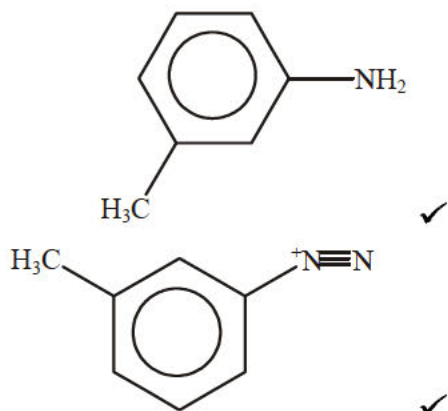


F324: Rings, Polymers and Analysis

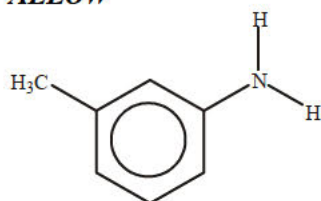
4.1.4 Amines / 74

1.



ALLOW ECF ✓✓ on incorrect amine

ALLOW

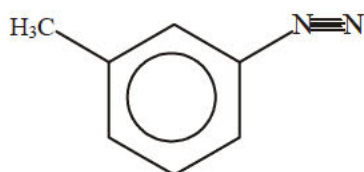


IGNORE Cl^- ion

DO NOT ALLOW if ring is connected to the N triple bond in the diazonium or if diazonium has a negative charge

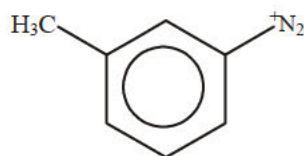
ALLOW one mark for correct displayed diazonium if alkyl group is not shown

ALLOW



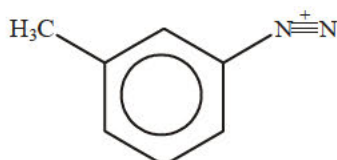
for both marks

ALLOW



for one mark

ALLOW



for one mark

ALLOW



for one mark

$\text{HNO}_2 + \text{HCl}$ and temp $< 10^\circ\text{C}$ **OR** $\text{NaNO}_2 + \text{HCl}$ and temp $< 10^\circ\text{C}$ ✓

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

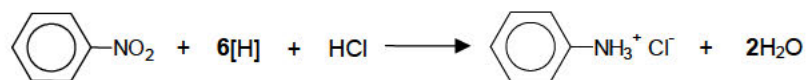
ALLOW NaOH **OR** KOH & $\text{C}_6\text{H}_5\text{OH}$ **OR** phenoxide ion **OR**

$\text{C}_6\text{H}_5\text{O}^-$

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^-)

$\text{C}_6\text{H}_5\text{NH}_2$ (1) balanced (1)

2

(c) moles $\text{C}_6\text{H}_5\text{NO}_2$ used = 0.0300 (mol) (1)

theoretical yield of $\text{C}_6\text{H}_5\text{NH}_2$ = 2.79(3) (g) (1) or ecf

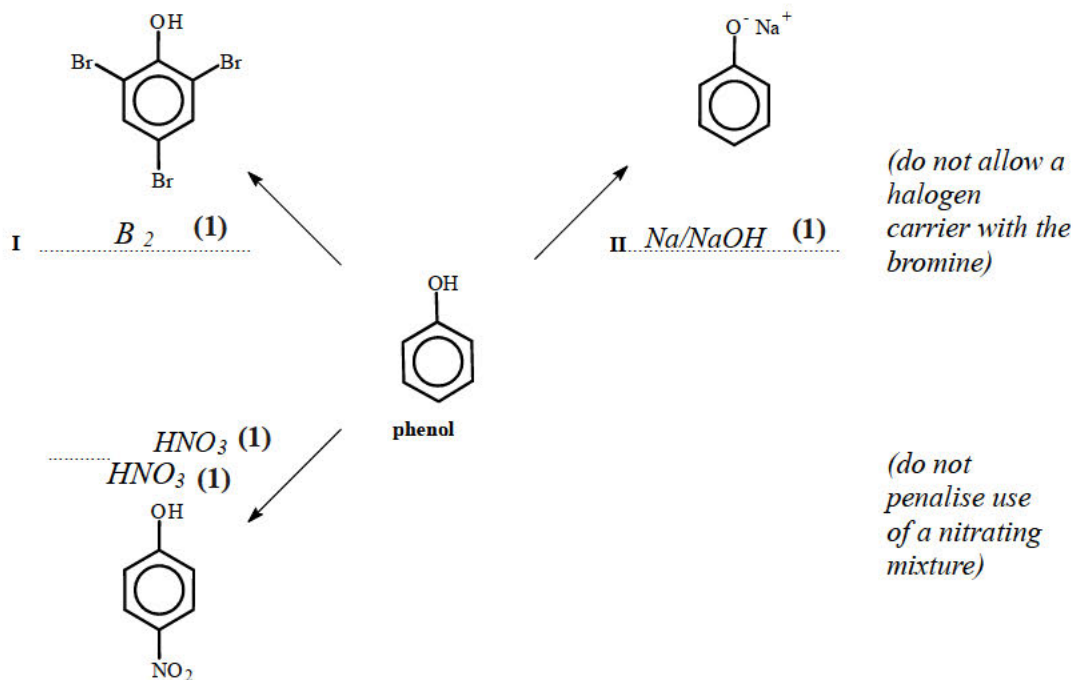
actual 72.1% yield = 2.014 (g) / (calculator value 2.013753) (1) or ecf

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

4

[9]

3. (i)



3

(ii) dye / colouring / indicator (1)

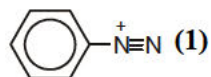
1

(iii) phenylamine (1)
 $NaNO_2 / HNO_2$ (1) + HCl (1)
 $< 10^\circ C$ (1)
 add to alkaline phenol (1)

5

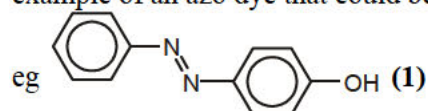
[9]

4. sodium nitrite + HCl / nitrous acid (1)
 $< 10^\circ C$ (1)



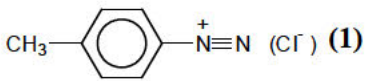
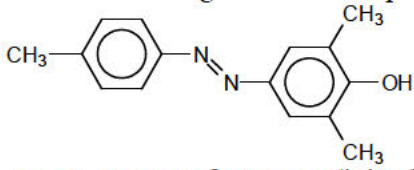
phenol/named example (added to the products from above) AW (1)
 alkaline conditions / OH^- (1)

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



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.
- 
- $-\text{N}=\text{N}-$ (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. $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$ (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.: $\text{C}_6\text{H}_5\text{CH}_3 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2 + \text{H}_2\text{O}$ (1)

intermediate – name or unambiguous structure (1)

4 marks

reduction stage

tin/iron (1)

HCl (1)

equation – e.g.: $\text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2 + 6[\text{H}] \rightarrow \text{C}_6\text{H}_4(\text{CH}_3)\text{NH}_2 + 2\text{H}_2\text{O}$

or with H^+ also on left to give $\text{C}_6\text{H}_4(\text{CH}_3)\text{NH}_3^+$ (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)

HCl/H₂SO₄ (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

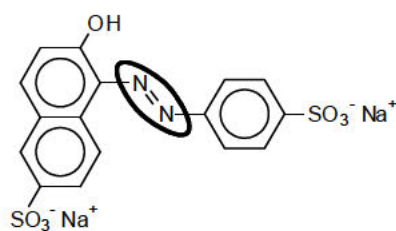
the product from the first stage mixed with the phenol AW (1)

(in excess) hydroxide / alkali (1)

allow correct formulae for the reagents

7

(b) (i)



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)

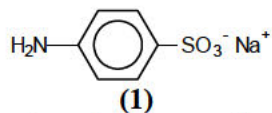
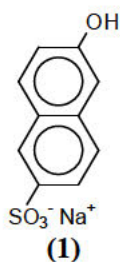
(1)

2

(c) Na / NaOH / OH⁻ etc (1)

1

(d)



2

*allow 1 mark if they are both correct, but in the wrong boxes
only penalise a slip with $\text{SO}_3^- \text{Na}^+$ once*

[13]

8. (a) (i) Diamino
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)

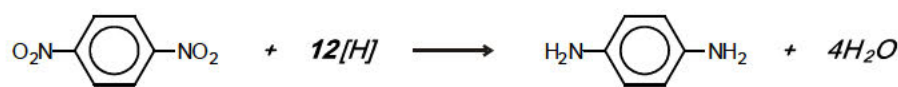
1

- (ii) tin and HCl (1)
conc acid under reflux (1)

2

or H_2 gas + Ni/Pd catalyst

(iii)



H_2O as product (1)

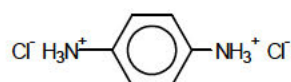
and the equation balanced (1)

2

- (c) (i) accepts H^+ using the lone pair (on N) (1)
which is donated/forms a (dative) covalent bond (1)
either mark can be obtained with a good diagram

2

(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]