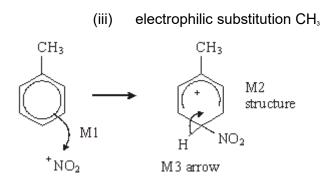
M1. (a) (i) conc
$$HNO_3$$

conc H₂SO₄ allow 1 for both acids if either conc missing	1
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^{+} + H_3O^{+} + 2HSO_4^{-}$	
or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$	1



horseshoe must not extend beyond C2 to C6 but can be smaller + must not be too close to Cl

(b) Sn or Fe / HCl (conc or dil or neither) or Ni / H_2 not NaBH₄ LiAlH₄

1

3

1

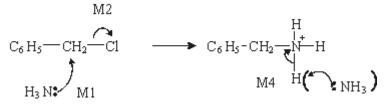
1

1

(ii) nucleophilic substitution

Use an excess of ammonia

M3 structure



Page 2

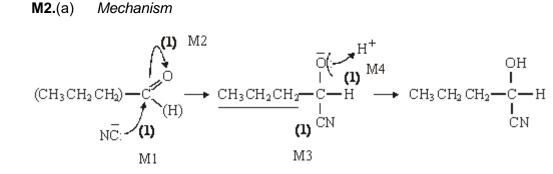
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(c)

(i)

NH₃

1

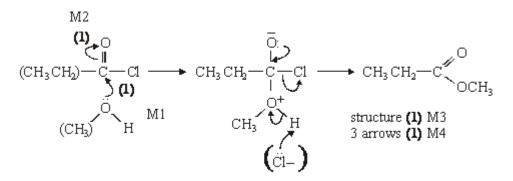


Allow C_3H_7 if structure shown elsewhere penalise HCN splitting if wrong

Name of product: 2-hydroxypenta(neo)nitrile (1)

or 1-cyanobutan-1-ol

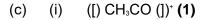
(b) Mechanism



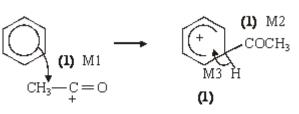
Name of organic product: methylpropanoate (1)

5

5







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4

Notes

(abc) extra curly arrows are penalised

- (a) be lenient on position of negative sign on : CN⁻ but arrow must come from lp
- (a)/(b) C = 0 alone loses M2 but can score M1 for attack on C+, similarly C = 0
- (a) allow 2-hydroxypentanonitrile or 2-hydroxypenta(ne)nitrile ... pentylnitrile
- (b) in M4, allow extra: CI⁻ attack on H, showing loss of H⁺
- (c) (i) allow formula in an "equation"(balanced or not) be lenient on the position of the + on the formula
 - (ii) for M1 the arrow must go to the C or the + on the C don't be too harsh about the horseshoe, but + must not be close to the saturated C M3 must be final step not earlier; allow M3 even if structure (M2) is wrong

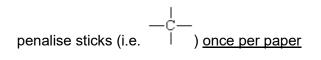
[14]

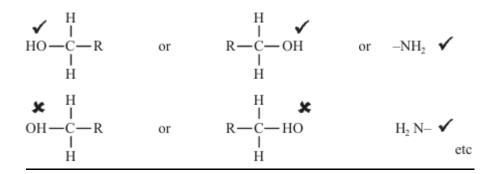
Organic points

 <u>Curly arrows:</u> must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space e.g.



(2) <u>Structures</u>





Penalise once per paper

 $\frac{\text{allow}}{\text{or } H_3-\text{ or }-CH_3 \text{ or } \stackrel{CH_3}{|} \text{ or } CH_3$

M3.

(a) Cyclohexane evolves 120 kJ mol⁻¹

 \therefore (expect triene to evole) 360 kJ mol⁻¹ (1) or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

QofL: benzene lower in energy / <u>more</u> (stated) stable (1) Not award if mentions energy required for bond breaking due to <u>delocalisation</u> (1) or explained

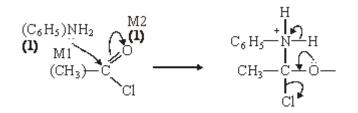
4

(b) (i) phenylamine weaker (1) *if wrong no marks*

lone pair on N (less available) (1) delocalised into ring (1) or "explained"

3

(ii) addition – elimination (1)



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structure (1) M3 3 arrows (1) M4

N-phenyl ethanamide (1)

(iii) conc HNO₃ (1) conc H₂SO₄ (1) HNO₃ + 2H₂SO₄ $\rightarrow \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$ (1) $\stackrel{+}{\longrightarrow} O_2 + H_3O^+ + 2HSO_4^-$ (1) (1) M3 (1) M2

6

6

(iv) peptide / amide (1)

NaOH (aq) **(1)** HCl conc or dil or neither H₂SO₄ dil NOT conc NOT just H₂O

2

Notes

- (a) 360 or 3 × 120 or in words (1);
 - 152 NOT 150 (1); (152 can get first two marks)
 - Q of L benzene more stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene (1);
 - delocalisation or explained (1)
- (b) (ii) or N-phenylacetamide or acetanilide mechanism: if shown as substitution can only gain M1 if CH₃CO+ formed can only gain M1 lose M4 if Cl- removes H⁺ be lenient with structures for M1 and M2 but must be correct for M3 C alone loses M2

 (iii) <u>No marks for name of mechanism in this part</u> if conc missing can score one for both acids (or in equation) allow two equations

allow HNO₃ + H₂SO₄ \rightarrow NO²⁺ + HSO₄⁻ + H₂O ignore side chain in mechanism even if wrong arrow for M1 must come from niside hexagon arrow to NO₂⁺ must go to N but be lenient over position of + + must not be too near "tetrahedral" Carbon horseshoe from carbons 2-6 but don't be too harsh

 (iv) reagent allow NaOH
HCl conc or dil or neither
H₂SO₄ dil or neither but not conc not just H₂O

[21]