## 4.4, 4.5 HW MS

1. (a) nucleophilic addition

(b) (i) 2-hydroxybutanenitrile 1

(allow 1 for amide even if not $\mathrm{C}_{4} \mathrm{H}_{7} \mathrm{NO}$, i.e. $\mathrm{RCONH}_{2}$ ) (if not amide, allow one for any isomer of $\mathrm{C}_{4} \mathrm{H}_{7} \mathrm{NO}$ which shows geometric isomerism)
(c) (i)

$\mathrm{COOCH}_{3}$

2. (a) (i) 2, 3-dimethylbutan - 2 - ol (1)
(ii) elimination (1)

Mechanism
(1)


$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2} \longleftarrow\left(\mathrm{CH}_{3}\right)_{2} \stackrel{\left.+()^{\mathrm{C}} \stackrel{\mathrm{H}}{\square} \stackrel{+}{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right)}{ }$
(1)
(iii) Structure


Name of isomer 2, 3 - dimethylbut - 1 - ene (1)
Explanation loss of $\mathrm{H}^{+}$or H (1) from end C also possible (1)
(b) (i) Equation


Name of mechanism addition - elimination (1)
Mechanism

allow loss of $\mathrm{H}^{+}$here

(ii) Type of reaction esterification (1)

Reagent(s) $\quad \mathrm{CH}_{3} \mathrm{COOH}$ or ethanoic acid (1)
Conditions strong acid catalyst (1)
3. (a) (i) propyl methanoate (1)
not propanyl

- A wrong reagent or no reagent scores zero
- An incomplete reagent such as silver nitrate for Tollens, or potassium dichromate loses the reagent mark, but can get both observation marks
- penalise observations which just say colour change occurs or only state starting colour
(ii) Reagent: $\mathrm{NaHCO}_{3}(\mathbf{1})$

Observation with C: no reaction (1)
Observation with $\boldsymbol{D}$ : effervescence (1)
for $\boldsymbol{C}$ and $\boldsymbol{D}$ NOT Tollens

| Test | an identified <br> (hydrogen) <br> carbonate | acidified <br> $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ | acidified <br> $\mathrm{KMnO}_{4}$ | correct <br> metal | UI or stated <br> indicator | $\mathrm{PCl}_{5}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Observation <br> with $\mathbf{C}$ | no reaction | goes green | goes <br> colourless | no <br> reaction | no change | no reaction |
| observation <br> with $\mathbf{D}$ | bubbles or <br> $\mathrm{CO}_{2}$ | no change | no change | bubbles or <br> $\mathrm{H}_{2}$ | red or correct <br> colour <br> $\mathrm{pH} 3-6.9$ | (misty) <br> fumes |

(b) (i) Reagent: pentan-2-one (1)
or 2-pentanone
but not pent-2-one or pentyl
(ii) Reagent: Tollen's or Fehling's (1)

Observation with $\boldsymbol{E}$ : no reaction (1)
Observation with $\mathbf{F}$ : silver mirror or red ppt (1)
for $\mathbf{E}$ and $\mathbf{F}$

| Test | Tollens | Fehlings or <br> Benedicts | iodoform or <br> $\mathrm{I}_{2} / \mathrm{NaOH}$ | acidified <br> $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ | Schiff's |
| :--- | :--- | :--- | :--- | :--- | :--- |
| observation with <br> E | no reaction | no reaction | yellow (ppt) | no change | no reaction |
| observation with <br> F | silver or mirror <br> or grey or ppt | red or ppt <br> not red solution | no reaction | goes green | goes pink |

(c)

(1)
must be aldehyde. Allow $\mathrm{C}_{2} \mathrm{H}_{5}$ for $\mathrm{CH}_{3} \mathrm{CH}_{2}$ otherwise this is the only answer
4. (a) (i) B: propanoyl chloride (or consequentially on part (a) (ii)) (1)

C: propanoic anhydride (or consequentially on part (a) (ii)) (1) do not allow formulae
(ii) effervescence / misty fumes / steamy fumes / fumes / solution becomes warm / fizzing not just gas (1)
(iii)

(1)
(the minimum necessary for the mark is $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}-\mathrm{N}$ shown)
(iv) $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}\right)_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ (1)
allow $\mathrm{C}_{2} \mathrm{H}_{5} \ldots$.
(b) (i) methanol (1)
methyl propanoate (or consequentially on part (a) (ii)) (1)
do not allow formulae
(ii) A: in presence of (concentrated) sulphuric acid
/ $\mathrm{H}_{2} \mathrm{SO}_{4}$ / strong acid / gaseous hydrogen chloride or HCl
allow dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ (1)
heat / reflux (but only if first mark awarded) (1)
allow 1 mark for acidic conditions / $\mathrm{H}+$ and heat
B: room temperature / in the cold / not heated / cooling not acid (1)
C: heat / reflux not acid (1)
5. (a) (i)

(ii) ester (1)
solvent, flavourings (1)
(iii) conc $\wedge \mathrm{H}_{2} \mathrm{SO}_{4}$ (1)
in same physical state (1) 6
(b) $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}+6 \mathrm{O}_{2} \rightarrow 4 \mathrm{CO}_{2}+5 \mathrm{H}_{2} \mathrm{O}$ (1) 1
(c) (i)

(1)

(1)


$$
\mathrm{CH}_{2}=\mathrm{CHCH}_{2} \mathrm{CH}_{3}
$$

(ii) two H on carbon in double bond (1)
(iii)


$$
\text { cis but-2-ene (1) trans but-2-ene } 7
$$

6. (a) Reagents
$\mathrm{NaBH}_{4}(\mathbf{1})$
Type of reaction reduction (1)
(b) (i) Reagents(s) $\quad \mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}(\mathbf{1}) \mathrm{H}_{2} \mathrm{SO}_{4}$ (1)

Conditions reflux (1)
(ii) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}+2[\mathrm{O}] \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O}$ (1) 4
(c) Reagents

HCN or $\mathrm{NaCN} / \mathrm{H}^{+}$(1)
Name of mechanism nucleophilic $\cap$ addition (1)
(d) (i) mirror images (1)
(ii) plane polarized light (1)
rotated in opposite directions (1)
(e) (i) Structure

Name

propyl propanoate (1)
(ii)

(1)
(f) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}$ or $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}+4 \mathrm{O}_{2}{ }^{(\mathbf{1})} \rightarrow 3 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}$ (1)
7. (a) (i) correct graphical formula for tertiary alcohol allow $\mathrm{CH}_{3}$ not $\mathrm{C}_{2} \mathrm{H}_{5}(\mathbf{1})$
2-methylbutan-2-ol / 2-hydroxy-2-methylbutane / 2-methyl-2-hydroxybutane award name mark even if it follows incorrect formula (1)
(ii) graphical formula of pent-1-ene (1)
graphical formula of pent-2-ene (1)
accept geometrical isomers of pent-2-ene if clearly shown to be different
(iii) dehydration / elimination (1)
(iv) no H atoms on C atom next to $\mathrm{C}-\mathrm{OH} /$ three methyl groups on C (1) 1
(b) (i) ethanenitrile / ethanonitrile / methyl cyanide /
cyanomethane / acetonitrile (1)
(ii) any hydrolysis (1) 1
(iii) $\mathrm{CH}_{3} \mathrm{COCl}+\mathrm{CH}_{3} \mathrm{NH}_{2}{ }^{\circledR} \mathrm{CH}_{3} \mathrm{CONHCH}_{3}+\mathrm{HCl}$
for correct formula of methylamine / HCl product (1)
overall correct (1)
8. (a) $\mathrm{NaBH}_{4} \mathbf{( 1 )} 1$
(b) nucleophilic ${ }^{\wedge}$ addition (1)

(1) (1)

5
(c) (i) hexanedioic acid (1)
(ii) $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O} \quad \rightarrow \quad \mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}$
$\mathrm{Mr}=98$ (1) $\quad \mathrm{Mr}=146$ (1)
$2.40 \mathrm{~g} \quad \rightarrow \quad \frac{2.40}{98} \times 146=3.58 \mathrm{~g}(\mathbf{1})$
9. (a) (i) ethyl ethanoate

(1)

2
(ii) esterification / condensation / addition - elimination (1) 1
(b) (i) aqueous / dilute sulphuric / hydrochloric acid (allow $\mathrm{HCl}(\mathrm{aq}) ; \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ not water) (1)
temp. $<100^{\circ}$ / warm / heat / reflux (this mark dependent on sensible reagent) (1)
(ii) $\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$
(allow $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{2}, \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$ but must have $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ ) (1)
(c) (i) sodium hydroxide / sodium carbonate / sodium hydrogen carbonate (allow formula) (1) room temperature / aqueous (2nd mark dependent on correct reagent) (1)2
(ii) ethanoic anhydride

(1)
(methyl groups can be shown as $-\mathrm{CH}_{3}$ but the $\mathrm{C}-\mathrm{C}$ bond must be drawn)
(iii) addition of water / hydrolysis (1)
$\left(\mathrm{CH}_{3} \mathrm{CO}\right)_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{CH}_{3} \mathrm{COOH}$ (1)
(d) (i) ethanamide not ethylamide.

(1)
(ii) ammonia (not if dilute implied) / ammonium carbonate $/ \mathrm{PCl}_{5}$ followed by $\mathrm{NH}_{3}$ (allow formulae) (1)
heat or temperature $<100^{\circ}$ (1)
(iii) $\mathrm{CH}_{3} \mathrm{CONH}_{2}+\mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NH}_{4} \mathrm{Cl}$ (1)
10. (a) (i) An appropriate alkene; $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCH}_{2}$ or $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CCH}_{2}$ ..... 1
Isomer 1 ..... 1
Isomer 2 ..... 1
Position isomerism ..... 1
Mechanism
electrophilic attack and electron shift to Br (Unless $\mathrm{H}^{+}$used) ..... 1
carbocation ..... 1
reaction with carbocation ..... 1
[Allow mechanism marks for the alkene $\mathrm{CH}_{3} \mathrm{CHCHCH}_{3}$ ]
[Allow one mark if mechanism for minor product given]
(ii) An appropriate carbonyl; $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ ..... 1
Mechanism nucleophilic attack and electron shift to O ..... 1
anion intermediate ..... 1
reaction with anion ..... 1[Allow mechanism marks for the carbonyl $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$ ]
Isomer 1 ..... 1
Isomer 2 ..... 1
Optical isomerism ..... 1
NB Isomer structures must be tetrahedralNB Penalise "stick" structures once in part (a)
(b) QoL Large charge on carbonyl carbon atom due to bonding to O and Cl ..... 1
Nucleophiles have electron pairs which can be donated ..... 1
Equation Species ..... 1
Balanced ..... 1

