1. (a)

Element	%	Atomic Mass	% ÷ Atomic Mass	Simplest ratio
Carbon	70.5	12	5.875	5.95 = 6
Hydrogen	13.7	1	13.7	13.87 = 14
Oxygen	15.8	16	0.9875	1
			(1)	**(1)**

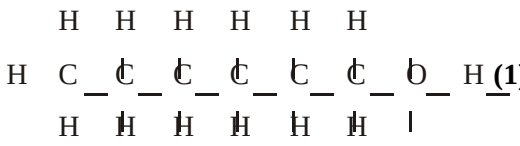
2

(b) 1 Infra red absorption at 3300 suggest alcohol / –OH **(1)**
absorption at 2900 suggests alkane (and aldehyde) **(1)**
NOT –CH *on its own*

2 Mass spectrum
Peak at 17 or 102–17 (ie 85) suggests alcohol / OH
OR
Peak at 31 suggests CH_2OH **(1)**

Peak at 15	suggests methyl	)	
Peak at 29	suggests ethyl	)	
Peak at 43	suggests propyl	)	*three needed*
Peak at 57	suggests butyl	)	*for 2nd mark* **(1)**
Peak at 71	suggests pentyl	)	
Peak at 85	suggests hexyl	)	

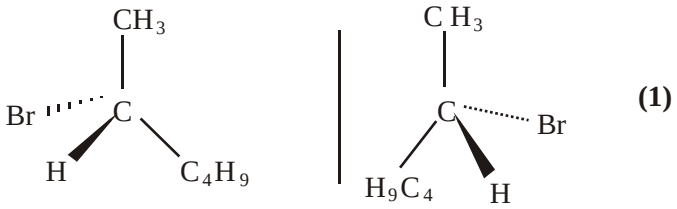
3 Only one dehydration isomer suggests that the OH group must be on the end of the chain ie a primary alcohol **(1)**



(1) 6

(c) 1

(d) (i)



(1)

QWC*

Rotate plane of plane polarised light in opposite directions **(1)** 2

(ii) Hexan–2–ol 1

(e) Primary halogenoalkanes are second order

Tertiary halogenoalkanes are first order **(1)**
Difficult to predict for secondary halogenoalkanes an experiment is needed to decide **(1)** 2

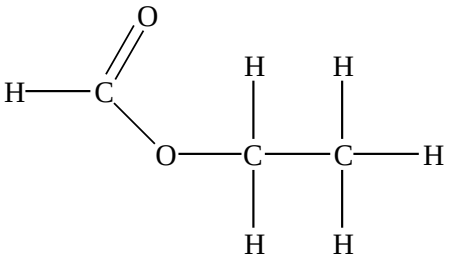
(f) (A) would produce hexanal and hexanoic acid **(1)**
(E) would produce hexan–2–one **(1)**
Ketone / aldehyde / carboxylic acid **1 (out of 2)** 2

[16]

2. B

[1]

3. (a)



1

(b) ester 1

(c) (i) Moles: C_2H_5OH: 3.75 **(1)**

Moles: $HCOOC_2H_5$: 2.50 and moles H_2O : 2.50 **(1) for both** 2

(ii) $K_c = \dfrac{[HCOOC_2H_5][H_2O]}{[HCOOH][C_2H_5OH]}$ 1

Reject obviously round brackets ***"( )"***

(iii) $K_c = \dfrac{2.50/0.485 \times 2.50/0.485}{0.50/0.485 \times 3.75/0.485}$ **(1)**

Must have clearly divided moles of each component by 0.485 for 1st mark e.g.

$[HCOOC_2H_5] = [H_2O] = 5.16$ (mol dm^{-3})

and $[HCOOH] = 1.03$ (mol dm^{-3})

and $[C_2H_5OH] = 7.73$ (mol dm^{-3})

= 3.33 **(1) stand alone mark**

IGNORE sig.figs. 2

Accept $K_c = \dfrac{(2.50)^2}{0.50 \times 3.75}$ *= 3.33 only scores* ***(2)*** *if it is stated that V cancels either here or in (iv)*

If $[H_2O]$ *omitted in (ii), then answer*
$K_c = 0.647\ mol^{-1}\ dm^3$
(2) *but this will give*
$K_c = 1.33\ mol^{-1}\ dm^3$ *with V omitted from calculation* ***(1)***

Reject 1st mark if 485 used as V in expression

(iv) No, (as) equal numbers of moles on both sides
OR volumes cancel
OR mol dm^{-3} cancel
OR units cancel
OR crossing out units to show they cancel 1

Accept "equal powers/moles on both sides"
OR "powers cancel"

Mark CQ on K_c *expression in (ii)*

Reject ***"****concentrations cancel****"***

(d) (i) (as reaction) endothermic **(1)**

Accept exothermic in backward direction (or words to that effect)

K_c decreases **(1)**

If state exothermic in forward direction, ***1 mark only (out of 4)*** *for CQ "increase in* K_c*"*

numerator in quotient (has to) decrease
OR denominator in quotient (has to) increase
OR fraction (has to) decrease **(1)**

yield of $HCOOC_2H_5$ decreases **(1)** 4

(ii) no effect as catalysts do not affect (the value of) K
OR
no effect as catalysts do not affect the position of equilibrium
OR
no effect as catalysts do not affect the yield
OR
No effect as catalysts increase the rate of the forward and backward reactions equally/to the same extent
OR
no effect as catalysts **only** increase the rate
OR
no effect as catalysts **only** alter the rate

"no effect" can be stated or implied
IGNORE any references to activation energy 1

Reject just "catalysts increase rate"

[13]

4. (a)

Element	Mass of 1 mole	%	No. of moles	Simplest Ratio
C	12	73.2	6.10	5
H	1	7.3	7.30	6
O	16	19.5	1.22	1

Empirical formula C_5H_6O **(1)**
The mass of the empirical formula is
$12 \times 5 + 1 \times 6 + 16 \times 1 = 82$
Therefore the molecular formula is empirical $\times 2 = C_{10}H_{12}O_2$ **(1)**
OR

Mass of Carbon is $73.2/100 \times 164 = 120$ so 10 C atoms

Mass of Hydrogen is $7.3/100 \times 164 = 11.97$ so 12 H atoms

Mass of Oxygen is $19.5/100 \times 164 = 31.98$ so 2 O atoms

Therefore the molecular formula is $C_{10}H_{12}O_2$ **(1)** 2

Empirical formula is C_5H_6O **(1)**

(b) (i) arene/benzene ring
OR high carbon to hydrogen ratio/low hydrogen to carbon ratio aryl. 1
ALLOW “arene or alkene”

(ii) contains an OH group/“acid or alcohol” 1

(iii) phenol/"not a carboxylic acid" 1

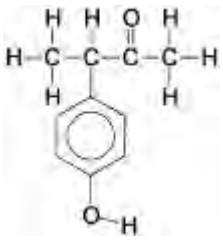
(iv) contains a C=O group/carbonyl/"aldehyde or ketone" 1

(v) a ketone/ “not an aldehyde” 1

(vi) contains a carbon atom with four different groups around it/chiral compound/optical isomers 1

(vii) an arene **(1)**
with two adjacent hydrogen atoms **(1)** 2

(c)



1

[11]

5. (a) (i) Elimination / dehydration 1

(ii) **Concentrated** sulphuric acid / **concentrate**d phosphoric acid / aluminium oxide 1

ACCEPT correct formula

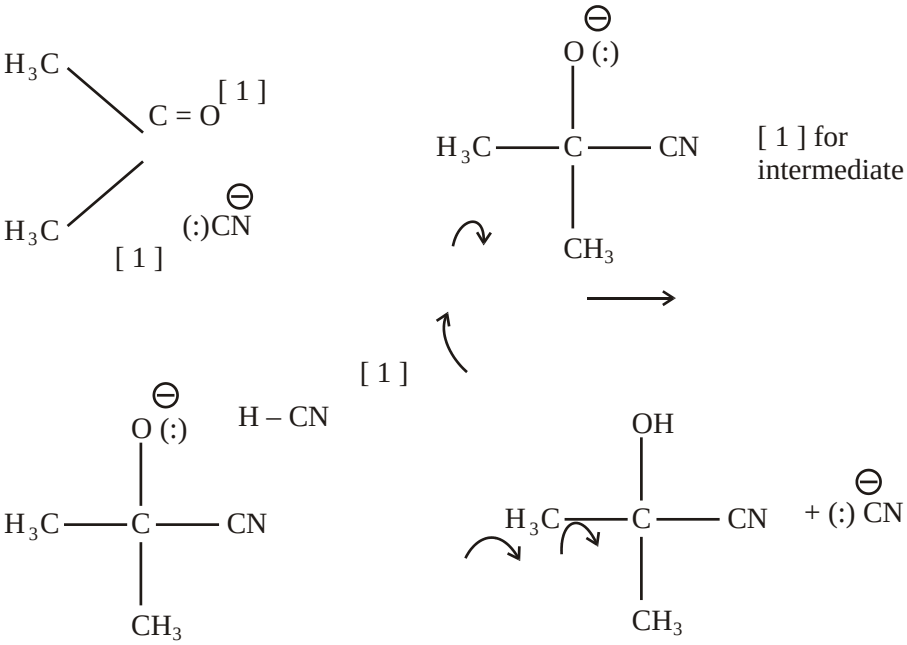
(iii) Hydrolysis 1

(iv) Esterification 1

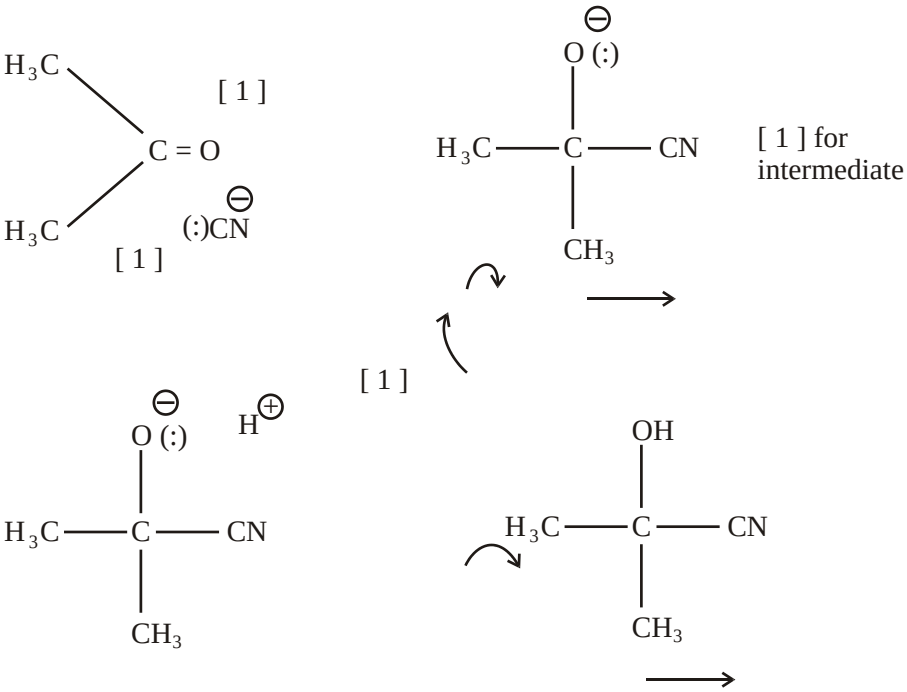
(v) CH_3OH / methanol 1

(b) (i)

EITHER



OR



Lone pairs not essential

Arrows may start from minus of O^-

ALLOW CN^- OR ^-CN

(ii) High $[H^+]$

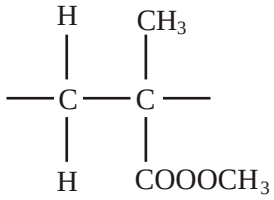
insufficient CN^- (available for nucleophilic attack) **(1)**

Low $[H^+]$
insufficient H^+ / HCN for the second stage **(1)**

High $[H^+]$ surpasses ionisation / shifts equilibrium to left and low $[H^+]$ shifts equilibrium to right **max (1)** 2

(c) (i) (Free) radical / peroxide 1

(ii)



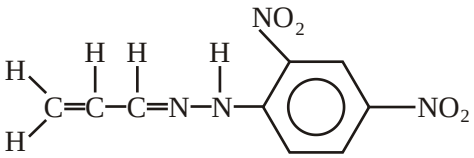
Correct repeating unit **(1)**
Continuation bonds dependent on a 2 carbon skeleton unit **(1)** 2

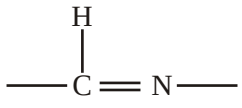
(iii) The polymer chain lengths are different (due to different termination steps) different size molecules / different numbers of monomer (units) 1

[15]

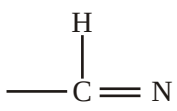
6. (a) (i) Yellow/orange precipitate (allow red/any shades of red) 1

(ii)





(1)



Must be formed by C atom from the C = O group

rest of molecule correct **(1)** 2

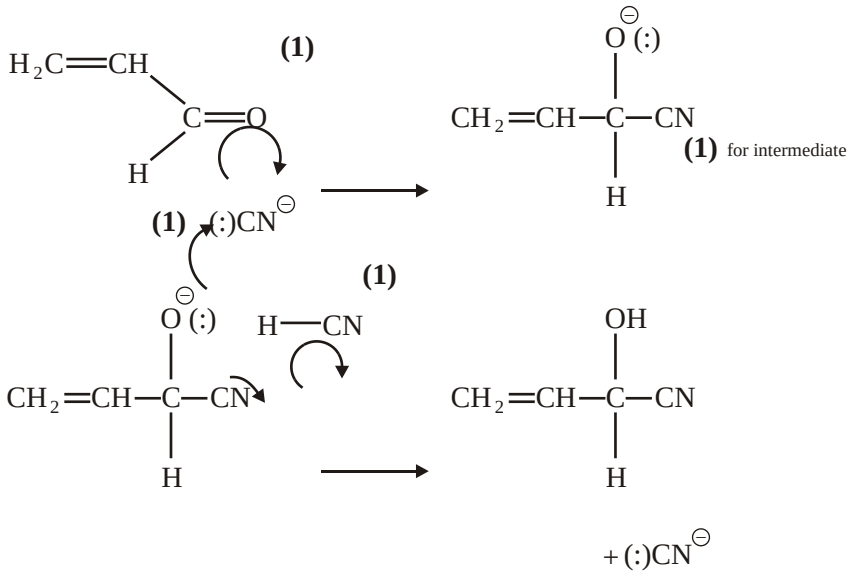
(b) Hydrogen nuclei OR hydrogen atoms OR hydrogen(s) OR protons **(1)**

in (three) different environments (may be shown by diagram) **(1)**

Ratio 2:1:1 **(1)**

Any reference to fragments or bonds scores zero 3

(c) (i) EITHER



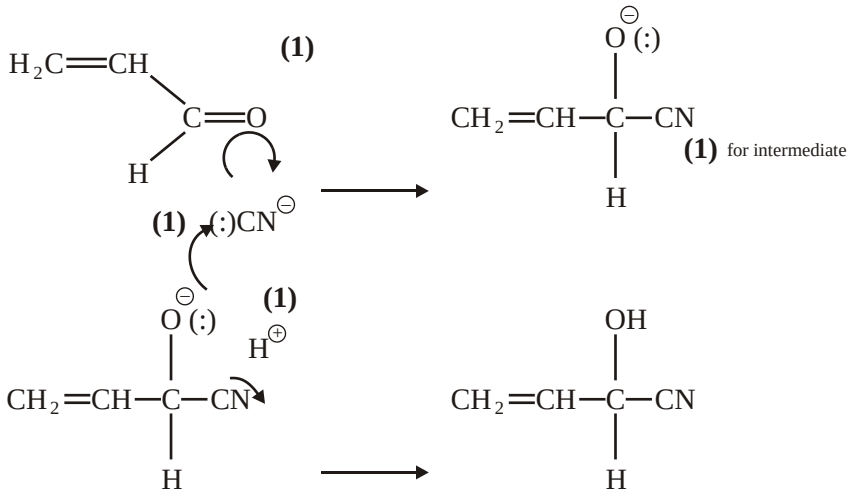
Lone pairs not essential.

Arrow may start from minus of O^-

- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of ^-CN in step 1 (but not from the minus of CN^-) and can start from the minus of O^- in step 2
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN scores zero
- Autoionisation of C=O can only score the last two marks
  ie max 2

4

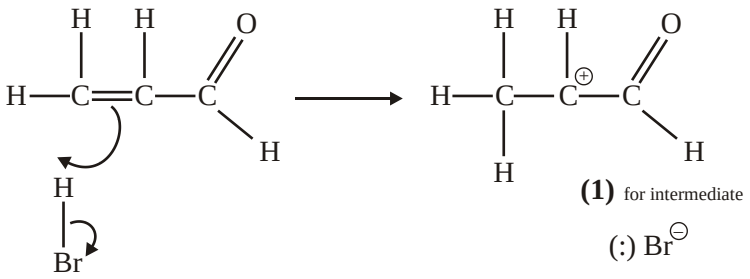
OR



- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of ^{-}CN in step 1 (but not from the minus of CN^{-}) and can start from the minus of O^{-} in step 2
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN scores zero
- Autoionisation of C=O can only score the last two marks
  ie max 2 4

(ii) Nucleophilic addition 1
Stand alone

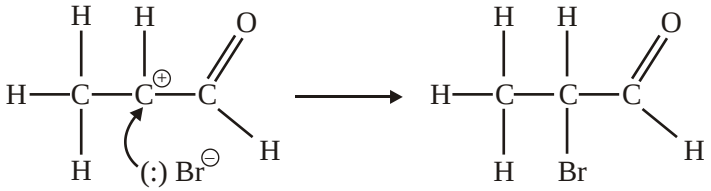
(d) (i)



(1) for both arrows

(1) for intermediate

(:) $Br^{\ominus}$



(1) for arrow

Note: If Br is on the wrong carbon atom, only third mark available 3

(ii) Electrophilic addition
Stand alone 1

(e)
- C = O is a polar bond OR O more electronegative than C **(1)**

QWC
- C = C has high electron density OR C = C is electron rich **(1)**
  IGNORE "C=C is non-polar" *and* references to ∏ bond
- $C^{\delta+}$ can be attacked by a nucleophile OR (C in) C = O can be attacked by nucleophile
  OR C = C attacked by electrophile **(1)** 3

[18]

7. (a) (i) $K_a = \dfrac{[CH_2ClCO_2^-][H^+]}{[CH_2ClCO_2H]}$ 1

Accept $[H_3O^+]$ in place of $[H^+]$
allow one set of sq brackets to be missing

(ii) $[H^+]^2 = 1.3 \times 10^{-3} \times 0.001$ **(1)**

$= 1.3 \times 10^{-6}$

$[H^+] = \sqrt{1.3 \times 10^{-6}}$

1.14×10^{-3} **(1)**

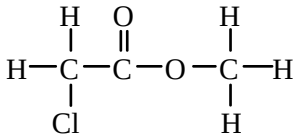
pH = $-\log 1.14 \times 10^{-3} = 2.9(4)$ **(1)**

[IGNORE SF] 3

(iii) Trichloroethanoic, as it has the largest K_a value **(1)**

and has (3 electron withdrawing) chlorine atoms to stabilise the anion formed (on dissociation). **(1)** 2

(b) (i)



ester group **(1)**
rest of molecule **(1)** dependent on first mark
(must be fully displayed)
methyl chloroethanoate **(1)** 3

No transferred error for name

(ii) ester(s) 1

Reject ether

(iii) nucleophile, **(1)**

as it has a lone pair (of electrons) on the (hydroxyl) oxygen **(1)**

which can attack the **positive carbonyl carbon** on the acid **(1)** 3

2nd and 3rd marks could be obtained by use of a diagram

Reject attack by CH_3O^-

(iv) (reflux) heat with NaOH(aq) **(1)**
(cool) and add HCl(aq) **(1)**

OR
reflux **(1)** [must be in context]
with HCl **(1)** 2

[15]

8. (a) All three compounds can form hydrogen bonds **to water** molecules 1

(b) *Brady's reagent / 2,4 DNP* **(1)**
Red–yellow/ yellow/red–orange / orange precipitate / crystals solid **(1)** 2

(c) (i) Benedict's solution
OR acidified potassium / sodium dichromat(VI)
OR potassium manganate(VII) 1

(ii) Blue to red
OR orange to green / blue
OR purple to colourless 1

(iii) C–H (stretching) frequency for an **aldehyde**
OR
carbonyl, C=O, frequency different value 1

(d) $Na_2CO_3(aq) + 2CH_3CH_2CO_2H(aq)/(l) \rightarrow 2CH_3CH_2CO_2Na(aq) + CO_2(g) + H_2O(l)$
Reactants **(1)** 2
Products **(1)**

(e) Sodium)
sodium hydroxide) *Anytwo*
sodium hydrogencarbonate)
sodium oxide) 2

[10]

9. (a) Restricted rotation / lack of free rotation around C=C **(1)**
NOT cannot rotate

There are two different groups on **each** carbon of C=C / four different groups around **two** carbon atoms **(1)** 2

(b) Potassium dichromate **(1)**
If given oxidation state must be correct

dilute H_2SO_4 / H_2SO_4 solution **(1)**
(Heat and) distil off (citral as it is formed) **(1)**
IF $KMnO_4$ ***2*** **max** *ie 2nd and 3rd marks* 3

(c) (i) *Brown / orange / yellow → colourless / decolourises / disappears* 1

(ii) Yellow/ orange/ red **precipitate** / crystals / solid 1

(iii) Red **precipitate** / crystals/ solid 1

[8]

10. (a) (i) CH_3COCH_3 (use expts 1 + 2) as conc doubles, rate doubles
first order **(1)**

I_2 (use expts 1 + 3) as conc changes / halves, rate is constant
zero order **(1)**

if no explanations ***max 1*** *for both orders*

H^+ explanation **(1)** first order **(1)**

e. g.
expts 1 + 4 or 3 + 4 as $[CH_3COCH_3]$ doubles and $[H^+]$ doubles, rate × 4
but 1st order w. r. t. $[CH_3COCH_3]$ so must be 1st order w. r. t. $[H^+]$
OR
Expts 2 + 4 as $[I_2]$ doubles and $[H^+]$ doubles, rate doubles but zero order
w.r.t. $[I_2]$ so must be 1st order w.r.t. $[H^+]$ 4

(ii) *2 consequential on (a)* 1

(b) rate = $k[CH_3COCH_3][H^+]$ *consequential on (a)* **(1)**

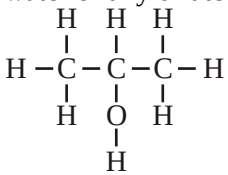
k (= e.g $1.5 \times 10^{-5} / 0.4 \times 0.4$) = 9.4×10^{-5} **(1)**
consequential on their rate equation units $dm^3\ mol^{-1}\ s^{-1}$ **(1)** 3

QWC (c) step 1 – slow / rate determining step / step 2 – faster **(1)**
iodine has zero order (or is not in rate eqn) so.. does not take part in
a slow step / r.d.s. **or** is in a fast step **or** is in mechanism after r.d.s. **(1)** 2

(d) Expt 2 starts at 0.004 and Expt 3 at 0.002 **(1)**
Expt 2 line steeper **(1)**
Expt 3 line parallel **(1)** 3

(e) (i) (aqueous) sodium (or potassium) hydroxide / carbonate or formulae 1

(ii) water or any dilute acid or formula **(1)**



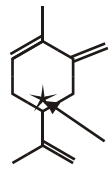
(1)
ALLOW OH 2

(f) 1 peak propanone, 3 peaks propanal **(1)**
hydrogen in one environment, hydrogen in three environments **(1)**
[These could be shown on structural formulae]

ALLOW e.g. 1 peak propanone because H in one environment, for 1 mark 2

[18]

11. (a) (i)

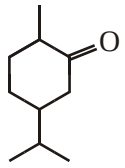


chiral centre 1

(ii) rotation of plane of polarisation (of plane) polarised (monochromatic) light 1

(b) 2,4-dinitrophenylhydrazine **(1)** orange / red / yellow ppt **(1)**
NOT "DNP" *OR* "DNPH"
Warm ammoniacal silver nitrate / Fehlings / Benedicts / $K_2Cr_2O_7 + H_2SO_4$
(1) no silver mirror / red ppt *OR* stays blue / stays orange **(1)** 4

(c) Amount of carvone used
= 2.70g/ 150 g mol^{-1} = 0.018 mol **(1)**
amount of hydrogen used
= 0.864 dm^3/24 dm^3 mol^{-1} = 0.036 mol **(1)**
Ratio carvone : hydrogen is 1:2 **(1)**
therefore two / π / double / both C=C bonds reduced per molecule **(1)**
and so the structure is



(1) 5

(d) (i) Dry **(1)** ethoxyethane **(1)** 2

(ii) Attack by H^- / AlH_4^- / or by nucleophilic addition **(1)**
C=O polar, C=C non–polar **(1)** 2

(iii) Carvone shows peak near 1700 cm^{-1} **(1)**
characteristic of C= O / because it is a ketone **(1)**
Z shows (broad) peak around 3300 cm^{-1} due to O –H group (from reduction of C=O) **(1)** 3

(e) Several possibilities:

NaOH (1) $C_6H_5OH + NaOH \rightarrow C_6H_5 ONa + H_2O$ (1) ethanol no reaction **(1)**;
OR
(aqueous) bromine **(1)**
$C_6H_5OH + 3Br_2 \rightarrow C_6H_3Br_3 OH + 3HBr$ (ignore substitution pattern if structural formulae are used) **(1)** ethanol no reaction **(1)**
OR conc sulphuric acid
nitration
R–halogen (Friedel –Crafts)
Phosphorus (V) chloride
Potassium dichromate(VI) / sulphuric acid
ethanoic acid (+ conc H_2SO_4) 3

[21]

12. (a) Yellow/orange solid/precipitate/crystals formed 1

Reject red

(b) **F** : $CH_3CH(CH_3)CHO$ **(1)**
G : $CH_3CH_2COCH_3$ **(1)**
H : e.g. $CH_2(=)CHCH_2CH_2OH$ **(1)** 3

H** : other alkenols and cyclic alcohols, e.g. cyclobutanol / correct enols / cyclic ethers **(1)

Allow displayed formulae

(c) (i) Prevents **reagents/products** from **boiling/volatilising /evaporating** away/being lost to the surroundings
Reactants have greater chance of reacting since they condense and rejoin the mixture 1

*Accept reduces the risk of fire; **(1)***

*Accept prevents potentially harmful vapours from entering the lab **(1)***

(ii) Ethyl butanoate 1

(iii) Ethanol **(1)**
Sodium butanoate **(1)** 2

Accept T.E. from (ii)

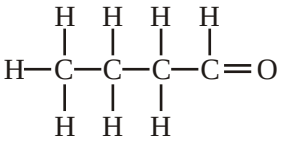
Reject butanoic acid

(iv) Hydrolysis / saponification 1

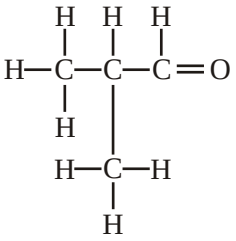
Reject hydration

[9]

13. (a) (i)



(1) Butanal / butan-1-al **(1)**



(1) (2-) methylpropanal / (2-)methylpropan-1-al **(1)**
NOT methylpropan-2-al

Aldehyde must be displayed but rest of molecule not displayed (1 **out of 2)**

Name must match correct compound. No marks for correctly naming an incorrect compound 4

(ii) Any one from

Infrared spectra **(1)**
different in 'fingerprint'
OR differences in frequencies/wavelengths absorbed
OR different peak/trough patterns **(1)**
NOT different peaks/troughs

Measure Boiling point **(1)**
Different boiling points and suggest why e.g.straight chain higher boiling point **(1)**

nmr spectra **(1)**
A + B would have a different number of peaks **(1)**

Mass spec **(1)**
Different fragmentation pattern **(1)**

X-ray diffraction **(1)**
Electron density maps identify branching **(1)**

Prepare 2,4-dinitrophenylhydrazone **(1)**
and measure melting point **(1)**

NOT measure melting point 2

(b) (i) 2,4-dinitrophenylhydrazine / 2,4-DNP(h) / Brady's reagent **(1)**

orange/yellow/orange-red/yellow-orange **precipitate**/**crystals**
[a solid must be mentioned] **(1)**
NOT 'Red'
2nd mark dependent on 1st 2

(ii) (Heat with) Benedict's reagent/Fehling's reagent **(1)**

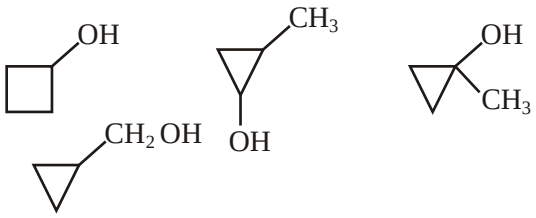
Result for C remains blue **(1)**
ALLOW no change if blue mentioned somewhere

Result for A and B orange/red/green/yellow/brown
precipitate/**crystals** *[a solid must be mentioned]* **(1)**

OR
Acidified dichromate **(1)**
Result for C remains orange **(1)**
Result for A + B green/blue **(1)**
Same rules as above but precipitate not needed

2nd and 3rd marks dependent on 1st 3

(c) (i)



Any two
ALLOW fully displayed

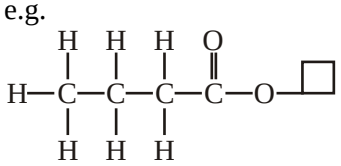
ALLOW $CH_2CH_2CH_2CHOH$

ALLOW OH *NOT* OH

NOT $CH_2CH_2CH_2CHOH$ etc 2

(ii) Esters
NOT esterification 1

(iii) e.g.



ester group - *must be displayed* **(1)**
rest of molecule - *need* ***not*** *be fully displayed* **(1)**
- *2nd mark dependent on 1st*

ALLOW TE from $CH_2CH_2CH_2CHOH$ *etc in (c)(i) for* ***2 marks*** *in (iii)*

If enol in (c)(i) ***max 2*** *(out of 5) for (c) ie (ii) and ester displayed in (iii) can be awarded* 2

[16]

14. (a) Ethylmagnesium bromide of formula, or any other halide *NOT* C_2H_5BrMg, **(1)**
Dry ether / ethoxyethane
Followed by hydrolysis / acid / water **(1)**

Grignard reagent / named reagent with incorrect alkyl group scores **(0)** *for* **(1)** *reagent but can score both condition marks.*
If halogenoalkane given as reagent, can score 1st mark if Mg included under conditions. 3

(b) (i) <u>*Observation*</u>
<u>*effervescence/ bubbles/ fizzing*</u> **(1)**
<u>NOT *gas evolved*</u>

$2C_2H_5COOH + Na_2CO_3 \rightarrow 2C_2H_5COONa + CO_2 + H_2O$ **(1)** 2

(ii) <u>*Observation*</u>

steamy/ misty/ white fumes **(1)**
NOT smoke
$C_2H_5COOH + PCl_5 \rightarrow C_2H_5COCl + POCl_3 + HCl$ **(1)** 2

(c) Reagents potassium dichromate ((VI)) / $K_2Cr_2O_7$, **(1)**
sulphuric acid / H_2SO_4 / hydrochloric acid / HCl but conseq. on an oxidising **(1)** agent
ALLOW acidified potassium dichromate / H^+ and $Cr_2O_7^{2-}$ **(2)**
ALLOW acidified dichromate ions **(2)**
Acidified dichromate (without ion) scores just **(1)**
ACCEPT
Potassium manganate(VII) / potassium permanganate / $KMnO_4$ / Tollens'* / Fehling's* **(1)**
Acidified / alkaline* / neutral **(1)** 2
(*) need to acidify to liberate free acid for 2nd mark

(d) (i) <u>*Reagent*</u> <u>*Condition*</u>

(any one of)	*(to match)*
HCN	and KCN
HCN **or** KCN	(buffered between) pH between 6 and 9
KCN	+ acid / H^+ *NOT* excess
HCN	+ base / OH^- *NOT* excess **(2)**

Type of reaction

Nucleophilic addition - *both words needed* **(1)** 3

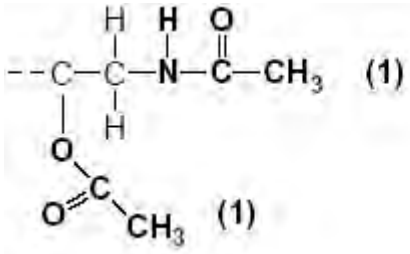
(ii)

Reagent	*Condition*
(any one of)	*(to match)*
Hydrogen	Pt / Ni / Pd (catalyst) – *IGNORE ref to temp.*
Sodium	(in) ethanol
Lithium aluminium hydride	**dry** ether / ethoxyethane
Sodium borohydride	(in) aqueous / water / ethanol / methanol **(2)**

Type of reaction

Reduction
ACCEPT redox / hydrogenation (not addition)
ACCEPT nucleophilic addition if metal hydrides used **(1)** 3

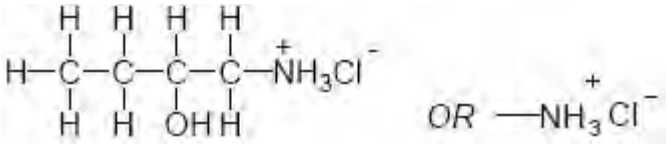
(e) (i) 2



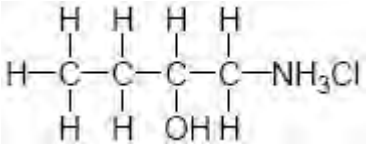
ALLOW —NHCH$_3$

If >C=O represented as CO, penalise once only

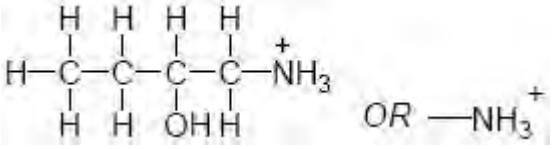
(ii)



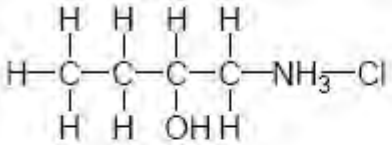
OR



OR

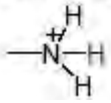


NOT



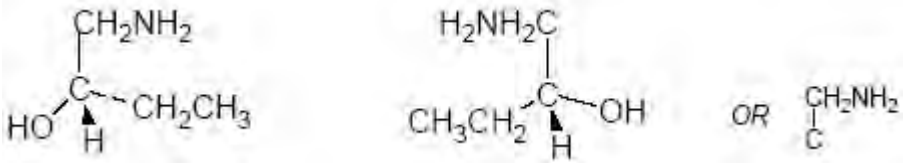
If show all bonds in NH_3, + charge must be shown on N atom

ie



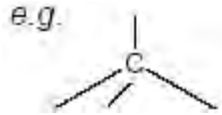
1

(f) Optical
NOT stereo **(1)**



ALLOW – C_2H_5 *for* – CH_2CH_3

MUST show the two as object and mirror image **(2)**

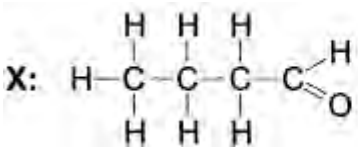
e.g.  OR  *are acceptable*

but NOT

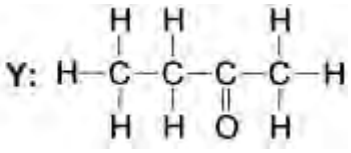
C must not be bonded to H in OH group
Near-miss molecule plus mirror image **(1)** 3
The two solid lines in 3D structure must not be at 180 °

[21]

15. (a)



(1)



(1) 2

(b) **Y** = butanone **(1)** 1

(c) C = O polar so attracted to water / forms hydrogen bonds with water 1

(d) (i) $CH_3CH_2CH(OH)CH_3$ 1

(ii) Potassium/sodium dichromate + sulphuric acid
OR
potassium manganate(VII) + sulphuric acid
NOT acidified dichromate 1

(e) (i) C = O / carbon double bonded to oxygen **(1)** 1

(ii) O – H / bond between oxygen and hydrogen **(1)**
Hydrogen/ H bonded **(1)** 2

[9]

16. (a) (i) Reagent: potassium dichromate (VI)/potassium manganate (VII) **(1) or** formulae sulphuric acid or hydrochloric acid **(1) or** formulae

If potassium manganate(VII) chosen **not** HCl or conc H_2SO_4 for second mark

'Acidfied dichromate' or H^+ / $Cr_2O_7^{2-}$(1) 2

(ii) amount of propanol = 5.67/60 = 0.0945 mol **(1)**
amount of propanoic acid produced = 0.64 × 0.0945
= 0.06048 mol **(1)**
yield of propanoic acid = 74 × 0.06048 = 4.5 / 4.48 / 4.476 g **(1)**

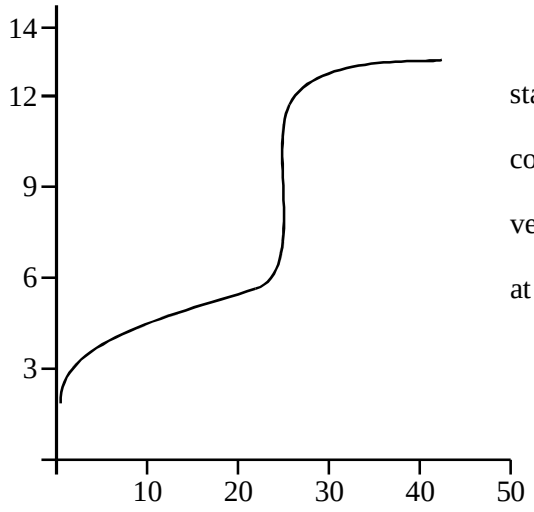
OR by mass ratio: ratio acid/alcohol = 74/60 = 1.23 **(1)**
100% yield = 1.23 × 5.67g = 6.99 g **(1)**
64% yield = 6.99 g × 0.64 = 4.5 / 4.48 / 4.476 g **(1)** 3

(b) (i) increase in temperature:

(position of) equilibrium goes to the right **(1)**
as endothermic left to right **(1)**
on the addition of sodium propanaoate
the position of equilibrium goes to left **(1)**
higher concentration of / more **propanoate ions**
or
sodium propanoate produces **propanoate ions (1)** 4

(ii) pH rises (consequential on above) **(1)** 1

(c) (i)



start pH 2 to 4 (**1**)

correct general shape (**1**)

vertical 6/7.6 to 10/12 (**1**)

at 25 cm^3 (**1**) 4

(ii) indicator : thymol blue **(1)** consequential on vertical part of graph

reason: pH change sharp around pK_{in} value / its colour changes around end point
pH / band pH8 to 10 shown on graph **(1)** 2

(d) (i) fully dissociated **and** reactions identical
OR
$H^+ + OH^- \rightarrow H_2O$ **(1)** 1

(ii) HCN weak acid / partially dissociated **(1)**
$\Delta H_{ionisation}$ of HCN endothermic **(1)** 2

[19]

17. (a) (i) impurities lower / change the melting point /(impure solid)
melts over a range of temperatures
or the pure solid has a sharp melting point **(1)** 1

(ii) C=O / carbonyl responsible for peak at $1720cm^{-1}$ **(1)** 1

(iii) because of hydrogen bonding **(1)**
between (alcohol) molecules **(1)** 2

(iv) **A** is $CH_3–CH_2–CH_2–CHO$ **(1)** or in full
B is $CH_3–CH_2–CH_2–CH_2–O–H$ **(1)** or in full

Incorrect **B** can score consequentially on **A** being a carbonyl <u>from data</u> 2

(b) (i) Reagent: potassium hydroxide / sodium hydroxide **(1)** or KOH / NaOH
Solvent: ethanol/alcohol **(1)** but aqueous alcohol(0) 2

(ii) $CH_3–CH_2–CH=CH_2$ or in full **(1)**

if answer incorrect, consequential on **B** in (a)(iv) 1

(iii) $CH_3–CH_2–CHBr–CH_3$ or in full **(1)**
consequential on **D** in (b)(ii) 1

(iv) Because $CH_3CH_2CH^+CH_3$/secondary ion / secondary intermediate is more stable than the $CH_3CH_2CH_2CH_2^+$/primary ion / primary intermediate **(1)**

(do not allow Markovnikov as the **reason**) 1

[11]

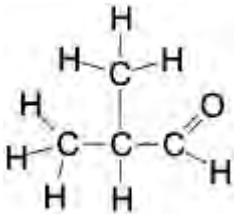
18. (a) Sodium dichromate/potassium dichromate/$Na_2Cr_2O_7$/ $K_2Cr_2O_7$/ $KMnO_4$/potassium manganate (VII)/ permanganate. **(1)**
Sulphuric acid/H_2SO_4 **(1)** 2

(b) Acid: Donates protons/produces $\mathbf{H^+}$ **ions** in solution **(1)**
Weak: An acid that has only partly ionised/slightly dissociated. **(1)** 2

19. (a) (i) Add Brady's Reagent / 2,4-dinitrophenylhydrazine **(1)**
Yellow/orange **precipitate** / crystals/ solid produced **(1)** 2

(ii) $CH_3CH_2COCH_3$ **(1)**
Butanone **(1)** 2

(iii)



(1) 1

(b) (i) Esters **(1)** 1

(ii) $CH_3CH_2CH_2CO_2CH_2CH_3$ + **H_2O (1)** 1

(iii) Ethyl butanoate **(1)** 1

(iv) Nucleophile/ nucleophilic **(1)** 1

(c) Cloudy/misty/steamy fumes/vapour/gas 1

(d) Cl is **more** electron withdrawing/electronegative **(1)**
Which makes carbonyl carbon more electrophilic/positive/susceptible to nucleophilic attack
OR Cl is a better leaving group (than OH)
as Cl^- is more stable (than ^-H) **(1)** 2

[12]

20. (a) pentyl dichloroethanoate **(1)**
ALLOW 1,1 OR 2,2-
ALLOW pent-1-yl /*all one word*
NOT penten
NOT pentan
NOT pentanyl

ester **(1)**
ALLOW esther 2

(b) (i) using a pipette remove a known volume (say 20 cm^3) **(1)**

remove some solution – either with a pipette
OR a known volume / 20 cm^3

titrate with an alkali (such as sodium hydroxide) **(1)**

of known concentration **(1)**
– *dependent on previous mark ie must have mentioned alkali*

IGNORE quenching

using a named indicator eg. phenolphthalein/methyl orange **(1)**
NOT litmus / universal indicator

Measure pH on its own 1 (out of 4)
But if calculation fully explained from pH can get full marks 4

(ii) $K_c = \dfrac{[CHCl_2COOC_5H_{11}(l)]}{[CHCl_2COOH(l)] \times [C_5H_{10}(l)]}$

State symbols not required 1

(iii) C_5H_{10} 1.7 **(1)** $\dfrac{1.7}{0.3}$ = 5.67(5.7) *NOT* 5.66

$CHCl_2COOC_5H_{11}$ 0.6 **(1)** $\dfrac{0.6}{0.3}$ = 2

(1) *for ÷ moles at eq by 0.3 in both cases* 3

(iv) $2K_c = \dfrac{0.6 / 0.3}{1.33} \times 1.7 / 0.3$ **(1)** $= \dfrac{2}{1.33 \times 5.67}$

= 0.265 (1) $dm^3\ mol^{-1}$ / $mol^{-1}\ dm^3$ **(1)**

NOT dm^{-3}
ALLOW 0.27 / 0.26 / 0.264
Penalise 1 SF or 4SF or more SF but only take off 1 mark maximum in *(iii) and (iv) for significant figure errors*

ALLOW TE from expression in (ii)
TE using numbers for (iii) full marks possible 3

[13]

21. (a) (i) Pairs: acid NH_4^+ /ammonium ion and base NH_3 /ammonia
acid H_3O^+ / hydronium ion and base H_2O / water 1

Accept hydroxonium ion

(ii) $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ ignore lower case k 1

Accept $K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$

Reject answers including $[H_2O]$

(iii) $[H_3O^+] = 10^{-5}$ mol dm^{-3} **(1)**

Assumption ionization of NH_4^+ (negligibly) small **(1)**

Assumption $[NH_3] = [H_3O^+]$ **(1)**

Accept $[NH_4^+] = [NH_4Cl]$ *or* NH_4Cl *totally ionized*

thus $[NH_4Cl] = (1 \times 10^{-5})^2 / 5.62 \times 10^{-10}$
$= 0.178$ mol dm^{-3} **(1)**
Answer to 2 or more S.F. 4

(iv) QWC

methyl red **(1)**

indicator constant or pK_{In} must be near the endpoint pH
OR indicator constant or pK_{In} must be near 5 **(1)**
2nd mark conditional on correct indicator 2

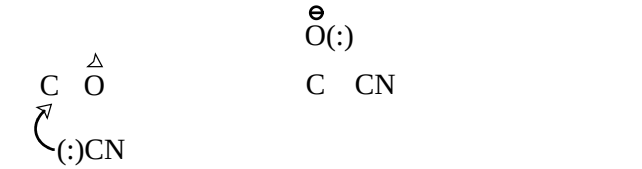
Accept pK_{In} *in the steep part of the graph or it is a weak base-strong acid titration*

(b) $CN^- + H_2O \rightleftharpoons HCN + OH^-$
IGNORE state symbols 1

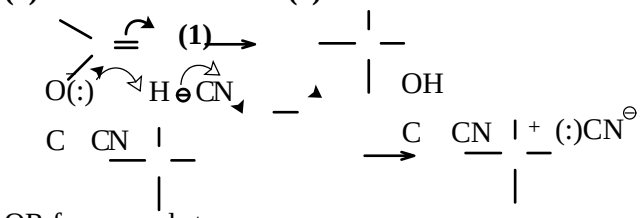
Accept "→" instead of "⇌"

(c) (i) nucleophilic addition 1

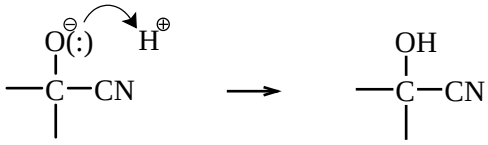
(ii)



(1) for both arrows **(1) for intermediate**



OR for second step



(1) 3

Fish hook arrows (penalise once)

- Ignore the groups attached to the carbonyl carbon throughout
- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of $^{-}$CN in step 1 (but not from the minus of CN^{-}) and can start from the minus of O^{-} in step 2
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN or initial attack by H^{+}/HCN scores zero
- Autoionisation of C=O can only score the last two marks ie max 2

(iii) QWC

if too acidic too small a concentration of cyanide ions **(1)**

Accept not enough / too little CN^{-}

if too alkaline too little HCN to donate the proton in the last step
OR H^{+} ion concentration too low **(1)** 2

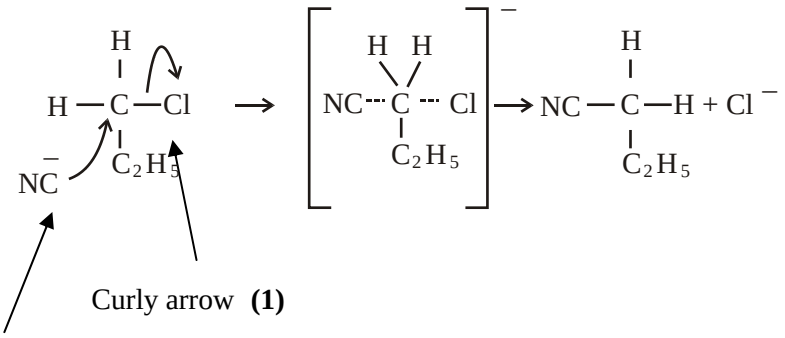
(d) (i) rate = $k[CH_3CH_2CH_2Cl]\ [CN^-]$
Must be an equation
Must be [ ] NOT ( )
Ignore upper case K 1

Accept 'R' or 'r' for rate $C_3H_7Cl]$ / [1-chloropropane]/ [chloropropane]

Accept [cyanide ion]/[cyanide]

Reject [KCN]

(ii)



Curly arrow **(1)**

Curly arrow **(1)** Transition state **(1)**

- Must have partial bonds in transition state
- CN and Cl must be on opposite sides of central C in the transition state
- Accept negative charge on N of cyanide ion 3

Mechanism based on S_N1 scores 0

Reject fish hook arrows (penalise once)

Reject arrow from N of CN

[19]

22. (a) methyl butanoate
Accept Methyl butaneoate 1

Reject 'an' missing

(b) the other three substances can form
intermolecular hydrogen bonds with themselves but the ester cannot. 1

Reject Discussion of London Forces

(c) Hydrolysis 1

(d) QWC

Must cover advantages and disadvantages. Must **not** be contradictory

Advantages to manufacturers: (any two)

- not dependent on weather, seasons etc
- consistent taste /concentration/more consistent
- quality
- or alternative ideas

Disadvantages to consumers : (any two)

- some people put off by 'non-natural' food
- may not taste the same as natural product which may contain other impurities
- unable to describe the product as organic

or alternative ideas 4

Reject cost with no justification

(e) $Kc = \frac{[C_3H_7COOH(l)][CH_3OH(l)]}{[C_3H_7COOCH_3(l)][H_2O(l)]}$ **(1)**

Accept eq subscripts

	Moles at equilibrium	**Concentration / mol dm^{-3}**
butanoic acid = 4.4/88 =	0.05	1.67
methanol	0.05	1.67
ester (methyl butanoate)	0.05	1.67
water	0.95	31.7

all four equilibrium moles = **(1)**
Conc at equilibrium = equilibrium moles ÷ 0.030 **(1)**

$Kc = \frac{1.67 \times 1.67}{1.67 \times 31.7}$ **(1)** = 0.053 **(1)**

ignore significant figures unless value given to 1 s.f.

The units cancel because both the top and bottom of the fraction have units of concentration squared.
Or same number of moles on both sides of the equation **(1)** 5

Reject absence of square brackets

[12]

23. (a) A 1

(b) D 1

(c) A 1

[3]

24. (a) *IGNORE 'alkane'* in any answer

X : ester **(1)**

Reject carbonyl

Y : **both** alkene **and** alcohol or hydroxyl **(1)**

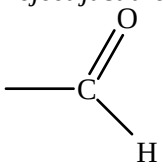
Accept carbon–carbon double bond
Accept "hydroxy"

Reject ***OH***$^-$ *or "hydroxide"*

Z : **both** alcohol or hydroxyl **and** aldehyde **(1)** 3

Accept "hydroxy"

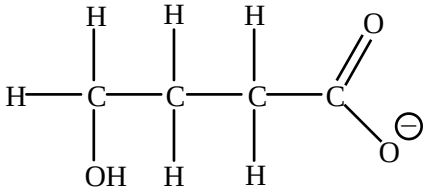
Reject ***OH***$^-$ *or "hydroxide" or "carbonyl"*
Reject just the formula



(b) X : no reaction **(1)**

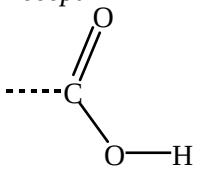
Y : no reaction **(1)**

Z :



(1) do not award if the bond from the carbon atom is **clearly** to the H of the OH group 3

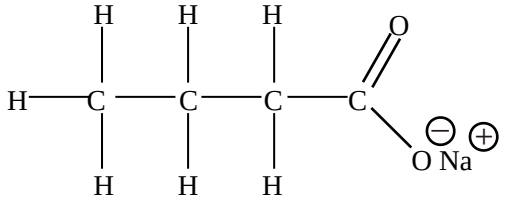
Accept



–O$^-$ *Na+ or –ONa*

Reject any formula with the alcohol group oxidised

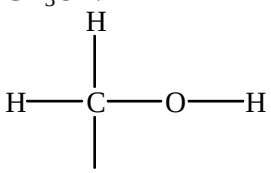
(c) (i) $CH_3CH_2CH_2COONa/CH_3CH_2CH_2COO^-Na^+/$



(1)

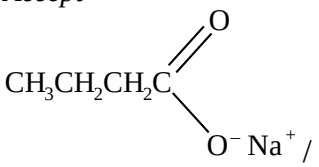
Allow C_3H_7 / $C_2H_5CH_2$

$CH_3OH/$



2

Accept



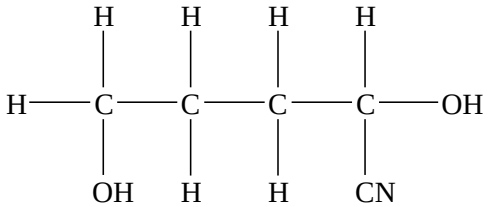
$CH_3CH_2CH_2COO^-$ /
$CH_3CH_2CH_2CO_2Na$ /
$CH_3CH_2CH_2CO_2^-Na^+$

Reject carboxylic acid

Or

…O^- —Na^+

(ii)



$/CH_2(OH)CH_2CH_2CH(CN)OH$
/ $CH_2(OH)CH_2CH_2CH(OH)CN$ **(1)** 1

[9]

25. (a) Aldehyde(s) 1

(b) (blue to) red **(1)**
precipitate/solid **(1)** 2

Accept green/yellow/ brown/orange instead of red

[3]

26. (a) **Can be given in either order**

1st functional group
alkene or C=C or carbon-carbon double bond **(1)**

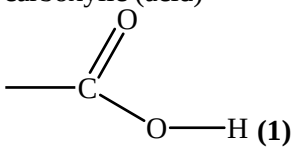
*Reject **just** 'double bond' or just 'carbon double bond'*

bromine water/Br_2 turns (from orange/brown etc. to)
colourless/decolorised **(1)**
INITIAL COLOUR NOT REQUIRED

Accept $KMnO_4$
Accept acidified decolorised
Accept alkaline green

Reject 'clear' instead of 'colourless'

2nd functional group
carboxylic (acid)



(1)

Accept carboxyl

Reject "carbonyl"

on addition of Na_2CO_3 or $NaHCO_3$ or CaCO3 or Mg, fizzing occurs **(1)**

Accept gas evolved which turns limewater milky
OR
or universal indicator/ blue litmus turns red

Reject just "a gas/CO_2/H_2 evolved" for fizzing

OR

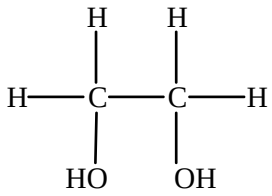
(warm with) a **named** alcohol plus **conc. acid** (as catalyst),
pleasant/fruity smell

Ignore references to testing with PCl_5 4

(b) (i) **W** as it contains an aldehyde group / –CHO group
OR
W can be oxidised (whereas X cannot)
OR
X cannot be oxidised
OR
W as X is a ketone (which cannot be oxidised) 1

*Reject W with no reason or an incorrect reason **(0)***
Contains C=O

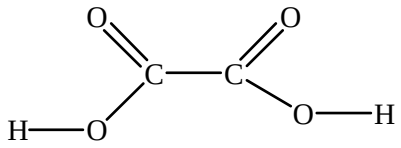
(ii) $CH_2\ OHCH_2\ OH$
OR



OR
Ethan(e)-1-2-diol 1

Accept $(CH_2OH)_2$

(iii)



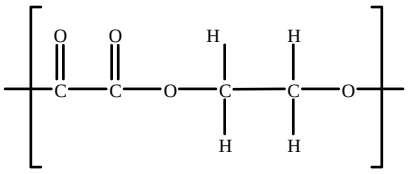
OR
HOOCCOOH
OR
Ethanedioic acid/oxalic acid 1

Accept $(COOH)_2$

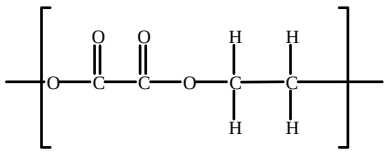
Accept ethan(e)-1,2-dioic acid or ethandioic acid

Reject any other name

(c) (i)



OR

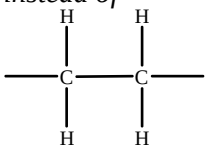


(2) for a correct structure
IF STRUCTURE IS INCORRECT, BUT A CORRECT ESTER LINKAGE IS FULLY DRAWN **(1)**

the correct repeat unit **must contain** only 4 carbon and 4 oxygen atoms 2

Accept CQ polyester on basis of monomers in (b)(ii) and (iii)

Accept $-CH_2CH_2-$
instead of



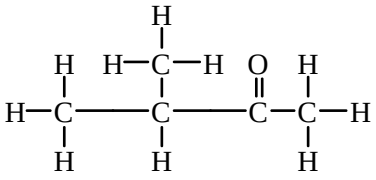
in relevant part of structure

***only (1)** if STRUCTURE IS CORRECT, BUT the ester linkage has been written as COO/CO_2*

(ii) Condensation 1

[10]

27. (a)



Ketone + five carbon atoms (could be straight chain) **(1)**
Branched chain + rest of molecule **(1)** 2

Allow 1 CH_3 group not displayed

Reject aldehyde

Reject if any hydrogen atoms missing (1 max)

(b) 2-methylbutan(e)-3-one/
3-methylbutan(e)-2-one
Ignore punctuation 1

Accept 2-methylbutanone
Accept 3-methylbutanone
Allow TE from (a) provided it is a ketone
e.g. pentan-2-one, pentan-3-one

Reject 2-methylbuta(-3)one
Reject 2-methylbut(-3-)one
Reject 2-methylbutan-2-one
Reject methylbutanone

(c) $C_5H_{12}O$ 1

Accept $C_5H_{11}OH$

Reject structural or displayed formula

(d) The reactants don't distil over before they can react
Owtte 1

Accept higher % of alcohol will be oxidised/not all of the alcohol will react/maximum chance of oxidising

Accept more time to oxidise to condense (any evaporated) reactants

Reject BP of alcohol low
Reject explanation of what happens during refluxing
Reject to get a higher yield
Reject discussion of rate of reaction

[5]