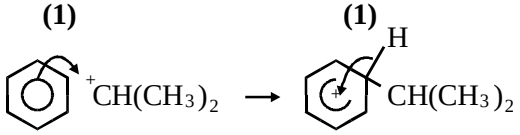
4.6, 4.7 TEST ms

1. (a) (i) $CH_3CH{=}CH_2 + HCl + AlCl_3 \rightarrow (CH_3)_2\overset{+}{C}H$ **(1)** $AlCl_4^-$ **(1)**

(ii) *Type of substitution* electrophilic <u>or</u> alkylation **(1)**

Mechanism

(1) **(1)**



(1) 6

(b) $CH_3CH_2\overset{+}{C}H_2$ <u>or</u> primary carbonium ion **(1)**
less stable <u>or</u> 1 & 2 inductive effects **(1)**
than $(CH_3)_2CH^+$ <u>or</u> secondary **(1)** 3

(c) $CH_3CHClCH_3$ **(1)** 1

[10]

2. (a) $\Delta H = -119.6 \times 3$ **(1)**
$= -358.8$ kJ mol^{-1} **(1)**

(b) benzene is more stable or of lower energy **(1)**
due to delocalisation **(1)** 4

[4]

3. (a) Lone pair on N **(1)**
accepts a proton **(1)** 2

(b) Lone pair less available **(1)**
due to delocalisation **(1)** 2

(c) (i) Nucleophilic substitution <u>or</u> alkylation **(1)**

(ii) *Compound 1* $(CH_3CH_2)_2NH$ **(1)**

Compound 2 $(CH_3CH_2)_3N$ **(1)**

Compound 3 $(CH_3CH_2)_4N^+Br^-$ 4

(d) *Equation* $CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$ **(1)**

Reason only one product formed **(1)** 2

[10]

4. (a) (i) cone HNO_3 1

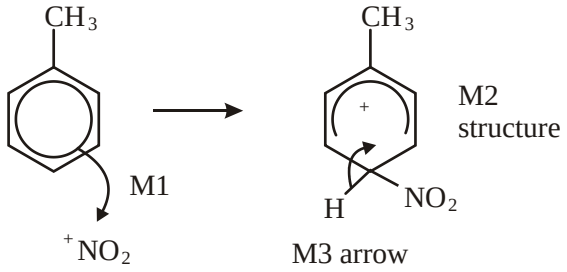
cone H_2SO_4 1

allow 1 for both acids if either cone missing

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

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

(ii) electrophilic substitution CH_3 1



3

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

+ must not be too close to Cl

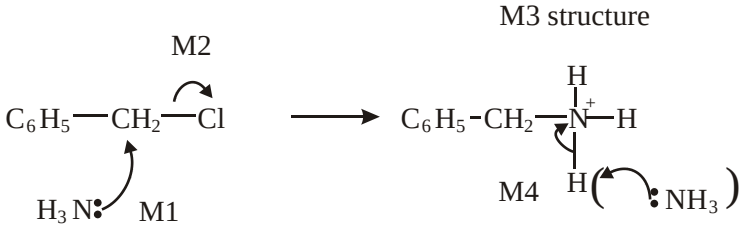
(b) Sn or Fe / HC1 (cone or dil or neither)

or Ni / H_2 not $NaBH_4$ $LiAlH_4$ 1

(c) (1) NH_3 1

Use an excess of ammonia 1

(ii) nucleophilic substitution 1

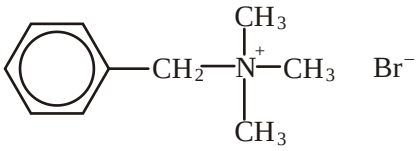


4

(d) lone pair on N less available (in correct context) 1

delocalised into the ring (Q of L) 1

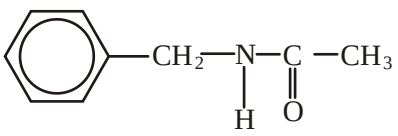
(e)



ignore Br

+ must be on N or outside a square bracket 1

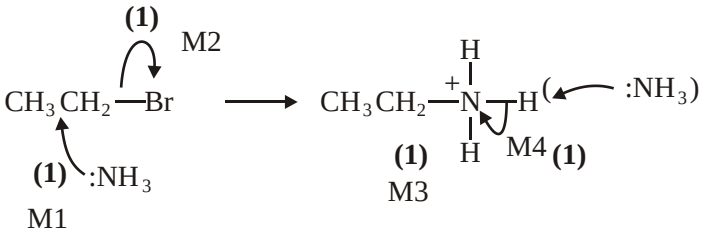
(f)



1

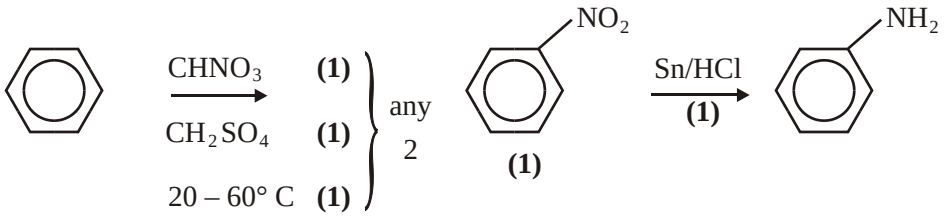
[19]

5. (a)



Further reaction / substitution / formation of II° / III° amines etc **(1)**
use an excess of NH_3 **(1)** 6

(b)  repels nucleophiles (such as NH_3) **(1)** 5



Notes

(a) allow SN1
penalise: Br^- intead of NH_3 removing H^+ for M4
not contamination with *other amines* (this is in the question) not diamines

(b) allow because NH_3 is a nuclephile or benzene is (only) attacked by electrophiles
or C–Br bond (in bromobenzene) is stronger / less polar or Br lp delocalized

HNO_3 / H_2SO_4 without either conc scores **(1)** allow 20 – 60° for **(1)** (any 2 ex 3)

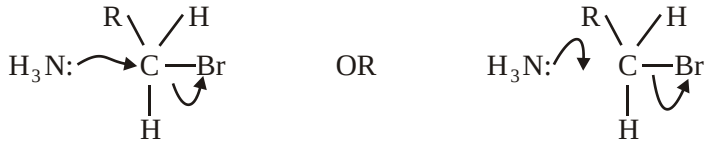
allow name or structure of nitrobenzene

other reducing agents: Fe or Sn with HCl (conc or dil or neither)
not conc H_2SO_4 or conc HNO_3
allow Ni/H_2
Not $NaBH_4$ or $LiAlH_4$
ignore wrong descriptions for reduction step e.g. hydrolysis or hydration

[11]

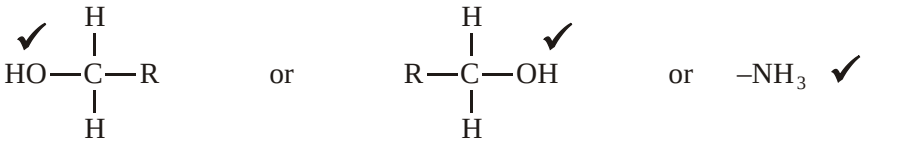
Organic points

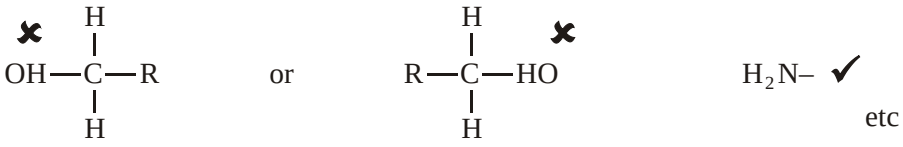
(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper





Penalise once per paper

allow CH_3– or –CH_3 or  or CH_3

or H_3C–