OCR

RECOGNISING ACHIEVEMENT

A2

CHAINS, RINGS + SPECTROSCOPY

Mark Scheme 2814
June 2004

Abbreviations, annotations and conventions used in the mark scheme

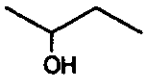
/	= alternative and acceptable answers for the same marking point
;	= separates marking points
NOT	= answers not worthy of credit
( )	= words which are not essential to gain credit
___	(underlining) = key words which must be used
ecf	= allow error carried forward in consequential marking
AW	= alternative wording
ora	= or reverse argument

Marking structures in organic chemistry

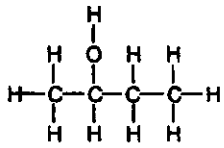
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3, C_2H_5, OH, COOH, $COOCH_3$) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient).

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

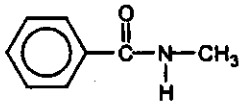
- a **structural formula** – e.g. $CH_3CH(OH)C_2H_5$,



- a **skeletal formula** – e.g.



- a **displayed formula** – e.g.

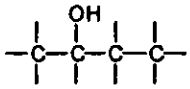


or as a hybrid of these – e.g.

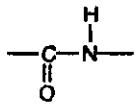
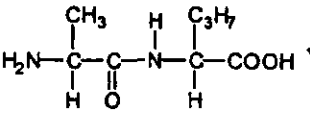
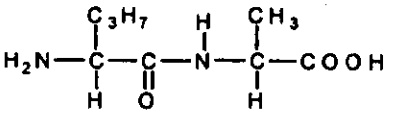
The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

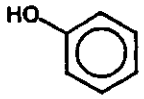
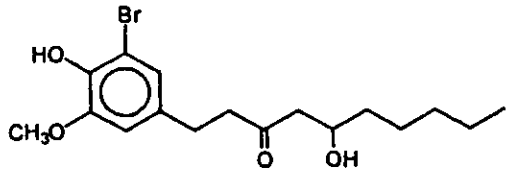
- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms

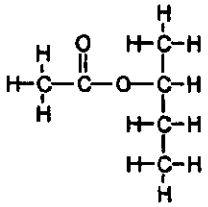
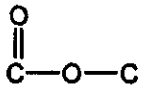
e.g.



Benzene rings may be represented as  as well as  in any of the types of formula above.

1 (a) (i)	carboxylic acid ✓		NOT 'carboxyl'	[1]
(ii)	$CH_3CH(NH_2)COO^-Na^+$	or a displayed structure	Allow 1 overall for covalent O – Na or missing charge on COO but otherwise correct	
	where...			
	COO^- / COONa ✓			
	rest of the structure including Na also correct ✓			[2]
(iii)	*water* / H_2O ✓			[1]
(b)	H_3N^+ becomes H_2N ✓ rest of the molecule unchanged ✓			[2]
(c)	condensation / water molecule removed / created (or shown) ✓			
	NH_2 (from one molecule) reacts with the COOH (from the other molecule) (or shown by drawing around the groups) ✓ **AW**		allow any correct displayed isomer of C_3H_7	
	 displayed at least once ✓		allow ALA-ALA and VAL-VAL	
	one correct dipeptide structure - eg  ✓		allow -CO-NH- on the dipeptides	
	second correct dipeptide structure – eg 			
	/ or ecf which clearly shows the idea of amino acids swapping ✓			
				[5]
				[Total: 11]

2 (a)	**A** phenol ✓ **B** ketone / Carbonyl ✓ **C** (secondary) alcohol ✓	**NOT** 'hydroxyl' for **A** or **C**	[3]
(b) (i)	**B** / ketone / carbonyl ✓		[1]
(ii)	yellow/orange/red ✓ precipitate/crystals/solid ✓		[2]
(iii)	(gingerol would not react because) ... it does not contain an aldehyde group / only aldehydes can react with Tollens' Reagent / only aldehydes can be easily oxidised / ketones cannot be oxidised further ✓	**NOT** just "ketones don't react" etc	[1]
(c)	 / phenol / **A**	do not penalise the CH_3O- if included	[1]
(d) (i)	bromination of the benzene ring ✓ eg  other functional groups unaffected ✓	allow mono, di or tri-bromination at any position	[2]
(ii)	HBr / hydrogen bromide		[1]
(e)	Peak at 3400cm^{-1} labelled O-H ✓ Peak at 1700cm^{-1} labelled C=O ✓	if more than two peaks labelled, mark incorrect peaks first	[2]
(f) (i)	same structural / displayed formula / same order of bonds ✓ different spatial /3-d arrangement ✓		[2]
(ii)	optical isomerism ✓		[1]
			[Total: 16]

3 (a) (i)	(conc) H_2SO_4	**NOT** just H^+ / acid .... or anything suggesting the acid is dilute	[1]
(ii)	to prevent loss (of reactants / products) by evaporation / vapours ***AW***		[1]
(b) (i)			
	correct displayed ester group ✓ 		[2]
	rest of the structure also correct ✓		
(ii)	butan-2-ol ✓	**NOT** just butanol	[1]
(c)	flavouring / perfume	**NOT** any solvent type uses such as nail-varnish nor medicines etc	[1]
			[Total: 6]

4 (a) **% O = 45.1** ✓

C = 50.7/12.0 = **4.2**	4.225 / 2.819 = 1.499 ≈	1.5 = 3
H = 4.2 / 1.0 = **4.2**	4.2 / 2.819 = 1.490 ≈	1.5 = 3
O = 45.1 / 16.0 = **2.8** (ecf)	2.819 / 2.819 = 1.000 =	1.0 = 2

calculation of moles ✓

$C_3H_3O_2$ clearly deduced from the ratio of moles ✓

NOT any method which works back from the molecular formula

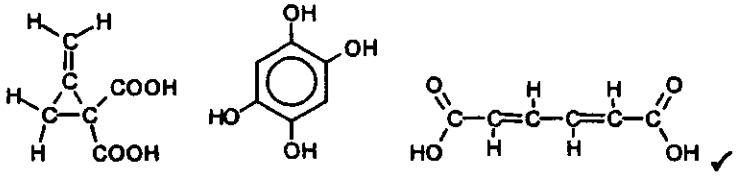
(b) (i) empirical formula has M_r = 36 + 3 + 32 = 71 (or ect) ✓

2 x empirical M_r = **142** / within range 138-144 ✓

Only allow ecf on 2nd Mark if 2 × M_r is still 138 - 144

(ii) mass spectrometry ✓

(c) any valid structure eg

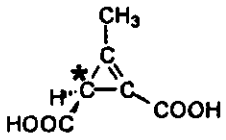


✓

(d) (i) carbon with 4 different groups attached ✓

Allow "functional groups"

(ii)



✓

(e) (i) carboxylic acid / COOH protons

NOT "OH protons"

(ii) D replaces protons on OH groups/ OH protons are labile ✓
Peak for (CO) OH protons disapears ✓

(iii) (E is correct structure because …)

ignore which they assign to peaks Y and Z

peaks **Y** and **Z** are due to two (equivalent) protons ✓

EITHER COMPARING PEAK AREAS…

structure **E** has groups: = CH_2 / two CH ✓
structure **F** would give a peak with area 3 / area 1

ignore any reference to shift values or (lack of) splitting

OR COMPARING THE NUMBER OF PEAKS…

structure **E** has three environments / H_{a1} H_{b1} H_c are labelled on the structure ✓
structure **F** would give four peaks (incl. COOH)

[3

[Total: 15]

5 (a) stage 1 HCN and KCN ✓
nucleophilic addition ✓

$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$ ✓

allow KCN with HCl/H_2SO_4 or HCN with NaOH for the first two marks, but acid / alkali does not score on its own.

stage 2 (named) dilute acid /$H^+(aq)$ ✓
heat/reflux ✓
hydrolysis ✓

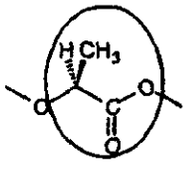
reagents and conditions can be on either line

$CH_3CH(OH)CN + 2H_2O \longrightarrow CH_3CH(OH)COOH + NH_3$
Or including H^+ on the left to give NH_4^+ ✓

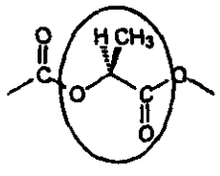
[8]

(b) (i) condensation ✓ **[1]**

(ii)



or



etc ✓

[1]

(iii) (fermentation because …)
natural processes (often) produce one (optical) isomer ✓
synthetically gives a mixture of (both optical) isomers ✓

Allow "racemic" **[2]**

(c) (i) poly(propene), poly(phenylethene) etc ✓

must be a hydrocarbon
allow new or old names **[1]**

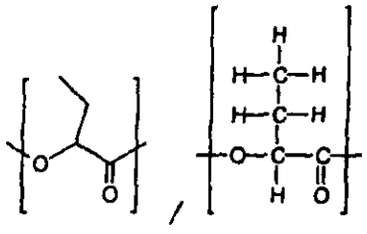
(ii) atactic ✓
syndiotactic ✓

[2]

(d) a correct repeat of a polyester with 'sticks' / bracketed …
the ester bond displayed/skeletal ✓

Do **NOT** allow H or OH at either end if no brackets

side chain / hydrogens **also** correct and the repeat shows only one monomer ✓



[2]

[Total: 17]

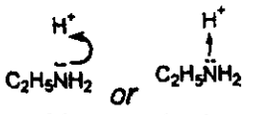
6 (a) ethylamine/bases react with/accept a proton/H^+ ✓

must be stated somewhere

to give $C_2H_5NH_3^+$ ✓

(using the) lone pair of electrons on the N atom of the amine / lone pair shown on N of a correct structure of the amine ✓

a dative covalent bond forms between N and H / curly arrow shown from lone pair towards H^+ / dative bond shown from N to H ✓



could score the last two marks

[4]

(b) (phenylamine is a weaker base because ...)

the phenyl group pulls electrons away from the nitrogen ✓

Must be clear which way electrons are going

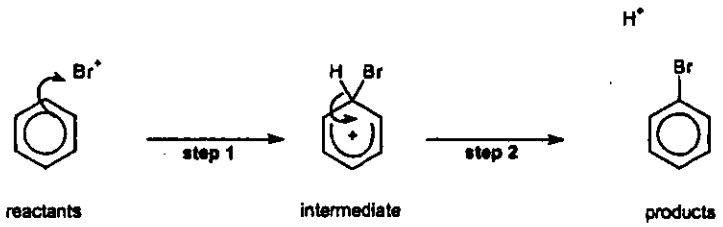
the lone pair is delocalised / interacts with the π electrons over the ring / or shown in a suitable diagram – eg

✓

[3

the lone pair is not donated as easily / is less available / H^+ is not accepted as easily ✓

[Total: 7

7 (a) (i)	iron / iron(III)bromide / aluminium chloride etc ✓	accept any iron(III) or aluminium chloride/bromide but **NOT** just "iron bromide" [1
(ii)	halogen carrier ✓	accept Lewis but **NOT** "Friedel-Crafts catalyst " [1
(iii)	$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$ HBr as product ✓ rest of the equation also correct ✓	allow H^+ and Br^- allow a balanced equation for di or tri but bromination [2
(iv)	bromobenzene	allow name from di or tribromination in (iii) as long as they are correct [1
(b)	 curly arrow from benzene π-bond to Br^+ ✓	check curly arrows clearly start and finish at the correct atom / bond
	correct intermediate ✓ curly arrow from C-H bond to gap in π-bond ✓	the 'smile' must reach round all 5 carbons with the + clearly **not** on the tetrahedral carbon
	H^+ and bromobenzene as products ✓	[4

Question 7 continues overlea

7 (c) (i) p-orbitals overlap above and below the ring / stated in words or shown in either diagram ✓

correct diagrams of π-bonds in cyclohexene and benzene:

✓

✓

Do **NOT** give the diagram mark if a double bond is also shown

allow any reasonable attempt at the benzene π-bonding, but not a simple 

π–bond(s)/electrons are labelled in either diagram or their position is described in words. ✓

π-bonding is drawn: in cyclohexene ✓
in benzene ✓

π-bond(s)/ electrons are labelled in either diagram or their position is described in words ✓

4 marks on π-bonding **[4]**

(ii) the negative charge/π electrons are more spread out / delocalised (in benzene **ora**) ✓

the bromine is less polarised / a catalyst is needed to polarise the bromine (in benzene **ora**) ✓

electophiles / bromine are less attracted (to benzene **ora**) ✓

more energy is needed (to break the π-bond) due to the delocalisation (in benzene **ora**)

AW

these marks can be gained from the explanation of the relative reactivity of either benzene or cyclohexene but a comparison must be made for each mark

do **NOT** give the last mark for just saying that benzene is more stable than cyclohexene

ANY 3 out of **4** marks explaining the different reactivity **max [3]**

Quality of Written Communication

one mark for the correct use and organisation of the following terms: **p-orbitals, delocalised** ✓

one mark for correct spelling, punctuation and grammar in at least two sentences ✓

[2]

[Total: 18]