Mark Scheme 2814
January 2006

CHAINS, RINGS + SPECTROSCOPY

ADVICE TO EXAMINERS ON THE ANNOTATION OF SCRIPTS

1. Please ensure that you use the **final** version of the Mark Scheme.
   You are advised to destroy all draft versions.

2. Please mark all post-standardisation scripts in red ink. A tick (✓) should be used for each answer judged worthy of a mark. Ticks should be placed as close as possible to the point in the answer where the mark has been awarded. The number of ticks should be the same as the number of marks awarded. If two (or more) responses are required for one mark, use only one tick. Half marks should never be used.

3. The following annotations may be used in when marking. No comments should be written on scripts unless they relate directly to the mark scheme. Remember that scripts may be returned to centres.

x	=	incorrect response (errors may also be underlined)
^	=	omission of the correct response
bod	=	"benefit of the doubt" (where professional judgement has been used in deciding a response is worthy of a mark)
ecf	=	"error carried forward" (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response). No mark awarded, even if one response was correct. [1]
sf	=	error in the number of significant figures (only penalised once on the paper).

4. The marks awarded for each part question should be indicated in the margin provided on the right hand side of the page. The mark total for each question should be ringed at the end of the question, on the right hand side. These totals should be added up to give the final total on the front of the paper.

5. In cases where candidates are required to give a specific number of answers, (e.g. 'give three reasons ...'), mark the first answer(s) given up to the total number required. Strike through the remainder. In specific cases where this rule cannot be applied, the exact procedure to be used is given in the mark scheme

6. Correct answers to calculations should gain full credit even if no working is shown, unless otherwise indicated on the mark scheme. (An instruction to 'Show your working' is to help candidates, who may then gain partial credit even if their final answer is not correct.)

7. Strike through all blank spaces and/or pages in order to give clear indication that the whole of the script has been considered.

8. An element of professional judgement is required in the marking of any written paper, and candidates may not use the exact words that appear in the mark scheme. If the science is correct and answers the question, then the mark(s) should normally be credited. If you are in doubt about the validity of any answer, contact your Team Leader/Principal Examiner for guidance.

[1] 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.

Abbreviations, annotations and conventions used in the mark scheme

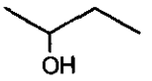
/ = alternative and acceptable answers for the same marking point
; = separates marking points
NOT = answers not worthy of credit
( ) = words which are not essential to gain credit
___ (underlining) = key words which must be used
ecf = allow error carried forward in consequential marking
AW = alternative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

Marking structures in organic chemistry

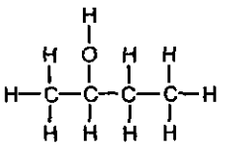
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3, C_2H_5, OH, COOH, $COOCH_3$) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient).

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

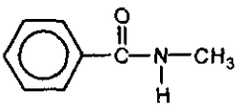
- a **structural formula** – e.g. $CH_3CH(OH)C_2H_5$,



- a **skeletal formula** – e.g.



- a **displayed formula** – e.g.

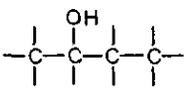


or as a hybrid of these – e.g.

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 –

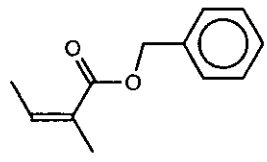
e.g.



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

1 (a) (i) *alkene* ✓ *allow "C=C double bond"*
ester ✓ **[2]**

i.



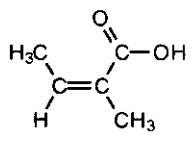
✓ **[1]**

ii. $C_{12}H_{14}O_2$ ✓ **[1]**

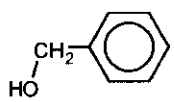
b. *same structural formula/order of bonds,*
different spacial arrangement **AW** ✓

description or diagram showing **B** *and how it is different from* **A** ✓ **[2]**

c.



✓



✓ **[2]**

d. i. *peak at 1680-1750 (cm^{-1}) due to C=O* ✓

peak at 1000-1300 (cm^{-1}) due to C-O / ✓ **[2]**

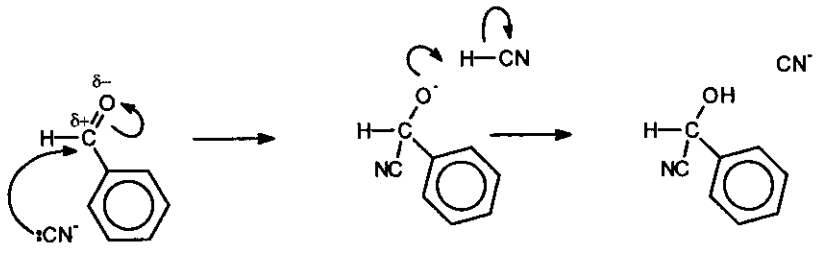
ii. *2500-3300 / 3230-3550 (cm^{-1})* ✓

O-H /carboxylic acid/alcohol is ***not*** *present in* **A** ✓

allow 1 mark for ~500-1500 (cm^{-1}) which is a unique fingerprint region etc **[2]**

[Total: 12]

2 (a) (i)



polarisation of $C^{\delta+}=O^{\delta-}$ and curly arrow breaking C=O ✓

curly arrow from lone pair on $:CN^-$ to C ✓

structure of intermediate ✓

curly arrows from O^- to H-CN/H_2O and breaking the H-CN/H-OH bond ✓ — *allow just a curly arrow from from O^- to H* **[4]**

iii. *nucleophilic addition* ✓ **[1]**

e. *lengthening the carbon chain* **AW** ✓ **[1]**

f. i. *heat/reflux .... with a suitable strong acid /acid /H^+* ✓
which is dilute / (aq) / stated concentration ✓ — *allow 'conc' for HCl* **[2]**

ii. $C_6H_5CH(OH)CN + 2H_2O + H^+ \longrightarrow C_6H_5CH(OH)COOH + NH_4^+$ ✓ **[1]**

g. *mandelic acid is chiral / has optical isomers /enantiomers* ✓

synthetic gives a mixture / natural gives only one (optical) isomer ✓

only <u>one</u> of the (optical) isomers is the (pharmacologically) active one **AW** ✓ — *ignore references to side effects and dosage* **[3]**

h. i. $C_6H_5CH(OH)CH_2NH_2$ / *2-amino-1-phenylethanol*
any unambiguous formula/name ✓ **[1]**

ii. *reduction / redox* ✓ **[1]**

[Total: 14]

3 (a) *low boiling point / easily turns to a gas* **AW** ✓ **[1]**

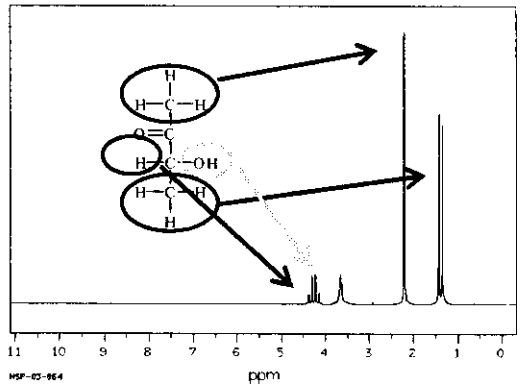
i. *2,4-dinitrophenylhydrozine / 2,4-DNP(H) / Brady's reagent* ✓

purify/recrystallise the product/solid (derivative) ✓

measure the melting point /mp ✓

compare the result with data book/known values ✓ **[4]**

j. i.



one mark for two peaks assigned ✓

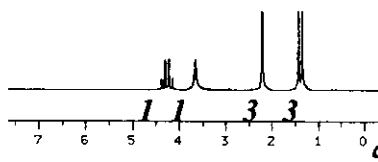
two marks for all three ✓ **[2]**

ii. *re-run in/add D_2O* ✓
peak (due to OH) disappears ✓ **[2]**

iii. ***Peak at 1.4ppm***
(1:1 due to) one H on the neighbouring /adjacent carbon ✓

Peak at 4.3ppm
(1:3:3:1 due to) three H on the neighbouring /adjacent carbon ✓ **[2]**

iv.



all four correct ✓ **[1]**

v. *no of H/protons in the same (chemical) environment/of that 'type'* ✓ **[1]**

[Total: 13]

4 (a) *Correct structure of 3-nitrophenol or any multiple nitrated phenol* ✓ **[1]**

k. *M_r phenol (C_6H_6O) = 94.0* ✓

M_r 4-nitrophenol ($C_6H_5NO_3$) = 139.0 ✓

expected mass/moles of nitrophenol from 100 g = 148 g/1.06 mol (or ecf *from wrong M_rs)* ✓

at 27% yield gives ***40 / 39.9*** *(g) (or* ecf*)* ✓

last mark is for 0.27 x expected mass to 2 or 3 sf **[4]**

l. ***conditions for nitration of benzene:***
HNO_3 is concentrated ✓

conc H_2SO_4 is present ✓

heating or stated temp above 50°C ✓

[3]

explanation for greater reactivity of phenol
lone pair from O atom is delocalised into the ring ✓

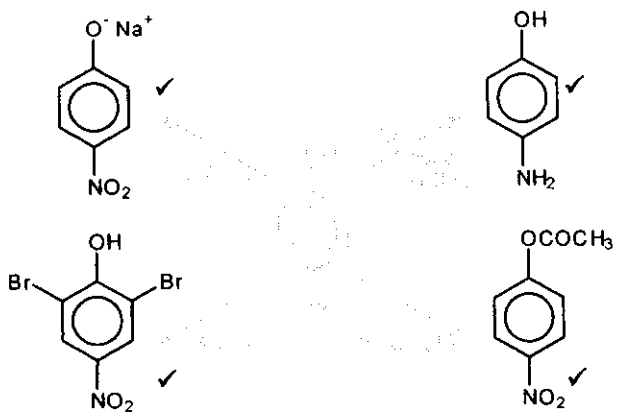
greater (π) electron density around the ring ✓

(the benzene ring in phenol) is activated ✓

attracts electrophiles/ NO_2 more / makes it more susceptible to electrophiles **AW** ✓ **[4]**

quality of Written Communication *mark for at least two legible sentences with correct spelling, punctuation and grammar* **[1]**

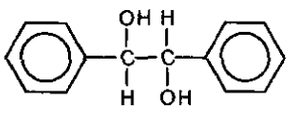
m.



allow bromination in any positions on the ring **[4]**

[Total: 17]

5 (a) (i)



✓ **[1]**

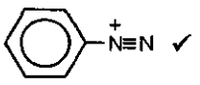
i. $C_{14}H_{10}O_2$ + 4[H] ⟶ $C_{14}H_{14}O_2$ ✓ *allow* ecf *from (i)* **[1]**

n. ***delocalised electrons***
electrons are spread over more than two atoms **AW** ✓

π-bond
formed by overlap of p-orbitals/ diagram to show ✓ **[2]**

o. *sodium nitrite + HCl / nitrous acid* ✓

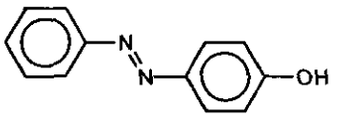
<10°C ✓



✓

phenol/named example (added to the products from above) **AW** ✓
alkaline conditions / OH^- ✓

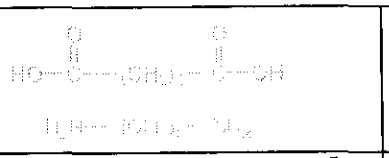
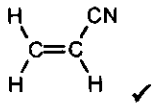
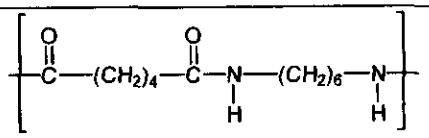
example of an azo dye that could be formed from phenylamine,
eg ✓



[6]

[Total: 10]

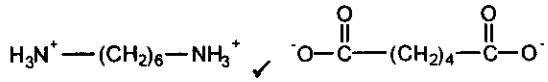
6 (a)

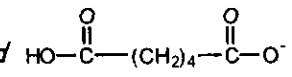
	 ✓
 *monomers connected by NHCO ✓* *correct repeat shown ✓*	
condensation	*addition*

✓ *for both* **[4]**

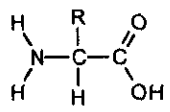
p. i. PCl_5 / $SOCl_2$ **[1]**

ii. *HCl* **[1]**

q.  ✓

allow 1 mark for: both $H_3N^+—(CH_2)_6—NH_2$ *and*  **[2]**

r. i. *4* **[1]**

ii.  *where R = H, CH_3, CH_2OH or $CH_2C_6H_5$ ✓* **[1]**

iii. *any three different chemically or biologically correct differences between amino acids and the nylon monomers ✓✓✓ - eg*

- *protein monomers are amino acids / nylon monomers are a (di)amine/base and a (di)acid*
- *protein monomers have different types/R groups / nylon monomers are two types/no variation*
- *protein monomers have stereo/optical isomers/are chiral*
- *protein monomers have higher melting points/form zwitterions*

other possible answers include:

- *nylon monomers have longer chain length/no other functional groups / no aromatic content / are symmetrical etc*

don't allow comparisons of solubility or M_r **[3]**

[Total: 13]

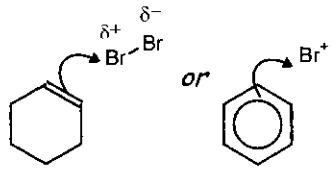
7 (a) (i) ***bromine as an electrophile***

an electrophile accepts an electron pair ✓ *NOT a lone pair*

bromine is polarised/has + charge (centre)/dipole on Br-Br/Br^+ shown in diagram ✓

appropriate diagram showning a curly arrow from a double/π bond to the $Br^{\delta+}$/Br^+ ✓

eg



[3]

iv. ***comparison of reactivity of cyclohexene and benzene***

benzene is (more) stable / more energy required ✓

benzene (π) electrons are delocalised ✓

benzene has lower electron/- charge density ✓

so bromine is less polarised /attracted to it /
benzene is less susceptible to electrophiles ✓

ora *for cyclohexene* **[4]**

quality of written communication *mark for any* ***two*** *of the the terms:*

delocalised/localised, π-electrons/bonds/system, electron density, dative covalent, activation/stabilisation energy, halogen carrier, heterlytic fission, addition/substitution, polarity *used appropriately* ✓ **[1]**

s. i. *iodobenzene because ...*

Br is more electronegative than I ✓ **ora**

so the I atom will be positive /δ^+ /the electrophile ✓ **[2]**

ii. $C_6H_6 + IBr \longrightarrow C_6H_5I + HBr$ ✓

or ecf *giving* $C_6H_5Br + HI$ **[1]**

[Total: 11]