



RECOGNISING ACHIEVEMENT

CHAINS, RINGS +
SPECTROSCOPY
Mark Scheme 2814
January 2003

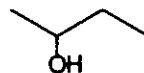
Marking structures in organic chemistry

When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3 , C_2H_5 , OH , COOH , COOCH_3) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient).

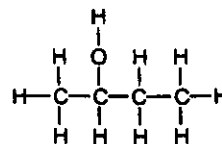
If not specified by the question, this may be given as either:

- a **structural formula** – e.g. $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$.

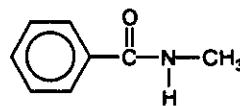
- a **skeletal formula** – e.g.



- a **displayed formula** – e.g.

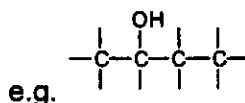


or as a hybrid of these – e.g.



The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –



Benzene rings may be represented as



as well as

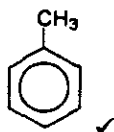


in any

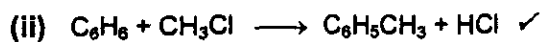
of the types of formula above.

[†] Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

1 (a) (i)



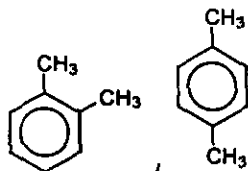
[1]



[1]

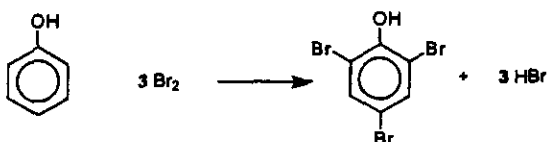
(iii) iron / aluminium chloride / iron(III)chloride etc
Fe / AlCl₃ / FeCl₃ ✓

[1]

(iv) any polymethylated benzene ring ✓
egname ✓ eg 1,2-dimethylbenzene/
1,4-dimethylbenzene

[2]

(b) (i)

brominated phenol ✓ 2,4,6 substituted ✓
balancing ✓

[3]

(ii)

phenoxide ✓
balancing ✓

[2]

(c) any general use that contains phenols - eg
antiseptics / disinfectants / dyes / plastics / pharmaceuticals / pesticides/explosives ✓

[1]

[Total: 11]

- 2 (a) (i) (trigonal) pyramidal ✓ [1]
- (ii) tetrahedral ✓ [1]
- (iii) trigonal (planar) ✓ [1]
- (b) (i) $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$ ✓ [1]
- (ii) $\text{NH}_2\text{CH}_2\text{COO}^-$ ✓ [1]
- (c) (i) H^+ / acid / HCl / H_2SO_4 / OH^- / alkali ✓
/heat / reflux ✓
(or use of an enzyme at 37°ish) [2]
- (ii) hydrolysis ✓ [1]
- (d) (i) carbon with four different / distinguishable groups attached ✓
(or carbon / part of the molecule / atom which is assymmetric / non-superimposable on its mirror image) [1]
- (ii)
- $$\begin{array}{c} \text{NH}_2 \\ | \\ \text{CH}_3 - \text{C} - \text{H} \\ | \\ \text{COOH} \end{array}$$

$$\begin{array}{c} \text{NH}_2 \\ | \\ \text{HOOC} - \text{C} - \text{CH}_3 \\ | \\ \text{H} \end{array}$$
- one structure of alanine with at least one 3-d bond ✓
two optical isomers / reflections of a 3-d structure ✓ [2]
- (iii) one stereoisomer ✓
natural / from a living system / made by enzymes etc ✓ [2]

[Total: 13]

3 (a) ester ✓
(primary) amine ✓ [2]

(b) (i) $C_8H_9NO_2$ ✓ [1]

(ii) M_r of A = 151 (or ecf from (i)) ✓

$$\text{moles A} = 0.100\text{g}/151 = 0.000662$$

$$\text{conc. A} = 0.000662/0.330\text{dm}^3$$

$$= 0.002 / 0.0020 \text{ (ecf from a wrong } M_r) \text{ ✓}$$

[2]

(c) (i) peaks identified
peak X – benzene ring protons ✓
peak Y – CH_2 protons ✓
peak Z – CH_3 protons ✓

3 identification marks

reasoning from δ value ... for each, either:

- quotes the relevant functional group in the Data Sheet (eg $-O-CH_2-R$) / or
- quotes the relevant Data Sheet range (eg 3.3–4.3) / or
- from first principles using the expected deshielding to assign the peaks ✓✓✓

reasoning from the splitting pattern ...

Y peak is a quadruplet/1:3:3:1 etc
this is due to 3 neighbours / adjacent to a CH_3 ✓

Z peak is a triplet / 1:2:1 etc
this is due to 2 neighbours / adjacent to a CH_2 ✓

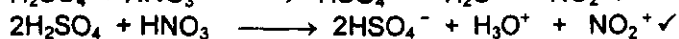
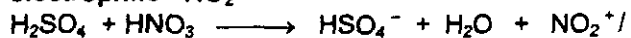
ANY 3 out of 5 reasoning marks [6]

(ii) peak at 1700cm^{-1} and/or at 1280cm^{-1} marked ✓ [1]

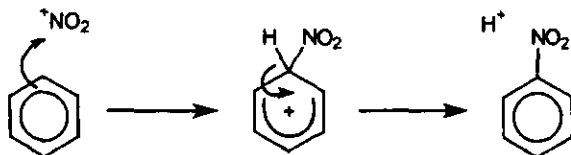
[Total: 12]

4 (a) (i) reagents conc H₂SO₄ + HNO₃ ✓

electrophile NO₂⁺ ✓



mechanism

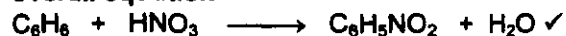


curly arrow from benzene π -bond to electrophile ✓

correct intermediate (*ecf* on electrophile formula) ✓

curly arrow from C-H bond to π -bond and H⁺ formed ✓

overall equation



ANY 6 out of 7 [6]

(ii) NO₂⁺ accepts an electron pair ✓
H is replaced / substituted by NO₂ ✓

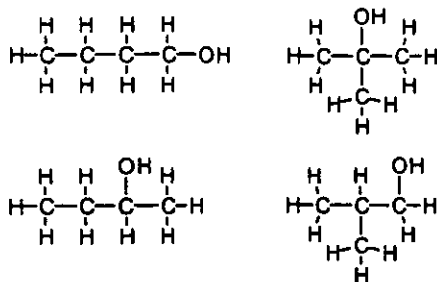
[2]

(b) two peaks ✓
peak at/between 2.3-2.7 ✓
peak at/between 7.1-7.7 ✓

[3]

[Total: 11]

5 (a)



any unambiguous type of formula ✓✓✓✓

[4]

- (b) (i) butan-1-ol gives butanal /butanoic acid / an aldehyde / a carboxylic acid
 butan-2-ol gives butanone / a ketone
 2-methylpropan-2-ol gives no reaction ✓✓✓

3 marks for the alcohol reactions

D is methylpropan-1-ol ✓

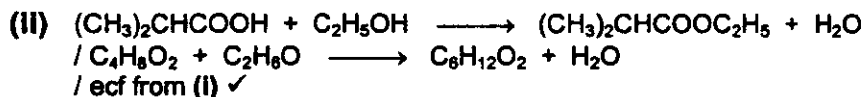
E is methylpropanoic acid ✓✓

(where any carboxylic acid for E gets the first mark)

3 marks for identifying D and E
Any 5 out of 6**Quality of Written Communication**

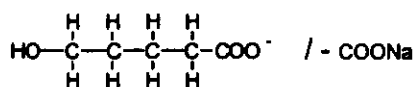
information is organised clearly and coherently using at least two specialist terms not mentioned in the question (eg correct names of compounds, primary, secondary, aldehyde, ketone, oxidised etc) ✓

[6]



[1]

(c)



where:

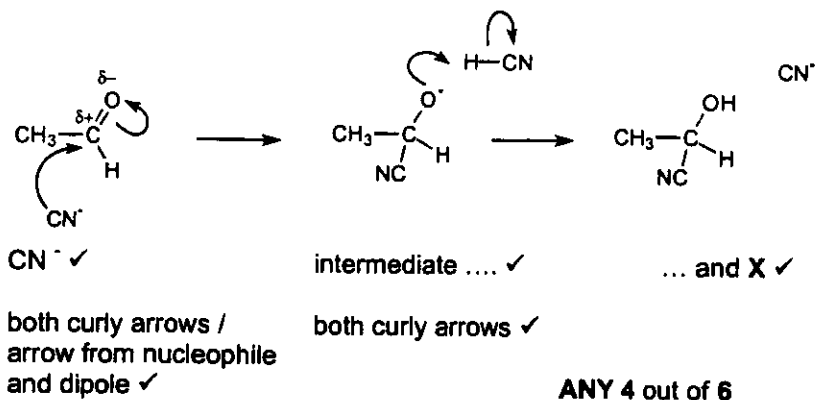
-OH ✓

-COO⁻ / COO⁻ Na⁺ / COONa ✓

2]

[Total: 13]

6 (a) (i) nucleophilic addition ✓

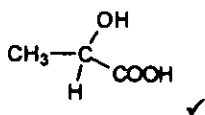


[4]

(ii) HCl / H_2SO_4 / H^+ / acid ✓
hydrolysis ✓

[2]

(iii)



[1]

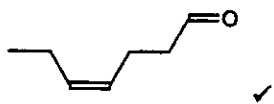
(b) 1 doublet and 1 quadruplet / 1:3:3:1 and 1:1 ✓
correct reason for at least one peak ✓
(eg 1:3:3:1 due to 3 neighbours / next to CH_3 / use of $n+1$ rule)

[2]

(c) (i) $\text{C}_7\text{H}_{12}\text{O}$ ✓

[1]

(ii)



[1]

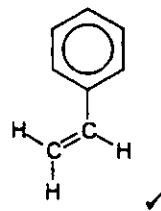
(iii)



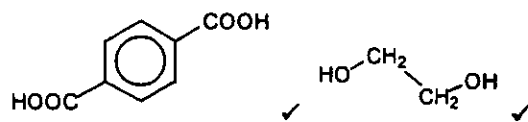
[2]

[Total: 13]

7 (a) L:

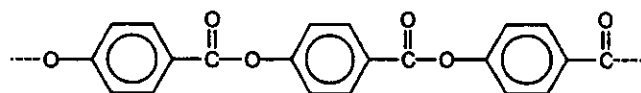


M:



[3]

(b)



at least one correct ester link ✓
rest of the structure and repeat also correct ✓

[2]

(c)

condensation ✓
loss of water / small molecule ✓

[2]

(d)

fibres / clothing / bottles etc ✓

[1]

[Total: 8]

8 to detect the presence of C=O ...

2,4-dinitrophenylhydrazine / 2,4-DNPH ✓
red/orange/yellow ppt/solid/crystals ✓

or

i.r. spectrum ✓
has peak at 1680-1750 cm⁻¹ ✓

2 marks

to confirm it is a ketone not an aldehyde ...

Tollens' reagent /(acidified) K₂Cr₂O₇ ✓
aldehyde: silver mirror / green colour ✓
ketone: no silver mirror / no green colour ✓

or

n.m.r. spectrum ✓
aldehyde: peak at 9.5-10 ✓
ketone: no peak at 9.5-10 ✓

3 marks

a chemical method to identify the ketone ...

use the product / solid / ppt from 2,4-DNPH / 2,4-dinitrophenylhydrazine ✓
(re)crystallise / purify (the product) ✓
measure the melting point ✓
compare with known compounds / data book ✓

4 marks

ANY 8 marks out of 9 [8]

Quality of Written Communication

at least two sentences with legible text, accurate spelling, grammar and punctuation, so the meaning is clear ✓

[1]

[Total: 9]