**4.10, 4.11 EXAM QUESTIONS mark scheme**

**1.** (a) electrophilic substitution; 1

 cone HN03; 1
cone H2SO4 either or both cone missing scores one for both acids; 1

(b) Sn or Fe/HCl (cone or dil or neither); 1

(ignore extra NaOH)

Sn or Fe/H2SO4 (dil or neither)

(not HNO3 at all)

or H2/Ni

(not NaBH4/ LiAlH4 or Na/C2H5OH)



 1

(c) 77 or 92; 1

(d)


 1

(allow -NH3+)

(e) **G**

 **H** 1


 1

[9]

**2.** (a) CH3OH + CH3CH2COOH  CH3CH2COOCH3 + H2O 1

(b) (nucleophilic) addition–elimination NOT acylation 1
 4

M3 for structure

M4 for 3 arrows and lone pair

ignore use of Cl– to remove H+

(c)  ****

allow C2H5 and –CO2–

allow CH3CH2COOCOCH2CH3

 or (CH3CH2CO)2O 1

(d) (i) faster/not reversible/bigger yield/purer product/no(acid) (catalyst)
required 1

(ii) anhydride less easily hydrolysed or reaction less violent/exothermic
no (corrosive) (HCl) fumes formed or safer or less toxic/dangerous
expense of acid chloride or anhydride cheaper 1

any one

(e) (i) C8H8O2 1

(ii) **any** two **from**



Allow –CO2– allow C6H5

 2

[12]

**3.** (a) butanoyl chloride 1

(b) (i) Cl has (two) isotopes or 35Cl and 37C1 1

(ii) 106 **and** 108 1

(c) (nucleophilic) addition-elimination, penalise electrophilic ...not esterification 1



 4

 M3 for structure
M4 for 3 arrows and lone pair
(only allow for correct M3 or close)

 M2 not allowed independent of Ml,
but allow Ml for correct attack on C+ if M2 shown as independent first.

[8]

**4.** (a) 5 **(1)** 1

(b) 2:2:2:3:3 **(1)**

any order but not multiples

 1

(c)  **(1)** 1

(d) CH3CH2 or C2H5 or ethyl **(1)**4.13 (quartet) : CH2 peak split by CH3 / next to CH3 **(1)**1.26 (triplet) : CH3 peak split by CH2 / next to CH2 **(1)** 3

(e) CH2CH2 **(1)** 1

(f) **(2)**
allow **(1)** for CH3COCH2OCOCH2CH3
or CH3COOCH2COCH2CH3

Must be C7H12O3

 2

[9]

**5.** (a) C=O **(1)** 1

or “carbonyl”

(b) (i) Cl has (2) isotopes **(1)**

Allow 35Cl and 37Cl without word isotope – but must be correct isotopes

must have 3 different elements, i.e. not C3H7+ but allow balanced equation including C3H7+ for the equation mark

(ii) *Fragmentation*:  **(1)**

must be an ion (\*)

*Equation*: C4H7ClO+   + C2H4Cl **(1)** 3

(\*) allow C2H3O+ or any form of it (i.e. CH2CHO+ or CH2COH+) in equation, be generous with position of + or 

if fragment ion completely wrong (not m/z = 43) no further marks

(c) (i) CDCl3 or CCl4 **(1)** or D2O, C6D6

(ii) Si(CH3)4 **(1)** or SiC4H12 2

(d)

|  |  |  |  |
| --- | --- | --- | --- |
|  | Peak 1 | Peak 2 | Peak  |
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |
| Number of adjacent, non-equivalent protons | 1 | **0** | **3** |

 **(1)** 1

(e)  **(1)** 1
or CH3COCHClCH3

(f)

  **(1)** 1

[9]

**6.** (a)  **(1)** 1

(b) *Name of mechanism*: (nucleophilic) addition- elimination **(1)**

*Mechanism*:



 5

(c) CH3CH2COOCH2CH3+** ** CH3CH2C+=O **(1)**+ CH3CH2O****

equation (1)

 2

(d) CH3CH2CH2COOCH3 or (CH3)2CHCOOCH3 **(1)**

Allow C3H7COOCH3

 1

[9]

**7.** (a) (i) molecular formula **(1)**

(ii) 13C isotope **(1)** 2

(b) (i) (CH3)2CHCOCH3+  (CH3)2CHCO+ + H3

 **(1)** **(1)** **(1)**

(ii) *Structure 1* *Structure 2*

 CH3CO+ (CH3)2CH+
**(1)** **(1)** 5

(c) two isotopes **(1)**

C3H735Cl = 78 C3H737Cl = 80 **(1)**

relative abundances 35Cl:37Cl = 3:1 **(1)** 3

[10]

**8.** (a) 2-chloropropanoic acid **(1)** 1

(b) 1.72 Doublet  next to CH **(1)**4.44 Quartet  next to CH3 **(1)** 2

(c) Two triplets **(1)** 1

(d) 

Allow SN1 5

(e) (i) 

(ii) 

(iii)



Or anhydride

 3

[12]

**9.** (a) (i)  + 2 [H]  CH3CH(OH)CH2CH2CH3 **(1)
or C5H10O or C5H11OH**

(ii) *Name of mechanism*: nucleophilic addition **(1)**

QoL

Mechanism:


(iii) racemic (racemate) mixture formed **(1)**OR explained e.g. 2 enantiomers in equal amounts 7

(b) *Fragment 1*: 43 ; 43
*Fragment 2:* 71 ; 15

Any two × (1)

 2

[9]

**10.** (a) ***R***: O-H (alcohols) **(1)**

 ***S***: C=O or carbonyl **(1)**

 2

(b) aldehyde **(1)** -CHO or RCHO **(1)**

 1

(c) (i) *Reason 1*: TMS inert or non-toxic or volatile / easily removed
*Reason 2*: single (intense) peak
 peak of 12 protons
 has 12 equivalent protons
 all protons in same environment
OR
 peak / signal upfield of others
 highly shielded
 more shielded
 peak away from others or  = 0 or low

not solvent, not cheap

any 2 reasons × (1)

(ii) *Solvent*: CDCl3 or CCl4 **(NOT D2O)***Reason*: proton free **(1)** allow no hydrogens (atoms)

NOT H+ / hydrogen ions

 4

(d) (i)  **(1)**

(ii) –OH **(1)**

(iii) –CH2–CH2– **(1)** 3

(e)  **(1)** 1

[11]

**11.** (a) (i) HCN or KCN/HCl **(1)**
nucleophilicaddition **(1)**

(ii) C4H8O  C5H9NO

Mr = 72 **(1)** Mr = 99 **(1)**

*If MF shown lose 1 for wrong Mr.*

*If no MF shown max 2 if Mr wrong*

5g   × 99 **(1)** (= 6.88g)

64% yield = 0.64 ×  × 99 = 4.40g **(1)**

*(allow answer 4.36 – 4.42)* 6

(b) (i) NaBH4 or LiAlH4 or  or Na/C2H5OH **(1)**

(ii) racemic mixture formed **(1)**
or equal amounts of enantiomers

(iii) butanone has peak at ~ 1700 cm–1 **(1)**

(but not at ~ 3350 cm–1)

B has peak at ~ 3350 cm–1 **(1)**

(but not at ~ 1700 cm–1) 4

(c)



 4

(d)  1

[15]

**12.** (a) A is RCOOR **(1)**

R + R = 102 – 44 = 58 **(1)**  C4H10

C5H10O2 **(1)** 3

(b) 2 : 2 : 3 : 3 **(1)** 1

(c) Two CH2CH3 groups present **(1)** 1

(d) CCCOOCC **(1)** 1

(e)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Chemical shift, /ppm | 1.09 | 1.33 | 2.32 | 4.13 |
| Label of group | a **(1)** | d **(1)** | b **(1)** | c **(1)** |

 4

[10]

**13.** (a) (CH3)4 Si or tetramethylsilane  **(1)** 1

(b) 4  **(1)** 1

(c) 2 : 1 : 6 : 3  **(1)** 1

(d) –CH2CH3  **(1)**

CH3 splits CH2 to form a quartet  **(1)**

CH2 splits CH3 to form a triplet  **(1)** 3

(e) two equivalent CH3 groups  **(1)** 1

(f)  1

[8]

**14.** (i) CH3COOCH2CH3 or CH3COOC2H5 **(1)**

(ii) 3 **(1)**

(iii) 3 + 4 or triplet + quartet **(1)** 3

 [3]

**15.** (a) same molecular formula / same number of each type of atom **(1)**

 different arrangements of atoms (in the molecule) **(1)**
(**not** just same structural formula) 2

(b) (i)


 **(1) (1)** 2

(ii) 43: CH3CH2CH2+/ CH3C+HCH3 / C3H7+ **(1)**
29: CH3CH2+ / C2H5+ **(1)**
15: CH3+ **(1)**

(2 max if +ve sign omitted or –ve) (+ can be anywhere) 3

(iii) Isomer 1 (dependent on candidate’s order) **(1)**

Isomer 2 could not (easily) give peak at 29 / C2H5+ **(1)** 2

(c) (i)  **(1)**

 **(1)** 2

(ii) ester **(1)**
carboxylic acid **(1)**

 names must be appropriate way round relative to (i)
these marks dependent on correct answers in (i) 2

[13]

**16.** (a) **A** **B**

CH3COOH **(1)** HCOOCH3
 or HOCH2**(1)** 2

(b) **C** **D**

CH3CH2CH2OH CH3CH2–O–CH3 **(1)**
or CH3CH(OH)CH3 **(1)** 2

(c) **E F**

   2

(d) **G** **H**

CH3CH2CHO **(1)** CH3COCH3 **(1)** 2

(e) **I** **J**

  2

(f) **K L**
one alkene e.g. one cycloalkane e.g.
 

 2

[12]

**17.** (a) *Name*  nucleophilic addition **(1)**

*Mechanism*

 5

(b) (i) *Equation*  CH3COCH3 + 2[H]  CH3CH(OH)CH3 **(1)**

Reducing agent NaBH4 **(1)**

(ii)



 6

[11]

**18.** A 1715 cm–1 C=O group **(1)**

B 3350 cm–1 O–H group alcohol **(1)**

A 

 two environments or two kinds of proton **(1)**
CH3CH2 adjacent or coupled **(1)**
ratio 2:3 or 4:6 **(1)** symmetric **(1)**

[CH3CH2COCH2CH3]+**.**  CH3CH2CO+ + CH3CH2**.** **(1)**

m/z = 86 **(1)** **(1)**

or Mr for **A**



CH3CH2HCH2CH3 **(1)** and CH3HCH2CH2CH3 **(1)**

 both secondary **(1)**

hydration gives **B** and 

about 50% of each **(1)**

A  B reduction

B  C dehydration or elimination **(1)**

C is an alkene **(1)** cis/trans isomers **(1)**

D is a racemate **(1)** or optical isomers any 20

[20]

**19.** (a) X (O–H) (alcohols) penalise acid or missing “alcohol” 1
Y C=O allow carbonyl 1

 4

NOT acid

(b)


 3

Allow conseq dibromocompounds following incorrect unbranched alkenes

NOT allow dibromocompound consequent on a duplicate alkene

NOT allow monobromocompounds if HBr added



 6:3:1 either next to correct structure or to none 1

 Allow a mark for identifying correct dibromocompound with three peaks
even if integration ratio is wrong 1

 if 6:3:1 missing or wrong, no marks for splitting 1

 Only award a mark for splitting if it is clear which integration number it
refers to 1

 6 singlet or drawn 1

 3 doublet or drawn 1

 1 quartet/quadruplet or drawn 1

[16]

 **20.** (a) (i) 3 peaks or shown in a list 1

*m/z* = 126, 128 and 130 (56 +70/72/74) *(all 3 scores 2)* 2

*(if 56 wrong allow (x + 70/72/74) for1(x cannot be zero)*

(any two scores 1)

(ii) 3


(1) (1) (1)

(b) (i) optical 1

equal mixture of enantiomers 1

(optically) inactive or effects cancel 1

plane polarised light use stereospecific reagent (QoL) 1

rotated in opposite/different

directions (QoL) reacts with one isomer only 1

(ii) carbocation 1

planar – *(must refer to carbocation or intermediate)* 1

attack from either side equally likely –

*(must refer to carbocation /intermediate)* 1

 7 max

(c) (i) 2 peaks *(if 4 peaks allow splitting only)* 1

ratio 6:2 or 3:1 1

doublet (6 or 3) 1

quartet (2 or 1) 1

(ii) **S**
  1

**T**
 1

[19]

**21.** (a)  1

 1

NB The bonds shown in the structure must be correct

 Isomerism: Geometric or cis-trans 1

If written answer is correct, ignore incorrect labelling of structures.
If no written answer, allow correctly labelled structures.

 Both COOH groups must be on the same side/ close together/ cis . 1

 No rotation about C=C axis 1

 Structure

 1

(b) Br2 / HBr / H2SO4 / H+ / Br+ / NO2+ (Mark M1) 4



NB If electrophile H+ / Br+ / NO2+ allow M1, M2 and M4
If the acid is incorrect, M2 and M3 can still be scored
Allow M4 consequentially if repeat error from part (a)

(c) e.g. 2NaOH + HO2CCHCHCO2H  NaO2CCHCHCO2Na + 2H2O

 Both H replaced 1
Balanced for atoms and charges 1

NB Allow ionic equations and 2NaOH + C4H4O4 
 C4H2O4Na2+ 2H2O

 Allow one if structure incorrect but molecular formula
 correct

 Allow one for a correct equation showing one H replaced

(d) *M1* Two peaks 1
*M2* No splitting or singlets 1
*M3* (Two) non-equivalent protons or two proton environments 1
*M4* No adjacent protons 1
*M5* Same area under the two peaks or same relative intensity 1
 Max 3

NB Doublet could score M1 and M3 or M5 (Max 2)

 More than two peaks CE = 0

 Apply the “list principle” to incorrect answers if more
 than 3 given

[15]

**22.** (a) [CH3CH2CO]+ 1
CH3CH2COCl + AlCl3  [CH3CH2CO]+ + AlCl4– 1

(Penalise wrong arrows in the equation or lone pair on Al
In the equation, the position of the + on the electrophile can be on O or C or outside square brackets,
Can score electrophile mark in mechanism if not previously gained)

 3

(Arrow for M1 must be to C or to the + on C

penalize + in intermediate if too close to C1 ;

horseshoe should extend from C2 to C6 )

(b) *m/z* = 105 C6H5CO+ 1

 *m/z* = 77 C6H5+ 1

(not Wheland intermediate)
(Penalise missing + once)

Allow position of + on O or C of CO or outside [ ] for the fragment ion [C6H5CO]+

Allow position of + on H or C or outside [ ] for the fragment ion [C6H5]+
[C6H5COCH2CH3]+˙  C6H5CO+ + CH3CH2˙
(˙ must be on H or C of CH2 or outside bracket)

 **(1)** for molecular ion **(1)** for RHS 2
Allow molecular formulae, i.e. C9H10O+ **.**  C7H5O+ + C2H5 **.**

(c) Nucleophilic addition 1

 1 Q contains asymmetric carbon or chiral centre or are chiral molecules
2 with 4 different groups/atoms attached (stated)

not molecules attached

 3 planar C=O
4 attack from each side
5 equally likely or equal amounts of each isomer formed
6 Racemic mixture or racemate (Q of L)
7 of mirror images or enantiomers or d/l or +/– or R/S or drawn max 6

(d) Conc H2SO4 or conc H3PO4 or Al2O3 or iron oxides Not HCl or HBr 1
Geometrical or cis-trans 1
Double bond or C=C not just  cloud 1

(stated not just drawn)

 2 Different atoms/groups on each C (not molecules) 1

(stated not just drawn)

[20]

**23.** **X** is methyl propanoate 1



 M1 for arrow and lone pair, 4
M2 for arrow
addition-elimination 1

 Spectrum 2 1

if thinks Spectrum 1 = X can only score for structure of Y

 **Y** is CH3COOCH2CH3 1
The two marks for explanation are awarded for discussing one or more of the 2
four peaks (not those for the CH3 of the ethyl groups)
for stated  values the integration or the splitting should be related to the
structure: e.g. structure of **X** shows that
 at  3.7 – 4.1 **(1)** spectrum of **X** should have integration 3 / singlet **(1)**

or

 at  2.1 – 2.6 **(1)** spectrum of **X** should have integration 2 / quartet **(1)**

 Spectrum 2 has these
[OR Spectrum 1 has
 at 3.7 – 4.1 **(1)** quartet / integration 2 **(1)** so not **X**
 at 2.1 – 2.6 **(1)** singlet / integration 3 **(1)** so not **X**]

[10]

**24.** (a) K2Cr2O7/H2SO4 reuced by

 CH3CH2CH2CH2OH **(1)**

 oxidised to CH3(CH2)2CHO **(1)**
and CH3(CH2)2COOH **(1)**

CH3CH2CH2CHO **(1)**

 oxidised to CH3(CH2)2COOH **(1)**

Equation: Cr2O72– + 14H+ + 6e–  2Cr3+ + 7H2O **(1)** 6

Note: Deduct one if all three compounds given as reducing agents.

(b) Tollens’ reduced by
 CH3CH2CH2CHO **(1)**

 oxidised to CH3(CH2)2COOH **(1)**

Equation [Ag(NH3)2]+ + e–  Ag + 2NH3 **(1)** 3

(c) CH3CH2CH2CH2OH **(1)**
 Product CH3CH2CH2CH2OOCCH3 **(1)**

(CH3)3COH
 Product (CH3)3COOCCH3 **(1)** 4

(d) CH3CH2CH2OH has five peaks **(1)**

(CH3)3COH has two peaks **(1)** 2

[15]

**25.** (a) 3 Ketones:



 3: 2: 2: 3  **(1)** 6: 1: 3  **(1)** 6: 4 or 3: 2 **(1)**

6

(b) 4 aldehydes:

 7

(c) nucleophilic addition  **(1)**

equal  **(1)** mixture of optical isomers  **(1)**

e.g  4

(d) Reagents are oxidizing agents  **(1)**

Aldehydes can be (easily) oxidized  **(1)**

Ketones are not (easily) oxidized  **(1)** 3

[20]

**26. Part (a)** for each section:

 A totally wrong reagent scores zero
An incomplete reagent such as silver nitrate for Tollens, loses the reagent mark, but can get both observation marks.
A wrong reagent such as [Ag(NH3)2]2+ or bromide water loses the reagent mark and the next mark “gained”, i.e. can only score 1/3 if both observations correct

 If two test given and results given correctly for both compounds in both tests then full marks
If one test on A and a different test on B with only these results given
 if both results correct then score 2/3
 if either result wrong then score 1/3
if either test would not work as a distinction, then score 0/3

 If the candidate says A = ketone (or C = benzene), lose this mark.

 If the candidate omits the letters when referring to the pair of compounds,
e.g. says alkene decolourises / alkane no reaction penalise one mark only.

(a) (i) penalise observations which just say colour change occurs or only state starting colour

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Tollens | [1] | Fehlings / Benedicts | [1] | Brady’s or 2,4-dnph | [1] | sodium | [1] |
| No reaction A | [1] | no reaction A | [1] | no reaction A | [1] | bubbles or hydrogen A | [1] |
| silver mirror or grey or ppt B | [1] | red or ppt B | [1] | (Yellow / orange) Xtals or ppt | [1] | no reaction B | [1] |
| (not silver solution) | [1] | not red solution | [1] | not yellow / orange solution | [1] |  |  |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Carboxylic acid / H2SO4 | [1] | Schiff’s | [1] | iodoform or I2 / NaOH | [1] | PCl5 | [1] |
| (sweet) smell A | [1] | no reaction A | [1] | yellow (ppt) A | [1] | (misty) fumes A | [1] |
| no reaction B | [1] | goes pink B | [1] | no reaction B | [1] | no reaction B | [1] |

 (ii)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Bromine (water) | [1] | KMnO4 | [1] | KMnO4 / H2SO4 | [1] |  | [1] |
| no reaction C | [1] | no reaction C | [1] | no reaction C | [1] |  | [1] |
| decolourised D | [1] | goes brown D | [1] | goes colourless D | [1] |  | [1] |
| not clear not discolour (is)ed |  |  |  |  |  |  |  |

(iii) not just smell for E

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| an identified (hydrogen) carbonate | [1] | correct metal | [1] | UI or stated indicator | [1] | PCl5 | [1] |
| no reaction e | [1] | no reaction E | [1] | no change E | [1] | (misty) fumes E | [1] |
| bubbles or CO2 F | [1] | bubbles or H2 F | [1] | red or correct colour F | [1] | no reaction F | [1] |

 note MAX 8

(b) F has absorption at 2500 - 3000 cm–1 (due to COOH) **(1)**
**N.B.** Qu asks “How fingerprinting is used” i.e. no marks for simply
stating fingerprint region unique.
Compare with (spectrum of) known compound or database **(1)**(exact) match 3

(c) major peak [CH3CO]+ **(1)**m / z 43 **(1)**CH3COOCH3+**.**  CH3CO++ OCH3**.**

(1 for molecular ion) (1 for correct other fragment)

 **Alternative:**

 major peak [CH3]+ **(1)**m /z 15 **(1)**CH3COOCH3+**.**  CH3++ CH3COO**.** or COOCH3**.** or C2H3O2**.** or C3H6O2+**.**

(1) (1 for radical)

 If major peak wrong but possible e.g. CH3OO+ m/z = 59
no marks so far, but can score up to 2 for
CH3COOCH3+**.**  CH3++ CH3COO+ or +COOCH3 + CH3

1 for correct other fragment]

 4

[15]

**27.** (a) X contains >C=O **(1)**

if X and Y reversed lose this mark but allow remaining max 6/7

 X is CH3CH2COOH **(1)**

 Y is CH3CH2CH2OH **(1)**

 A is  **(1)**



Conc H2SO4 : catalyst **(1)** 7

(b) 4



(c)  3.1 – 3.9 **(1)**
 2.1 – 2.6 **(1)**

a: quartet **(1)**  3 adjacent H **(1)**

b: triplet **(1)**  2 adjacent H **(1)** 6

(d) 3269 cm–1 OH  alcohol **(1)**

 G is  (1) 2

 **Notes**

(a) first mark for C=O stated or shown in **X**

Ignore wrong names

 **Y** CH3CH2CH2OH
allow C3H7 in **A** if **Y** correct or vice versa
Allow **(1)** for **A** if correct conseq to qrong **X** and **Y**

 other oxidising agents: acidified KMnO4; Tollens; Fehlings

 other reducing agents: LiAlH4; Na/ethanol; NiH2; Zn or Sn or Fe/HCl

(b) give **(1)** for carboxylic acid stated or COOH shown in each suggestion
**(1)** for correct E
any 2 out of 3 for **B**, **C** or **D**
allow C3H7 for either the **B** or **D** shown on the mark schme
i.e. a correct structure labelled **B**, **C** or **D** or **E** will gain 2.

(c) protons a – *quartet* must be correct to score *3 adjacent H* mark. Same for b

(d) allow **(1)** for any OH (alcohol) shown correctly in any structure – ignore extra functional groups. Structure must be completely correct to gain second mark

[19]

 Organic points

(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

 allow CH3– or –CH3 or  or CH3
 or H3C–

**28.** (a) Identity of **X**; 2-methylpropene **(1)**Absorption at 1650 cm–1 indicates an alkene present **(1)**

OR a chemical answer e.g. Br2 (aq) brown to colourless 2

(b) Reagents
Step 1 KOH (allow NaOH) **(1)** alcoholic **(1)** warm **(1)**

Only allow solvent and warm if reagent correct

Step 2 HBr **(1)**

Mechanism: A  **X**



Or a carbocation mechanism

Mechanism **X**  B



 11

(c) A gives three peaks **(1)**B gives one peak **(1)**

Allow one for “A has more peaks than B” when no number of
peaks is given

 2

[15]

**29.** B 1685 cm–1  C=O **(1)**

C 3340 cm–1  OH or alcohol **(1)**

D 1630 cm–1  C=C or alkene **(1)**only 1,4-dimethylbenzene will give B as a single compound **(1)**



[18]

**30.** A: 4 peaks or 4 different environments **(1)**

1 : 2 : 2 : 3 **(1)** OH singlet **(1)** CH3 singlet **(1)**

2 triplets **(1)** CH2CH2 coupled **(1)**

B: 4 peaks or 4 different environments **(1)**
1 : 2 : 2 : 3 **(1)** OH singlet **(1)** OCH2O singlet **(1)**
quartet + triplet **(1)** CH2CH3 coupled **(1)**

C: 2 peaks or 2 different environments **(1)**
2 : 6 or 1 : 3 **(1)** CH3 groups equivalent **(1)**
2 singlets **(1)** no coupling **(1)**

[max 15]

**31.** (a) (i) *electrophile* lone pair acceptor/electron deficient species / electron
 seeking group / electron lover
 (**not just** positive group / species) **(1)**

*substitution* replacement / swap / substitution of one atom / group
 (in a molecule) by another atom / group **(1)** **not** molecules replaced 2

(ii) nitronium ion / NO2+ **(1)**

 HNO3+ + H2SO4  H2NO3+ + HSO4 **(1)**

 H2NO3+ + H2SO4 NO2+ + H3O+ + HSO4– **(1)**

 allow 1 mark for HNO3 + H2SO4  NO2+ + HSO4 + H2O

 allow 2 marks for HNO3 2H2SO4  NO2+ + H3O+ + 2HSO4¯
1 for species, 1 for balancing

mechanism shows attack by NO2+ with curly arrow from ring **(1)**

 appropriate intermediate with ‘+’ charge in centre of ring,
incomplete circle or 2 double bonds **(1)**

mark consequentially on electrophile given

 curly arrow from C–H bond to ring / deprotonation to give H+
final product must be nitrobenzene **(1)** 6

(iii) above 60 °C likelihood of multiple substitution
/ nitration / **(1)** 1

likely to carry on reacting

(b) chlorine **(1)**

AlCl3 / FeCl3 / Fe / other suitable halogen carrier **(1)**

absence of sunlight / room temp / anhydrous **(1)** 3

(c) (i) 2-chloro(-2-)methylpropane / (2)methyl 2 chloropropane **(1)** 1

(ii) compound **D (1)**

 all same type of protons / hydrogen are all in same (chemical)
environment / equivalent as they are all CH3 **(1)** 2

(iii) compound **C (1)**

ratio = 6:2:1 **(1)**

 2 CH3 groups have 6 equivalent protons, CH2 has 2 protons,
CH 1 proton **(1)** 3

must say same type of proton / H

penalise first omission of ‘same type’

(iv) appropriate unambiguous formula for **either** but-1-ene **or** but-2-ene **(1)**

appropriate unambiguous formula for the remaining structural isomer

allow 1 mark if candidate draws cis and trans but-2-ene **(1)** 2

(v) unambiguous structure for 2-methylpropan-1-ol – may be
from mechanism **(1)**

 curly arrow / attack by OH– curly arrow from lone pair or
charge only **(1)**

do **not** allow if Na -OH

 curly arrow from bond to Cl / dipole shown on
C-Cl bond / intermediate showing 3 full and 2 partial bonds to C **(1)**

 loss of Cl– NaCl **or** Na+:Cl– **(1)**
– **not** allowed 4

 **if** SN1 mechanism given:
first mark as above - independent
second mark for correct carbocation formed including curly
arrow from C to Cl or CS+ –ClS –

 third mark for hydroxide attack as above
final mark notavailable (wrong mechanism)

penalise missing proton once only

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**32.** (a) (M–R)+. Is a radial-cation **(1)** covalent bond breaks **(1)**
to form a cation (M+) **(1)** and a radical (R.) **(1)** 4

(b) Cl has a two isotopes **(1)**
CH3CH235Cl = 64 and CH3CH237Cl = 66 **(1)**
relative abundances 35Cl : 37Cl = 3 : 1 **(1)**
CH3CH2Cl+  CH3CH + Cl **(1)** 4

(c) ClCH2CH2Cl or 3 isotopic combinations possible **(1)**
C2H435Cl2 = 98 **(1)** C2H435Cl37Cl = 100 **(1)** C2H437Cl2 = 102 **(1)** 4

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**33.** (a) A C6H14 **(1)**  Ratio 12:2 or 6:1 **(1)**

B/C C=O **(1)** C5H10O **(1)**

CH3CH2CH2 CH3 **(1)** ratio 6:4 or 3:2 **(1)**

**(1)** ratio 9:1 9

(b) Tollens **(1)** silver mirror with aldehyde **(1)**

 no reaction with ketone **(1)**

*(or Fehlings red ppt with aldehyde, no reaction with ketone)*

Fingerprint region **(1)**

Exact match with standard **(1)** 5

(c) 3300cm–1  OH group in both **(1)**

1650cm–1  C=C in D **(1)**

 D is CH2 = CH– CH2 CH2 CH2 OH **(1)**

(or others)

E is  etc **(1)** 4

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**34.** (a) Region 1500–400 cm –1 **(1)**
unique for each compound **(1)**
compare spectrum with that of known compound **(1)**
exact match **(1)** 4

(b) C5 esters

  **(2)**

  **(2)**

  **(2)**

 T (alcohol) is CH3CH(OH)CH3 **(2)**
(3 peaks)

 U (acid) is CH3COOH **(2)**
(2 peaks)

T absorption at 3250 cm–1 confirms OH (alcohol) **(1)**
U absorption at 2900cm–1 confirms OH (acid) or at 1700 cm–1 confirms C=O **(1)** max 11

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**35.** (a)



 **A** = butanal

 **B** = methylpropanal

 **C**= butanone

 **D** = ethyl ethanoate **(1)**

Ignore numbers in names unless they make them incorrect
spellings must be correct
accept alternative trivial names correctly spelled 8

(b) ethanol / correct formula **(1)**

 ethanoic acid / ethanoyl chloride / ethanoic anhydride / correct formula **(1)**

 temperature less than 100 °C / reflux heat / concentrated sulphuric acid **(1)**dilute sulphuric acid / acid conditions / H+
(this mark dependent on sensible answers for first two marks)

 for ethanoyl chloride, room temperature / dry / anhydrous

 for ethanoic anhydride, heat / up to 100 °C 3

(c)  **(1)**

 butanoic acid methylpropanoic acid **(1)** 2

(d) heat with Fehling’s solution / ammoniacal silver nitrate / Tollen’s reagent /
other suitable oxidising system eg acidified dichromate / Schiff’s reagent

 **B** gives red, green or brown (precipitate) / silver (mirror) or black/grey **(1)**
precipitate / other, dependent on reagent

 **C** shows no change **(1)**

 **B** and **C** can be referred to as ‘aldehyde’ and ‘ketone’ only if names correct
in (a) or if there is some other valid identification 3

(e) (i) **B**

 two methyl groups / 6 Hs in identical chemical environments **or (1)**2 Hs in unique environments 2

(ii) **A**

 four different chemical environments (for protons) **(1)**
in (i) and (ii), second mark is dependent on first mark 2

(iii) same number of hydrocarbon groups with same number of protons in each 1

(f) nucleophilic addition **(1)**



 **(1)** for intermediate **(1)** for product

 allow –ve charge on N
but curly arrow must come from **C** allow H from HCN or H2O 5

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