MEGA LECTURE

TOPIC 18 HW MS

1. (a) Cyclohexane evolves 120 kJ mol^{-1}

(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 / more (stated) stable **(1)***
Not award if mentions energy required for bond breaking

*due to delocalisation **(1)** or explained*

4

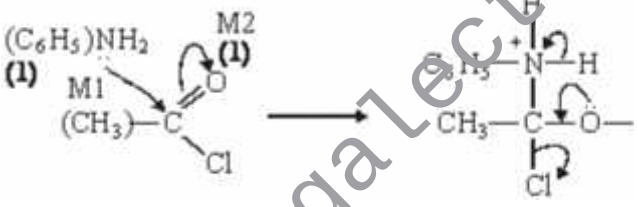
(b) (i) phenylamine weaker **(1)**

if wrong no marks

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

3

(ii) addition – elimination **(1)**



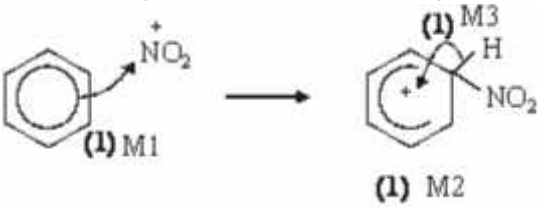
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)** →
conc H_2SO_4 **(1)**

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ **(1)**



6

(iv) peptide / amide **(1)**

1

NaOH (aq) **(1)**

HCl conc or dil or neither

H_2SO_4 dil NOT conc

NOT just H_2O

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 CH_3CO^+ 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
 alone loses M2

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

allow $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
ignore side chain in mechanism even if wrong
arrow for M1 must come from niside hexagon
arrow to NO_2^+ 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
H_2SO_4 dil or neither but not conc
not just H_2O

[21]

2. (a) (i) $C_6H_6 + CH_3CH_2COCl \xrightarrow{} C_6H_5COCH_2CH_3 + HCl$

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

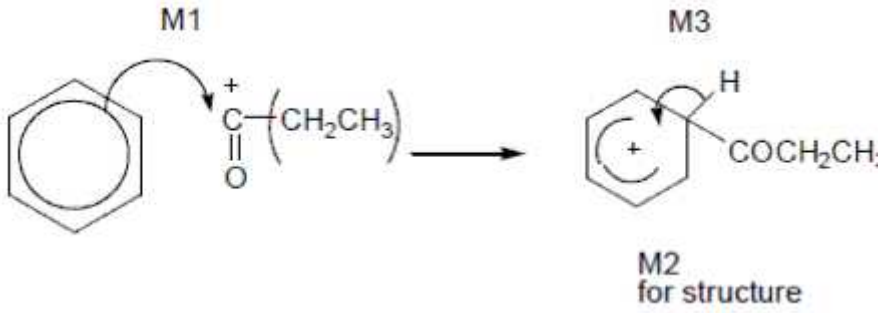
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

1

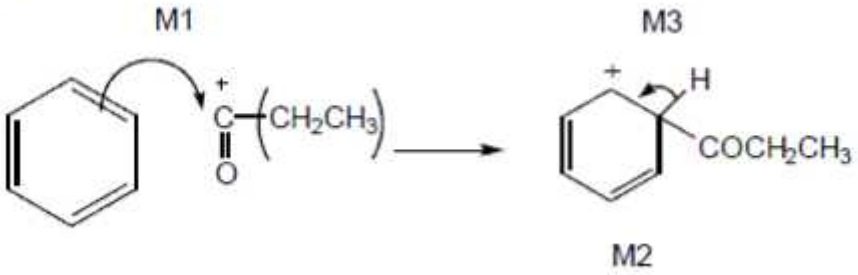
(ii) electrophilic substitution

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

[9]

3. (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

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

1

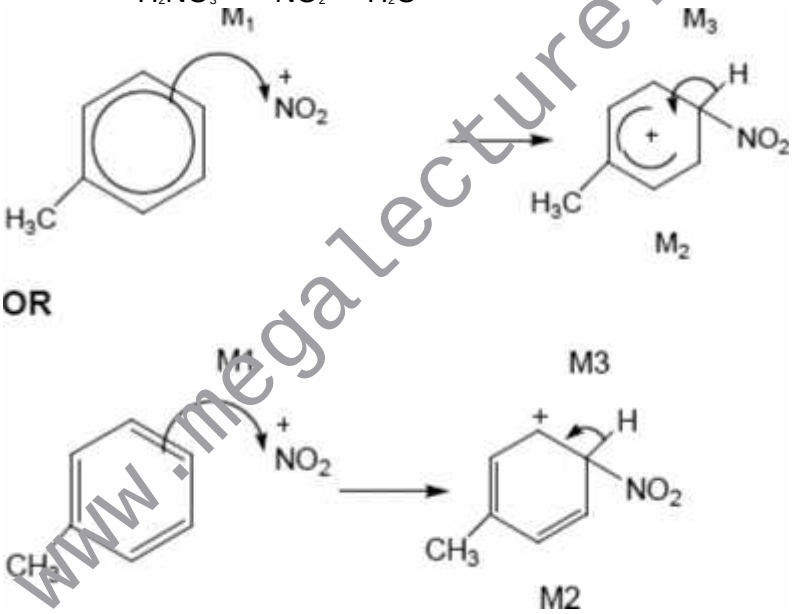
OR $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

OR via two equations

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

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$



(ii)

- *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) $2C_7H_5N_3O_6 \rightarrow 5H_2O + 3N_2 + 7C + 7CO$

Or halved

1

[7]

4. (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

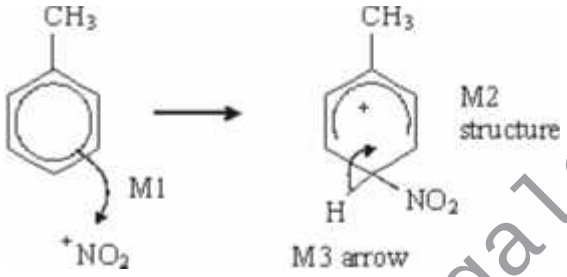
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

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

1

(ii) electrophilic substitution CH_3

1



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

3

(b) Sn or Fe / HCl (conc or dil or neither)
or Ni / H_2 not $NaBH_4$ $LiAlH_4$

1

(c) (i) NH_3

1

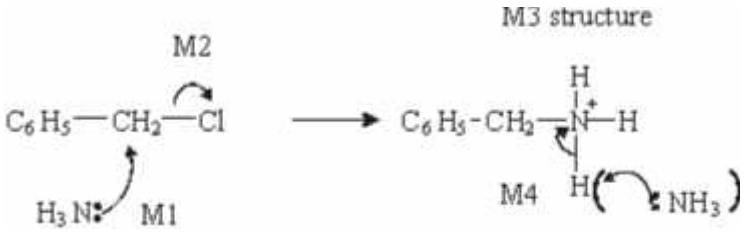
Use an excess of ammonia

1

(ii) nucleophilic substitution

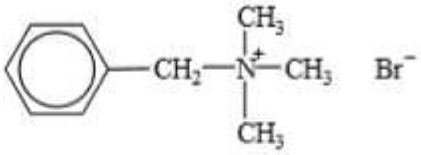
1

M3 structure

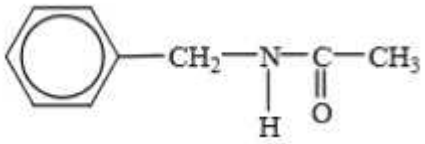


4

(d) lone pair on N less available (in correct context)
delocalised into the ring (Q of L)

(e) 

ignore Br^-
+ must be on N or outside a square bracket

(f) 

[19]

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

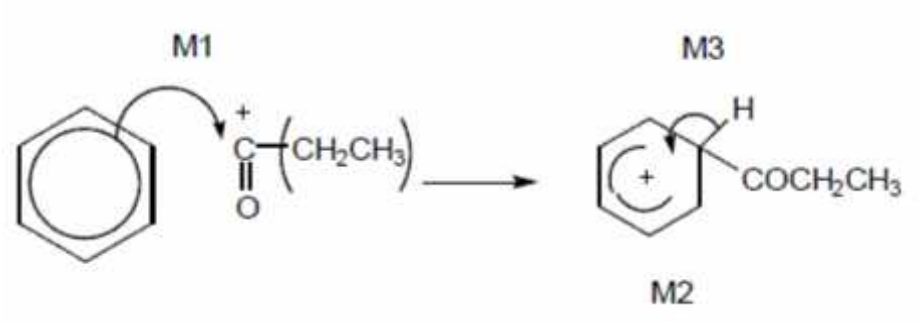
$AlCl_3$ or $FeCl_3$ or names
could score in equation

1

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

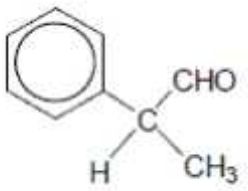
allow M3 arrow independent of M2 structure

Ignore base removing H in M3

3

(c) Tollens or ammoniacal silver nitrate

1



penalise wrong formula

1

[8]

6. (a) $CH_3COCl + AlCl_3 \rightarrow CH_3\overset{+}{C}O + \overset{-}{AlCl_4}$

(1) equation (1)

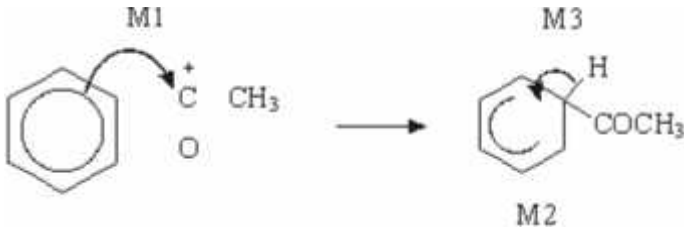
2

penalise wrong alkyl group once at first error
position of + on electrophile can be on O or C or outside [ ]
penalise wrong curly arrow in the equation or lone pair on $AlCl_3$ else ignore

Electrophilic substitution

NOT F/C acylation

1



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

M1 arrow from within hexagon to C or to + on C

M2 $\overset{+}{RCO}$

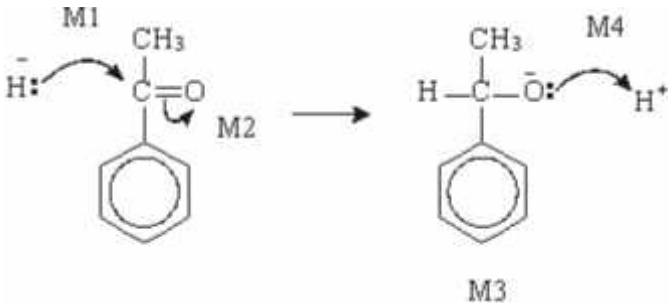
+ must be on C of

3

(b) Nucleophilic addition

NOT reduction

1



M2 not allowed independent, but can allow M1 for attack of H^- on C+ formed

4

1–phenylethan(–1–)ol or (1–hydroxyethyl)benzene

1

(c) dehydration or elimination

1

(conc) H_2SO_4 or (conc) H_3PO_4

allow dilute and Al_2O_3

Do not allow iron oxides

1

[14]

7. B

[1]

8. D

[1]