Mark Scheme 2814
June 2005

CHAINS, RINGS + SPECTROSCOPY

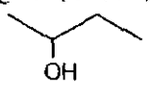
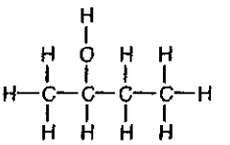
Abbreviations, annotations and conventions used in the mark scheme

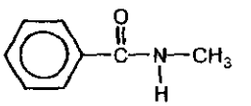
/ = alternative and acceptable answers for the same marking point
; = separates marking points
NOT = answers not worthy of credit
( ) = words which are not essential to gain credit
___ (underlining) = key words which must be used
ecf = allow error carried forward in consequential marking
AW = alternative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

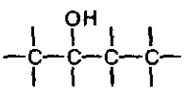
If not specified by the question, this may be given as either:

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

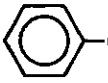
or as a hybrid of these – e.g. 

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. 

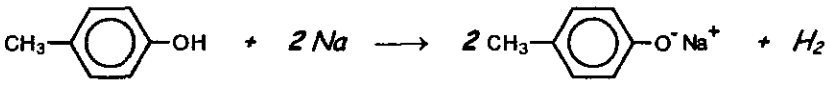
Benzene rings may be represented as  as well as  in any of the types of formula above.

1 (a)(i) *balanced equation to give*  ✓ + H_2O ✓ *allow* $C_7H_5O_2^-$ [2]

(ii) *4-methylphenol reacts (phenylmethanol does not)* ✓

... because phenols are (more) acidic / donate H^+ more easily AW ✓ [2]

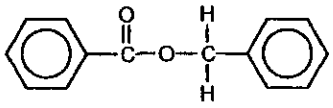
(b)(i) H_2 / *hydrogen* [1]

(ii) 

phenoxide/sodium phenoxide structure / formula ✓
rest the equation also correct and balanced ✓

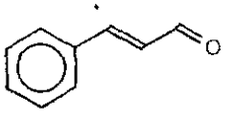
allow C_7H_7ONa *but* **NOT** *-NaO or O-Na* [2]

(c) (i) H^+ */acid / named strong acid eg* H_2SO_4 / HCl [1]

(ii) 

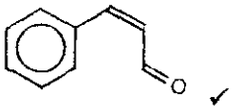
displayed ester group ✓
rest of the ester ✓ [2]

[Total: 10]

2 (a) (i)  ✓ [1]

(b) *C=C double bond does not rotate* ✓
two different groups on each carbon (of the C=C) AW ✓ *NOT on "each side" of the C=C* [2]

i. *trans because H / groups are on opposite sides AW* ✓ [1]

ii. *any formula that shows the H on the same side - eg*
 ✓ [1]

(c) (i) *aldehyde / C=O / carbonyl* ✓ [1]

(ii) $C_6H_5CHCHCHO + 2[H] \longrightarrow C_6H_5CHCHCH_2OH$ ✓ *allow* $C_9H_{10}O$ [1]

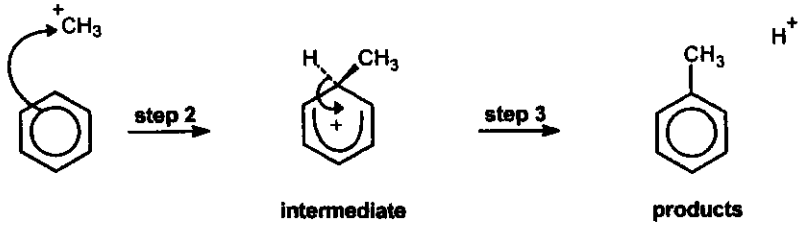
(d) ***method***
silver nitrate ✓
ammonia / ammoniacal ✓
warm / heat ✓
silver (mirror) / brown ppt forms ✓

explanation
silver ions reduced / $Ag^+ + e^- \rightarrow Ag$ ✓
aldehyde oxidised to a carboxylic acid ✓
correct structure - eg $C_6H_5CHCHCOO^-$ */COOH* ✓

quality of written communication
mark for correct spelling, punctuation and grammar in at least two sentences ✓ [8]

[Total: 15]

3 (a) (i)



intermediate products

curly arrow from π-bond towards the carbon of $^+CH_3$ ✓

intermediate
structure of the intermediate ✓
curly arrow from C-H bond ✓

intermediate must have the "+" within the delocalised area

products
structure of methylbenzene and H^+ shown ✓

allow HCl as product if Cl^- is shown with the intermediate **[4]**

(ii) *accepts an electron pair* ✓ *NOT a "lone" pair* **[1]**

(iii) $H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$ **[1]**

$C_6H_6 + CH_3Cl \longrightarrow C_6H_5CH_3 + HCl$
products ✓
rest of the equation also correct ✓ **[2]**

(b) (i) *(benzene) ring is activated* ✓

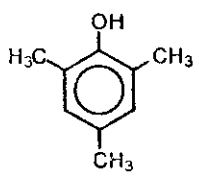
lone pair from oxygen is delocalised / interacts with the π electrons around the ring / AW or diagram ✓

ignore references to the inductive effect

greater electron density (around the ring) ✓

attracts $^+CH_3$ / electrophiles more easily ✓ **[4]**

(ii)



✓ **[1]**

[Total: 13]

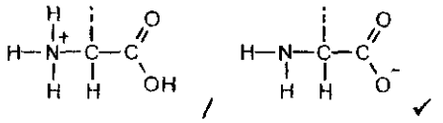
4 (a) (i) *water / evidence of a solution in water - eg (aq), 'dil', '6M' or 'conc' for HCl* ✓

NOT conc HNO_3 or conc H_2SO_4

a named strong acid or alkali (heated under) reflux / a suitable enzyme at around 37°C ✓ **[2]**

(ii) *amino acids* ✓ **[1]**

(iii) *correct structure for one of the amino acids* ✓
correct ionic form for reagent used in a(i) - eg



/

✓ **[2]**

(iv) *reaction with water to split/break down the compound* ✓

peptide bond in the compound is broken / diagram to show AW ✓ **[2]**

(b) (i) *a carbon with four different groups attached* ✓

a chiral carbon /centre ✓

different spatial / 3-D arrangement (of the groups) ✓

(stereo)isomers / mirror images are non-superimposable / molecules are asymmetric ✓

ANY 3 out of 4 marks **[3]**

(ii) *contains 2 chiral centres* ✓

*each can have 2 (stereo)isomers/ 2x2 possibilities **AW*** ✓ **[2]**

(iii) *use naturally occurring / enantiomerically pure amino acids*
OR
use a stereospecific catalyst / enzyme / micro-organisms
OR
separate the mixture using a suitable method ✓ **[1]**

(iv) *higher doses are required* ✓

the drug /other stereoisomers may have (harmful) side-effects ✓ **[2]**

[Total: 15]

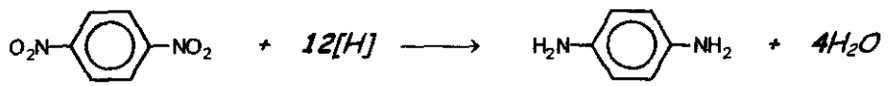
5 (a) (i) *Diamino*
two/2 amine groups ✓

1,4
their position on the ring / numbering of carbons around ring (or shown on a diagram) ✓ **[2]**

(b) (i) *reduction / redox* ✓ **[1]**

(ii) *tin and HCl* ✓
conc acid under reflux ✓
or H_2 gas + Ni/Pd catalyst **[2]**

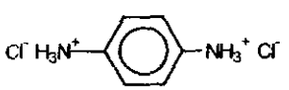
(iii)



H_2O as product ✓
and the equation balanced ✓ **[2]**

(c) (i) *accepts H^+ using the lone pair (on N)* ✓
which is donated/forms a (dative) covalent bond ✓
either mark can be obtained with a good diagram **[2]**

(ii)



correct structure with charges shown ✓✓
one mark for either: just one neutralised,
both neutralised, but without Cl^-,
both neutralised, but no charges shown **[2]**

(iii) *hexane-1,6-diamine is a stronger base because:*

electrons move towards the N (due to the inductive effect) (in hexane-1,6-diamine) ✓

the lone pair from N is (partially) delocalised around the ring (in diaminobenzene) ✓

so the electron pair is more easily donated / H more easily accepted (in hexane-1,6 diamine) **ora** ✓ **[3]**

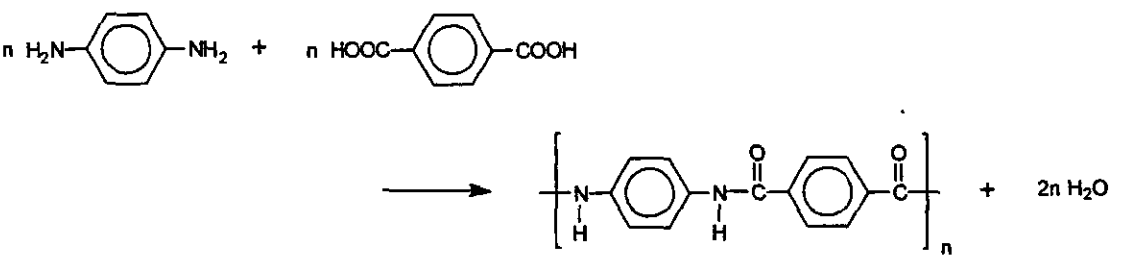
question 5 continued overleaf

Mark Scheme for 2814/01, June 2005 - ERRATUM

See page 34 of the main booklet.

As part of the printing process, part of the diagrams for Question 5(d)(ii) have become corrupted.

These diagrams should read:

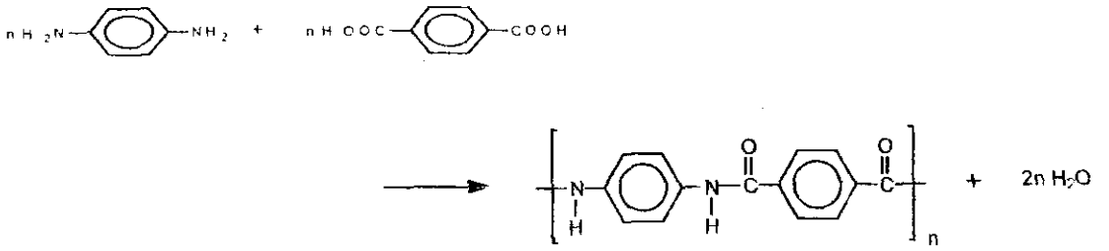


question 5 continued

(d) (i) *eg fire resistant / bullet proof clothing / cycle tyres / tennis rackets* ✓

allow any use where a tough flexible material is needed [1]

(ii) *condensation (polymerisation)* ✓



structure of benzene-1,4-dicarboxylic acid ✓

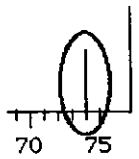
amide /peptide bond displayed ✓

repeat unit of correct polymer indicated ✓

formula of water shown as the product in an equation ✓ [5]

[Total: 20]

6 (a) *Molecular ion peak circled* ✓



Compound X has M_r = 74 ✓

Empirical formula has M_r = (36 + 6 + 32) = 74
(so must be the same as the molecular formula) ✓ **[3]**

(b) (i) *compound X is not an aldehyde or ketone / not a carbonyl compound* ✓ **[1]**

(ii) *compound X does not contain a C=C double bond/ is not an alkene / is not a phenol* ✓ **[1]**

(c) ***structure 1*** *ethyl methanoate* ✓
structure 3 *propanoic acid* ✓ **[2]**

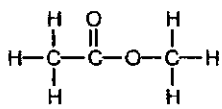
(d) ***presence or absence of relevant peaks*** *(in the context of any of the structures) ...*

peak at ~1750 / 1680-1750(cm^{-1}) for C=O ✓
peak at ~1250 / 1000-1300(cm^{-1}) for C-O ✓
no peak at 2500 - 3300(cm^{-1}) ✓

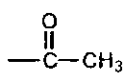
structures possible or ruled out ...
structures 3 is ruled out / can only be structure 1 or 2 ✓ **[4]**

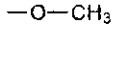
(e)

correct structure:



✓

reasoning: *peak at ~2 / 2.0-2.9(ppm) is due to*  ✓

peak at ~3.7 / 3.3-4.3(ppm) is due to  ✓

allow max 1 as ecf from the wrong structure for valid reasoning from the δ value

relative peak area is 1:1/equal as both groups have the same number of protons ✓ ***AW***

peak(s) not split as there are no protons on the neighbouring carbons ✓

quality of written communication
*for use and correct organisation of at least **two** of the scientific terms: ppm, environment, methyl, proton, adjacent, singlet (doublet etc)* ✓ **[6]**

[Total: 17]