4.10, 4.11 EXAM QUESTIONS mark scheme

1. (a) electrophilic substitution; 1

cone $HN0_3$; 1

cone H_2SO_4 either or both cone missing scores one for both acids; 1

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

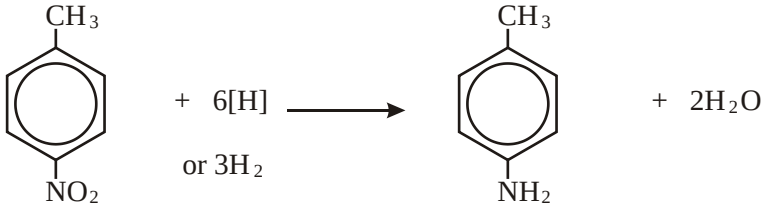
(ignore extra NaOH)

Sn or Fe/H_2SO_4 (dil or neither)

(not HNO_3 at all)

or H_2/Ni

(not $NaBH_4$/ $LiAlH_4$ or Na/C_2H_5OH)



1

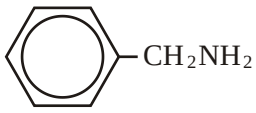
(c) 77 or 92; 1

(d)

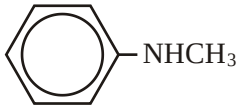
1

(allow -NH_3^+)

(e) **G**



H 1

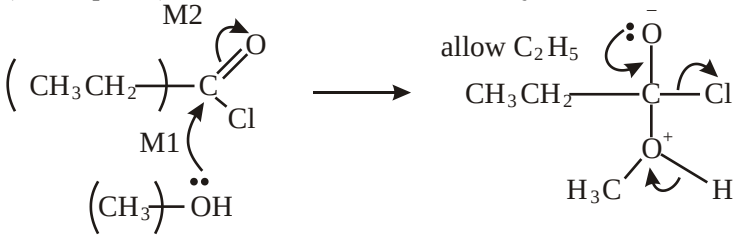


1

[9]

2. (a) $CH_3OH + CH_3CH_2COOH \rightarrow CH_3CH_2COOCH_3 + H_2O$ 1

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



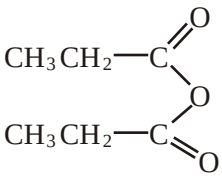
4

M3 for structure

M4 for 3 arrows and lone pair

ignore use of Cl^- to remove H^+

(c)



allow C_2H_5 and $–CO_2–$

allow $CH_3CH_2COOCOCH_2CH_3$

or $(CH_3CH_2CO)_2O$ 1

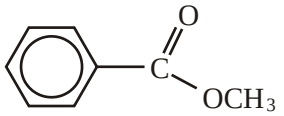
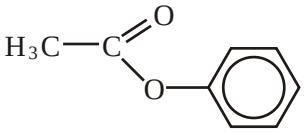
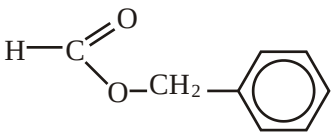
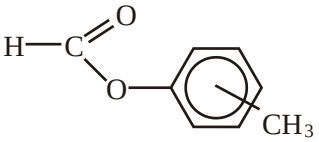
(d) (i) faster/not reversible/bigger yield/purer product/no(acid) (catalyst) required 1

(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) $C_8H_8O_2$ 1

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

Allow $–CO_2–$ allow C_6H_5

2

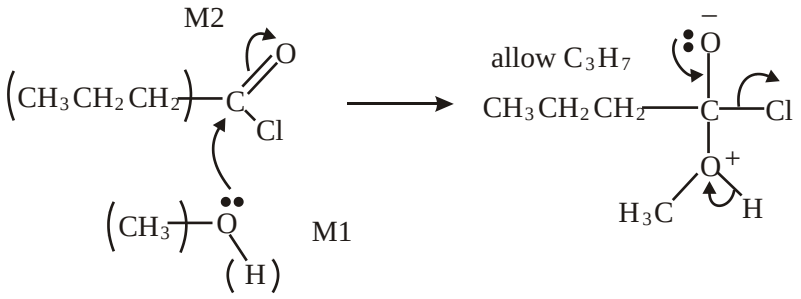
[12]

3. (a) butanoyl chloride 1

(b) (i) Cl has (two) isotopes or ^{35}Cl and $^{37}C1$ 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) $CH_3-\overset{\overset{O}{\|}}{C}-(R)$ **(1)** 1

(d) CH_3CH_2 or C_2H_5 or ethyl **(1)**
δ4.13 (quartet) : CH_2 peak split by CH_3 / next to CH_3 **(1)**
δ1.26 (triplet) : CH_3 peak split by CH_2 / next to CH_2 **(1)** 3

(e) CH_2CH_2 **(1)** 1

(f) $CH_3-\overset{\overset{O}{\|}}{\underset{(CO)}{C}}-CH_2CH_2-\overset{\overset{O}{\|}}{\underset{(CO)}{C}}-OCH_2CH_3$ **(2)**
allow **(1)** for $CH_3COCH_2OCOCH_2CH_3$
or $CH_3COOCH_2COCH_2CH_3$
Must be $C_7H_{12}O_3$

2

[9]

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

or "carbonyl"

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

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

must have 3 different elements, i.e. not $C_3H_7^+$ but allow balanced equation including $C_3H_7^+$ for the equation mark

(ii) *Fragmentation*: $CH_3-\overset{+}{C}=O$ **(1)**

must be an ion (*)

Equation: $C_4H_7ClO^{+\bullet} \rightarrow CH_3\overset{+}{C}O + C_2H_4Cl^{\bullet}$ **(1)** 3

(*) allow C_2H_3O+ or any form of it (i.e. CH_2CHO^+ or CH_2COH^+) in equation, be generous with position of + or •

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

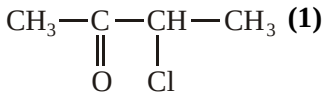
(c) (i) $CDCl_3$ or CCl_4 **(1)** or D_2O, C_6D_6

(ii) $Si(CH_3)_4$ **(1)** or SiC_4H_{12} 2

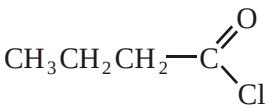
(d)

	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 $CH_3COCHClCH_3$

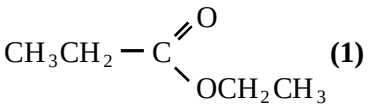
(f)  or $(CH_3)_2CHCOCl$

(1) 1

or

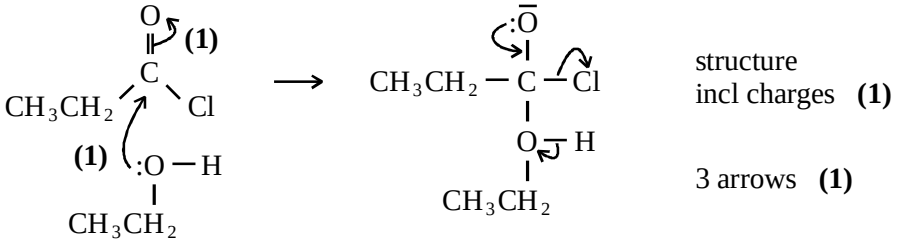
$CH_3CH_2CH_2COCl$

[9]

6. (a)  (allow — COO —) **(1)** **(1)** 1

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

Mechanism:



5

(c) $CH_3CH_2COOCH_2CH_3^{+\bullet} \rightarrow CH_3CH_2C^{+}=O$ **(1)** + $CH_3CH_2O\bullet$
equation (1)

2

(d) $CH_3CH_2CH_2COOCH_3$ or $(CH_3)_2CHCOOCH_3$ **(1)**
Allow $C_3H_7COOCH_3$

1

[9]

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

(ii) ^{13}C isotope **(1)** 2

(b) (i) $(CH_3)_2CHCOCH_3^{+\bullet} \rightarrow (CH_3)_2CHCO^{+} + \dot{C}H_3$

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

(ii) *Structure 1* *Structure 2*

CH_3CO^{+} $(CH_3)_2CH^{+}$

(1) **(1)** 5

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

$C_3H_7{}^{35}Cl = 78$ $C_3H_7{}^{37}Cl = 80$ **(1)**

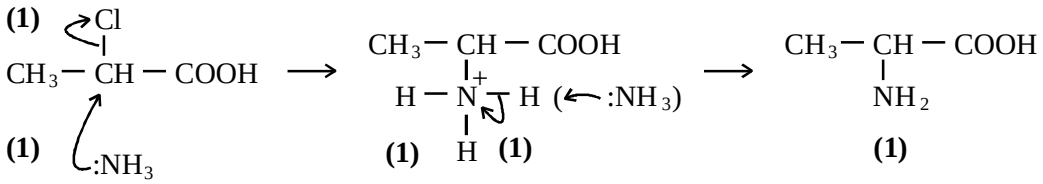
relative abundances ^{35}Cl:$^{37}Cl = 3:1$ **(1)** 3

[10]

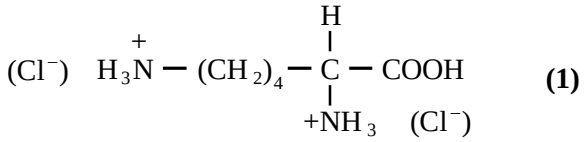
8. (a) 2-chloropropanoic acid **(1)** 1

(b) δ1.72 Doublet ∴ next to CH **(1)**
δ4.44 Quartet ∴ next to CH_3 **(1)** 2

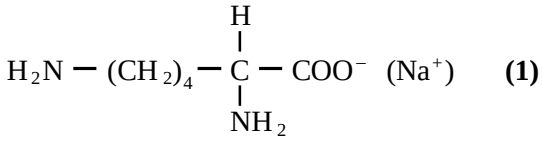
(c) Two triplets **(1)** 1

(d) 

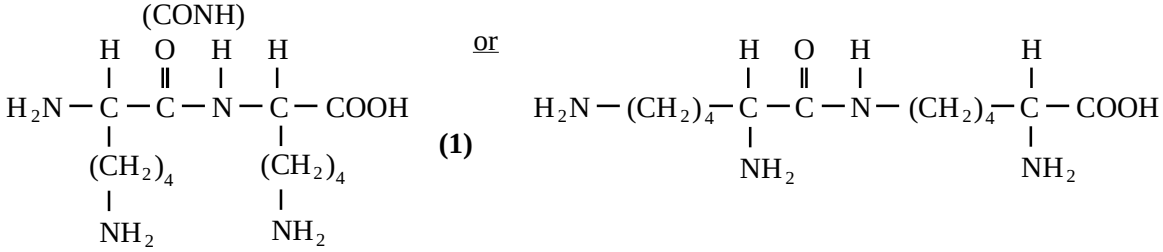
Allow S_N1 **5**

(e) (i) 

(1)

(ii) 

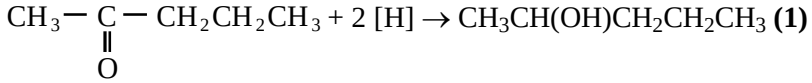
(1)

(iii) 

Or anhydride

3

[12]

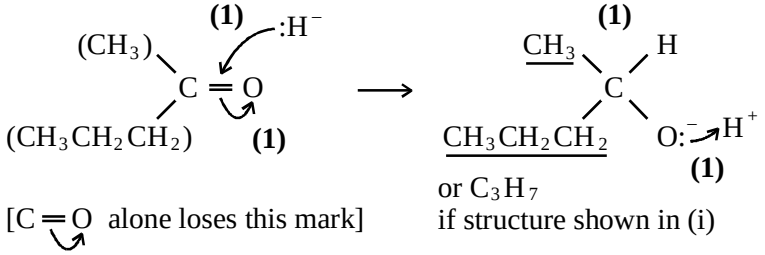
9. (a) (i) 

(1)

or $C_5H_{10}O$ **or $C_5H_{11}OH$**

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

Mechanism:



or C_3H_7 if structure shown in (i)

[C = O alone loses this mark]

(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 $\delta = 0$ or low
not solvent, not cheap
any 2 reasons × (1)

(ii) *Solvent*: $CDCl_3$ or CCl_4 **(NOT D_2O)**
Reason: proton free **(1)**
allow no hydrogens (atoms)
NOT H^+ / hydrogen ions

4

(d) (i) $CH_3-\overset{\overset{O}{\|}}{C}-$ **(1)**

(ii) –OH **(1)**

(iii) $-CH_2-CH_2-$ **(1)** 3

(e) $CH_3-\underset{(\overset{\overset{O}{\|}}{})}{C}-CH_2-CH_2-OH$ **(1)** 1

[11]

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

(ii) $C_4H_8O \rightarrow C_5H_9NO$

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

If MF shown lose 1 for wrong Mr.

If no MF shown max 2 if Mr wrong

5g $\rightarrow$ $\frac{5}{72} \times 99$ **(1)** (= 6.88g)

64% yield = $0.64 \times \frac{5}{72} \times 99 = 4.40$g **(1)**

(allow answer 4.36 – 4.42) 6

(b) (i) $NaBH_4$ or $LiAlH_4$ or H_2/Ni or Na/C_2H_5OH **(1)**

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

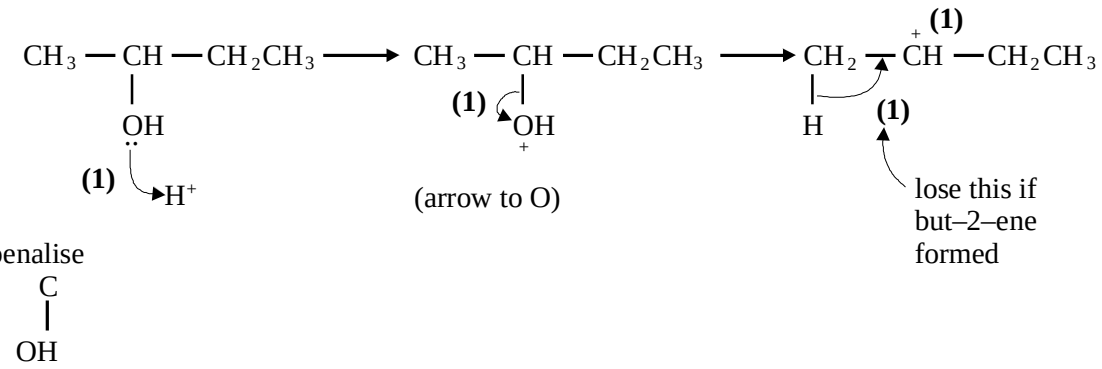
(iii) butanone has peak at ~ 1700 cm^{-1} **(1)**

(but not at ~ 3350 cm^{-1})

B has peak at ~ 3350 cm^{-1} **(1)**

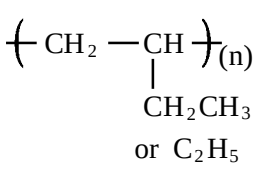
(but not at ~ 1700 cm^{-1}) 4

(c)



penalise

4

(d)  **(1)** 1

[15]

12. (a) A is RCOOR′ **(1)**

R + R′ = 102 – 44 = 58 **(1)** ≡ C_4H_{10}

∴ $C_5H_{10}O_2$ **(1)** 3

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

(c) Two CH_2CH_3 groups present **(1)** 1

(d) $\overset{a}{C}H_3\ \overset{b}{C}H_2COOC\overset{c}{H}_2\ \overset{d}{C}H_3$ **(1)** 1

(e)

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

4

[10]

13. (a) $(CH_3)_4$ Si or tetramethylsilane **(1)** 1

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

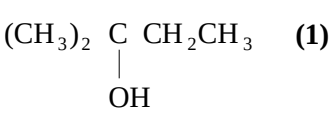
(c) 2 : 1 : 6 : 3 **(1)** 1

(d) $-CH_2CH_3$ **(1)**

CH_3 splits CH_2 to form a quartet **(1)**

CH_2 splits CH_3 to form a triplet **(1)** 3

(e) two equivalent CH_3 groups **(1)** 1

(f)  **(1)** 1

[8]

14. (i) $CH_3COOCH_2CH_3$ or $CH_3COOC_2H_5$ **(1)**

(ii) 3 **(1)**

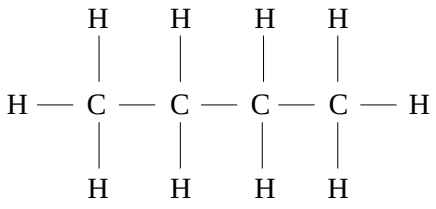
(iii) 3 + 4 or triplet + quartet **(1)** 3

[3]

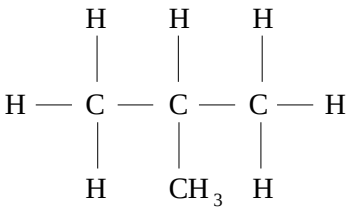
15. (a) same molecular formula / same number of each type of atom **(1)**

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

(b) (i)



(1)



(1) 2

(ii) 43: $CH_3CH_2CH_2^+$ / $CH_3C^+HCH_3$ / $C_3H_7^+$ **(1)**

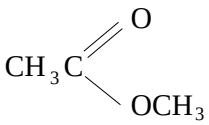
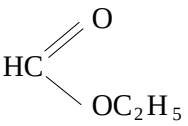
29: $CH_3CH_2^+$ / $C_2H_5^+$ **(1)**

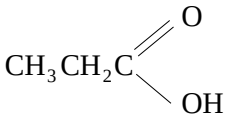
15: $CH3^+$ **(1)**

(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 / $C_2H_5^+$ **(1)** 2

(c) (i)  or  **(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

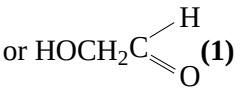
[13]

16. (a) **A**

CH_3COOH **(1)**

B

$HCOOCH_3$

or  **(1)** 2

(b) **C**

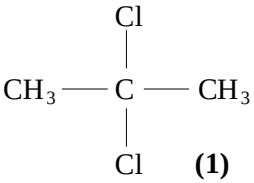
$CH_3CH_2CH_2OH$
or $CH_3CH(OH)CH_3$ **(1)**

D

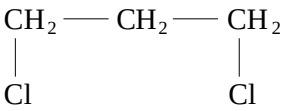
$CH_3CH_2–O–CH_3$ **(1)**

2

(c) **E**

 **(1)**

F

 **(1)** 2

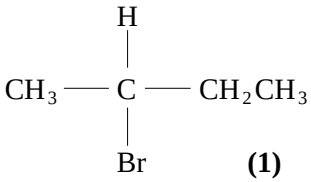
(d) **G**

CH_3CH_2CHO **(1)**

H

CH_3COCH_3 **(1)** 2

(e) **I**

 **(1)**

J

$CH_3CH_2CH_2CH_2Br$
or $(CH_3)_2CHCH_2Br$
or $(CH_3)_3CBr$ **(1)** 2

(f) **K**

one alkene e.g.

CH_2= CH $CH_2CH_2CH_3$

CH_3– CH = CH – CH_2CH_3

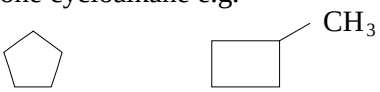
$(CH_3)_2C$ = $CHCH_3$ **(1)**

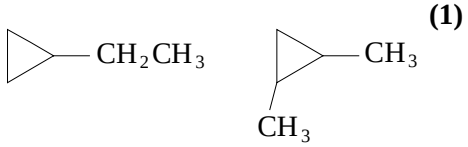
etc

H_2C = $C(CH_3)CH_2CH_3$

L

one cycloalkane e.g.



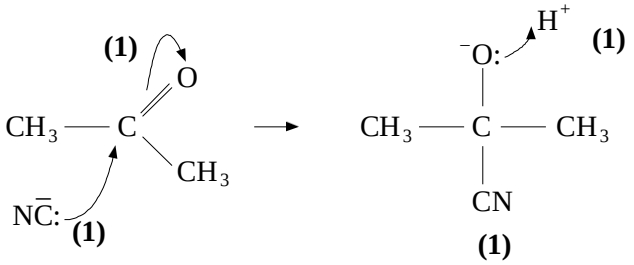
 **(1)**

2

[12]

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

Mechanism



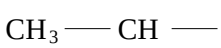
5

(b) (i) *Equation* $CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$ **(1)**

Reducing agent $NaBH_4$ **(1)**

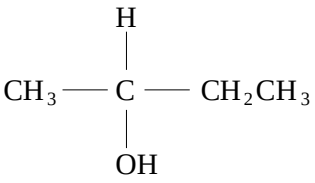
(ii)

*Carbonyl compound **A***



(1)

*Alcohol **C***

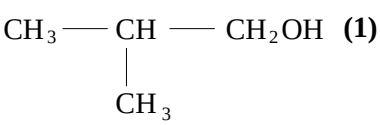


(1)

*Carbonyl compound **B***

(1)

*Alcohol **D***



(1)

6

[11]

18. A 1715 cm^{-1} C=O group **(1)**

B 3350 cm^{-1} O–H group alcohol **(1)**

A $CH_3CH_2COCH_2CH_3$ **(1)**

t **(1)** q **(1)**

two environments <u>or</u> two kinds of proton **(1)**
CH_3CH_2 adjacent <u>or</u> coupled **(1)**
ratio 2:3 <u>or</u> 4:6 **(1)** symmetric **(1)**

$[CH_3CH_2COCH_2CH_3]^{+\bullet} \rightarrow CH_3CH_2CO^+ + CH_3CH_2^{\bullet}$ **(1)**

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

<u>or</u> M_r for **A**

$CH_3CH_2CHCH_2CH_3 \rightarrow CH_3CH=CHCH_2CH_3$ **(1)**

B OH **(1)** **C**

$CH_3CH_2\overset{+}{C}HCH_2CH_3$ **(1)** and $CH_3\overset{+}{C}HCH_2CH_2CH_3$ **(1)**

both secondary **(1)**

hydration gives **B** and $CH_3CH(OH)CH_2CH_2CH_3$ **(1)**

D

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

A → B reduction

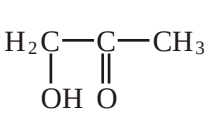
B → C dehydration <u>or</u> elimination **(1)**

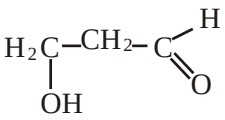
C is an alkene **(1)** cis/trans isomers **(1)**

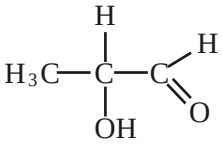
D is a racemate **(1)** <u>or</u> optical isomers any 20

[20]

19. (a) X (O–H) <u>(alcohols)</u> penalise acid or missing "alcohol" 1
Y C=O allow carbonyl 1



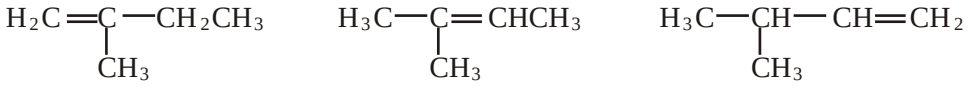




A 4

NOT acid

(b)

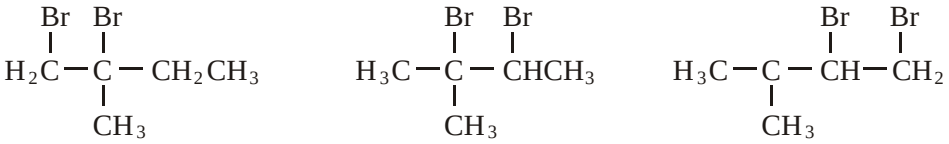


3

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

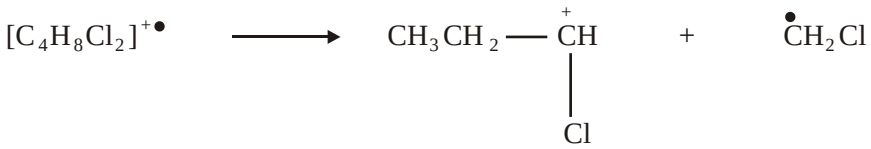
1 quartet/quadruplet or drawn 1

[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

<u>equal</u> mixture of enantiomers 1

(optically) inactive or effects cancel 1

plane polarised light use <u>stereospecific</u> reagent (QoL) 1

<u>rotated</u> 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

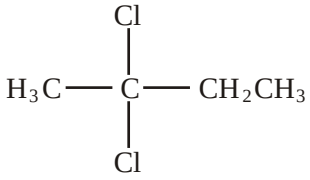
(c) (i) 2 peaks *(if 4 peaks allow splitting only)* 1

ratio 6:2 or 3:1 1

doublet (6 or 3) 1

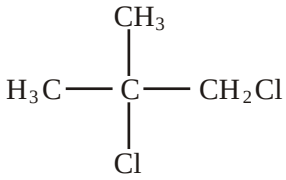
quartet (2 or 1) 1

(ii) **S**



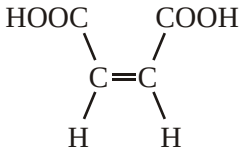
1

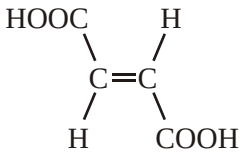
T



1

[19]

21. (a)  1

 1

NB The bonds shown in the structure must be correct

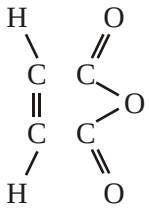
Isomerism: Geometric or cis-trans 1

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

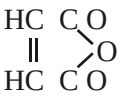
Both COOH groups must be on the same side/ close together/ cis . 1

No rotation about C=C axis 1

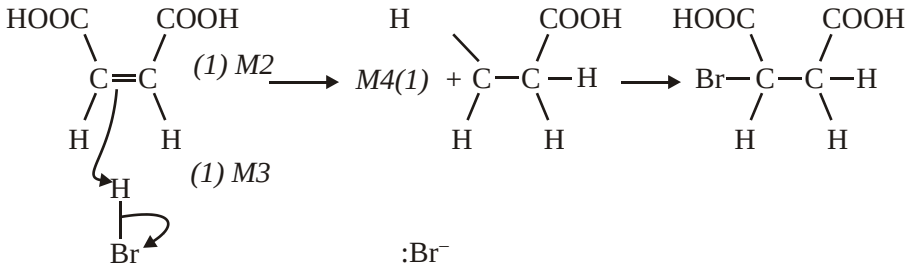
Structure



Allow 1



(b) Br_2 / HBr / H_2SO_4 / H^+ / Br^+ / NO_2^+ (Mark M1) 4



NB If electrophile H^+ / Br^+ / NO_2^+ 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. $2NaOH + HO_2CCHCHCO_2H \rightarrow NaO_2CCHCHCO_2Na + 2H_2O$

Both H replaced 1
Balanced for atoms and charges 1

NB Allow ionic equations and $2NaOH + C_4H_4O_4 \rightarrow C_4H_2O_4Na_2 + 2H_2O$

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

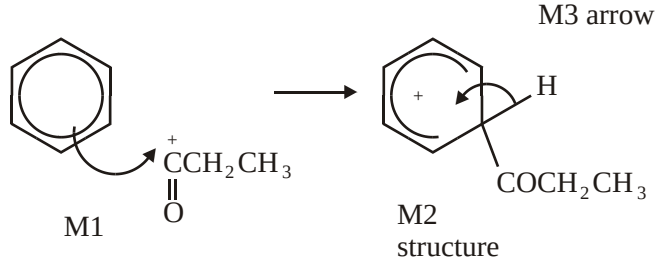
Apply the "list principle" to incorrect answers if more than 3 given

[15]

22. (a) $[CH_3CH_2CO]^+$ 1

$CH_3CH_2COCl + AlCl_3 \longrightarrow [CH_3CH_2CO]^+ + AlCl_4^-$ 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 $C_6H_5CO^+$ 1

m/z = 77 $C_6H_5^+$ 1

(not Wheland intermediate)
(Penalise missing + once)
Allow position of + on O or C of CO or outside [ ] for the fragment ion $[C_6H_5CO]^+$
Allow position of + on H or C or outside [ ] for the fragment ion $[C_6H_5]^+$
$[C_6H_5COCH_2CH_3]^{+\cdot} \longrightarrow C_6H_5CO^+ + CH_3CH_2^{\cdot}$
(· must be on H or C of CH_2 *or outside bracket)*

(1) for molecular ion **(1)** for RHS 2
Allow molecular formulae, i.e. $C_9H_{10}O^{+\cdot} \longrightarrow C_7H_5O^+ + C_2H_5^{\cdot}$

(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

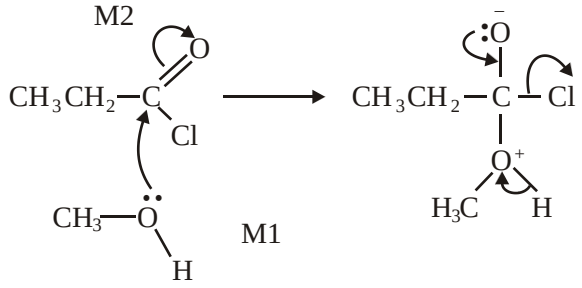
3 <u>planar</u> C=O
4 attack from each side
5 equally likely or equal amounts of each isomer formed
6 <u>Racemic</u> mixture or <u>racemate</u> (Q of L)
7 of mirror images or enantiomers or d/l or +/– or R/S or drawn max 6

(d) Conc H_2SO_4 or conc H_3PO_4 or Al_2O_3 or iron oxides Not HCl or HBr 1
Geometrical or cis-trans 1
Double bond or C=C not just π 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



M3 = structure

M4 = 3 arrows

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 CH_3COOCH_2CH3 1

The two marks for explanation are awarded for discussing one or more of the four peaks (not those for the CH_3 of the ethyl groups) 2

for <u>stated δ values</u> the integration or the splitting should be related to the structure: e.g. structure of **X** shows that

at δ 3.7 – 4.1 **(1)** spectrum of **X** should have integration 3 / singlet **(1)**

or

at δ 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) $K_2Cr_2O_7/H_2SO_4$ reuced by

$CH_3CH_2CH_2CH_2OH$ **(1)**

oxidised to $CH_3(CH_2)_2CHO$ **(1)**
and $CH_3(CH_2)_2COOH$ **(1)**

$CH_3CH_2CH_2CHO$ **(1)**

oxidised to $CH_3(CH_2)_2COOH$ **(1)**

Equation: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ **(1)** 6
Note: Deduct one if all three compounds given as reducing agents.

(b) Tollens' reduced by
$CH_3CH_2CH_2CHO$ **(1)**

oxidised to $CH_3(CH_2)_2COOH$ **(1)**

Equation $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ **(1)** 3

(c) $CH_3CH_2CH_2CH_2OH$ **(1)**

Product $CH_3CH_2CH_2CH_2OOCCH_3$ **(1)**

$(CH_3)_3COH$

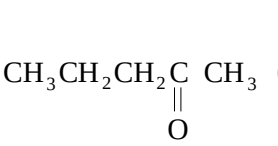
Product $(CH_3)_3COOCCH_3$ **(1)** 4

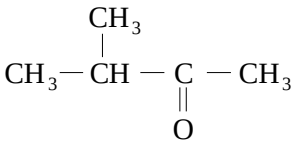
(d) $CH_3CH_2CH_2OH$ has five peaks **(1)**

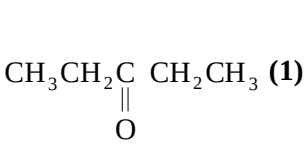
$(CH_3)_3COH$ has two peaks **(1)** 2

[15]

25. (a) 3 Ketones:

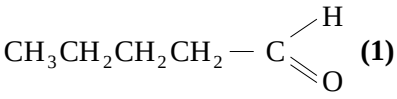

(1)

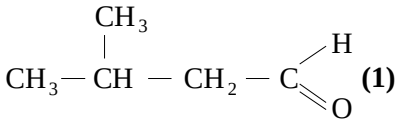

(1)

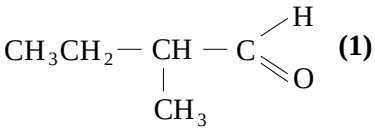

(1)

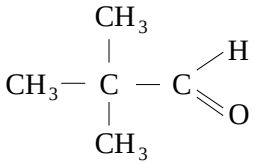
3: 2: 2: 3 **(1)** 6: 1: 3 **(1)** 6: 4 or 3: 2 **(1)** 6

(b) 4 aldehydes:


(1)


(1)

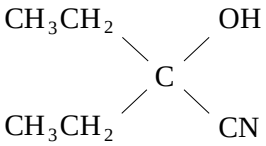

(1)


(1)

Y **(1)** Z **(1)** X **(1)** 7

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

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

e.g 
(1) 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 $[Ag(NH_3)_2]^{2+}$ 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 / H_2SO_4	[1]	Schiff's	[1]	iodoform or I_2 / NaOH	[1]	PCl_5	[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]	$KMnO_4$	[1]	$KMnO_4$ / H_2SO_4	[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]	PCl_5	[1]
no reaction e	[1]	no reaction E	[1]	no change E	[1]	(misty) fumes E	[1]
bubbles or CO_2 F	[1]	bubbles or H_2 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 $[CH_3CO]^+$ **(1)**
m / z 43 **(1)**
$CH_3COOCH_3^{+\cdot} \rightarrow CH_3CO^+ + OCH_3^{\cdot}$
(1 for molecular ion) (1 for correct other fragment)

Alternative:

major peak $[CH_3]^+$ **(1)**
m /z 15 **(1)**
$CH_3COOCH_3^{+\cdot} \rightarrow CH_3^+ + CH_3COO^{\cdot}$ or $COOCH_3^{\cdot}$ or $C_2H_3O_2^{\cdot}$ or $C_3H_6O_2^{+\cdot}$
(1) (1 for radical)

If major peak wrong but possible e.g. CH_3OO^+ m/z = 59
no marks so far, but can score up to 2 for
$CH_3COOCH_3^{+\cdot} \rightarrow CH_3^+ + CH_3COO^+$ or $^+COOCH_3 + CH_3$
1 for correct other fragment]

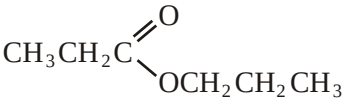
4

[15]

27. (a) X contains >C=O **(1)**
if X and Y reversed lose this mark but allow remaining max 6/7

$\therefore$ X is CH_3CH_2COOH **(1)**

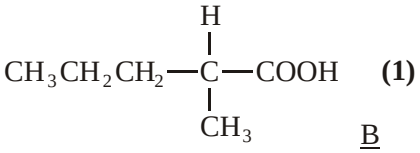
$\therefore$ Y is $CH_3CH_2CH_2OH$ **(1)**

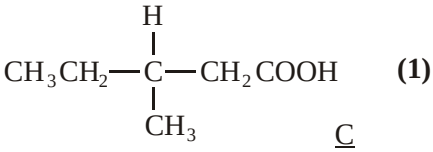
$\therefore$ A is  **(1)**

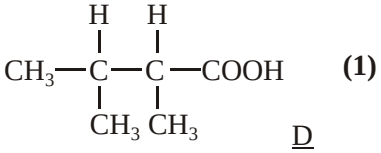
Propanol → X reagent: acidified $K_2Cr_2O_7$ **(1)**
Propanol → Y reagent: $NaBH_4$ **(1)**

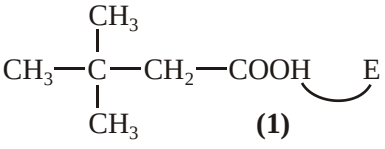
Conc H_2SO_4 : catalyst **(1)** 7

(b) 4

 **(1)** B

 **(1)** C

 **(1)** D

 **(1)** E

in any order

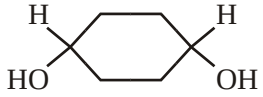
(c) $-O\overset{a}{C}H_2-$ 3.1 – 3.9 **(1)**

$-\overset{b}{C}H_2-\underset{\underset{O}{\|}}{C}-$ 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 $CH_3CH_2CH_2OH$
allow C_3H_7 in **A** if **Y** correct or vice versa
Allow **(1)** for **A** if correct conseq to qrong **X** and **Y**

other oxidising agents: acidified $KMnO_4$; Tollens; Fehlings

other reducing agents: $LiAlH_4$; Na/ethanol; NiH_2; 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 C_3H_7 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.

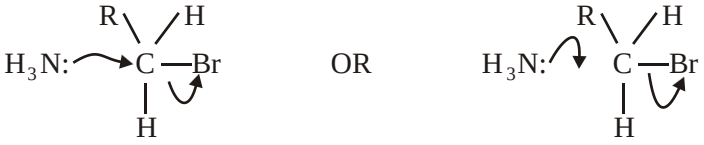
(c) protons a – *quartet* must be correct to score *3 adjacent H* mark. Same for b

(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]

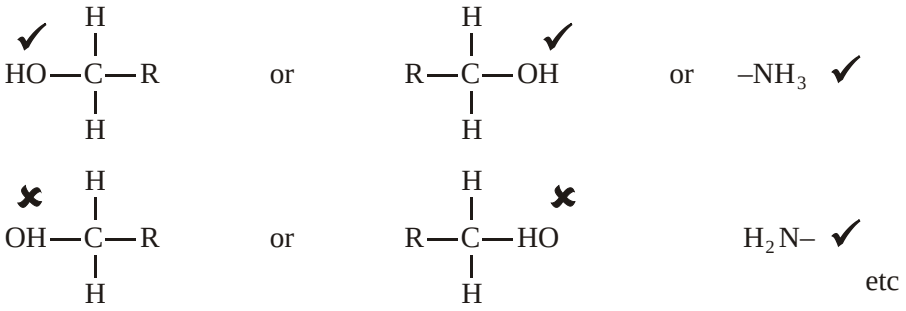
Organic points

(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 CH_3– or –CH_3 or  or CH_3

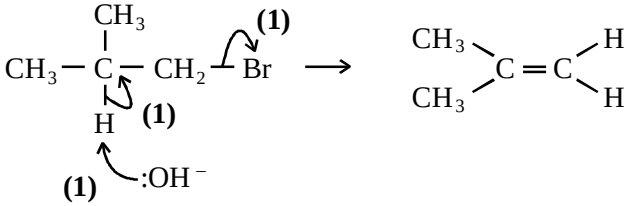
or H_3C–

28. (a) Identity of **X**; 2-methylpropene **(1)**
Absorption at 1650 cm^{-1} indicates an alkene present **(1)**
OR a chemical answer e.g. Br_2 (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

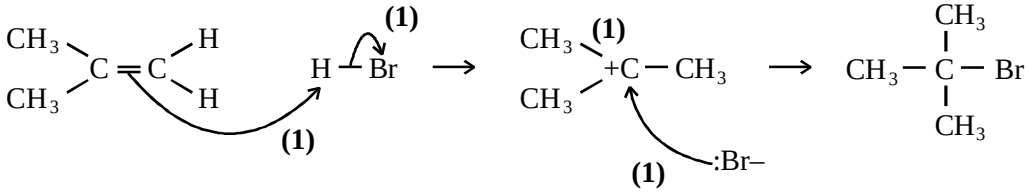
Step 2 HBr **(1)**

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

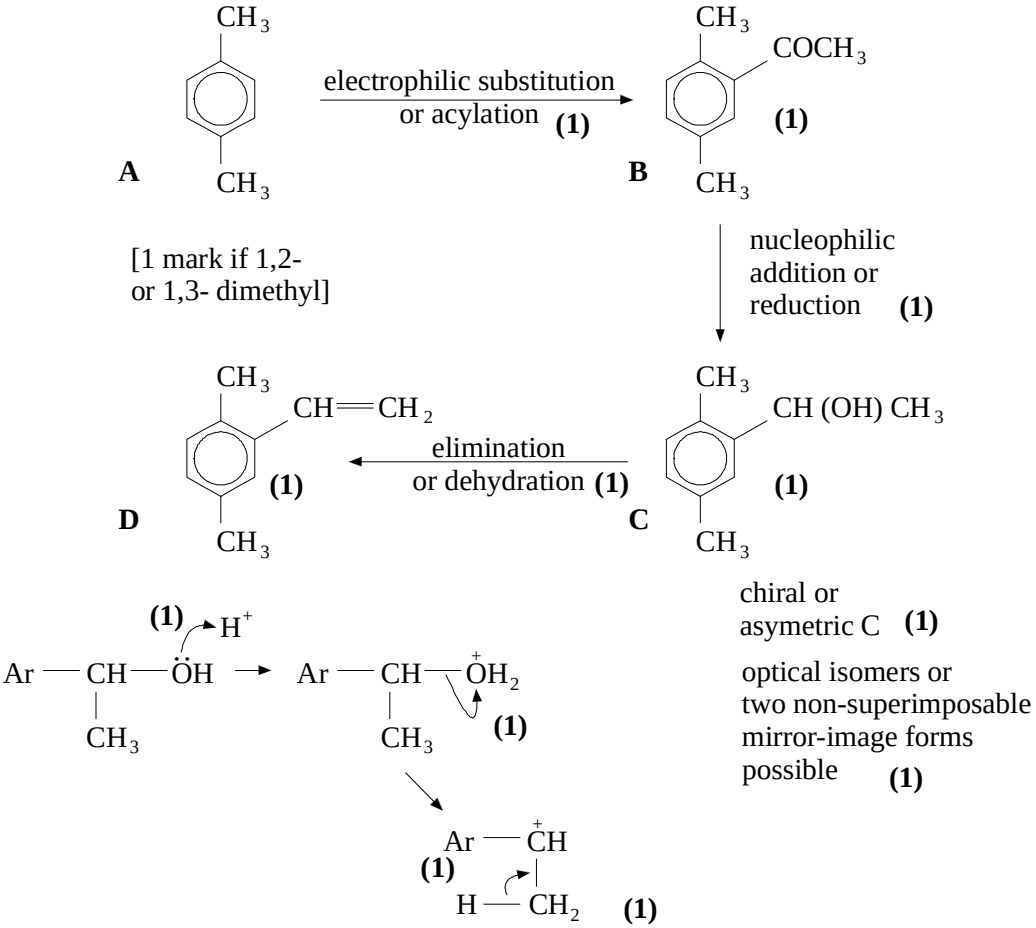
2

[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)** CH_3 singlet **(1)**

2 triplets **(1)** CH_2CH_2 coupled **(1)**

B: 4 peaks or 4 different environments **(1)**
1 : 2 : 2 : 3 **(1)** OH singlet **(1)** OCH_2O singlet **(1)**
quartet + triplet **(1)** CH_2CH_3 coupled **(1)**

C: 2 peaks or 2 different environments **(1)**
2 : 6 or 1 : 3 **(1)** CH_3 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 / NO_2^+ **(1)**

$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4$ **(1)**

$H_2NO_3^+ + H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + HSO_4^-$ **(1)**

allow 1 mark for $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4 + H_2O$

allow 2 marks for $HNO_3 \quad 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$
1 for species, 1 for balancing

mechanism shows attack by NO_2^+ 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)**

$AlCl_3$ / $FeCl_3$ / 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 CH_3 **(1)** 2

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

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

2 CH_3 groups have 6 equivalent protons, CH_2 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 S_N1 mechanism given:
first mark as above - independent
second mark for correct carbocation formed including curly arrow from C to Cl or $C^{S+}–Cl^{S-}$

third mark for hydroxide attack as above
final mark not available (wrong mechanism)

penalise missing proton once only

[24]

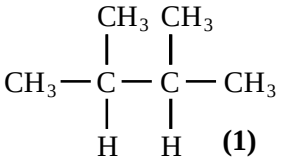
32. (a) $(M–R)^{+\cdot}$ Is a radial-cation **(1)** covalent bond breaks **(1)**
to form a cation (M^+) **(1)** and a radical ($R^{\cdot}$) **(1)** 4

(b) Cl has a two isotopes **(1)**
$CH_3CH_2{}^{35}Cl = 64$ and $CH_3CH_2{}^{37}Cl = 66$ **(1)**
relative abundances $^{35}Cl : {}^{37}Cl = 3 : 1$ **(1)**
$CH_3CH_2Cl^{+\bullet} \rightarrow CH_3CH_2^+ + Cl^{\bullet}$ **(1)** 4

(c) $ClCH_2CH_2Cl$ <u>or</u> 3 isotopic combinations possible **(1)**
$C_2H_4{}^{35}Cl_2 = 98$ **(1)** $C_2H_4{}^{35}Cl^{37}Cl = 100$ **(1)** $C_2H_4{}^{37}Cl_2 = 102$ **(1)** 4

[12]

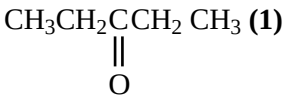
33. (a) A C_6H_{14} **(1)**



(1)

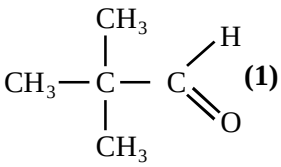
Ratio 12:2 or 6:1 **(1)**

B/C C=O **(1)** $C_5H_{10}O$ **(1)**



(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)**

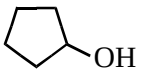
Exact match with standard **(1)** 5

(c) $3300cm^{-1}$ ∴ OH group in both **(1)**

$1650cm^{-1}$ ∴ C=C in D **(1)**

∴ D is $CH_2 = CH– CH_2 CH_2 CH_2 OH$ **(1)**

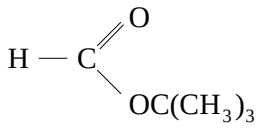
(or others)

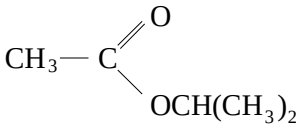
E is  etc **(1)** 4

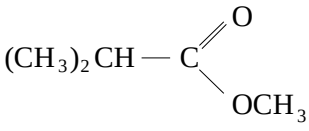
[18]

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) C_5 esters

Q is (2 peaks)  **(2)**

R is (3 peaks)  **(2)**

S is (3 peaks)  **(2)**

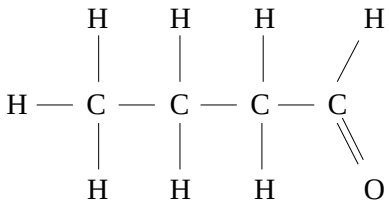
T (alcohol) is $CH_3CH(OH)CH_3$ **(2)**
(3 peaks)

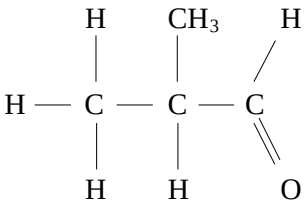
U (acid) is CH_3COOH **(2)**
(2 peaks)

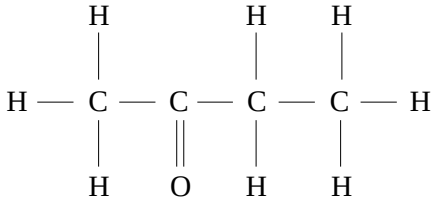
T absorption at 3250 cm^{-1} confirms OH (alcohol) **(1)**
U absorption at 2900cm^{-1} confirms OH (acid) or at 1700 cm^{-1} confirms C=O **(1)** max 11

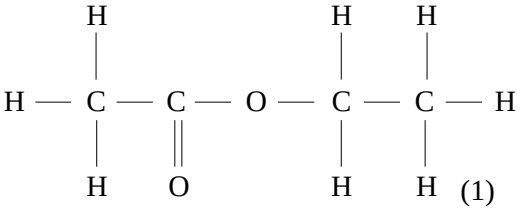
[15]

35. (a)

A  (1)

B  (1)

C  (1)

D  (1)

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)**

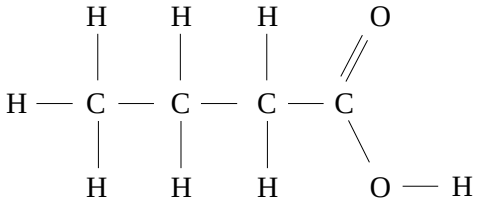
ethanoic acid / ethanoyl chloride / ethanoic anhydride / correct formula **(1)**

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)

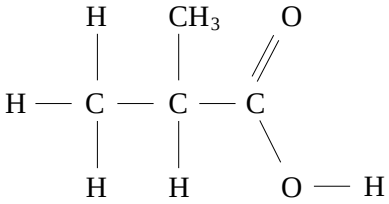
for ethanoyl chloride, room temperature / dry / anhydrous

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

(c)



or



(1)

(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**

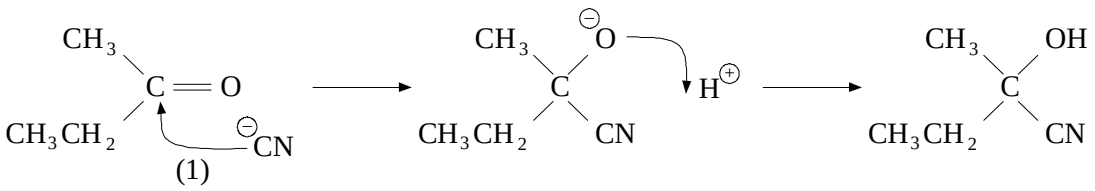
two methyl groups / 6 Hs in identical chemical environments **or (1)**
2 Hs in unique environments 2

(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 H_2O 5

[26]