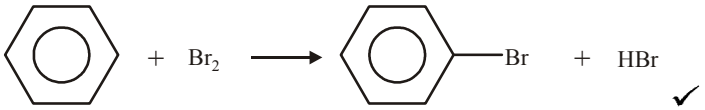
F324: Rings, Polymers and Analysis
4.1.1. Arenes Mark Scheme /114

1. (a)



✓

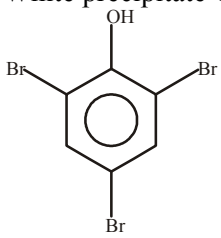
ALLOW $C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$

DO NOT ALLOW *multiple substitution*

DO NOT ALLOW Br^+

1

(b) (i) White precipitate **OR** white solid **OR** white crystals ✓



DO NOT ALLOW *colourless*

DO NOT ALLOW *white ppt <u>and</u> bubbles*

DO NOT ALLOW
$Br_3C_6H_2OH$ ***OR*** *2,4,6-tribromophenol* ***OR*** *tribromophenol*

2

(ii) 1,2-Dibromocyclohexane ✓

ALLOW *1,2dibromocyclohexane* ***OR*** *1-2dibromocyclohexane* ***OR*** *12dibromocyclohexane* ***OR*** *cyclo-1,2-dibromohexane*

DO NOT ALLOW *dibromocyclohexane* ***OR*** $C_6H_{10}Br_2$ ***OR*** *structures*

1

(iii) **MUST** spell delocalised/delocalized or localised/localized correctly once in the answer to obtain all 5 marks

benzene electrons or π-bonds are delocalised ✓

__ALLOW__ diagram to show overlap of all 6 p-orbitals for delocalisation
__DO NOT ALLOW__ benzene has delocalised structure or ring

phenol a lone or non-bonded pair of electrons on the oxygen or the OH group is (partially) delocalised into the ring ✓

__ALLOW__ diagram to show movement of lone pair into ring for phenol

cyclohexene electrons are localised **OR** delocalised between two carbons ✓

__ALLOW__ diagram or description of overlap of 2 adjacent p-orbitals for bonding in cyclohexene
__DO NOT ALLOW__ cyclohexene has a C=C double bond
__IGNORE__ slip if cyclohexene is written as cyclohexane but π-bonding correctly described

benzene has a lower **electron density OR** phenol has a higher electron density **OR** cyclohexene has a higher electron density ✓

*__DO NOT ALLOW__ charge density **OR** electronegativity instead of electron density*

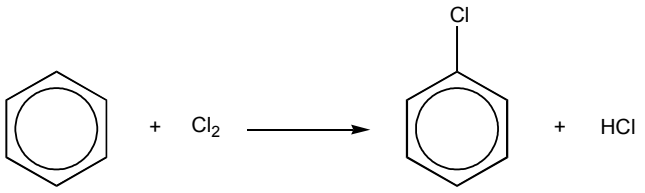
benzene cannot **polarise** or induce a dipole in Br_2 **OR** phenol can polarise the Br_2 **OR** cyclohexene can polarise Br_2 or the Br–Br bond ✓

*__ALLOW__ $Br^{\delta+}$ **OR** electrophile Br^+ as alternate to polarise*

5

[9]

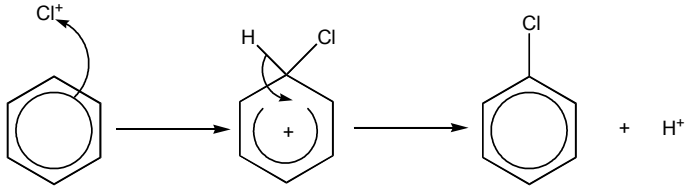
2. (a) (i)



(1) 1

(ii) Introduces a permanent dipole on Cl_2 / forms Cl^+/
$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$/
$AlCl_3 + Cl_2 \rightarrow Cl^{\delta+} - AlCl_3^{\delta-}$ **(1)** 1

(iii)



correct dipole / Cl^+ **(1)**
curly arrow from benzene ring to Cl^+ / $Cl^{\delta+}$ **(1)**
intermediate **(1)**
curly arrow from H to regenerate benzene ring in intermediate **(1)**
H^+ as other product **(1)** 4

(iv) electrophilic substitution **(1)**
with electrophilic spelt correctly 1

(b) In benzene, π electrons are delocalised/spread out **(1)**
In alkenes, π electrons are concentrated between 2 carbons **(1)**
Electrophiles attracted more to greater electron density in alkenes **(1)** 3

[10]

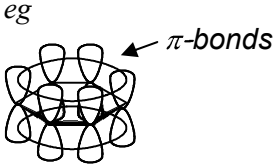
3. Discussion of the π-bonding

p-orbitals overlap **(1)**

above and below the ring **(1)**

(to form) π-bonds / orbitals **(1)**

any of the first three marks are available from a labelled diagram
eg



(π-bonds / electrons) are <u>delocalised</u> **(1)**

***4** marks*

Other valid points – any two of:

- ring is planar /
- C-C bonds are equal length / have intermediate length/strength between C=C and C-C /
- σ-bonds are between C-C and/or C-H
- bond angles are 120°

*MAX 2 out of 4 marks **(1)(1)***

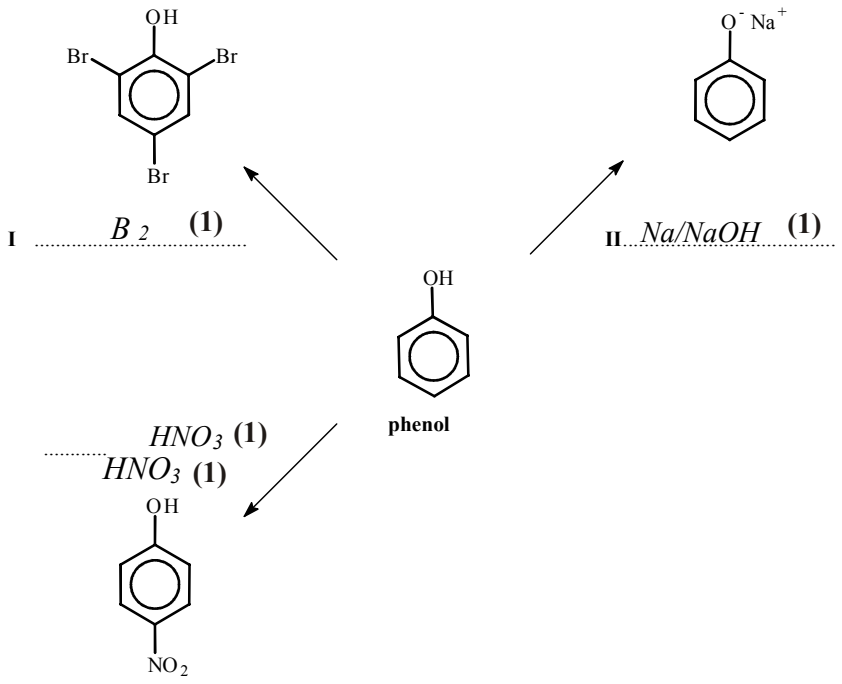
6

Quality of written communication
two or more sentences with correct spelling, punctuation and grammar

1

[7]

4. (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]

5. **bonding in benzene**
overlap of p-orbitals / π bonds/electrons (or labelled) **(1)**

above and below the ring (or shown in a diagram) **(1)**
electrons are <u>delocalised</u> (or labelled) **(1)**
C–C bonds are: same length/strength / in between single and double / σ-bonded **AW (1)**

greater reactivity of phenol
(the ring is activated because …)
<u>lone</u> pair from O is delocalised into the ring **(1)**
so electron density (of the ring) is increased **(1)**
so electrophiles are more attracted (to the ring) / dipole in electrophile more easily induced **(1)**
*(**NOT** just more easily "attacked" or "susceptible")*

Quality of written communication mark for at least two complete sentences in which the meaning is clear with correct spelling, punctuation and grammar **(1)** 8

[8]

6. (a) Correct structure of 3-nitrophenol or any multiple nitrated phenol **(1)** 1

(b) M_r phenol (C_6H_6O) = 94.0 **(1)**

M_r 4-nitrophenol ($C_6H_5NO_3$) = 139.0 **(1)**

expected mass/moles of nitrophenol from 100 g = 148 g/1.06 mol (or ecf from wrong M_rs) **(1)**

at 27% yield gives 40 / 39.9 (g) (or ecf) **(1)** 4
last mark is for 0.27 × expected mass to 2 or 3 sf

(c) **conditions for nitration of benzene:**
HNO_3 is concentrated **(1)**

conc H_2SO_4 is present **(1)**

heating or stated temp above 50°C **(1)** 3

explanation for greater reactivity of phenol
lone <u>pair</u> from O atom is delocalised into the ring **(1)**

greater (π) electron density around the ring **(1)**

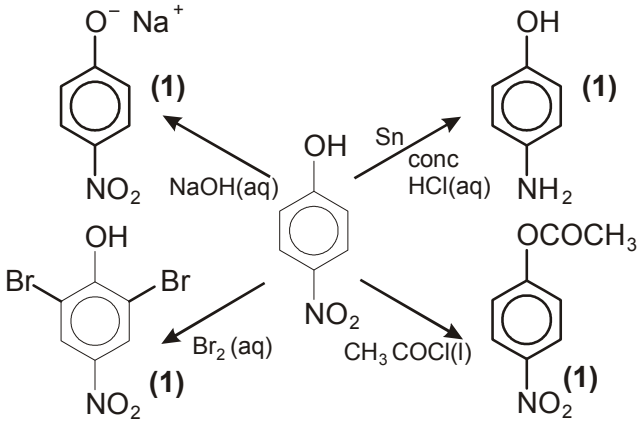
(the benzene ring in phenol) is <u>activated</u> **(1)**

attracts electrophiles/$^{+}NO_2$ more / makes it more susceptible to electrophiles **AW (1)** 4

quality of Written Communication mark for at least two legible sentences with correct spelling, punctuation and grammar 1

[13]

7.



4

allow bromination in any positions on the ring

[4]

8. **delocalised electrons**
electrons are spread over more than two atoms **AW (1)**

π-bond
formed by overlap of p-orbitals/ diagram to show **(1)** 2

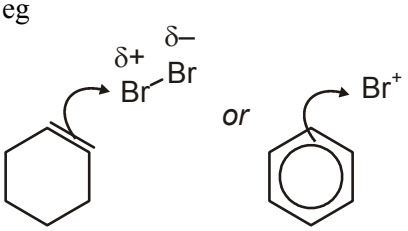
[2]

9. (a) (i) **bromine as an electrophile**
an electrophile accepts an electron pair **(1)**
***NOT** a lone pair*

bromine is polarised/has + charge (centre)/dipole on Br-Br/Br^+
shown in diagram **(1)**

appropriate diagram showning a curly arrow from a double/
π bond to the $Br^{\delta+}$/Br^+ **(1)**

eg



3

(ii) **comparison of reactivity of cyclohexene and benzene**
benzene is (more) stable / more energy required **(1)**

benzene (π) electrons are delocalised **(1)**

benzene has lower electron/- charge density **(1)**

so bromine is less polarised /attracted to it /
benzene is less susceptible to electrophiles **(1)**

ora for cyclohexene 4

quality of written communication mark for any **two** of the the terms:

delocalised/localised, π-electrons/bonds/system, electron density,
dative covalent, activation/stabilisation energy, halogen carrier,
heterlytic fission, addition/substitution, polarity used appropriately **(1)** 1

(b) (i) iodobenzene because …

Br is more electronegative than I **(1) ora**

so the I atom will be positive /δ^+ /the electrophile **(1)** 2

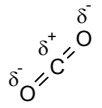
(ii) $C_6H_6 + IBr \rightarrow C_6H_5I + HBr$ **(1)**
or ecf giving $C_6H_5Br + HI$ 1

[11]

10. (a) (i) NaOH / Na **(1)** 1

(ii) $C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$ /
$C_6H_5OH + Na \rightarrow C_6H_5O^-Na^+ + ½H_2$ **(1)** 1

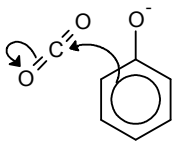
(b) (i)



(1) 1

allow a dipole on just one C=O bond

(ii)



(1)(1) 2

(iii) lone/electron pair from oxygen is delocalised into the ring /interacts with π-electrons **(1)**

increases π-electron density / negative charge (around the ring) **(1)**

attracts electrophiles more **(1)** 3

(c) M_r salicylic acid = 138 **(1)**

moles (in 1:1 reaction) = 3500 x 10^6/138 = 2.536 x 10^7 **(1)**

mass of phenol needed = 2.536 × 10^7 × 94 = 2384 tonnes **(1)**

allowing for 45% yield = 2384 × $^{100}/_{45}$ = **5298/5300** (tonnes) **(1)** 4

allow 5297.5–5300

allow ecf throughout

[12]

11. 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]

12. (a) any two of …
fibres / dyes / explosives / pharmaceuticals etc **(1)(1)** 2
*allow any specific examples as long as they do involve aromatic nitro or amine groups – eg **NOT** nylon, fertiliser etc*

(b) temp 50-60° **(1)**
concentrated (acids) **(1)** 2
allow abbreviations for concentrated

(c) $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
reactants **(1)** products **(1)** 2
allow a balanced equation for multiple nitration at any positions

(d) (i) a pair of electrons … **(1)**
… (electrons) move / transferred /
a (covalent) bond breaks/forms **(1)** 2

(ii) it accepts a pair of electrons (from the benzene) **(1)** 1
***NOT** a 'lone' pair*

(iii) $H(^+)$ (on the ring) is replaced by $NO_2(^+)$ **(1)** 1
allow 'substitutes'
ignore + charges

(iv) it is not used up / reformed at the end **AW (1)** 1

(e) π-bonding electrons are <u>delocalised</u> **(1)**

six π-electrons in benzene **(1)**
four π-electrons in the intermediate **(1)**

π-electrons are not over one carbon atom /
over **five** carbon atoms / p-orbitals in the intermediate **(1)**
this must be stated in words to compare benzene and the intermediate

π-electrons are over the **complete** ring / **all around** the ring
all six carbon atoms/ p-orbitals overlapping **(1)**

Quality of written communication
for at least two sentences/statements with legible text and
correct spelling, punctuation and grammar **(1)** 6

[17]