1. (a)

| Element | $\%$ | Atomic Mass | $\% \div$ 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 |  |
|  |  |  | $\mathbf{( 1 )}$ | $\mathbf{( 1 )}$ | 2 |

(b) $1 \quad$ 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 $\mathrm{CH}_{2} \mathrm{OH}(1)$

Peak at 15
Peak at 29
Peak at 43
Peak at 57
Peak at 71
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)


(d) (i)


(1)

QWC*
Rotate plane of plane polarised light in opposite directions (1)
(ii) Hexan-2-ol
(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)
(f) (A) would produce hexanal and hexanoic acid (1)
(E) would produce hexan-2-one (1)

Ketone / aldehyde / carboxylic acid $\mathbf{1}$ (out of 2)
2. B
3. (a)

(b) ester
(c) (i) Moles: $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}: 3.75$ (1)

Moles: $\mathrm{HCOOC}_{2} \mathrm{H}_{5}$ : 2.50 and moles $\mathrm{H}_{2} \mathrm{O}$ : 2.50 (1) for both
(ii) $\quad K_{c}=\frac{\left[\mathrm{HCOOC}_{2} \mathrm{H}_{5}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]}{[\mathrm{HCOOH}]\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right]}$

Reject obviously round brackets "()"
(iii) $\quad K_{c}=\frac{2.50 / 0.485^{\times 2.50} / 0.485}{0.50 / 0.485^{\times 3.75} / 0.485}$ (1)

Must have clearly divided moles of each component by 0.485 for $1^{\text {st }}$ mark e.g.
$\left[\mathrm{HCOOC}_{2} \mathrm{H}_{5}\right]=\left[\mathrm{H}_{2} \mathrm{O}\right]=5.16\left(\mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$
and $[\mathrm{HCOOH}]=1.03\left(\mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$
and $\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right]=7.73\left(\mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$
$=3.33$ (1) stand alone mark

IGNORE sig.figs.
Accept $K_{c}=\frac{(2.50)^{2}}{0.50 \times 3.75}=3.33$ only scores (2) if it is stated that $V$ cancels either here or in (iv)

If $\left[\mathrm{H}_{2} \mathrm{O}\right]$ omitted in (ii), then answer
$K_{c}=0.647 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$
(2) but this will give $K_{c}=1.33 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$ with $V$ omitted from calculation (1)

Reject $1^{\text {st }}$ 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
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)
$\mathrm{K}_{\mathrm{c}}$ 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 $\mathrm{HCOOC}_{2} \mathrm{H}_{5}$ decreases (1)
(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

Reject just "catalysts increase rate"
4. (a)

| Element | Mass of <br> 1 mole |
| :---: | :---: |
| C | 12 |
| H | 1 |
| O | 16 |


| \% | No. of <br> moles | Simplest Ratio |
| :---: | :---: | :---: |
| 73.2 | 6.10 | 5 |
| 7.3 | 7.30 | 6 |
| 19.5 | 1.22 | 1 |

Empirical formula $\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{O}(\mathbf{1})$
The mass of the empirical formula is
$12 \times 5+1 \times 6+16 \times 1=82$
Therefore the molecular formula is empirical $\times 2=\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{O}_{2}$ (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 $\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{O}_{2}$ (1)
Empirical formula is $\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{O}(\mathbf{1})$
(b) (i) arene/benzene ring

OR high carbon to hydrogen ratio/low hydrogen to carbon ratio aryl. 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
(vii) an arene (1)
with two adjacent hydrogen atoms (1) 2
(c)

5. (a) (i) Elimination / dehydration 1
(ii) Concentrated sulphuric acid / concentrated phosphoric acid / $\begin{aligned} & \text { aluminium oxide }\end{aligned}$

ACCEPT correct formula
(iii) Hydrolysis 1
(iv) Esterification 1
(v) $\mathrm{CH}_{3} \mathrm{OH} /$ methanol 1
(b) (i)

EITHER



OR

[1]

[1]




[1]
[1]
$\uparrow$

[ 1 ] for intermediate



[1]



Lone pairs not essential
Arrows may start from minus of $\mathrm{O}^{-}$ ALLOW CN ${ }^{-} \mathrm{OR}^{-} \mathrm{CN}$
(ii) $\operatorname{High}\left[\mathrm{H}^{+}\right]$
insufficient $\mathrm{CN}^{-}$(available for nucleophilic attack) (1)
Low $\left[\mathrm{H}^{+}\right]$
insufficient $\mathrm{H}^{+}$/ HCN for the second stage (1)
High $\left[\mathrm{H}^{+}\right]$surpasses ionisation / shifts equilibrium to left and low $\left[\mathrm{H}^{+}\right]$ shifts equilibrium to right max (1)
(c) (i) (Free) radical / peroxide
(ii)


Correct repeating unit (1)
Continuation bonds dependent on a 2 carbon skeleton unit (1)
(iii) The polymer chain lengths are different (due to different termination steps) different size molecules / different numbers of monomer (units)
6. (a) (i) Yellow/orange precipitate (allow red/any shades of red)
(ii)


(1)


Must be formed by C atom from the C = O group
rest of molecule correct (1)
(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
(c) (i) EITHER


Lone pairs not essential.
Arrow may start from minus of $\mathrm{O}^{-}$

- 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 ${ }^{-} \mathrm{CN}$ in step 1 (but not from the minus of $\mathrm{CN}^{-}$) and can start from the minus of $\mathrm{O}^{-}$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 $\mathrm{C}=\mathrm{O}$ can only score the last two marks ie $\max 2$

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 ${ }^{-} \mathrm{CN}$ in step 1 (but not from the minus of $\mathrm{CN}^{-}$) and can start from the minus of $\mathrm{O}^{-}$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 $\mathrm{C}=\mathrm{O}$ can only score the last two marks ie $\max 2$
(ii) Nucleophilic addition 1 Stand alone
(d) (i)



Note: If Br is on the wrong carbon atom, only third mark available
(ii) Electrophilic addition

Stand alone
(e) - $\mathrm{C}=\mathrm{O}$ 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 " $\mathrm{C}=\mathrm{C}$ is non-polar" and references to $\Pi$ bond

- $\quad \mathrm{C}^{\delta+}$ can be attacked by a nucleophile OR ( C in) $\mathrm{C}=\mathrm{O}$ can be attacked by nucleophile
OR C = C attacked by electrophile (1)

7. (a) (i) $K_{a}=\frac{\left[\mathrm{CH}_{2} \mathrm{ClCO}_{2}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{2} \mathrm{ClCO}_{2} \mathrm{H}\right]}$

Accept $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$in place of $\left[\mathrm{H}^{+}\right]$
allow one set of sq brackets to be missing
(ii) $\left[\mathrm{H}^{+}\right]^{2}=1.3 \times 10^{-3} \times 0.001(\mathbf{1})$
$=1.3 \times 10^{-6}$
$\left[\mathrm{H}^{+}\right]=\sqrt{ } 1.3 \times 10^{-6}$
$1.14 \times 10^{-3} \mathbf{( 1 )}$
$\mathrm{pH}=-\log 1.14 \times 10^{-3}=2.9(4)(\mathbf{1})$
[IGNORE SF]
(iii) Trichloroethanoic, as it has the largest $\mathrm{K}_{\mathrm{a}}$ value (1)
and has ( 3 electron withdrawing) chlorine atoms to stabilise the anion formed (on dissociation). (1)
(b) (i)

ester group (1)
rest of molecule (1) dependent on first mark
(must be fully displayed)
methyl chloroethanoate (1)
No transferred error for name
(ii) ester(s)

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)
$2^{\text {nd }}$ and $3^{\text {rd }}$ marks could be obtained by use of a diagram
Reject attack by $\mathrm{CH}_{3} \mathrm{O}^{-}$
(iv) (reflux) heat with $\mathrm{NaOH}(\mathrm{aq})(\mathbf{1 )}$ (cool) and add $\mathrm{HCl}(\mathrm{aq})(\mathbf{1})$
OR
reflux (1) [must be in context] with HCl (1)
8. (a) All three compounds can form hydrogen bonds to water molecules
(b) Brady's reagent / 2,4 DNP (1)

Red-yellow/ yellow/red-orange / orange precipitate / crystals solid (1)
(c) (i) Benedict's solution

OR acidified potassium / sodium dichromat(VI)
OR potassium manganate(VII)
(ii) Blue to red
$O R$ orange to green / blue
$O R$ purple to colourless
(iii) $\mathrm{C}-\mathrm{H}$ (stretching) frequency for an aldehyde

OR
carbonyl, $C=O$, frequency different value
(d) $\mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{aq})+2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq}) /(\mathrm{I}) \rightarrow 2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{Na}(\mathrm{aq})+\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ Reactants (1)
Products (1)
(e) Sodium )
sodium hydroxide ) Anytwo
sodium hydrogencarbonate )
sodium oxide ) 2
9. (a) Restricted rotation / lack of free rotation around $\mathrm{C}=\mathrm{C}$ (1)

NOT cannot rotate
There are two different groups on each carbon of $\mathrm{C}=\mathrm{C} /$ four different groups around two carbon atoms (1)
(b) Potassium dichromate (1)

If given oxidation state must be correct
dilute $\mathrm{H}_{2} \mathrm{SO}_{4} / \mathrm{H}_{2} \mathrm{SO}_{4}$ solution (1)
(Heat and) distil off (citral as it is formed) (1)
IF $\mathrm{KMnO}_{4} 2$ max ie $2^{\text {nd }}$ and $3^{\text {rd }}$ marks
(c) (i) Brown / orange / yellow $\rightarrow$ colourless / decolourises / disappears 1
(ii) Yellow/ orange/ red precipitate / crystals / solid 1
(iii) Red precipitate / crystals/ solid 1
10. (a) (i) $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ (use expts $1+2$ ) as conc doubles, rate doubles first order (1)
$\mathrm{I}_{2} \quad$ (use expts $1+3$ ) as conc changes / halves, rate is constant zero order (1)
if no explanations max $\mathbf{1}$ for both orders
$\mathrm{H}^{+}$explanation (1) first order (1)
e. g.
expts $1+4$ or $3+4$ as $\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]$ doubles and $\left[\mathrm{H}^{+}\right]$doubles, rate $\times 4$ but $1^{\text {st }}$ order w. r. t. $\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]$ so must be $1^{\text {st }}$ order w. r. t. $\left[\mathrm{H}^{+}\right]$
OR
Expts $2+4$ as $\left[\left[_{2}\right]\right.$ doubles and $\left[\mathrm{H}^{+}\right]$doubles, rate doubles but zero order
w.r.t. $\left[l_{2}\right]$ so must be $1^{\text {st }}$ order w.r.t. $\left[\mathrm{H}^{+}\right]$
(b) rate $=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]\left[\mathrm{H}^{+}\right]$consequential on (a) (1)
$\mathrm{k}\left(=\right.$ e.g $\left.1.5 \times 10^{-5} / 0.4 \times 0.4\right)=9.4 \times 10^{-5}(\mathbf{1})$
consequential on their rate equation units $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ (1)

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)
(d) Expt 2 starts at 0.004 and Expt 3 at 0.002 (1)

Expt 2 line steeper (1)
Expt 3 line parallel (1)
(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]
$A L L O W$ e.g. 1 peak propanone because H in one environment, for 1 mark
11. (a) (i)

(ii) rotation of plane of polarisation (of plane) polarised (monochromatic) light
(b) 2,4-dinitrophenylhydrazine (1) orange / red / yellow ppt (1) NOT "DNP" OR "DNPH"
Warm ammoniacal silver nitrate / Fehlings / Benedicts / $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}+\mathrm{H}_{2} \mathrm{SO}_{4}$
(1) no silver mirror / red ppt OR stays blue / stays orange (1)
(c) Amount of carvone used
$=2.70 \mathrm{~g} / 150 \mathrm{~g} \mathrm{~mol}^{-1}=0.018 \mathrm{~mol}(\mathbf{1})$
amount of hydrogen used
$=0.864 \mathrm{dm}^{3} / 24 \mathrm{dm}^{3} \mathrm{~mol}^{-1}=0.036 \mathrm{~mol} \mathbf{( 1 )}$
Ratio carvone : hydrogen is $1: 2$ (1)
therefore two / $\pi$ / double / both $\mathrm{C}=\mathrm{C}$ bonds reduced per molecule (1) and so the structure is

(1)
(d) (i) Dry (1) ethoxyethane (1)
(ii) Attack by $\mathrm{H}^{-} / \mathrm{AIH}_{4}^{-}$/ or by nucleophilic addition (1) $\mathrm{C}=\mathrm{O}$ polar, $\mathrm{C}=\mathrm{C}$ non-polar (1)
(iii) Carvone shows peak near $1700 \mathrm{~cm}^{-1}$ (1) characteristic of $\mathrm{C}=\mathrm{O} /$ because it is a ketone (1) Z shows (broad) peak around $3300 \mathrm{~cm}^{-1}$ due to $\mathrm{O}-\mathrm{H}$ group (from reduction of $\mathrm{C}=\mathrm{O}$ ) (1)
(e) Several possibilities:
$\mathrm{NaOH}(1) \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}+\mathrm{NaOH} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{ONa}+\mathrm{H}_{2} \mathrm{O}$ (1) ethanol no reaction
(1);

OR
(aqueous) bromine (1)
$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}+3 \mathrm{Br}_{2} \rightarrow \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Br}_{3} \mathrm{OH}+3 \mathrm{HBr}$ (ignore substitution pattern if
structural formulae are used) (1) ethanol no reaction (1)
$O R$ conc sulphuric acid
nitration
R-halogen (Friedel -Crafts)
Phosphorus (V) chloride
Potassium dichromate(VI) / sulphuric acid
ethanoic acid (+ conc $\mathrm{H}_{2} \mathrm{SO}_{4}$ )
12. (a) Yellow/orange solid/precipitate/crystals formed

Reject red
(b) $\quad \mathbf{F}: \mathrm{CH}_{3} \mathrm{CH}\left(\mathrm{CH}_{3}\right) \mathrm{CHO}(\mathbf{1})$

G: $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}$ (1)
H : e.g. $\mathrm{CH}_{2}(=) \mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (1)
$\boldsymbol{H}$ : 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

Accept reduces the risk of fire; (1)
Accept prevents potentially harmful vapours from entering the lab (1)

(ii) Ethyl butanoate
(iii) Ethanol (1)

Sodium butanoate (1)
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
(ii) Any one from

Infrared spectra (1)
different in 'fingerprint'
$O R$ differences in frequencies/wavelengths absorbed
$O R$ 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
(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’
$2^{\text {nd }}$ mark dependent on $1^{\text {st }} 2$
(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
$2^{\text {nd }}$ and $3^{\text {rd }}$ marks dependent on $1^{\text {st }}$
(c) (i)





OH

Any two
ALLOW fully displayed


ALLOW $\begin{aligned} & \text { OH } \\ & \mathrm{OH}\end{aligned} \underset{\mathrm{OH}}{\mid}$
NOT $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CHOH}$ etc
(ii) Esters

NOT esterification
(iii) e.g.

ester group - must be displayed (1)
rest of molecule - need not be fully displayed (1)
$-2^{\text {nd }}$ mark dependent on $1^{\text {st }}$
ALLOW TE from $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CHOH}$ 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
14. (a) Ethylmagnesium bromide of formula, or any other halide $\mathrm{NOT}_{\mathrm{C}}^{2} \mathrm{H}_{5} \mathrm{BrMg}$, (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 $1^{\text {st }}$ mark if Mg included under conditions.
(b) (i) Observation
effervescence/ bubbles/ fizzing (1)
NOT gas evolved
$2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow 2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COONa}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ (1)
(ii) Observation
steamy/ misty/ white fumes (1)
NOT smoke
$\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{PCl}_{5} \rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COCl}+\mathrm{POCl}_{3}+\mathrm{HCl}(\mathbf{1 )}$
(c) Reagents potassium dichromate ((VI)) / $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$, (1)
sulphuric acid / $\mathrm{H}_{2} \mathrm{SO}_{4}$ / hydrochloric acid / HCl but conseq. on an oxidising (1) agent
ALLOW acidified potassium dichromate $/ \mathrm{H}^{+}$and $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ (2)
ALLOW acidified dichromate ions (2)
Acidified dichromate (without ion) scores just (1)
ACCEPT
Potassium manganate(VII) / potassium permanganate / $\mathrm{KMnO}_{4}$ / Tollens’* /
Fehling's* (1)
Acidified / alkaline* / neutral (1)
${ }^{*}$ ) need to acidify to liberate free acid for $2^{\text {nd }}$ mark
(d) (i) Reagent Condition

| (any one of) | (to match) |
| :--- | :--- |
| HCN | and KCN |
| HCN or KCN | (buffered between) pH between 6 and 9 |
| KCN | + acid $/ \mathrm{H}^{+}$NOT excess |
| HCN | + base $/ \mathrm{OH}^{-}$NOT excess (2) |

Type of reaction
Nucleophilic addition - both words needed (1)
(ii) Reagent
(any one of)
Hydrogen
Sodium
Lithium aluminium hydride
Sodium borohydride

## Condition

(to match)
Pt / Ni / Pd (catalyst) - IGNORE ref to temp.
(in) ethanol
dry ether / ethoxyethane
(in) aqueous / water / ethanol / methanol (2)

Type of reaction
Reduction
ACCEPT redox / hydrogenation (not addition)
ACCEPT nucleophilic addition if metal hydrides used (1)
(e) (i)



If $\mathrm{C}=0$ represented as CO , penalise once only
(ii)


OR


OR


NOT


If show all bonds in $\stackrel{+}{\mathrm{NH}_{3}}+$ charge must be shown on N atom


1
(f) Optical

NOT stereo (1)


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

OR

are acceptable
but NOT


C must not be bonded to H in OH group
Near-miss molecule plus mirror image (1)
The two solid lines in 3D structure must not be at $180^{\circ}$
15. (a)


X:

(1)

(1)
(b) $\mathbf{Y}=$ butanone (1) 1
(c) $\mathrm{C}=\mathrm{O}$ polar so attracted to water / forms hydrogen bonds with water 1
(d) (i) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3} \quad 1$
$\begin{array}{llr}\text { (ii) } & \text { Potassium/sodium dichromate }+ \text { sulphuric acid } & \\ \text { OR } \\ \text { potassium manganate(VII) }+ \text { sulphuric acid } & \\ \text { NOT acidified dichromate } & 1\end{array}$
(e) (i) $\mathrm{C}=\mathrm{O} /$ carbon double bonded to oxygen (1) 1
(ii) O - $\mathrm{H} /$ bond between oxygen and hydrogen (1)
Hydrogen/ H bonded (1)
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 $\mathrm{H}_{2} \mathrm{SO}_{4}$ for second mark
'Acidfied dichromate' or $\mathrm{H}^{+} / \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}(1)$
(ii) amount of propanol $=5.67 / 60=0.0945 \mathrm{~mol}$ (1)
amount of propanoic acid produced $=0.64 \times 0.0945$

$$
=0.06048 \mathrm{~mol}(\mathbf{1})
$$

yield of propanoic acid $=74 \times 0.06048=4.5 / 4.48 / 4.476 \mathrm{~g} \quad$ (1)
OR by mass ratio: ratio acid/alcohol $=74 / 60=1.23$ (1)
$100 \%$ yield $=1.23 \times 5.67 \mathrm{~g}=6.99 \mathrm{~g}(\mathbf{1})$ $64 \%$ yield $=6.99 \mathrm{~g} \times 0.64=4.5 / 4.48 / 4.476 \mathrm{~g} \quad(\mathbf{1})$
(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)
(ii) pH rises (consequential on above) (1)
(c) (i)

(ii) indicator : thymol blue (1) consequential on vertical part of graph reason: pH change sharp around $\mathrm{pK}_{\text {in }}$ value / its colour changes around end point $\mathrm{pH} /$ band pH 8 to 10 shown on graph (1)2
(d) (i) fully dissociated and reactions identical OR
$\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O} \quad$ (1)
(ii) HCN weak acid / partially dissociated (1) $\Delta \mathrm{H}_{\text {ionisation }}$ of HCN endothermic (1) 2
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)
(ii) $\mathrm{C}=\mathrm{O} /$ carbonyl responsible for peak at $1720 \mathrm{~cm}^{-1}$ (1) 1
(iii) because of hydrogen bonding (1) between (alcohol) molecules (1)
(iv) $\mathbf{A}$ is
$\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CHO}$
(1) or in full
$\mathbf{B}$ is $\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{O}-\mathrm{H}$ (1) or in full

Incorrect $\mathbf{B}$ can score consequentially on $\mathbf{A}$ being a carbonyl from data
(b) (i) Reagent: potassium hydroxide / sodium hydroxide (1) or $\mathrm{KOH} / \mathrm{NaOH}$
Solvent: ethanol/alcohol (1) but aqueous alcohol(0)
(ii) $\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{CH}_{2}$ or in full (1) if answer incorrect, consequential on $\mathbf{B}$ in (a)(iv) 1
(iii) $\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CHBr}-\mathrm{CH}_{3}$ or in full (1) consequential on $\mathbf{D}$ in (b)(ii) 1
(iv) Because $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}^{+} \mathrm{CH}_{3}$ /secondary ion / secondary intermediate is more stable than the $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2}{ }^{+} /$primary ion / primary intermediate (1) (do not allow Markovnikov as the reason) 1
18. (a) Sodium dichromate/potassium dichromate/ $\mathrm{Na}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7} / \mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7} /$
$\mathrm{KMnO}_{4} /$ potassium manganate (VII)/ permanganate. (1)
Sulphuric acid $/ \mathrm{H}_{2} \mathrm{SO}_{4}$ (1)
(b) Acid: Donates protons/produces $\mathbf{H}^{+}$ions in solution (1)

Weak: An acid that has only partly ionised/slightly dissociated. (1)
19. (a) (i) Add Brady's Reagent / 2,4-dinitrophenylhydrazine (1)

Yellow/orange precipitate / crystals/ solid produced (1)
(ii) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}(\mathbf{1})$

Butanone (1)
(iii)

(1)

1
(b) (i) Esters (1) 1
(ii) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}+\mathbf{H}_{2} \mathbf{O}$ (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 $\mathrm{Cl}^{-}$is more stable (than ${ }^{-} \mathrm{H}$ ) (1) 2
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 $20 \mathrm{~cm}^{3}$ ) (1) (1)
remove some solution - either with a pipette
$O R$ a known volume / $20 \mathrm{~cm}^{3}$
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
(ii) $\quad \mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{CHCl}_{2} \mathrm{COOC}_{5} \mathrm{H}_{11}(\mathrm{l})\right]}{\left[\mathrm{CHCl}_{2} \mathrm{COOH}(\mathrm{l})\right] \times\left[\mathrm{C}_{5} \mathrm{H}_{10}(\mathrm{l})\right]}$

State symbols not required
1
(iii) $\mathrm{C}_{5} \mathrm{H}_{10}$
$\mathrm{CHCl}_{2} \mathrm{COOC}_{5} \mathrm{H}_{11}$
1.7 (1) $\frac{1.7}{0.3}=5.67(5.7)$ NOT 5.66
0.6 (1) $\frac{0.6}{0.3}=2$
(1) for $\div$ moles at eq by 0.3 in both cases
(iv) $2 \mathrm{~K}_{\mathrm{c}}=\frac{0.6 / 0.3}{1.33} \times 1.7 / 0.3 \quad$ (1) $=\frac{2}{1.33 \times 5.67}$
$=0.265(1) \mathrm{dm}^{3} \mathrm{~mol}^{-1} / \mathrm{mol}^{-1} \mathrm{dm}^{3}(\mathbf{1})$
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
21. (a) (i) Pairs: acid $\mathrm{NH}_{4}^{+} /$ammonium ion and base $\mathrm{NH}_{3}$ /ammonia acid $\mathrm{H}_{3} \mathrm{O}^{+}$/ hydronium ion and base $\mathrm{H}_{2} \mathrm{O}$ / water Accept hydroxonium ion
(ii) $K_{\mathrm{a}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}{ }^{+}\right]}$ignore lower case k

$$
\text { Accept } K_{a}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}
$$

Reject answers including [ $\mathrm{H}_{2} \mathrm{O}$ ]
(iii) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-5} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$

Assumption ionization of $\mathrm{NH}_{4}{ }^{+}$(negligibly) small (1)
Assumption $\left[\mathrm{NH}_{3}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$(1)
Accept $\left[\mathrm{NH}_{4}{ }^{+}\right]=\left[\mathrm{NH}_{4} \mathrm{Cl}\right]$ or $\mathrm{NH}_{4} \mathrm{Cl}$ totally ionized
thus $\left[\mathrm{NH}_{4} \mathrm{Cl}\right]=\left(1 \times 10^{-5}\right)^{2} / 5.62 \times 10^{-10}$
$=0.178 \mathrm{~mol} \mathrm{dm}^{-3}(\mathbf{1})$
Answer to 2 or more S.F.
(iv) QWC
methyl red (1)
indicator constant or $\mathrm{p} K_{\text {In }}$ must be near the endpoint pH
OR indicator constant or $\mathrm{p} K_{\text {In }}$ must be near 5 (1)
$2^{\text {nd }}$ mark conditional on correct indicator
Accept $p K_{\text {In }}$ in the steep part of the graph or it is a weak basestrong acid titration
(b) $\mathrm{CN}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCN}+\mathrm{OH}^{-}$

IGNORE state symbols
Accept " $\rightarrow$ " instead of " $\rightleftharpoons$ "
(c) (i) nucleophilic addition 1
(ii)

(1) for both arrows (1) for intermediate



OR for second step

(1)

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 ${ }^{-} \mathrm{CN}$ in step 1 (but not from the minus of $\mathrm{CN}^{-}$) and can start from the minus of $\mathrm{O}^{-}$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 $\mathrm{H}^{+} / \mathrm{HCN}$ scores zero
- Autoionisation of $\mathrm{C}=\mathrm{O}$ 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 $C N$
if too alkaline too little HCN to donate the proton in the last step $\mathrm{OR} \mathrm{H}^{+}$ion concentration too low (1)
(d) (i) rate $=k\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}\right]\left[\mathrm{CN}^{-}\right]$

Must be an equation
Must be [ ] NOT ( )
Ignore upper case K
Accept ' $R$ ' or ' $r$ ' for rate $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{Cl}$ ] / [1-chloropropane]/
[chloropropane]
Accept [cyanide ion]/[cyanide]
Reject [KCN]
(ii)


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

Mechanism based on $S_{N} 1$ scores 0
Reject fish hook arrows (penalise once)
Reject arrow from $N$ of $C N$
22. (a) methyl butanoate

Accept Methyl butaneoate
Reject 'an' missing
(b) the other three substances can form
intermolecular hydrogen bonds with themselves but the ester cannot.
Reject Discussion of London Forces
(c) Hydrolysis
(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
Reject cost with no justification
(e) $\quad \mathrm{Kc}=\frac{\left[\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}(\mathrm{l})\right]\left[\mathrm{CH}_{3} \mathrm{OH}(\mathrm{l})\right]}{\left[\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOCH}_{3}(\mathrm{l})\right]\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right]}$ (1)

Accept eq subscripts

| Moles at | Concentration / |
| :---: | :---: |
| equilibrium | $\mathrm{mol} \mathrm{dm}^{-3}$ |


| 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 $=(\mathbf{1})$
Conc at equilibrium $=$ equilibrium moles $\div 0.030$ (1)

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

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)
23. (a) A 1
(b) D 1
(c) A 1
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 $\mathbf{O H}$ or "hydroxide"
Z : both alcohol or hydroxyl and aldehyde (1)
Accept "hydroxy"
Reject $\mathbf{O H}$ 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

Accept

$-\mathrm{O}^{-} \mathrm{Na}+$ or -ONa
Reject any formula with the alcohol group oxidised
(c) (i) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COONa}^{2} / \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-} \mathrm{Na}^{+} /$

(1)

Allow $\mathrm{C}_{3} \mathrm{H}_{7} / \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CH}_{2}$


H
Accept

$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-} /$
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{Na} /$
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2}^{-} \mathrm{Na}^{+}$
Reject carboxylic acid
Or
... $\mathrm{O}^{-}-\mathrm{Na}^{+}$
(ii)

$/ \mathrm{CH}_{2}(\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{CN}) \mathrm{OH}$
$/ \mathrm{CH}_{2}(\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{CN}(\mathbf{1})$
25. (a) Aldehyde(s)
(b) (blue to) red (1)
precipitate/solid (1)
Accept green/yellow/ brown/orange instead of red
26. (a) Can be given in either order

## $1^{\text {st }}$ functional group

alkene or $\mathrm{C}=\mathrm{C}$ or carbon-carbon double bond (1)
Reject just 'double bond' or just 'carbon double bond'
bromine water/ $\mathrm{Br}_{2}$ turns (from orange/brown etc. to)
colourless/decolorised (1)
INITIAL COLOUR NOT REQUIRED
Accept $\mathrm{KMnO}_{4}$
Accept acidified decolorised
Accept alkaline green
Reject 'clear' instead of 'colourless'
$2^{\text {nd }}$ functional group
carboxylic (acid)


Accept carboxyl
Reject "carbonyl"
on addition of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ or $\mathrm{NaHCO}_{3}$ or CaCO 3 or Mg , fizzing occurs (1)
Accept gas evolved which turns limewater milky OR
or universal indicator/ blue litmus turns red
Reject just "a gas $/ \mathrm{CO}_{2} / \mathrm{H}_{2}$ evolved" for fizzing
OR
(warm with) a named alcohol plus conc. acid (as catalyst), pleasant/fruity smell
Ignore references to testing with $\mathrm{PCl}_{5}$
(b) (i) W as it contains an aldehyde group / - CHO group OR
W can be oxidised (whereas X cannot)
OR
$\mathbf{X}$ cannot be oxidised
OR
W as X is a ketone (which cannot be oxidised)
Reject $W$ with no reason or an incorrect reason (0) Contains $C=O$
(ii) $\mathrm{CH}_{2} \mathrm{OHCH}_{2} \mathrm{OH}$

OR


OR
Ethan(e)-1-2-diol
Accept $\left(\mathrm{CH}_{2} \mathrm{OH}\right)_{2}$
(iii)


OR
HOOCCOOH
OR
Ethanedioic acid/oxalic acid
Accept $(\mathrm{COOH})_{2}$
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
Accept CQ polyester on basis of monomers in (b)(ii) and (iii)
Accept $-\mathrm{CH}_{2} \mathrm{CH}_{2}-$ instead of

in relevant part of structure
only (1) if STRUCTURE IS CORRECT, BUT the ester linkage has been written as $\mathrm{COO} / \mathrm{CO}_{2}$
(ii) Condensation
27. (a)


Ketone + five carbon atoms (could be straight chain) (1)
Branched chain + rest of molecule (1)
Allow $1 \mathrm{CH}_{3}$ 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

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) $\mathrm{C}_{5} \mathrm{H}_{12} \mathrm{O}$

Accept $\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{OH}$
Reject structural or displayed formula
(d) The reactants don't distil over before they can react Owtte

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

