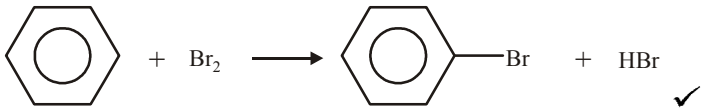
# F324: Rings, Polymers and Analysis
# 4.1.1. Arenes Mark Scheme /114

**1.** (a)




✓

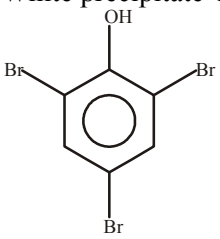
***ALLOW*** $C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$

***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*

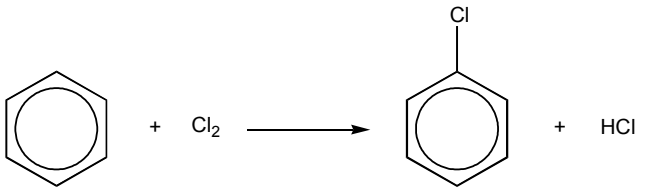
benzene cannot **polarise** or induce a dipole in $Br_2$ **OR** phenol can polarise the $Br_2$ **OR** cyclohexene can polarise $Br_2$ or the Br–Br bond ✓

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

**5**

**[9]**

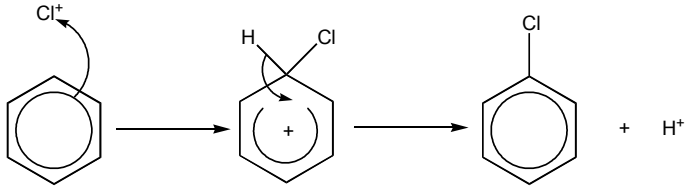
**2.** (a) (i)




**(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]**

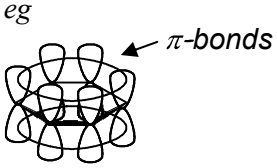
**3. Discussion of the π-bonding**

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:**

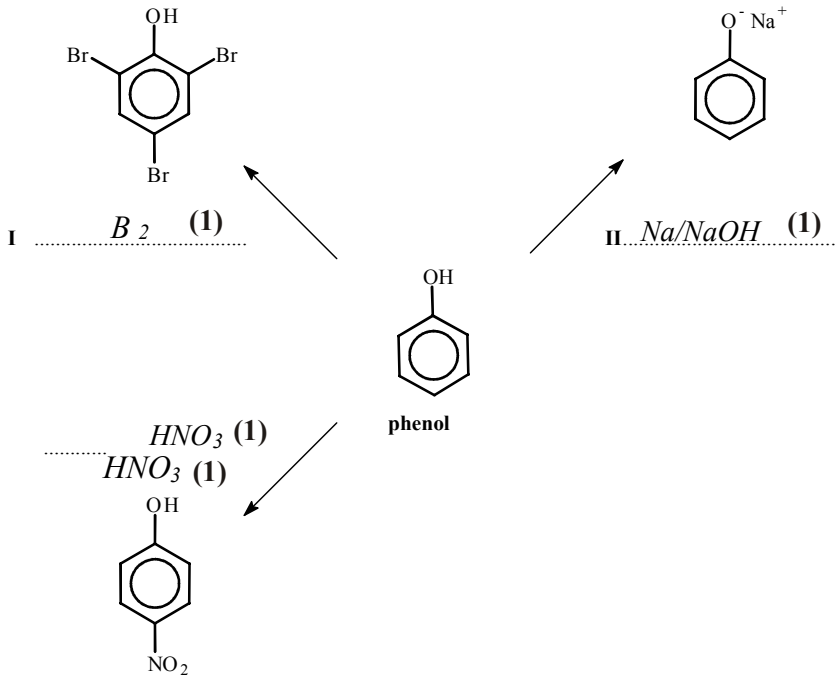
- ring is planar /
- C-C bonds are equal length / have intermediate length/strength between C=C and C-C /
- σ-bonds are between C-C and/or C-H
- bond angles are 120° 6

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

**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 $M_r$s) **(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)**

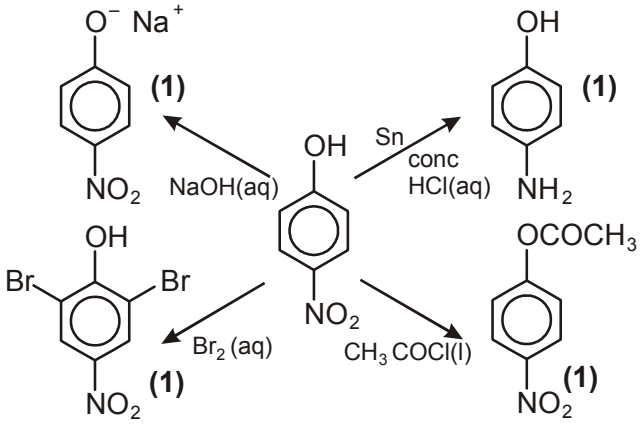
(the benzene ring in phenol) is <u>activated</u> **(1)**

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

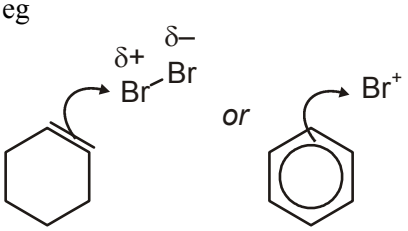
**[2]**

**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 /$\delta^+$ /the electrophile **(1)** 2

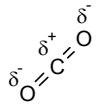
(ii) $C_6H_6 + IBr \rightarrow C_6H_5I + HBr$ **(1)**
or ecf giving $C_6H_5Br + HI$ 1

**[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

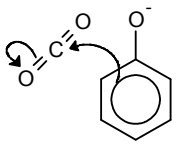
(b) (i)



**(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]**