



CHAINS, RINGS
+ SPECTROSCOPY
Mark Scheme 2814
June 2003

The following annotations may be used when marking:

X	=	incorrect response (errors may also be underlined)
^	=	omission mark
bod	=	benefit of the doubt (where professional judgement has been used)
ecf	=	error carried forward (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response)
sf	=	error in the number of significant figures

Abbreviations, annotations and conventions used in the Mark Scheme:

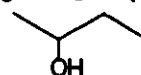
/	=	alternative and acceptable answers for the same marking point
;	=	separates marking points
NOT	=	answers not worthy of credit
()	=	words which are not essential to gain credit
<u> </u> (underlining)	=	key words which <u>must</u> be used
ecf	=	allow error carried forward in consequential marking
AW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

Marking structures in organic chemistry

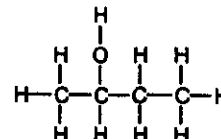
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH₃, C₂H₅, OH, COOH, COOCH₃) to unambiguously define the arrangement of the atoms. (E.g. C₃H₇ would not be sufficient).

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

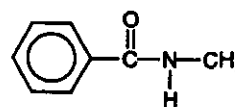
- a structural formula – e.g. CH₃CH(OH)C₂H₅,



- a skeletal formula – e.g.



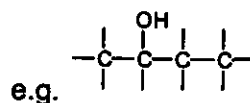
- a displayed formula – e.g.



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.

1 (a) (i) ethanal ✓ [

(ii) aldehyde / carbonyl ✓ [

(iii) CH₃CH₂OH / C₂H₅OH ✓CH₃COO⁻ / CH₃COOAg / CH₃COOH ✓allow displayed formulae, but
penalise poor connections to the
OH, sticks etc [(b) (i) (nucleophile/CN⁻) is an electron/lone pair donor ✓ **ESSENTIAL MARK**

then look for the following points:

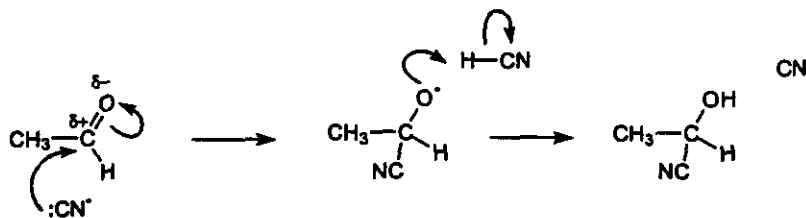
in the diagram ...

or a written alternative ...

CN⁻the nucleophile is CN⁻ ✓curly arrow clearly starts from a
lone pair drawn on the Cthe electron/lone pair is donated
from the C of the CN⁻ ✓curly arrow towards C^{δ+} and
breaking C=O(nucleophile/ CN⁻) is attracted to
an electron deficient carbon ✓correct structure of the
intermediate(nucleophile/ CN⁻) forms a
covalent/dative bond (to the
carbon) ✓

correct structure of the product

HCN is added ✓



ANY 4 out of 5 [

(ii) HCN / KCN / CN⁻ is toxic / AW

NOT dangerous or explosive [

(iii) Yes, because ...

(the product) has a chiral centre/carbon ✓

four different groups around the carbon ✓

asymmetric ✓

cannot be superimposed on its mirror image ✓

NOT "four different atoms" or
"molecules"

allow ecf from b(i)

ANY 2 out of 4 [

[Total: 12

2814

Mark Scheme

June 2003

2 (a) (i) $\text{CH}_3\text{CHClCH}_3$ ✓ allow any formula that is unambiguously 2-chloropropane [1]

(ii) $\text{CH}_3\text{CHClCH}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2 + \text{HCl}$ ✓ [1]

(iii) halogen carrier ✓ [1]

(b) (i) peaks identified
 peak X – CH_3 (protons) ✓
 peak Y – CH (proton) ✓
 peak Z – benzene ring (protons) ✓

3 identification marks

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

- quotes a δ value for the peak and refers explicitly to the Data Sheet /or
- quotes the relevant functional group in the Data Sheet (eg R-CH_3 for X) /or
- quotes exactly the relevant Data Sheet range, ie (0.7–1.6 for X)
 (2.3 – 2.7 for Y)
 (7.1 – 7.7 for Z) ✓✓✓

ignore any attempts to reason from the splitting here, but look out for credit to parts (ii) and (iii) if not given below

3 reasoning marks

[6]

(ii) 1 proton / CH/ 'n' = 1 (using the n+1 rule) ✓

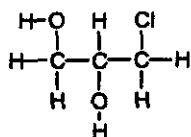
on the neighbouring/adjacent carbon ✓ [2]

(iii) the CH_3 protons are all equivalent/in the same (chemical) environment / there are six protons adjacent to the CH ✓

[1]

[Total: 12]

3 (a) (i)



the correct compound ✓

shown as a correctly displayed formula ✓

[2]

(ii) yes, because there are four different groups
around the central carbon ✓
(or ecf on the structure given in (i)) AW

allow asymmetric / non-super-
imposable on its mirror image

[1]

(b) infra-red/i.r. (spectroscopy) ✓
peak/absorption at 3230 - 3550 (cm⁻¹) ✓

n.m.r. (spectroscopy) ✓
peak at 3.5–5.5 (ppm) ... ✓
... which disappears in D₂O ✓

Quality of Written Communication

mark for good organisation / a logical response and
technical terms, using at least two of the following
words:

infra-red, nuclear magnetic resonance, spectroscopy,
wavenumber, cm⁻¹, chemical shift, ppm) ✓

[6]

(c) (i) dil/conc/(aq)
or dil/(aq)
or dil/conc/(aq)

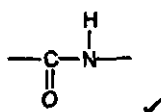
HCl
H₂SO₄ /H⁺/acid
OH⁻/alkali/NaOH etc ✓

if a formula given, there must be
some indication that it is aqueous

allow an enzyme as long as aq

[1]

(ii)



[1]

(iii) amino acids ✓

allow peptides

[1]

[Total: 12]

- 4 (a) carboxylic acid / phenol / amino acid / named example or correct formula ✓
- equation to give the correct negative ion ✓
eg $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
/ $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
- (b) (i) $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$ ✓
- (ii) (base, phenylamine, ethylamine) accepts H^+ ✓
/ donates lone pair
- (uses the) lone pair on the nitrogen ✓
- the lone pair (in phenylamine) is delocalised
/interacts with the delocalised/ π electrons in the ring
or
inductive effect pulls electrons (from the nitrogen)
- ora ✓
- (c) amino acid / $\text{RCH}(\text{NH}_2)\text{COOH}$
/ named example or correct formula ✓
- contains both carboxylic acid/ COOH and basic amine/ NH_2 groups ✓
- NOT 'HX' or any inorganic acid
- allow ecf on the formula or an inorganic acid from above as long as donation of H^+ shown [2]
- do not penalise a correct equation using H^+ or another acid [1]
- allow AW throughout

(or shown on a diagram)
- It must be clear which way the electrons are going" [3]
- do not allow non-organic acids for the first mark, but give ecf on good explanation
- allow any explanation describing acidity and basicity eg "can donate and accept H^+ " [2]

[Total: 8]

5 (a) planar molecule (or shown in diagram) ... ✓



p-orbitals (or shown in diagram) ✓
... overlap (or shown in a diagram) ✓

(p-orbital overlap forms) π -bonds ✓
electrons are delocalised ✓
C-C bonds are all the same length ✓

ANY 5 out of 6

Quality of Written Communication

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

(b) (i) $C_6H_5CHBrCH_2Br$ ✓

(ii) phenylethene has a double bond ✓

benzene (π) electrons are:
spread out / delocalised / lower electron density
✓ ora for 2 marks

then either ...
so the bromine molecule gets less polarised / needs the catalyst to help polarise it ... ✓

and the bromine/electrophile is less strongly attracted (to the π electrons) ✓
ora and AW for 2 marks

or ...
(delocalised (π) electrons make) benzene stable ... ✓

so more energy is needed (to overcome it) / higher E_a / it is not easily disrupted ✓
ora and AW for 2 marks

TOTAL 2 + 2 marks

(c) (to make) poly(phenylethene) / polymers / plastics / a named use of poly(phenylethene) ✓
eg packaging, insulation, toys, moulded casings etc

[Total: 12]

6 (a) 184

[1]

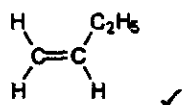
(b) (i) Identification of the compounds ...

any type of formula that unambiguously identifies the compound – eg

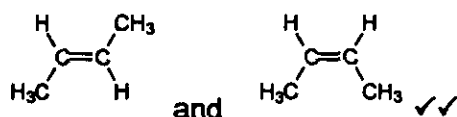
B



C



D and E



F



5 marks

reasoning ...

H can be taken from either carbon 1 or carbon 3 ✓ AW

D and E are cis-trans/geometric (isomers) ✓

double bond does not rotate ✓

explanation why but-2-ene gives cis/trans isomers or why but-1-ene doesn't ✓

ANY 3 out of 4 marks

[8]

(ii) addition / hydrogenation / reduction ✓

[1]

[Total: 10]

7 (a) (i) tin/iron ✓

hydrochloric acid / HCl ✓

allow LiAlH₄ ✓ anyhydrous/ether ✓

[2]

(ii) M_r of C₆H₅NO₂ = 123(.0) ✓
M_r of C₆H₅NH₂ = 93(.0) ✓(use of correct M_r s get 2 marks)theoretical mass of C₆H₅NH₂ = 7.56(g) /ecf
/ moles of C₆H₅NH₂ = 0.08(13) /ecf ✓

answer in the range 89.8-90.0(%) /ecf 3 sf ✓

(correct answer gets 2 more marks)

answer in the range 87-92% due to
rounding errors and/or with sig figs ≠
3 gets 3 marks max

[4]

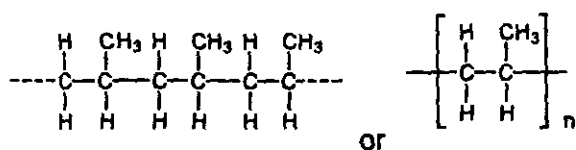
(b) sodium nitrite + (hydrochloric) acid
/ nitrous acid / HNO₂ ✓✓

< 10°C ✓

[3]

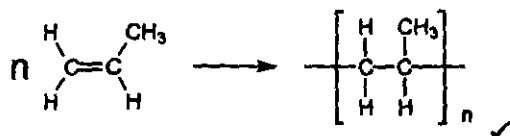
[Total: 9]

8 (a) (i) a correct structure for poly(propene), eg



bonds must extend outside any brackets ✓

equation showing 'n' monomers



[2]

(ii) addition:

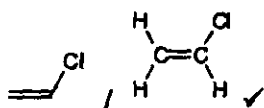
monomer has C=C double bond / is an alkene / double bond breaks/ no (other) substance lost ✓ NOT just "monomer has a double bond"

condensation:

water / small molecule lost ✓

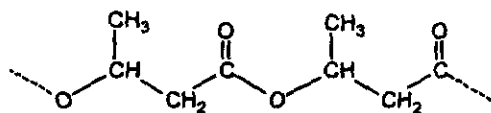
[2]

(b)



[1]

(c) (i)



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

allow a break in the repeat at any point

[2]

(ii) H reacts with NaOH / poly(propene) does not ✓

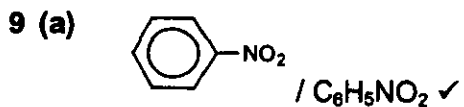
H is an ester / is polar ... ✓
will be hydrolysed by NaOH ✓
poly(propene) is non-polar ✓

"hydrolysed by NaOH" gets the reacts with NaOH mark as well

ANY 3 out of 4 marks

[3]

[Total: 10]



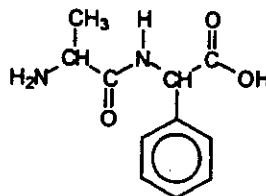
allow poly-nitrated benzene in any positions

[1

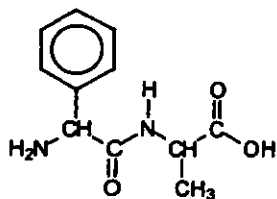


[2

(c) two structures made by joining the amino acids



either way round – eg



peptide bond in one structure ✓

two dipeptides with R groups swapped ✓

allow H_2O ✓ and one correct dipeptide ✓ as an alternative answer

[2

[Total: 5]