M1.(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^+

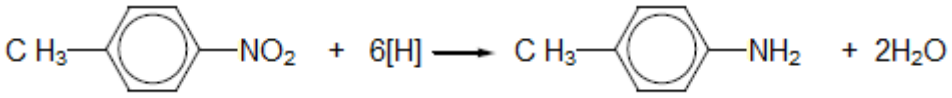
Ignore NaOH after Sn / HCl

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

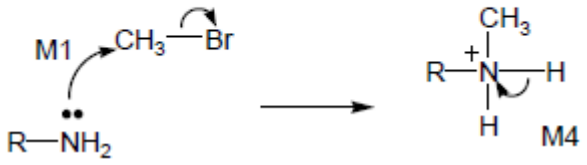
OR making fabric softener

OR making detergents

1

(c)

M2



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) <u>lone or electron pair on N</u>

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

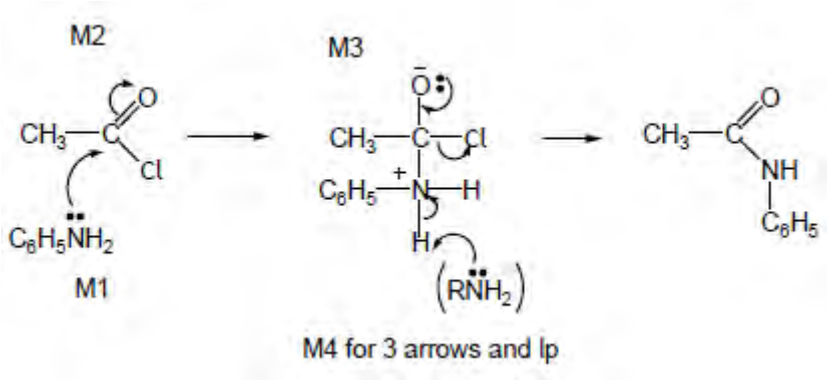
1

[11]

M2.(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

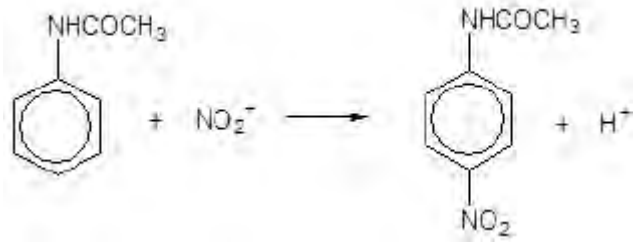
1

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

Answer must be given to this precision

1

(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

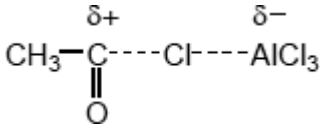
(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

M3.(a) $CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$



Allow RHS as

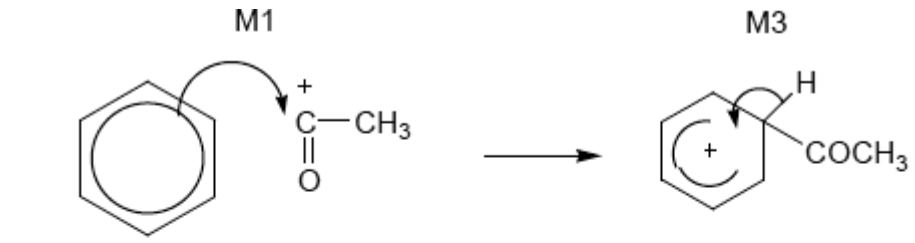
Allow + on C or O in equation but + must be on C in mechanism below

Ignore curly arrows in equation even if wrong.

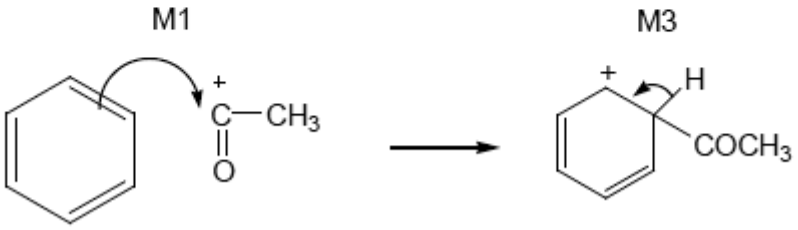
1

$AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$

1



OR



- *M1 arrow from within hexagon to C or to + on C*
- *+ must be on C of RCO in mechanism*
- *+ in intermediate not too close to C1*
- *gap in horseshoe must be centred approximately around C1*
- *M3 arrow into hexagon unless Kekule*
- *allow M3 arrow independent of M2 structure*
- *ignore base removing H for M3*
- ***NO** mark for name of mechanism*

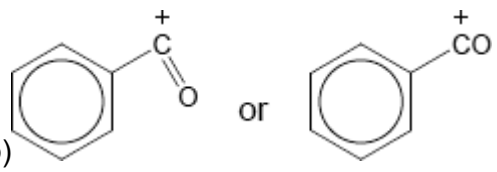
3

Phenylethanone ignore 1 in name, penalise other numbers

Note: this is the sixth marking point in (a)

1

(b)



+ must be on C

But allow $[C_6H_5CO]^+$

1

(c) M1 about electrons

methyl group has (positive) inductive effect OR increases electron density on benzene ring OR pushes electrons OR is electron releasing

Ignore reference to delocalisation

1

M2 about attraction

electrophile attracted more

or benzene ring better nucleophile

Allow intermediate ion stabilised

M2 only awarded after correct or close M1

1

[9]

M4.(a) Hydrogen bond(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) conc HNO_3

conc H_2SO_4 **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

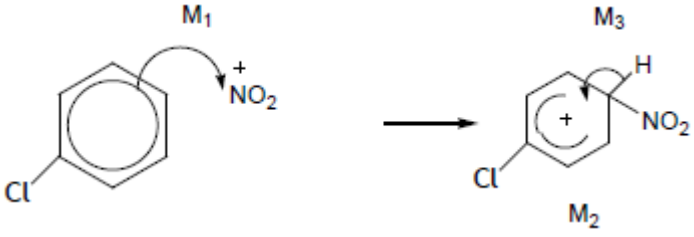
$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$

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

Allow 1:1 equation.

$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$. **1**

(iv) Electrophilic substitution **1**



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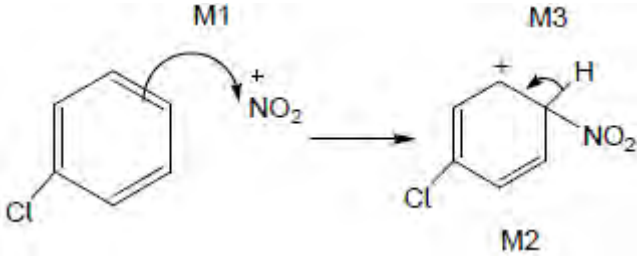
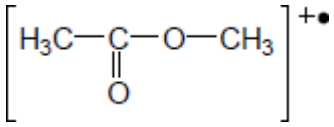


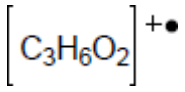
- *Ignore position or absence of Cl in M1 but must be in correct position for M2.*
- *M1 arrow from within hexagon to N or + on N.*
- *Allow NO_2^+ in mechanism.*
- *Bond to NO_2 must be to N for structure mark M2.*
- *Gap in horseshoe must be centered around correct carbon (C1).*
- *+ in intermediate 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

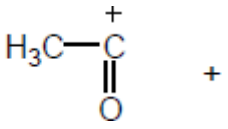
[11]

M5.(a) 

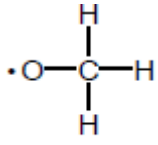
OR 

NOT penalise missing brackets.
If wrong ester, no further mark.

1

→ 

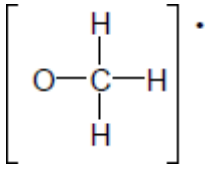
Must be displayed formula



(1)

Radical dot must be on O
Ignore lone pair(s) on O in addition to single electron

Allow radical with brackets as



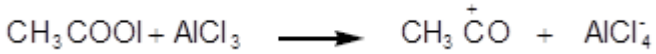
Ignore errors in acylium ion.

1

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

If wrong no further marks.

1



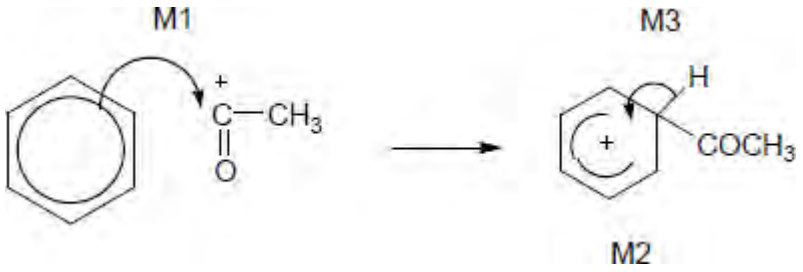
Correct equation scores 2 - contrast with (b)(iii)
Allow + on C or O in equation.

1

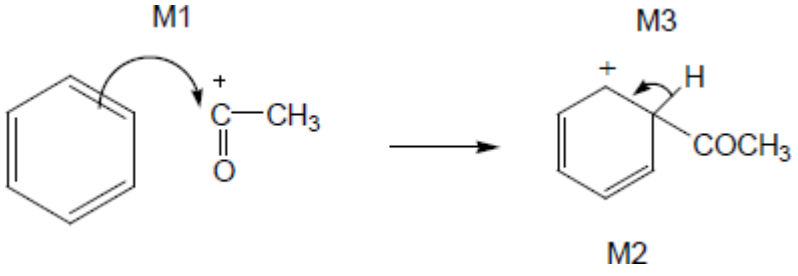
(ii) Electrophilic substitution

Ignore Friedel crafts.

1



OR

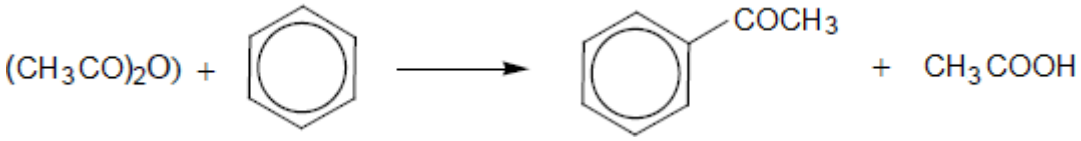


- *+ must be on C of RCO here*
- *M1 arrow from within hexagon to C or to + on C*
- *Gap in horseshoe must approximately be centred around C1 and not extend towards C1 beyond C2 and C6*
- *+ not too close to C1*
- *M3 arrow into hexagon unless Kekule*
- *allow M3 arrow independent of M2 structure, i.e.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