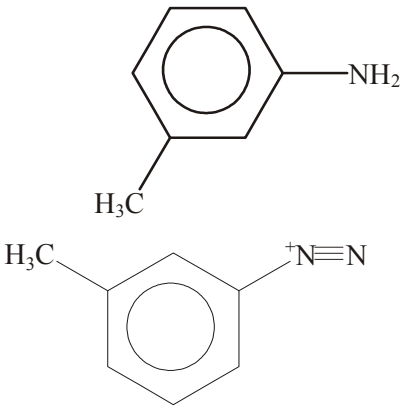
F324: Rings, Polymers and Analysis
4.1.4 Amines / 74

1.

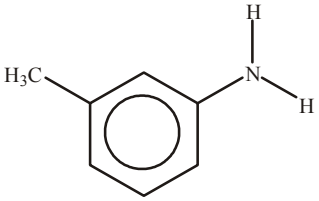


✓

✓

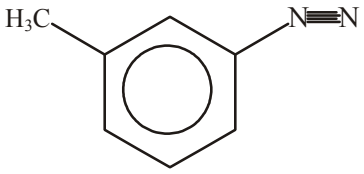
ALLOW ECF ✓✓ on incorrect amine

ALLOW



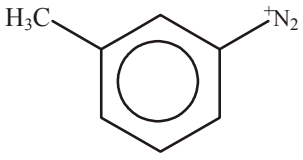
IGNORE *Cl^- ion*
DO NOT ALLOW *if ring is connected to the N triple bond in the diazonium or if diazonium has a negative charge*
ALLOW *one mark for correct displayed diazonium if alkyl group is not shown*

ALLOW



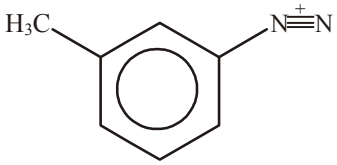
for both marks

ALLOW



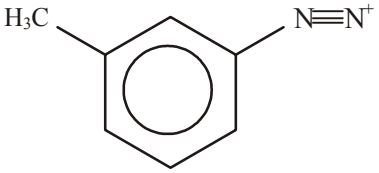
for one mark

ALLOW



for one mark

ALLOW



for one mark

HNO_2 + HCl and temp < 10 °C **OR** $NaNO_2$ + HCl and temp < 10 °C ✓

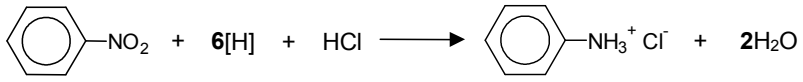
alkaline **AND** phenol (if temperature stated must be below 10 °C) ✓

ALLOW *NaOH* ***OR*** *KOH &* C_6H_5OH ***OR*** *phenoxide ion* ***OR*** $C_6H_5O^-$

ALLOW *reagents and conditions from the equations*

[5]

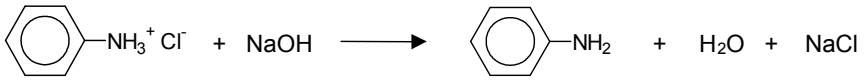
2. (a) (i)



H_2O as product **(1)** balancing **(1)** 2

(ii) reducing agent **(1)** 1

(b)



(or as the ionic equation without Na^+ or Cl^-)

$C_6H_5NH_2$ **(1)** balanced **(1)** 2

(c) moles $C_6H_5NO_2$ used = **0.0300** (mol) **(1)**

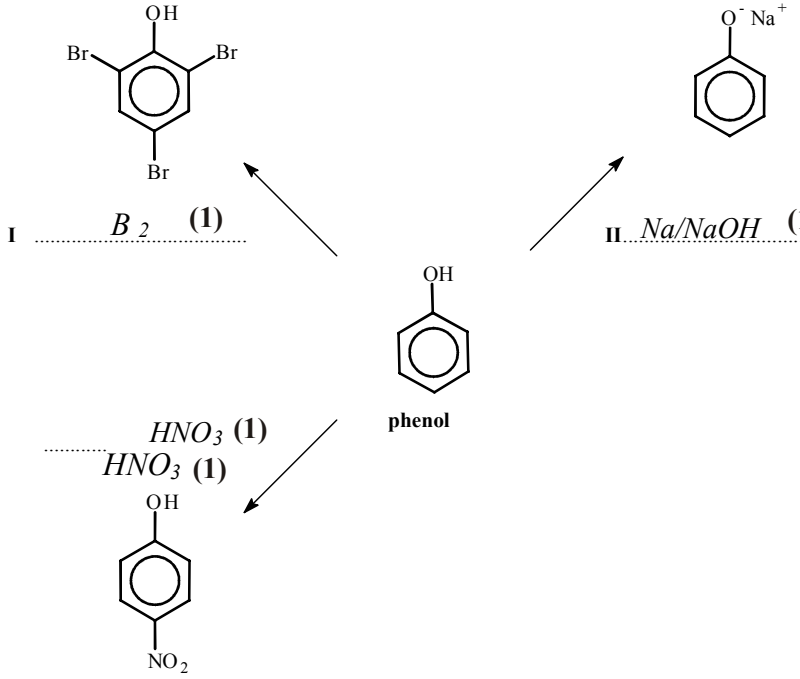
theoretical yield of $C_6H_5NH_2$ = **2.79(3)** (g) **(1)** or ecf

actual 72.1% yield = **2.014** (g) / (calculator value 2.013753) **(1)** or ecf

to three sig figs = **2.01** (g) **(1)** or ecf 4

[9]

3. (i)



(do not allow a halogen carrier with the bromine)

(do not penalise use of a nitrating mixture)

3

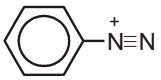
(ii) dye / colouring / indicator **(1)** 1

(iii) phenylamine **(1)**
$NaNO_2$ / HNO_2 **(1)** + HCl **(1)**
< 10°C **(1)**
add to alkaline phenol **(1)** 5

[9]

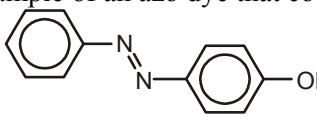
4. sodium nitrite + HC*l* / nitrous acid **(1)**

<10°C **(1)**

 **(1)**

phenol/named example (added to the products from above) **AW (1)**
alkaline conditions / OH^- **(1)**

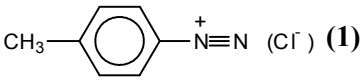
example of an azo dye that could be formed from phenylamine,

eg  **(1)** 6

[6]

5. (i) nitrous acid / HNO_2 1

(ii)

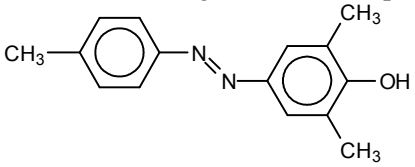


(1) 1

(iii) diazonium (ion /salt) **(1)** 1

(iv) to prevent decomposition / it reacting (diazonium ion) is unstable **AW** 1

(v) structure showing the amine coupled to the phenol or its salt – e.g.



–N=N– **(1)** rest of structure (joined by two nitrogens) **(1)** 2

[6]

6. **methylation stage (can come anywhere)**
CH_3Cl / CH_3Br **(1)**
$AlCl_3$ / $FeBr_3$ etc. **(1)**
equation – e.g. $C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$ **(1)**
intermediate name or unambiguous structure **(1)**
4 marks

intermediates and equations will vary if methylation is done after nitration or reduction

nitration stage
(conc) H_2SO_4 **(1)**
(conc) HNO_3 **(1)**
equation – e.g.: $C_6H_5CH_3 + HNO_3 \rightarrow C_6H_4(CH_3)NO_2 + H_2O$ **(1)**
intermediate – name or unambiguous structure **(1)**
4 marks

reduction stage
tin/iron **(1)**
HC*l* **(1)**
equation – e.g.: $C_6H_4(CH_3)NO_2 + 6[H] \rightarrow C_6H_4(CH_3)NH_2 + 2H_2O$
or with H^+ also on left to give $C_6H_4(CH_3)NH_3^+$ **(1)**
3 marks

allow other suitable reducing agents:

Quality of Written Communication mark for a well organised answer with the three stages clearly distinguished and sequenced **(1)**
1 mark 12

[12]

7. (a) 1st stage
aromatic amine / named aromatic amine / structure **(1)**
sodium nitrite / nitrous acid **(1)**
HC*l*/H_2SO_4 (but not conc) /H^+ **(1)**
at <10°C **(1)**

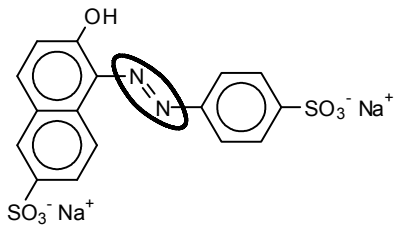
which forms a diazonium salt / ion **(1)**

if more than four are given, mark any wrong reagents, conditions first

2nd stage
the product from the first stage mixed with the phenol AW **(1)**
(in excess) hydroxide / alkali **(1)** 7

allow correct formulae for the reagents

(b) (i)



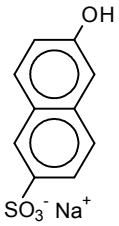
(1) 1

allow any benzene rings as well as N=N circled, as long as no other groups are

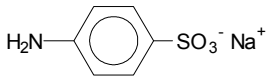
(ii) …16… carbon and ……10….. hydrogen atoms
(1) **(1)** 2

(c) Na / NaOH / OH^- etc **(1)** 1

(d)



(1)



(1) 2

allow 1 mark if they are both correct, but in the wrong boxes

only penalise a slip with SO_3^- Na^+ once

8. (a) (i) Diamino **[13]**

two/2 amine groups **(1)**

1,4

their position on the ring / numbering of carbons around ring (or shown on a diagram) **(1)** 2

(b) (i) reduction / redox **(1)** 1

(ii) tin and HC*l* **(1)**

conc acid under reflux **(1)** 2

or H_2 gas + Ni/Pd catalyst

(iii)

H_2O as product **(1)**

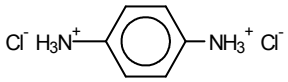
and the equation balanced **(1)** 2

(c) (i) accepts H^+ using the lone pair (on N) **(1)**

which is donated/forms a (dative) covalent bond **(1)** 2

either mark can be obtained with a good diagram

(ii)



correct structure with charges shown **(1)(1)**

one mark for either: just one neutralised,

both neutralised, but without Cl^-,

both neutralised, but no charges shown 2

(iii) hexane-1,6-diamine is a stronger base because:

electrons move towards the N (due to the inductive effect) (in hexane-1,6-diamine) **(1)**

the lone pair from N is (partially) delocalised around the ring (in diaminobenzene) **(1)**

so the electron pair is more easily donated / H^+ more easily accepted (in hexane-1,6 diamine) **ora (1)** 3

[14]