RAFFLES INSTITUTION H2 CHEMISTRY
2011 YEAR 6 PRELIMINARY EXAMINATION
PAPER 3 SUGGESTED SOLUTIONS

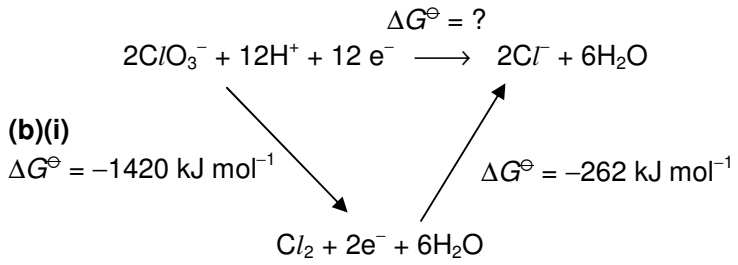
1 (a) (i) Cold: $Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$
Hot: $3Cl_2(g) + 6OH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

(ii) $F_2(g)$ is highly oxidizing and will react with water (violently) to give $O_2(g)$.

(b) (i) $2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$
$\Delta G^\ominus = -(10)(1.47)(96500) = -1418.6$
$= \mathbf{-1420\ kJ\ mol^{-1}}$

(ii) ① $2ClO_3^- + 12H^+ + 12\ e^- \longrightarrow 2Cl^- + 6H_2O$

②



Applying Hess Law,

$\Delta G^\ominus = -1420 + (-262) = \mathbf{-1682\ kJ\ mol^{-1}}$

$E^\ominus = -[-1682 \times 10^3 / (12 \times 96500)] = \mathbf{+1.45\ V}$ (shown)

(iii) Using Latimer diagram: $E^\ominus_{cell} = +1.45 - (+1.19) = \mathbf{+0.26\ V}$

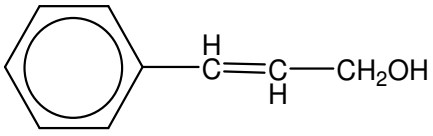
Amount of electrons transferred = 6 mol
$\Delta G^\ominus = -(6)(96500)(+0.26) = \mathbf{-150\ kJ\ mol^{-1}}$

(c) (i) **A** : $Cl_2 = 6.7/134 : 1.2/24 = 0.05 : 0.05 = 1 : 1$
1 mol of **A** undergoes electrophilic addition with 1 mol of chlorine gas
➔ **A** contains 1 alkene functional group (or C=C)

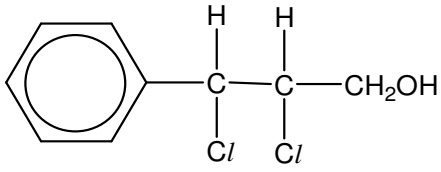
Compound **A** undergoes nucleophilic substitution with PCl_5 to give white fumes of HCl
➔ **A** is an alcohol (cannot be carboxylic acid, not enough O)
NaBr + conc. H_2SO_4 → HBr
➔ **A** undergoes both electrophilic addition **and** nucleophilic substitution to give **C** and **D**.

Since **C** and **D** each only contains 1 chiral centre,

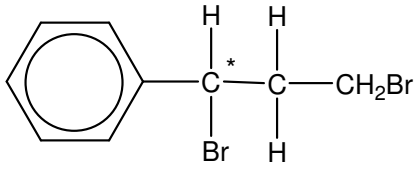
A can only be



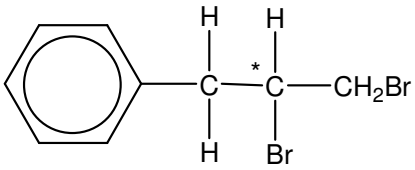
B:



C and **D**:



major

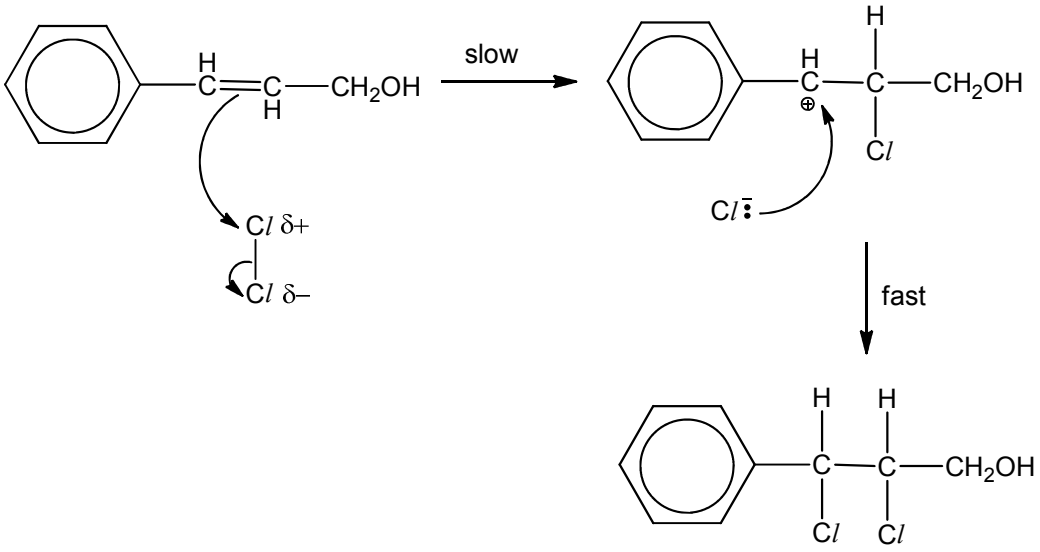


minor

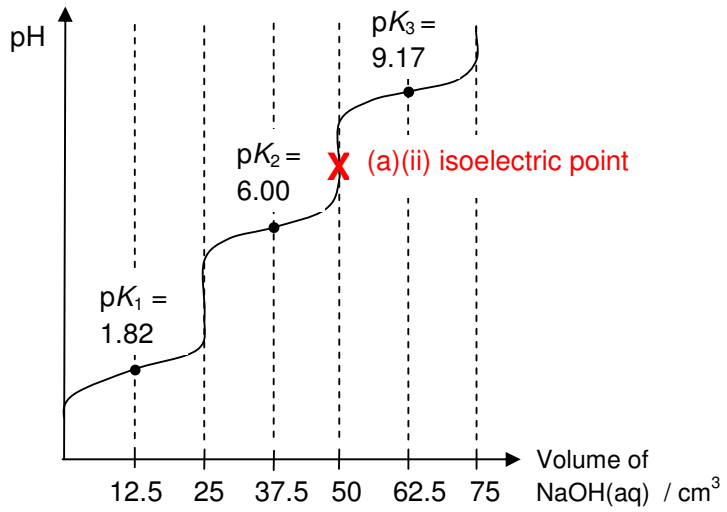
(ii) Compound **C** is the major product while **D** is the minor product.

This is because benzylic carbocation intermediate is more stable due to resonance / positive charge dispersed into the benzene ring.

(iii) Name of mechanism: Electrophilic Addition

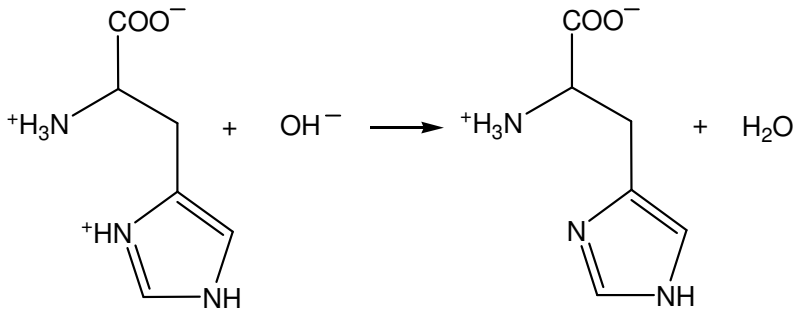


2 (a) (i)



(ii) Mark **X** at 50 cm^3

(iii)



(iv) <u>Before addition of HC*l*:</u>

Amount of histidine present = 0.100 dm^3 x 0.1 mol dm^{-3} = 0.01 mol

pH = pK_2 + lg [A$^-$]/[HA]
6 = 6.00 + lg [A$^-$]/[HA]
lg [A$^-$]/[HA] = 0
[A$^-$]/[HA] = 1

Amount of HA = amount of A$^-$ = 0.01/2 = **<u>0.005 mol</u>**

<u>On addition of HC*l*:</u>

Amount of H$^+$ added = 1 dm^3 x 0.001 mol dm^{-3} = 0.001 mol

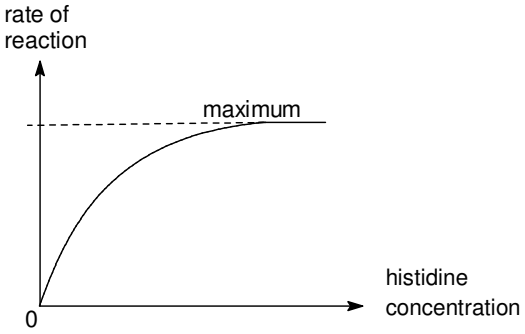
	HA	⇌	H$^+$(aq)	+	A$^-$(aq)
Before adding HC*l*	0.005				0.005
H$^+$ added			+0.001		
After adding HC*l*	0.005 + 0.001 = 0.006				0.005 – 0.001 = 0.004

pH = pK_2 + lg $[A^-]/[HA]$
= 6.00 + lg (0.004/0.006)
= **5.82**

(b) **(i)** sp^2

more s character / lone pair more strongly attracted by nucleus than the lone pair in the sp^3 hybridised N and less available for protonation

(ii)

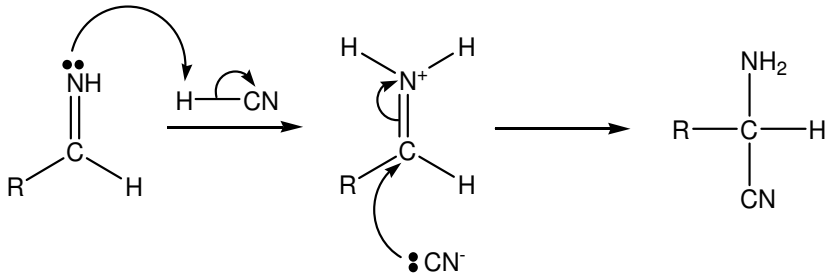


(c) **(i)** Step I: (acid-catalysed) nucleophilic addition

Step II: Dehydration / elimination

(ii) Any acid, heat (under reflux)

(iii)



(iv) Strecker's synthesis produces racemic products and hence, do not display optical activity while naturally occurring amino acid is present as one of the enantiomers (usually L enantiomer) and will rotate plane polarised light.

3 (a) (i) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

(ii) The copper electrode in <u>half-cell 1</u> is the negative electrode.

When aqueous ammonia is added to the half-cell 1, complex $[Cu(NH_3)_4]^{2+}$ is formed and the <u>concentration of Cu^{2+} ions decreases</u> , causing the equilibrium position of $Cu^{2+} + 2e^- \rightleftharpoons Cu$ to <u>shift to the left</u>, favouring oxidation (loss of electrons).

(iii) $$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} \text{ mol}^{-4} \text{ dm}^{12}$$

(iv) $$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{2} \lg \frac{[Cu^{2+}]_{\text{half-cell 1}}}{[Cu^{2+}]_{\text{half-cell 2}}}$$

$$0.129 = 0.00 - \frac{0.0592}{2} \lg \frac{[Cu^{2+}]_{\text{half-cell 1}}}{0.0100}$$

$[Cu^{2+}]_{\text{half-cell 1}}$ = **<u>4.38×10^{-7} mol dm^{-3}</u>**

(v) Initial amount of $Cu^{2+} = 90/1000 \times 0.0100 = 9.00 \times 10^{-4}$ mol
Initial amount of $NH_3 = 10/1000 \times 0.500 = 5.00 \times 10^{-3}$ mol

New volume of solution in half-cell 1 = 10 + 90 = 100 cm^3
Eqm. amount of $Cu^{2+} = 100/1000 \times 4.384 \times 10^{-7} = 4.384 \times 10^{-8}$ mol
Amount of NH_3 reacted = $4(9.00 \times 10^{-4} - 4.384 \times 10^{-8}) = 3.60 \times 10^{-3}$ mol

	$Cu^{2+}(aq)$	+	$4NH_3(aq)$	$\rightleftharpoons$	$[Cu(NH_3)_4]^{2+}(aq)$
Initial amt	9.00×10^{-4}		5.00×10^{-3}		–
Eqm amt	4.384×10^{-8}		$5.00 \times 10^{-3} - 3.60 \times 10^{-3} = 1.40 \times 10^{-3}$		$9.00 \times 10^{-4} - 4.384 \times 10^{-8} = 8.9996 \times 10^{-4} \approx 9.00 \times 10^{-4}$
÷ 0.100 Eqm [ ]	4.384×10^{-7}		1.40×10^{-2}		9.00×10^{-3}

$K_f = (9.00 \times 10^{-3}) / (4.384 \times 10^{-7}) (1.40 \times 10^{-2})^4$
= **<u>5.34×10^{11} mol^{-4} dm^{12}</u>**

(b) **F** – $Cr(OH)_3$
G – $Na_3Cr(OH)_6$
H – Na_2CrO_4
J – $Na_2Cr_2O_7$

(c)

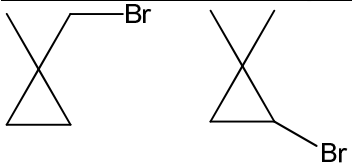
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E^{\ominus} = +0.77$ V
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	$E^{\ominus} = +0.68$V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$E^{\ominus} = +1.77$ V

$E^{\ominus}_{cell} = +0.77 - (+0.68) = +0.09$ V >0
Step 1: $2Fe^{3+}(aq) + H_2O_2(aq) \longrightarrow 2Fe^{2+}(aq) + O_2(g) + 2H^+(aq)$

$E^{\ominus}_{cell}$ = +1.77 – (+0.77) = +1.00 V > 0
Step 2: $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

(d) **(i)**

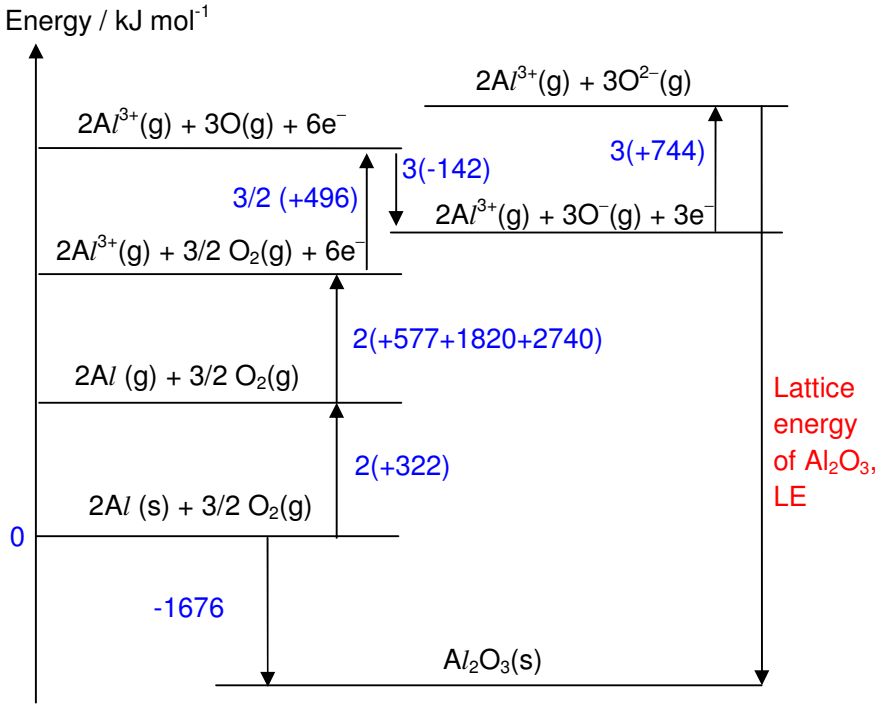
Two mono-brominated products:



(ii) Ratio of the above products = 6:4 = **3:2**

(iii) **Step I**: KCN(aq) in ethanol, heat (under reflux)
Step II: any dilute acid, heat (under reflux)
Step III: PCl_5 or $SOCl_2$
Step IV: excess conc. NH_3 in ethanol, heat in a sealed tube

4 (a)



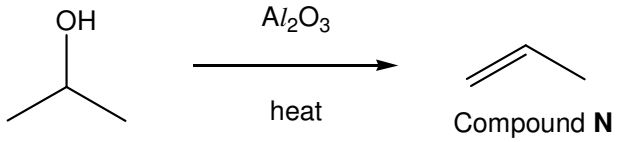
By Hess' law
$-1676 = 2(+322) + 2(+577+1820+2740) + 3/2\ (+496) + 3(-142) + 3(+744) + LE$

lattice energy of Al_2O_3, LE = -15144 = **-1.51×10^4 kJ mol^{-1}**

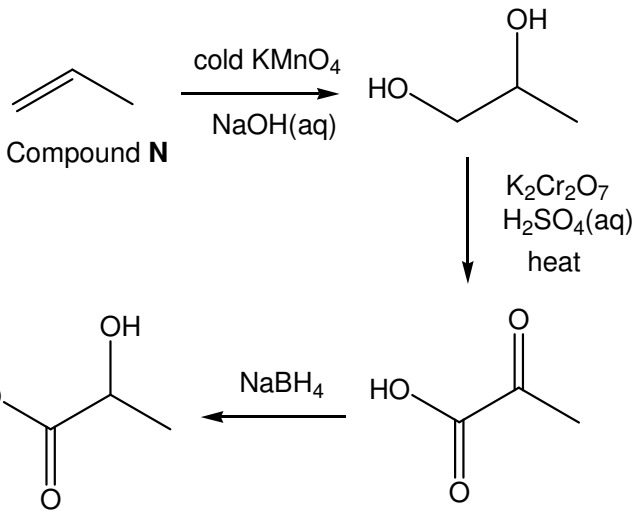
(b) First, add dilute HCl to the sample. If the solid is insoluble in acid, it must be the acidic oxide SiO_2

If the solid dissolves in acid, add NaOH(aq). If the solid is insoluble in NaOH(aq), it must be the basic oxide MgO. If the solid dissolves in both acid and base, it must be the amphoteric oxide Al_2O_3

(c) **(i)**



(ii)



2-hydroxypropanoic acid

(d) Solution of beryllium sulfate is <u>acidic</u> (pH ≈ 3) thus causing skin irritations.

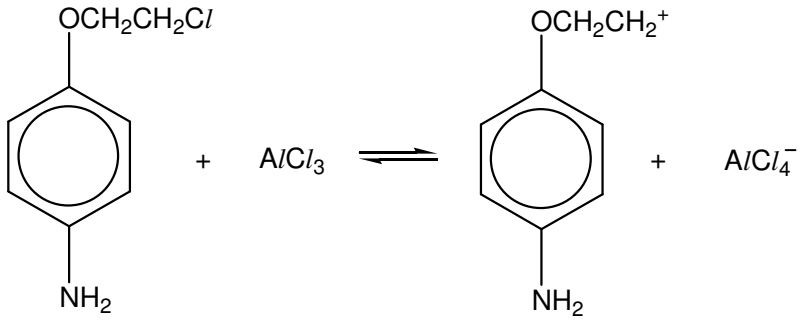
$[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(OH)(H_2O)_3]^{+} + H_3O^{+}$

The <u>small, highly polarising beryllium cation</u> weakens the O–H bonds of the water molecules in its surrounding sphere of coordination and results in the release of hydrogen ions in solution.

(e) **(i)** Step I: Sn, conc. HC*l*, heat (under reflux)

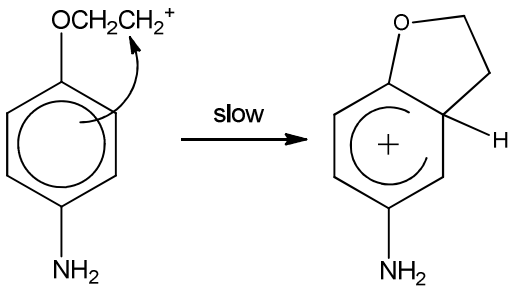
Step II: NaOH(aq)

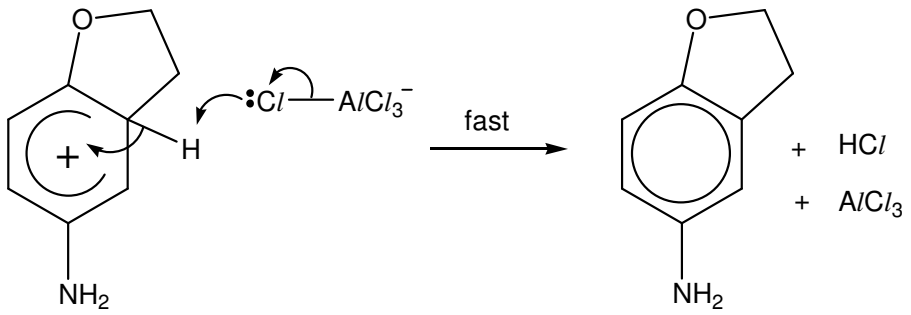
(ii)



A*l* <u>is electron deficient/ has vacant low-lying orbitals to act as electron pair acceptor</u>, thus acting as a Lewis acid catalyst.

(iii) Name: Electrophilic aromatic substitution





(iv) $AlCl_3$, being a Lewis acid, can react with the basic phenylamine / intermolecular electrophilic substitution may take place instead of intramolecular substitution.

5 (a) (i) In aqueous solution, Fe^{3+} exists as $[Fe(H_2O)_6]^{3+}$.

The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Fe^{3+} ion into two sets of slightly different energy levels.

Since the 3d orbitals are partially filled, the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed in $Fe^{3+}(aq)$.

The colour observed is complementary to the colour absorbed.

(ii) The energy absorbed for the d-d transition is out of the range of the visible spectrum. i.e. white light is not absorbed.

Hence white light is transmitted and solution of $[FeF_5(H_2O)]^{2-}$ appears colourless.

(b) K_{stab} for $[Zn(edta)]^{2-}$ is greater than that of $[Fe(edta)]^{2-}$.

Hence Zn will also be complexed and flushed out of the body via the kidneys together with the complexed Fe.

Zinc can be given as dietary supplement for patients undergoing such therapy. (OR use an alternative chelating agent which gives the highest K_{stab} for Fe.)

(c) (i)

Show 2 sp hybrid orbitals

(ii)

$$K_p = \frac{p_{CO}^{\ 4}}{p_{Ni(CO)_4}}$$

(iii) $(2.00)^4 / p_{Ni(CO)4} = 1.01$

$p_{Ni(CO)4} = 15.842 =$ **15.8 atm**

total pressure of system = 15.842 + 2.00 = **17.8 atm**

(iv)

	$Ni(CO)_4(g)$	$\rightleftharpoons$	$Ni(s) + 4CO(g)$
Initial p/atm	15.8 + (2.00/4) = **16.3**	-	0
Eqm p/atm	15.8	-	2.00

Let mass of $Ni(CO)_4$ be m.
$pV = nRT = (m/M)RT$
$16.3 \times 101 \times 10^3 \times 2 \times 10^{-3}$
$= \{m / [58.7 + 4 \times (12.0 + 16.0)]\} \times 8.31 \times (227 + 273)$

m = 135.27 = **135 g**

(d)

- **P** dissolves in dilute acid
  ⇒ **P** undergoes <u>acid-base reaction</u>, likely to contain an <u>amine</u> group

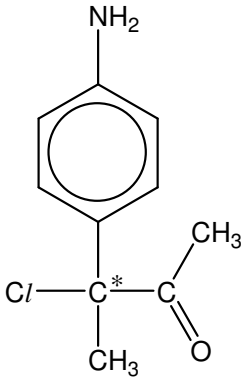
- **P** undergoes <u>condensation</u> with 2,4–DNPH to form a orange precipitate, but does not undergo oxidation with Tollens' reagent
  ⇒ **P** contains a <u>ketone</u>

- **P** undergoes <u>reduction/catalytic hydrogenation</u> with H_2/Ni to give **Q**
  ⇒ Ketone in **P** is reduced to a <u>secondary alcohol</u>

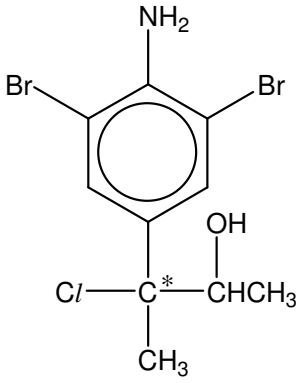
- **P** undergoes <u>electrophilic (aromatic) substitution</u> with aqueous Br_2 to give **Q**, which is disubstituted
  ⇒ **P** contains a <u>phenylamine</u> and <u>an H atom is substituted for a Br atom at the 2, 4 or 6-position, with respect to $–NH_2$, on the benzene ring</u>.

- **Q** undergoes <u>step-down oxidation</u> with aq alkaline I_2
  ⇒ yellow ppt is CHI_3
  ⇒ **Q** likely to contain **$CH_3CH(OH)–$**
  ⇒ **R** must be a <u>carboxylic acid</u>

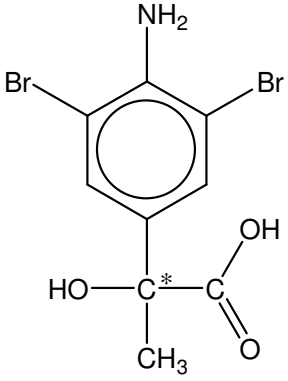
- **Q** also undergoes <u>nucleophilic substitution</u> with excess alkali due to loss of C*l* in the molecular formula
  ⇒ **Q** is a <u>chloroalkane</u> and **R** is an <u>alcohol</u>



P



Q



R