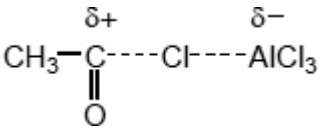
Mark schemes

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

Allow RHS as 

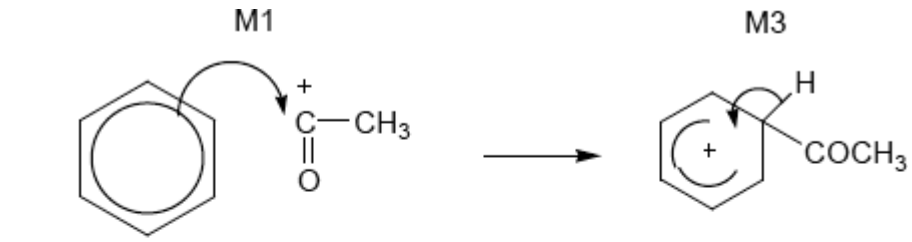
Allow + on C or O in equation but + must be on C in mechanism below

Ignore curly arrows in equation even if wrong.

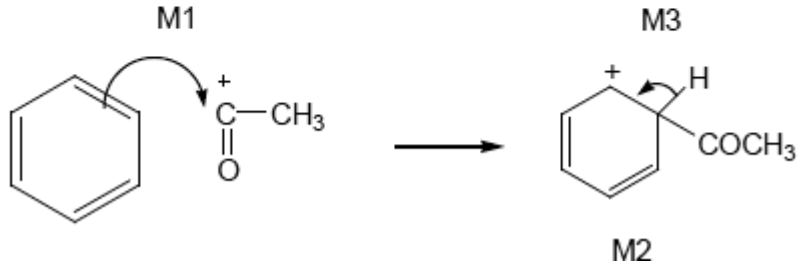
1

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

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*

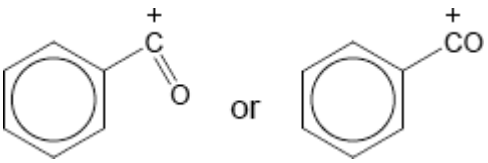
3

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]

2

(a) (i) Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation`

1

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

1

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

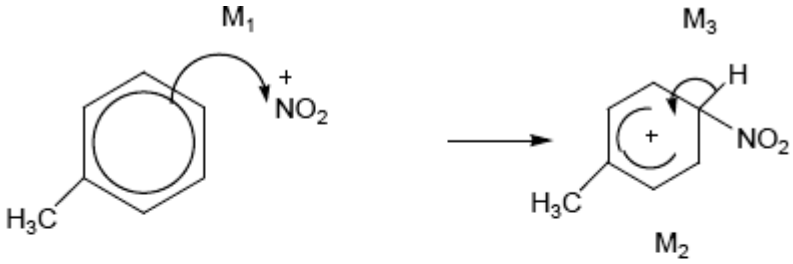
Allow + anywhere on NO_2^+

OR via two equations

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

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

(ii)



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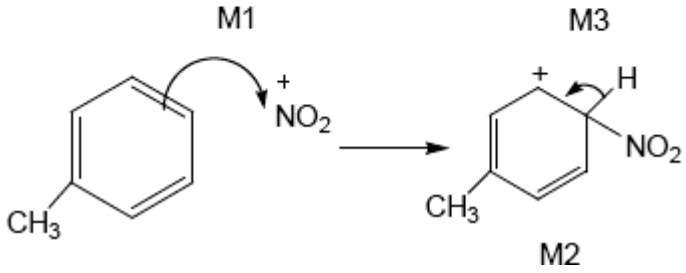


- *ignore position or absence of methyl group in M1 but must be in correct position for M2*
- *M1 arrow from within hexagon to N or <u>+ on N</u>*
- *Allow NO_2^+ in mechanism*
- *Bond to NO_2 must be to N*
- *horseshoe must not extend beyond C2 to C6 but can be smaller*
- *+ not too close to C1*
- *M3 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

(b) 5

1

(c) 2

1

(d) $2C_7H_5N_3O_6 \longrightarrow 5H_2O + 3N_2 + 7C + 7CO$

Or halved

1

[9]

3

(a) **M1** Benzene is <u>more stable than cyclohexatriene</u>

more stable than cyclohexatriene must be stated or implied

If benzene more stable than cyclohexene, then penalise M1 but mark on

If benzene less stable: can score M2 only

1

M2 Expected ΔHº hydrogenation of C_6H_6 is 3(–120)

$= -360 \text{ kJ mol}^{-1}$

Allow in words e.g. expected ΔHº hydrog is three times the ΔHº hydrog of cyclohexene

1

M3 Actual ΔHº hydrogenation of benzene is

152 kJ mol^{-1} (less exothermic)

or 152 kJ mol^{-1} different from expected

Ignore energy needed

1

M4 Because of delocalisation or electrons spread out or resonance

1

(b) **No mark for name of mechanism**

Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation

1

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

OR

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

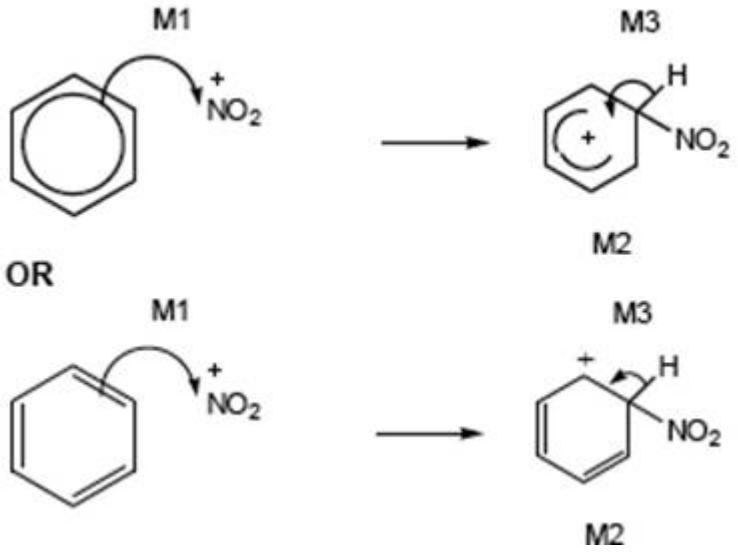
OR via two equations

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

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



M1 arrow from within hexagon to N or + on N

Allow NO_2^+ in mechanism

horseshoe must not extend beyond C2 to C6 but can be smaller

+ not too close to C1

M3 arrow into hexagon unless Kekule

allow M3 arrow independent of M2 structure

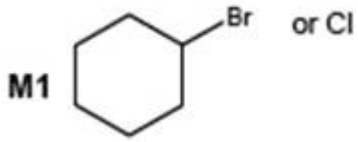
ignore base removing H in M3

+ on H in intermediate loses M2 not M3

3

(c) **If intermediate compound V is wrong or not shown, max 4 for 8(c)**

M1



or chlorocyclohexane or bromocyclohexane

1

Reaction 3

M2 HBr

1

M3 Electrophilic addition

Allow M2 and M3 independent of each other

1

Reaction 4

M4 Ammonia if wrong do not gain M5

1

Allow M4 and M6 independent of each other

M5 Excess ammonia or sealed in a tube or under pressure

1

If CE e.g. acid conditions, lose M4 and M5

M6 Nucleophilic substitution

1

(d) Lone or electron pair on N

No marks if reference to "lone pair on N" missing

1

Delocalised or spread into ring in U

1

Less available (to accept protons) or less able to donate (to H^+)

1

[19]

4 (a) (i) $C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$

OR

$C_6H_6 + CH_3CH_2CO^+ \rightarrow C_6H_5COCH_2CH_3 + H^+$

allow C_2H_5

penalise $C_6H_5–CH_3CH_2CO$

allow + on C or O in equation

1

Phenylpropanone

OR ethylphenylketone **OR** phenylethylketone

Ignore 1 in formula, but penalise other numbers

1

$AlCl_3$

can score in equation

1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$

allow C_2H_5

allow + on C or O in equation

1

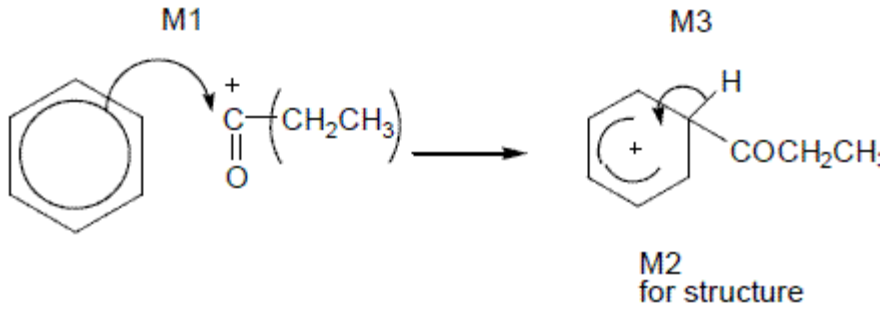
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

1

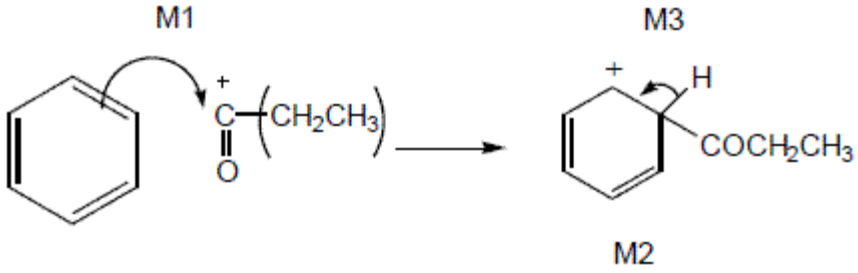
(ii) electrophilic substitution

can allow in (a)(i) if no contradiction

1



OR



M1 arrow from circle or within it to C or to + on C
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1

M2 penalise C_6H_5–CH_3CH_2CO (even if already penalized in (a)(i))

M3 arrow into hexagon unless Kekule

allow M3 arrow independent of M2 structure

ignore base removing H in M3

3

(b) (i) $CH_3CH_2\underline{CHO} + HCN \rightarrow CH_3CH_2CH(OH)CN$ **OR** $C_2H_5CH(OH)CN$

aldehyde must be –CHO brackets optional

1

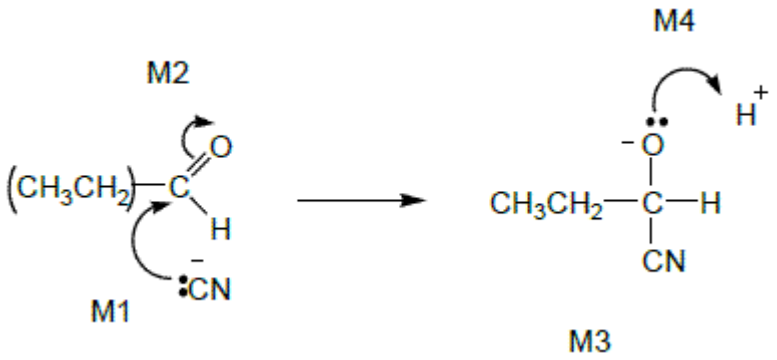
2-hydroxybutanenitrile **OR** 2-hydroxybutan<u>o</u>nitrile

no others

1

(ii) nucleophilic addition

1



M1 includes lp and arrow to Carbonyl C and minus charge (on either C or N)

Not allow M2 before M1, but allow M1 to C^+ after non-scoring carbonyl arrow

Ignore δ+, δ– on carbonyl group, but if wrong way round or full + charge on C lose M2

M3 for correct structure including minus sign. Allow C_2H_5

M4 for lp and curly arrow to H^+

4

(iii) (propanone) slower ***OR*** propanal faster

1

inductive effects of alkyl groups
OR
C of C=O less δ+ in propanone
OR
alkyl groups in ketone hinder attack
OR
easier to attack at end of chain

if wrong, no further marks

1

[18]

5

(a) CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride
OR $(CH_3CH_2CO)_2O$ OR propanoic anhydride
penalize contradiction in formula and name e.g. propyl chloride

could score in equation

1

$AlCl_3$ or $FeCl_3$ or names

could score in equation

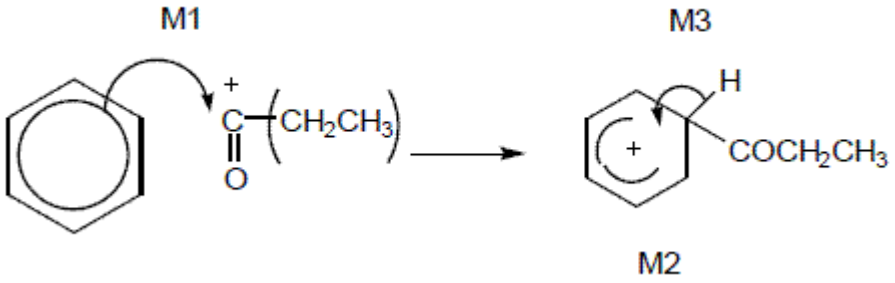
1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$
Allow RCOCl in equation but penalise above

allow + on C or O in equation

1

(b)



M1 arrow from circle or within it to C or to + on C

Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1

M3 arrow into hexagon unless Kekule

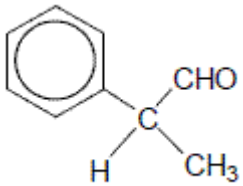
allow M3 arrow independent of M2 structure

Ignore base removing H in M3

3

(c) Tollens or ammoniacal silver nitrate

1



penalise wrong formula

1

[8]

6

Mark Range	The marking scheme for this part of the question includes an overall assessment for the Quality of Written Communication (QWC). There are no discrete marks for the assessment of QWC but the candidates' QWC in this answer will be one of the criteria used to assign a level and award the marks for this part of the question **Descriptor** an answer will be expected to meet most of the criteria in the level descriptor
4-5	– claims supported by an appropriate range of evidence – good use of information or ideas about chemistry, going beyond those given in the question – argument well structured with minimal repetition or irrelevant points – accurate and clear expression of ideas with only minor errors of grammar, punctuation and spelling
2-3	– claims partially supported by evidence – good use of information or ideas about chemistry given in the question but limited beyond this – the argument shows some attempt at structure – the ideas are expressed with reasonable clarity but with a few errors of grammar, punctuation and spelling
0-1	– valid points but not clearly linked to an argument structure – limited use of information or ideas about chemistry – unstructured – errors in spelling, punctuation and grammar or lack of fluency

(a) (i) M_r of $C_6H_5NH_2$ = 93 M_r of CH_3COCl = 78.5
total M_r of reagents = 264.5

1

$$\% \text{ atom economy} = \frac{M_r \text{ of wanted product}}{\text{total } M_r \text{ of all reagents}} \times 100 \text{ QWC}$$

1

$$= \frac{135}{264.5} \times 100 = 51.0\ \%$$

1

(ii) expected yield = $\frac{10}{93}$ × 0.5 × 135 = 7.26 kg

1

% yield = $\frac{5.38}{7.26}$ × 100 = 74.1 %

1

(iii) Although yield appears satisfactory (74%) % atom economy is only 51% QWC

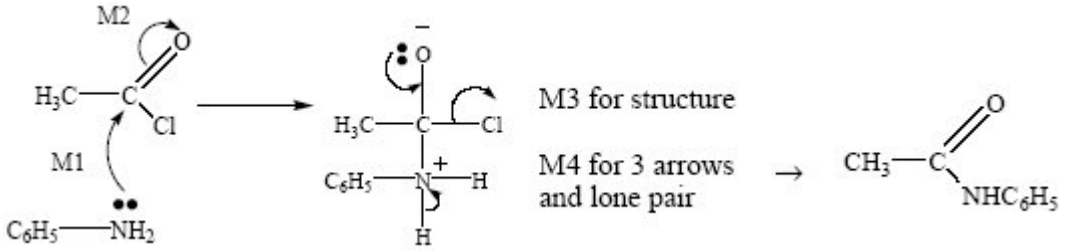
1

nearly half of the material produced is waste and must be disposed of QWC

1

(b) (nucleophilic) addition-elimination

1

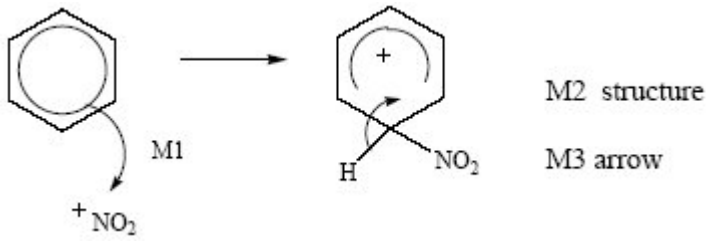


QWC (2)

4

(c) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

1



3

[16]