) S_N1 ***[1]***

(d) (i) **acidified** (potassium) manganate(VII) / permanganate / potassium dichromate(VI);
purple to colourless / orange to green; ***[2]***

(ii)



compound X



compound Y ***[2]***

(iii) O — H / hydroxyl bond in acids is more polar because of the (electron-withdrawing) C ═ O group / carbonyl O attracts electrons to itself;
$RCOO^-$ is more stable than RO^- (because of delocalization); ***[2]***

4. M02/5

(a) **A** contains O—H because 3400 ***[1]***;
B contains C═O because 1720 ***[1]***;
C contains C═O and O—H because 1720 and 3100 ***[1]***;
D contains C═C because 1650 ***[1]***.
(Accept names e.g. hydroxyl instead of O–H) ***[4]***

(b) (**A**) butan-**1**-ol / 1-butanol / $CH_3CH_2CH_2CH_2OH$ ***[1]***
(**B**) butanal, $CH_3CH_2CH_2CHO$ ***[1]***
(**C**) butanoic acid, $CH_3CH_2CH_2COOH$ ***[1]***
(**D**) but-1-ene, $CH_3CH_2CHCH_2$ ***[1]*** *(allow butene but not but-2-ene)*
*(Accept answers based on identifying **A** as 2-methylpropan-1-ol)*
*(There are 8 marking points, 4 names and 4 structures. Award marks as follows: 8 correct **[4]**, 6 or 7 correct **[3]**, 4 or 5 correct **[2]**, 2 or 3 correct **[1]**, 0 or 1 correct **[0]**.* ***[4]***

(c) (i) oxidation / redox ***[1]***;
potassium dichromate(VI) / potassium manganate(VII) *(accept formulas)* ***[1]***;
acidified / heat ***[1]***. ***[3]***

(ii) it is more easily oxidised / it is oxidised to compound **C** unless it is removed / *OWTTE* ***[1]***

(d) elimination / dehydration ***[1]***;
(concentrated) sulfuric acid /phosphoric acid / Al_2O_3 / porous pot ***[1]***;
water ***[1]***. ***[3]***

(e) hydrogen / H_2 ***[1]***;
($2CH_3CH_2CH_2CH_2OH + 2Na$) → $\mathbf{2CH_3CH_2CH_2CH_2ONa}$ ($+ H_2$) ***[1]***;
($2CH_3CH_2CH_2COOH + 2Na$) → $\mathbf{2CH_3CH_2CH_2COONa}$ ($+ H_2$) ***[1]***;
(Only the correct formula of each product is needed. Accept C_4H_9ONa, etc.)
sodium butanoate ***[1]***. ***[4]***

(f) **B**, **A**, **C** ***[1]***;
B has dipole–dipole attractions / no hydrogen bonding ***[1]***;
A has hydrogen bonding ***[1]***;
C has more/stronger hydrogen bonding / forms dimers *(difference with **A** must be clear)* ***[1]***.
(Explanation marks can be gained if order is wrong.) ***[4]***

(g) Asymmetric carbon atom / chiral centre / C atom joined to 4 different atoms/groups ***[1]***.
$CH_3CH(OH)CH_2CH_3$ ***[1]*** ***[2]***

(a) **A** contains O—H because 3400 ***[1]***;
B contains C=O because 1720 ***[1]***;
C contains C=O and O—H because 1720 and 3100 ***[1]***;
D contains C=C because 1650 ***[1]***.
(*Accept names e.g. hydroxyl instead of O–H*) ***[4]***

(b) (**A**) butan-**1**-ol / 1-butanol / $CH_3CH_2CH_2CH_2OH$ ***[1]***
(**B**) butanal, $CH_3CH_2CH_2CHO$ ***[1]***
(**C**) butanoic acid, $CH_3CH_2CH_2COOH$ ***[1]***
(**D**) but-1-ene, $CH_3CH_2CHCH_2$ ***[1]*** (*allow butene but not but-2-ene*)
*(Accept answers based on identifying **A** as 2-methylpropan-1-ol)*
*(There are 8 marking points, 4 names and 4 structures. Award marks as follows: 8 correct **[4]**, 6 or 7 correct **[3]**, 4 or 5 correct **[2]**, 2 or 3 correct **[1]**, 0 or 1 correct **[0]**.* ***[4]***

(c) (i) oxidation / redox ***[1]***;
potassium dichromate(VI) / potassium manganate(VII) *(accept formulas)* ***[1]***;
acidified / heat ***[1]***. ***[3]***

(ii) it is more easily oxidised / it is oxidised to compound **C** unless it is removed / *OWTTE* ***[1]***

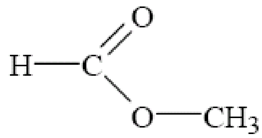
(d) elimination / dehydration ***[1]***;
(concentrated) sulfuric acid /phosphoric acid / Al_2O_3 / porous pot ***[1]***;
water ***[1]***. ***[3]***

(e) hydrogen / H_2 ***[1]***;
$(2CH_3CH_2CH_2CH_2OH + 2Na) \rightarrow \mathbf{2CH_3CH_2CH_2CH_2ONa}\ (+H_2)$ ***[1]***;
$(2CH_3CH_2CH_2COOH + 2Na) \rightarrow \mathbf{2CH_3CH_2CH_2COONa}\ (+H_2)$ ***[1]***;
(*Only the correct formula of each product is needed. Accept C_4H_9ONa, etc.*)
sodium butanoate ***[1]***. ***[4]***

(f) **B**, **A**, **C** ***[1]***;
B has dipole–dipole attractions / no hydrogen bonding ***[1]***;
A has hydrogen bonding ***[1]***;
C has more/stronger hydrogen bonding / forms dimers (*difference with **A** must be clear*) ***[1]***.
(Explanation marks can be gained if order is wrong.) ***[4]***

(g) Asymmetric carbon atom / chiral centre / C atom joined to 4 different atoms/groups ***[1]***. ***[2]***
$CH_3CH(OH)CH_2CH_3$ ***[1]***

5. N01/7

(a) (i) $HCOOCH_3$ **OR**  *[1]*

Heat *[1]*

Acid catalyst / H^+ *[1]*

HCOOH / methanoic acid *[1]*

CH_3OH / methanol *[1]*

$HCOOH + CH_3OH \rightleftharpoons HCOOCH_3 + H_2O$ *(accept $\rightarrow$ instead of $\rightleftharpoons$)* *[1]*

(ii) CH_3COOH (*but not* $C_2H_4O_2$) *[1]*

Physical:

Boiling point: acid is higher (due to greater H-bonding) / ester is lower

pH: acid < 7; ester = 7 (*need both for mark*). *[1]*

OR Smell: acid: vinegar/pungent smell; ester: sweet smell. *[1]*

Chemical:

acid reacts with OH^- to form salt and water. *[1]*

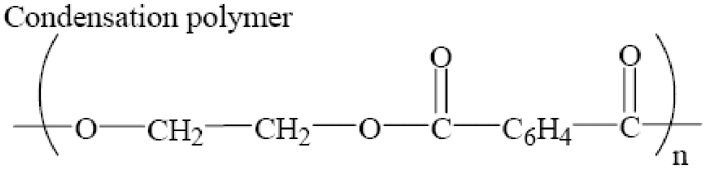
Ester reacts with OH^- to form salt plus methanol / acid can be esterified; ester cannot *[1]*

(b) (i) When two (small) molecules combine to form a larger one **with** the elimination of a smaller molecule (such as water). *[1]*

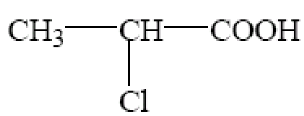
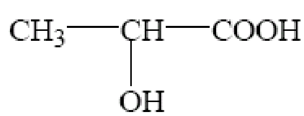
The need for two functional groups on each of the two monomers. *[1]*

Addition polymerisation: process in which unsaturated monomers combine to form a polymer **without** the elimination of any atoms/molecules. *[1]*

(ii) Condensation polymer *[1]*



*(Award **[1]** for ester group and **[1]** for* CH_2CH_2 *and* C_6H_4 *groups.)* *[2]*

(c) (i)   (*award **[1]** for each.*) *[2]*

(ii) Negatively charged or neutral species containing electron pairs / electron pair donors / Lewis bases *[1]*

OH^- (*no mark for* H_2O *– water does not react*) *[1]*

(iii) Each compound contains a C with four different groups on it / contains a chiral centre / molecules are asymmetric / contains asymmetric C / optically active starting materials. *[1]*

Reaction must involve S_N1 mechanism. *[1]*

Forming a planar carbocation. *[1]*

The nucleophile can attach from either side producing an equal mixture of enantiomers / racemic mixture (thus optically inactive). *[1]*

6. M01

7. N00/8

(a) $C = C$: add bromine (or bromine water) *[1]*
its colour is discharged **OR** changes from orange to clear. *[1]*
COOH: add sodium carbonate solution **OR** Na **OR** acid/base indicator. *[1]*
It would effervesce/gas bubbles produced. *[1]*

(b) (i) $C = C$ at 1610–1680 cm^{-1}
$C = O$ at 1680–1750 cm^{-1}
C—H at 2840–3095 cm^{-1} *[2]*
O—H at 2500–3300 cm^{-1}
*(Award **[2]** for three correct and **[1]** for any two.)*

(ii) CH_3 at 0.9 ppm
$C = C — H$ at 4.9–5.9 ppm
COOH at 11.5 ppm *[2]*
*(Award **[2]** for all three and **[1]** for any two.)*

Ratio of areas of peaks: 6:1:1 *[1]*

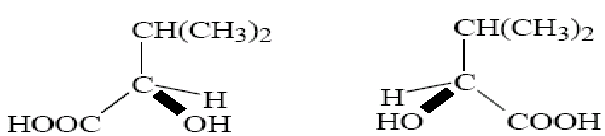
(c) (i) NMR *[1]*
because B would give 5 peaks *[1]*
whereas C would give only 4 peaks *[1]*
(Accept: because the chemical environments of the H atoms are different and the number of peaks would be different.)

(ii) Test based on fact that secondary alkanols (alcohols) area easily oxidised, whereas tertiary alkanols are not *[1]*
Warm (or reflux) with acidified dichromate or manganate(VII) *[1]*
With B orange dichromate would change to green (**OR** purple manganate(VII) would turn (almost) clear) *[1]*
With C it would remain orange (or purple) *[1]*

(d) (i) Optical activity is the ability to rotate the plane of polarised light (accept rotate plane polarised light). *[1]*

It has an asymmetric carbon atom **OR** a carbon bonded to four different groups **OR** the molecule is asymmetric **OR** chiral centre. *[1]*

(ii) Compound B can exhibit optical activity. *[1]*



(accept C_3H_7) *[2]*

*(Award only **[1]** if relationship is not clear.)*

One enantiomer rotates plane of polarised light clockwise (or +), the other anticlockwise (or –); accept dexrorotatory and levorotatory. *[1]*

(a) C ═ C: add bromine (or bromine water) *[1]*
its colour is discharged **OR** changes from orange to clear. *[1]*
COOH: add sodium carbonate solution **OR** Na **OR** acid/base indicator. *[1]*
It would effervesce/gas bubbles produced. *[1]*

(b) (i)

C ═ C	at 1610–1680 cm^{-1}
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(ii)

CH_3	at 0.9 ppm
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(Award only [1] if relationship is not clear.)

One enantiomer rotates plane of polarised light clockwise (or +), the other anticlockwise (or –); accept dexrorotatory and levorotatory. *[1]*

(e) For OH to be acidic, the O—H bond has to break/ H^+ or protons form

$$(\text{—C—O—H} \rightarrow \text{—C—O}^{\ominus} + H^{+})$$ *[1]*

In COOH the O—H bond breaks/ H^+ forms because the second O on carbon attracts e^- density from the O—H bond. *[1]*

Delocalisation stabilises the COO^- anion. *[1]*

8.