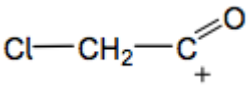
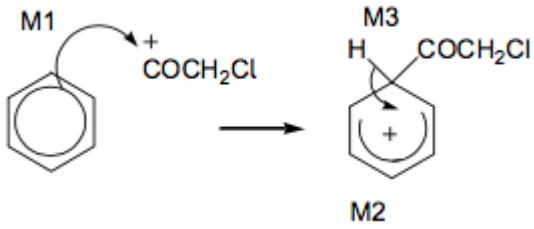
Mark schemes

1 (a) (i) 

Allow $[ClCH_2CO]^+$

1

(ii) 

M1 for arrow from inside hexagon to C or + on C on correct electrophile

M2 for structure of intermediate

- *Horseshoe centred on C1;*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6)*

M3 for Arrow from bond to H into ring

- *Allow M3 arrow independent of M2 structure*
- *+ on H in intermediate loses M2 not M3*
- *Ignore Cl- removing H^+*

1
1
1

(b) Reagent

Water

(Aqueous) silver nitrate

NaOH followed by acidified silver nitrate

(Water +) named indicator

Named alcohol

Na_2CO_3 or $NaHCO_3$

Ammonia

1

P

No reaction

No reaction (or slow formation of ppt)

No reaction (or slow formation of ppt)

No colour change

NVC

NVC

No reaction

Do NOT award

No observation

1

Q

Steamy /misty/ white fumes

White precipitate (immediately formed)

White precipitate (immediately formed)

Indicator turns to correct acid colour

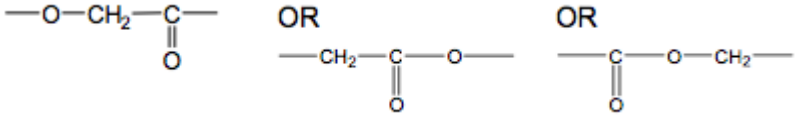
Fruity or sweet smell or misty fumes

Fizzing or effervescence (not just gas produced)

White smoke

1

(c) (i)



One unit only

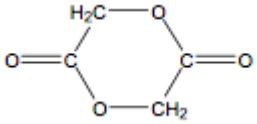
Must have trailing bonds

Ignore n and brackets

allow —O—CH_2—CO—

1

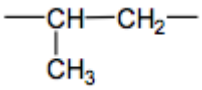
(i)



Allow CO for C=O

1

(d) (i)



One unit only

Must have trailing bonds

Ignore n and brackets

1

(ii) PGA sutures react/dissolve/break down/are biodegradable/ are hydrolysed / attacked by water or nucleophiles /no need to remove

OR Polypropene not biodegradeable/ not hydrolysed / not attacked by water/nucleophiles

1

(Ester links have) <u>polar bonds</u>

polypropene contains <u>non-polar bonds</u>

ignore intermolecular forces

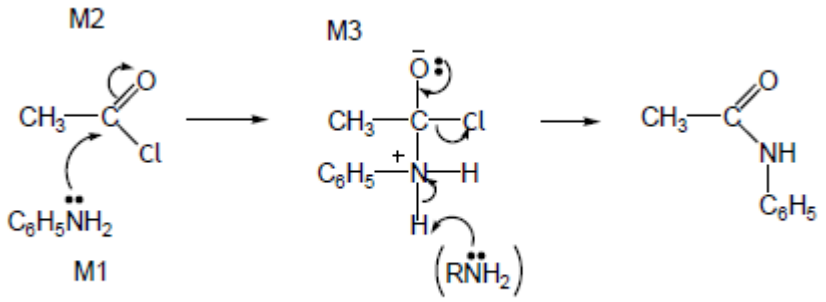
1

[12]

2 (a) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

1



Allow C_6H_5 or benzene ring

Allow attack by :$NH_2C_6H_5$

M2 not allowed independent of M1, but allow M1 for correct attack on C+

M3 for correct structure <u>with charges</u> but lone pair on O is part of M4

M4 (for three arrows and lone pair) can be shown in more than one structure

4

(b) **The minimum quantity of hot water was used:**

To ensure the hot solution would be saturated / crystals would form on cooling

1

The flask was left to cool before crystals were filtered off:

Yield lower if warm / solubility higher if warm

1

The crystals were compressed in the funnel:

Air passes through the sample not just round it

Allow better drying but not water squeezed out

1

A little cold water was poured through the crystals:

To wash away soluble impurities

1

(c) Water

Do not allow unreacted reagents

1

Press the sample of crystals between filter papers

Allow give the sample time to dry in air

1

(d) M_r product = 135.0

1

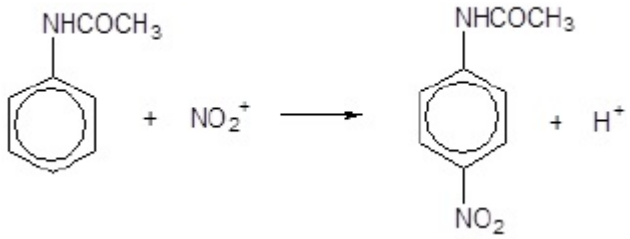
Expected mass = $5.05 \times \frac{135.0}{93.0} = 7.33$ g

1

Percentage yield = $\frac{4.82}{7.33} \times 100 = 65.75 = 65.8(\%)$

Answer must be given to this precision

(e)



OR

$C_6H_5NHCOCH_3 + NO_2^+ \rightarrow C_6H_4(NHCOCH_3)NO_2 + H^+$

1

(f) Electrophilic substitution

1

(g) Hydrolysis

1

(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

3

(a) Electrophilic substitution

Both words needed

Ignore minor misspellings

1

(b) (i) Sn / HCl

OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

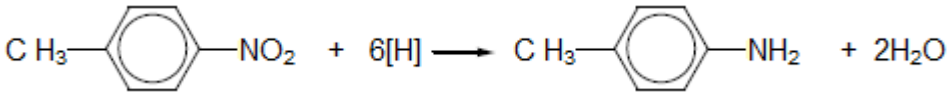
Ignore NaOH after Sn / HCl

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

OR



Allow molecular formulae as structures given

$C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

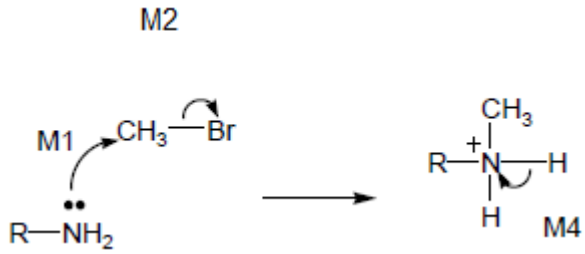
OR making hair conditioner

OR making fabric softener

OR making detergents

1

(c)



M3

NO Mark for name of mechanism

Allow SN1

M1 for lone pair on N and arrow to C or mid point of space between N and C

M2 for arrow from bond to Br

M3 for structure of protonated secondary amine

M4 for arrow from bond to N or + on N

For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br^-

4

(d) lone or electron pair on N

If no mention of lone pair CE = 0

If lone pair mentioned but not on N then lose M1 and mark on

M1

1

in **J** spread / delocalised into ring (or not delocalised in K)

Ignore negative inductive effect of benzene

*Allow interacts with **Π** cloud for M2*

M2

1

less available (for protonation or donation in **J**)

M3

OR

in **K** there is a positive inductive effect / electron releasing)

M2

more available (for protonation or donation in **K**)

M3

1

[11]

4

(a) (i) 3(-120) − (-208) = -152
OR
3(120) − 208 = 152 (kJ mol^{-1})

Must show <u>working</u> and answer and maths must be correct, but ignore sign

1

(ii) Electrons <u>delocalised</u> OR <u>delocalisation</u> (QOL)
OR
allow reference to <u>resonance</u> (QOL)

1

(b) x, y, w

Must be in this order

1

(c) (i) -240 (kJ mol^{-1})

Must have minus sign

1

(ii) between -239 and -121 (kJ mol^{-1})

Must have minus sign

1

(iii) Must specify which diene:

Proximity − for 1,3 C=C bonds are close together

allow converse for 1,4 diene

M1

1

Delocalisation − for 1,3 some delocalisation
OR
some overlap of electrons, π clouds or p orbitals

allow converse for 1,4 diene

M2 **1**

some extra stability for the 1,3- isomer

M3 **1**

[8]

5 (a) Hydrogen <u>bond</u>(ing)

Allow H bonding.

Penalise mention of any other type of bond.

1

(b) (i) Ammonia is a nucleophile

Allow ammonia has a lone pair.

1

Benzene repels nucleophiles

Allow (benzene) attracts / reacts with electrophiles.

OR *benzene repels electron rich species or lone pairs.*

OR *C–Cl bond is short / strong / weakly polar.*

1

(ii) H_2 / Ni **OR** H_2 / Pt **OR** Sn / HCl **OR** Fe / HCl

Ignore dil / conc of HCl.

Ignore the term 'catalyst'.

Allow H_2SO_4 with Sn and Fe but not conc.

Ignore NaOH following correct answer.

Not $NaBH_4$ nor $LiAlH_4$.

1

(iii) <u>conc HNO_3</u>

<u>conc H_2SO_4</u>

1

If either or both conc missed can score 1 for both acids.

1

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

OR using two equations

$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$

$H_2NO_3^+ \longrightarrow H_2O + NO_2^+$

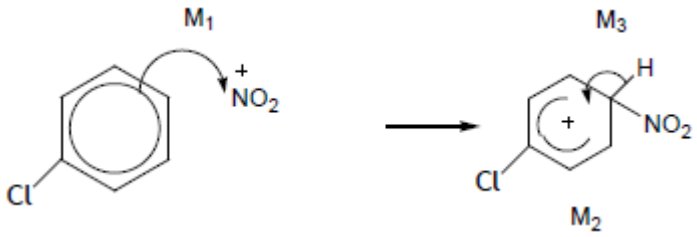
Allow 1:1 equation.

$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$.

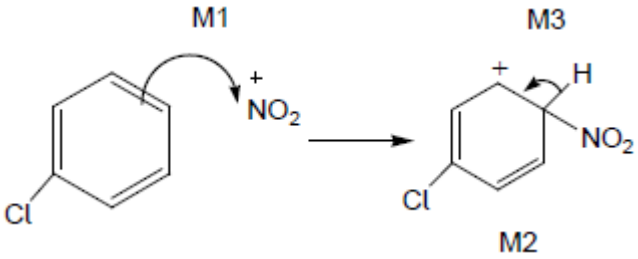
1

(iv) Electrophilic substitution

1



OR

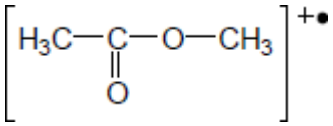


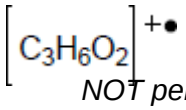
- *Ignore position or absence of Cl in M1 but must be in correct position for M2.*
- *M1 arrow from within hexagon to N or + on N.*
- *Allow NO_2^+ in mechanism.*
- *Bond to NO_2 must be to N for structure mark M2.*
- *Gap in horseshoe must be centered around correct carbon (C1).*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6).*
- *M3 arrow into hexagon unless Kekule.*
- *Allow M3 arrow independent of M2 structure.*
- *Ignore base removing H in M3.*
- *+ on H in intermediate loses M2 not M3.*

3

[11]

6

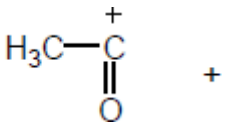
(a) 

OR 

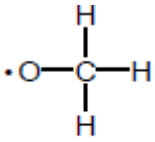
NOT penalise missing brackets.

If wrong ester, no further mark.

1

→ 

Must be displayed formula

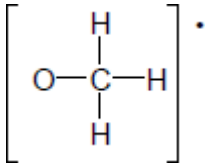


(1)

Radical dot must be on O

Ignore lone pair(s) on O in addition to single electron

Allow radical with brackets as



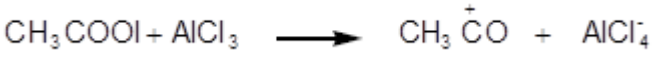
Ignore errors in acylium ion.

1

(b) (i) $AlCl_3$ or $FeCl_3$

If wrong no further marks.

1



Correct equation scores 2 - contrast with (b)(iii)

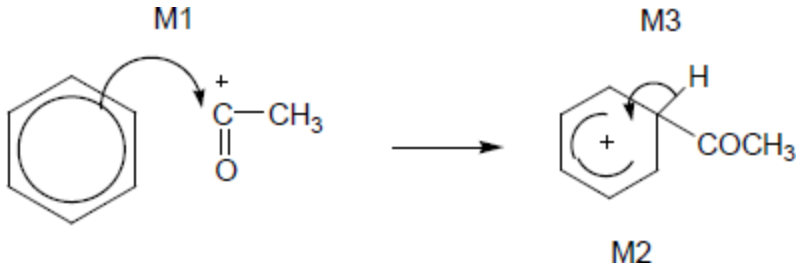
Allow + on C or O in equation.

1

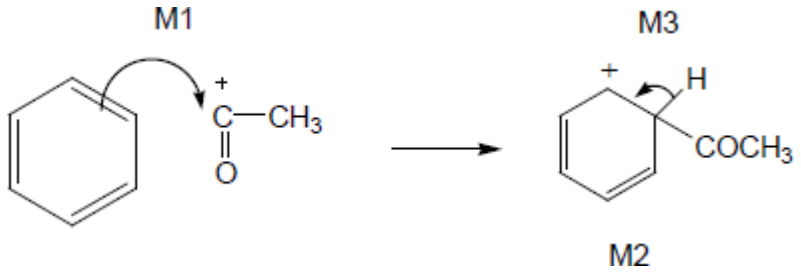
(ii) Electrophilic substitution

Ignore Friedel crafts.

1



OR

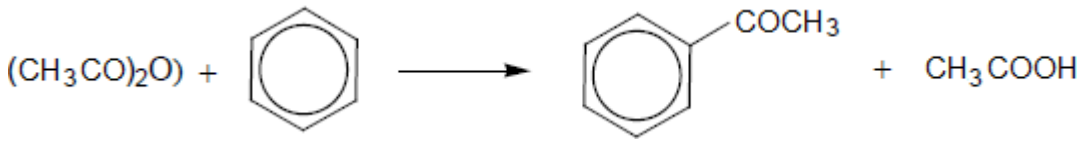


- *+ must be on C of RCO here*
- *M1 arrow from within hexagon to C or to + on C*
- *Gap in horseshoe must approximately be centred around C1 and not extend towards C1 beyond C2 and C6*
- *+ not too close to C1*
- *M3 arrow into hexagon unless Kekule*
- *allow M3 arrow independent of M2 structure, i.e. + on H in intermediate loses M2 not M3*
- *ignore base removing H for M3*

3

(iii) $(CH_3CO)_2O + C_6H_6 \longrightarrow C_6H_5COCH_3 + CH_3COOH$

OR



Correct equation scores 1 – contrast with (b)(i)

Not allow molecular formula for ethanoic anhydride or ethanoic acid.

1

[9]

7 (a) Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid

Allow H_2 (Ni / Pt) but penalise wrong metal

But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH

1

Equation must use molecular formulae

$C_6H_4N_2O_4 + 12\ [H]$

12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

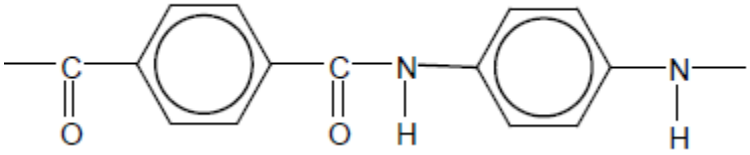
1

$\rightarrow C_6H_8N_2 + 4H_2O$

Allow .... + $6H_2$ if H_2 / Ni used

Allow −CONH− or −COHN− or $-C_6H_4-$

1



Mark two halves separately: lose 1 each for

- *error in diamine part*
- *error in diacid part*
- *error in peptide link*
- *missing trailing bonds at one or both ends*
- *either or both of H or OH on ends*

Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal

NOT Sn / HCl, $NaBH_4$ etc.

1

CH_2

1

In benzene 120°

1

In cyclohexane 109° 28’ or 109½°

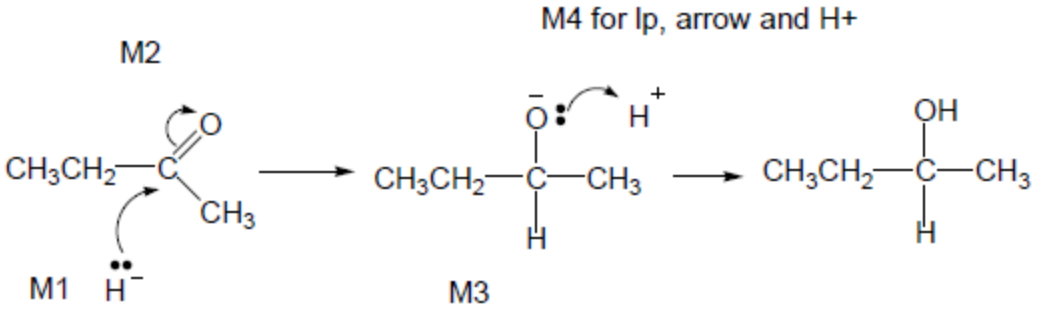
Allow 108° - 110°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

1



- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *M3 is for correct structure including minus sign but lone pair is part of M4*
- *Allow C_2H_5*
- *M1 and M4 include lp and curly arrow*
- *Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)*

4

(ii) M1 Planar C=O (bond / group)

Not just planar molecule

1

M2 Attack (equally likely) from either side

Not just planar bond without reference to carbonyl

1

M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely

1

[17]