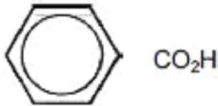


**Q1.**

- 4 (a)  $\text{Cl}_2 + \text{light/heat}$  (aq negates) [1] 1
- (b)  $\text{Cl}_2 + \text{AlCl}_3/\text{FeCl}_3/\text{Fe}$  etc. (aq negates) [1] 1
- (c)
- 
- [1] 1
- (d)  $\text{NaOH} + \text{I}_2(+ \text{aq})$  (or  $\text{I}^- + \text{OCI}^- + \text{aq}$ ) [1]
- C: (pale) yellow ppt.  
D: no reaction (both) [1] 2
- (e) mass of *CN* needed =  $0.03 \times 60 = 1.8\text{g}$  [1]
- $M_r = 154.5$ ,  $\therefore$  amount =  $1.8/154.5 = 0.0117$  (mol) (allow **0.012**) ecf [1] 2
- (f) (i) increasing ease:  $\text{H} < \text{D} < \text{G}$  [1]
- (ii) chlorine on the aryl ring is very inert or strong C-Cl bond or overlap between Cl lone pair and  $\pi$  bond on ring (OWTTE) [1]
- chlorine on C=O is reactive because of highly  $\delta^+$  carbon atom bonded to electronegative O and Cl (OWTTE) [1] 3

**Q2.**

5 (a) (i)  $\text{Cl}_2 + \text{AlCl}_3$  etc. (UV or aq negates) [1]

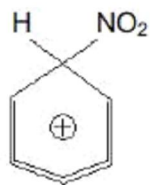
(ii)  $\text{Br}_2 + \text{AlCl}_3$  or  $\text{AlBr}_3$  etc. [1]

(iii)  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]

conc. +  $50^\circ < T < 60^\circ$  [1]

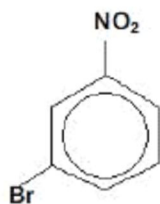
(b) (i)  $\text{A}^+ = \text{NO}_2^+$  or nitronium ion [1]

(ii) B is

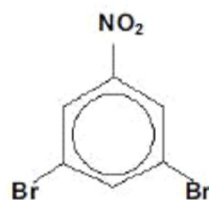


[1]

(c) (i)

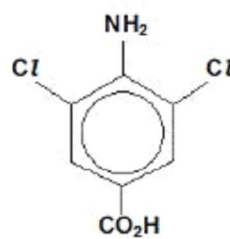
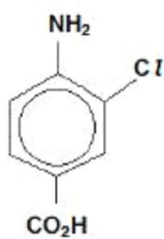


or



[1]

(ii)



[1]

Total = [8]

Q3.

(c) (i)  $Cl_2(aq)$   $AlCl_3$  or UV negates [1]

(ii) Electrophilic substitution **or** addition-elimination [1]

Nucleophilic substitution **or** electrophilic substitution on OH group  
If neither mark is awarded, could give "salvage" mark for substitution x2 [1]

(iii) **Either:** add  $Br_2(aq)$  phenol decolourises it, or gives a white ppt.

**or:** add  $FeCl_3(aq)$  phenol give a purple colour

**or:** add  $NaOH(aq)$  phenol dissolves

**or:** add  $UI$  solution phenol goes yellow/orange (**A** stays green)

**or:** add "diazonium" to solution in  $OH^-$   
phenol gives orange/red colour

(in each case, **A** give no reaction)

**or:** add  $Cr_2O_7^{2-}/H^+/warm$  **A** changes colour from orange to green

**or:** add  $MnO_4^-/H^+/warm$  **A** changes from purple to colourless

**or:** add  $PCl_5/POCl_3/PCl_3/SOCl_2$  **A** gives fumes

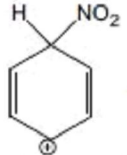
**or:** add  $CH_3CO_2H + conc. H_2SO_4$  **A** gives fruity smell

(in each case, no change with phenol)

Test + reagents [1] **Both** observations [1]

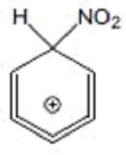
**Part (c): [5]**

Q4.

- 6 (a) (i) Electrophilic substitution **or** nitration [1]
- (ii)  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]  
(both) conc., and at  $50^\circ\text{C} \leq T \leq 60^\circ\text{C}$  [1]
- (iii)  $\text{NO}_2^+$  [1]
- 

Any  $\oplus$  on  $\text{NO}_2$  or H negates [1]

etc. or

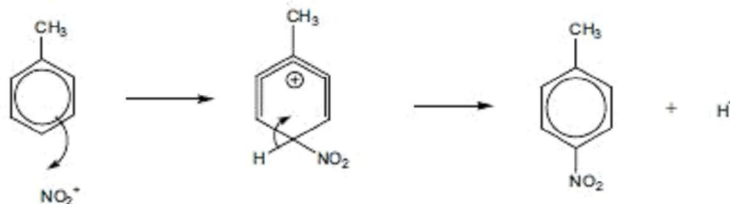

- $\text{H}^+$  [1]
- Part (a): [6]**
- (b) (i) Reduction [1]
- (ii)  $\text{Sn/Fe/Zn/SnCl}_2 + \text{HCl/H}^+/\text{H}_2\text{SO}_4$  (but not conc.  $\text{H}_2\text{SO}_4$ )  
**or**  $\text{H}_2 + \text{Ni/Pt}$  (**not**  $\text{LiAlH}_4$ ) [1]
- Part (b): [2]**
- (c)  $\text{PCl}_5/\text{PCl}_3/\text{SOCl}_2/\text{POCl}_3$  (+ heat) aq negates [1]
- Part (c): [1]**
- (d) (i) An amide, **not** peptide [1]
- (ii) Heat with  $\text{H}_3\text{O}^+$  **or** heat with  $\text{OH}^-$  (aq) [1]
- Or** warm (**not** heat/reflux) with aqueous amidase/peptidase/protease **not** enzyme/trypsin/chymotrysin/pepsin/papain etc. [1]
- Part (d): [2]**

Q5.

- 5 (a) I:  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  (or names) [1]  
 (both) conc. and at  $50^\circ\text{C} < T < 60^\circ\text{C}$  ✓ [1]  
 II:  $\text{KMnO}_4 (+\text{OH}^-) + \text{heat}$  [1]  
 III:  $\text{Sn} + (\text{conc}) \text{HCl}$  [1]  
 IV:  $\text{CH}_3\text{CH}_2\text{OH}$  (or name) [1]  
 + c.  $\text{H}_2\text{SO}_4 + \text{heat}$  [1]

[6]

(b)



intermediate, including  $\oplus$  [1]  
 $\text{NO}_2^+$  at start and  $\text{H}^+$  at finish [1]  
 (no marks for curly arrows, but if present, they must be in correct direction)

[2]

- (c) (i) ester and (primary) amine [2]  
 (ii) **more basic**: amine group is *not* adjacent to benzene ring **both** points [1]  
 (or lone pair (on N) is not delocalised)

[3]

[Total: 11]

Q6.

- 5 (a) I:  $Cl_2 + AlCl_3/Fe/etc$  [1]  
 II:  $Cl_2 + hf$  [1]  
 III:  $KMnO_4 + H^+$  [1]  
 IV:  $SOCl_2$  or  $PCl_5/PCl_3$  or  $P + Cl_2$  [1]  
 (for I, II and IV, deduct a mark ([1] only) for one or more mentions of (aq))  
 (for I, mention of hf negates the mark)  
 (for I and II, if  $Cl_2$  is omitted in one or both, deduct [1] mark only) [4]
- (b) I: electrophilic substitution [1]  
 III: oxidation or redox (NOT oxygenation) [1] [2]
- (c) H is  $C_6H_5-CH_2CN$  [1]  
 step V:  $NaCN/KCN$  [1]  
 heat (or  $50-80^\circ C$ ) + ethanol/alcohol [1]  
 step VI:  $LiAlH_4$  or  $H_2 + Ni/Pt/Pd/Rh$  or  $Na + ethanol$  [1] [4]

(d)

compound	reagent	
	cold water	hot NaOH(aq)
E	<i>no reaction</i>	<i>no reaction</i>
F	<i>no reaction</i>	$C_6H_5CH_2OH$
G	$C_6H_5CO_2H$	$C_6H_5CO_2^-Na^+$

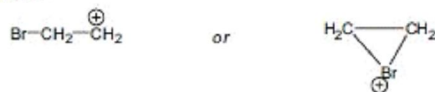
6 x [1] [6]

[Total: 16]

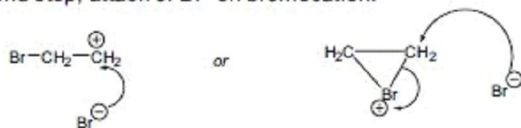
Q7.

- 5 (a) reaction I electrophilic addition [1]  
 reaction II electrophilic substitution [1]  
 (salvage: award [1] out of [2] for "addition" + "substitution", even if nucleophilic) [2]

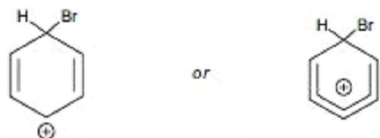
- (b) reaction I: intermediate [1]



second step, attack of  $\text{Br}^-$  on bromocation. [1]

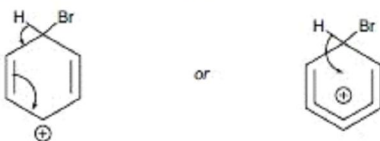


- reaction II: intermediate [1]



(or with  $\oplus$  in 2-position) (make sure  $\oplus$  is not at  $\text{sp}^3$  C-atom)

second step, loss of  $\text{H}^+$  from bromocation. [1]



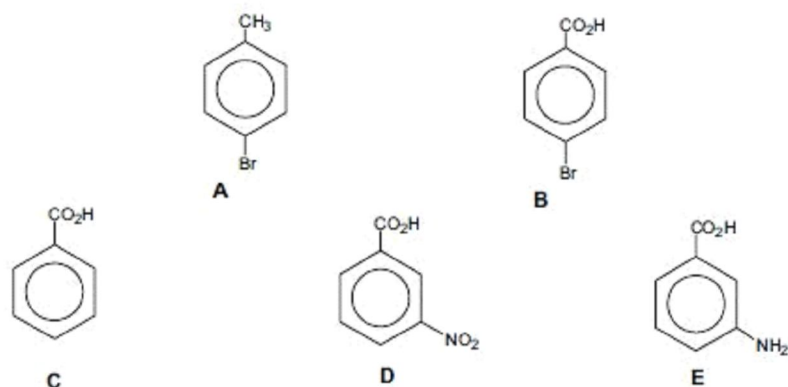
[4]

- (c) **Delocalised** ring of electrons (in benzene) is **stable**, (so is re-formed in second step in benzene.) [1] [1]  
 or electrons in the ethene  $\pi$  bond are localised/more available for reaction with electrophiles

**Total: 7**

Q8.

6



[deduct [1] mark if ring circle omitted more than once]  
 [allow ecf for **E** from structure of **D**]  
 [allow ecf for **B** from structure of **A**]  
 [allow  $-\text{CO}_2^-$  for **E**]

5 x [1]

[5]

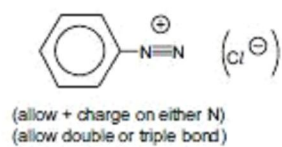
[Total: 5]

## Q9.

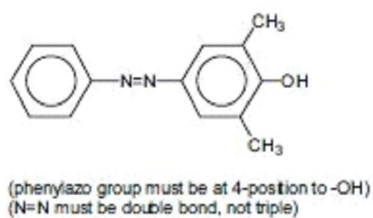
- 6 (a) (i) I:  $\text{SOCl}_2$  or  $\text{PCl}_5$  or  $\text{HCl} + \text{ZnCl}_2$  or  $\text{PCl}_3$  + heat or  $\text{Cl}_2 + \text{P}$  + heat [1]  
 [NOT  $\text{NaCl} + \text{H}_2\text{SO}_4$ ]  
 (mention of aq negates mark)
- II:  $\text{NH}_3$  (ignore any conditions stated) [1]
- (ii) nucleophilic substitution or  $\text{S}_\text{N}$  or  $\text{S}_\text{N}1$  or  $\text{S}_\text{N}2$  [1]
- (iii) delocalisation of lone pair on Cl over benzene ring produces a stronger C-Cl bond [1]
- [4]
- (b) (i) III:  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]  
 both conc., and at  $T < 60^\circ\text{C}$  [1]
- IV:  $\text{Sn} + \text{conc HCl}$  [NOT  $\text{LiAlH}_4$  or  $\text{H}_2 + \text{Ni}$ ] [1]
- (ii) III: electrophilic substitution [1]
- IV: reduction or redox [1]
- [5]
- (c) e.g. add bromine water or  $\text{Br}_2(\text{aq})$  (a solvent is needed for the mark) [1]  
 or add UI solution  
 phenylamine decolorises the bromine or gives a white ppt., hexylamine does not [1]  
 or hexylamine turns UI blue, with phenylamine it stays green [2]



(d)



[1]



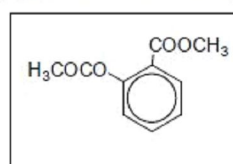
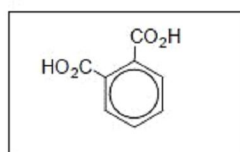
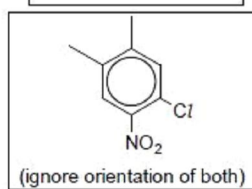
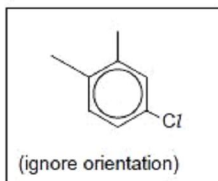
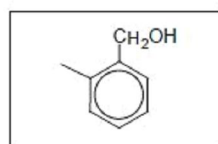
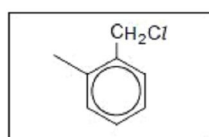
[1]

[2]

[Total: 13]

Q10.

7

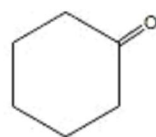


[6]

[Total: 6]

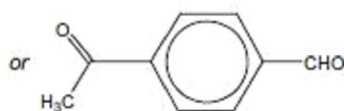
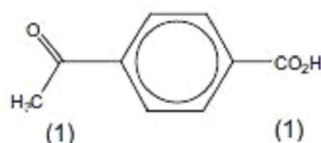
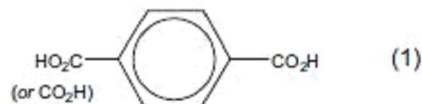
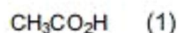
Q11.

(d)



(1)

and



[5]

(e) (i)  $(\text{CH}_3)_2\text{C}(\text{OH})\text{-CH}_2\text{OH}$  (1)

(ii) reaction I: (cold dilute)  $\text{KMnO}_4$  ("cold" not needed, but "hot" or "warm" negates) (1)

reaction II:  $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+$  + **distil** (1) [3]

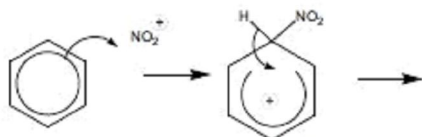
## Q12.

5 (a) (i) because the carbons are  $\text{sp}^2$  / trigonal planar / bonded at  $120^\circ$  or are joined by  $\pi$  bonds / orbitals (1)

(ii) because the  $\pi$  electrons / double bonds are delocalised / in resonance or electrons are evenly distributed / spread out (1) [2]

(b) (i)  $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$  (1)  
or  $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$  or  $\rightarrow \text{H}_2\text{O} + \text{NO}_2^+ + \text{HSO}_4^-$

(ii) electrophilic substitution (1)  
mechanism:



curly arrows from benzene to  $\text{NO}_2^+$ , **and** showing loss of  $\text{H}^+$  (1)

correct intermediate (with "+" in the 'horse-shoe') (1) [4]

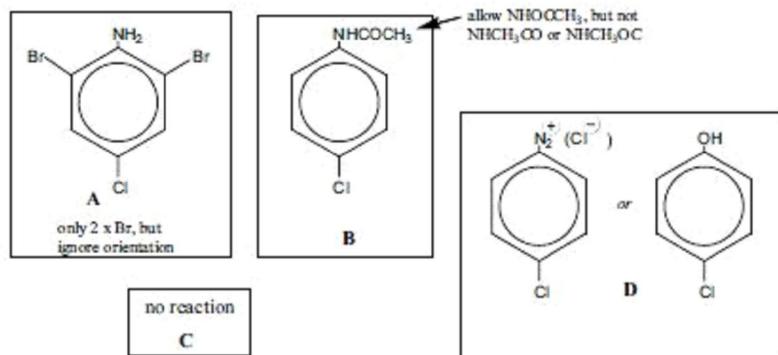
(c)  $\text{Cl}_2 + \text{AlCl}_3 / \text{FeCl}_3 / \text{Fe} / \text{Al} / \text{I}_2$  (aq or light negates this mark) (1) [1]

(d) (i) Y is chlorobenzene (1) Z is 4-chloronitrobenzene (1) (2)

(ii) Sn / Fe + (conc) HCl (1)

HCl is **conc.** and second step is to add NaOH(aq) (1)

(iii)


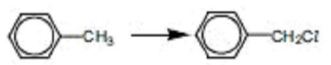


(4) [8]

[Total: 15]

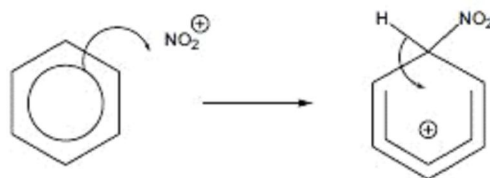
### Q13.

5 (a)

transformation	reagent + conditions
$C_2H_4 \rightarrow C_2H_5Cl$	HCl, no light or catalyst
$C_2H_5OH \rightarrow C_2H_5Cl$	conc HCl + ZnCl <sub>2</sub> or SOCl <sub>2</sub> or PCl <sub>5</sub> or PCl <sub>3</sub> and heat
$C_2H_6 \rightarrow C_2H_5Cl$	Cl <sub>2</sub> + light
$C_2H_4 \rightarrow C_2H_4Cl_2$	Cl <sub>2</sub> , no light or catalyst
$CH_3CO_2H \rightarrow CH_3COCl$	SOCl <sub>2</sub> or PCl <sub>5</sub> or PCl <sub>3</sub> and heat
	Cl <sub>2</sub> + AlCl <sub>3</sub>
	Cl <sub>2</sub> + light or heat

[6]

- (b) (i) production of  $\text{NO}_2^+$ :  $2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow 2\text{HSO}_4^- + \text{H}_3\text{O}^+ + \text{NO}_2^+$  [1]  
(accept  $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} + \text{NO}_2^+$ )



curly arrow from ring to  $\text{NO}_2^+$  **and** from C-H bond to ring [1]  
correct intermediate, including charge in the right place [1]  
*Note charge area must be more than half ring*

- (ii) **C** is  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  [1]  
(iii) step 1: reagent is hot acidified or alkaline  $\text{KMnO}_4$  [1]  
step 2: reagent is  $\text{Br}_2 + \text{FeBr}_3/\text{AlCl}_3$  etc. ( $\text{H}_2\text{O}$  or light negates) [1]

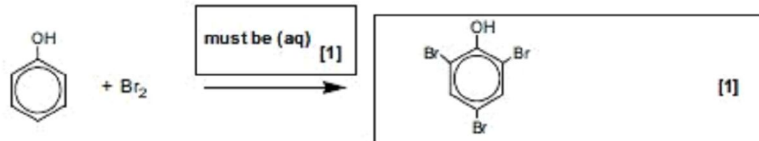
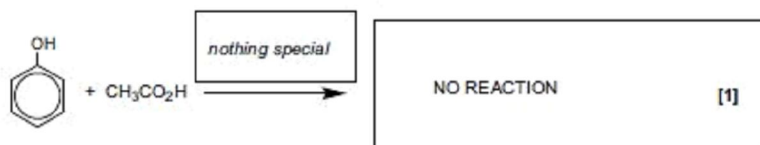
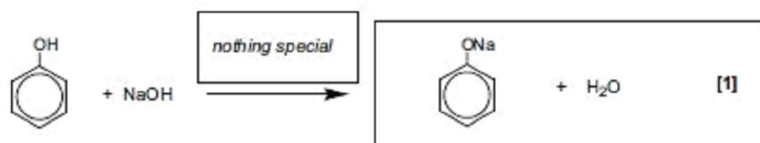
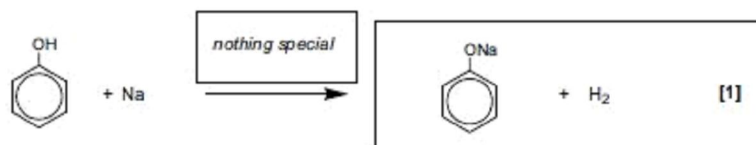
(If **C** is given as 3-bromotoluene, then allow the last [2] marks if steps 1 and 2 are reversed.)

**[Total: 12]**

**Q14.**

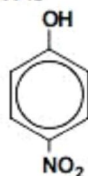
- 5 (a) acidity: ethanol < water [1]  
 due to +ve inductive effect of C<sub>2</sub>H<sub>5</sub> group or C<sub>2</sub>H<sub>5</sub> gives e<sup>-</sup> to oxygen or intensifies e<sup>-</sup> (in O-H bond) [1]  
 acidity: phenol > water [1]  
 due to stabilisation of the anion/anionic charge or makes the anion less basic [1]  
 [4]

(b)



[5]

(c) H is



[1]

reagents & conditions:

step 1 **dilute** HNO<sub>3</sub> (dilute, not just 'aq'. H<sub>2</sub>SO<sub>4</sub> negates)

[1]

step 2 Sn/SnCl<sub>2</sub>/Fe + HCl or H<sub>2</sub> + Ni/Pd (NOT H<sub>2</sub> + Pt. NOT LiAlH<sub>4</sub> or NaBH<sub>4</sub>)

[1]

step 3 CH<sub>3</sub>COCl or (CH<sub>3</sub>CO)<sub>2</sub>O ('aq.' negates)

[1]

[4]

[Total: 13]

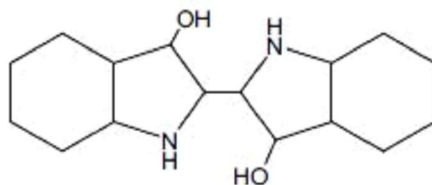
Q15.

3. (a) (i)  $C_{18}H_{10}N_2O_2$  [1]  
 (ii) ketone, alkene, amine, aryl (benzene/arene/phenyl) (any 3) [2]  
 [3]

- (b) (i) reduction or redox [1]  
 (ii)  $NaBH_4$  or  $LiAlH_4$  (NOT  $H_2 + Ni$ ) [1]  
 [2]

- (c) 1. 2,4-DNPH [1] red/yellow-orange/orange ppt. [1] no reaction  
 2. Na metal [1] no reaction gas given off/fizzing [1]  
 or  $PCl_5/SOCl_2$  [1] no reaction steamy fumes/fizzing [1]  
 or  $PCl_3 + warm$  misty/white fumes  
 2 x "no reaction" must be linked to "correct reagent" [1]  
 [5]

(d) (i)



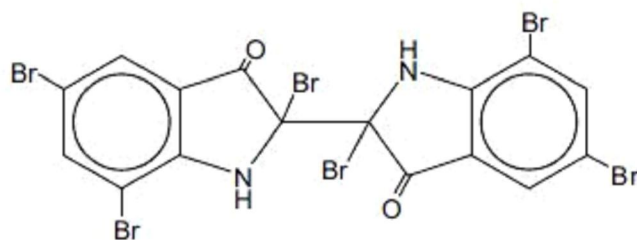
[1]

- (ii)  $M_r = 262$ , so  $2.5 \text{ g} = 2.5/262 = 9.54 \times 10^{-3} \text{ mol}$  [1]  
 (1 mol indigo absorbs 9 mol of  $H_2$ )  
 so volume of  $H_2 = 9 \times 24 - 9.54 \times 10^{-3} = 2.06 \text{ dm}^3$  (2060  $\text{cm}^3$ )

[1]

[1]  
 [3]

(e)

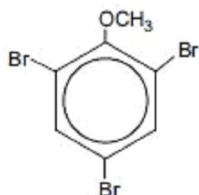


- 2 x Br on  $C=C$  [1]  
 a Br on each ring [1]  
 TWO non-adjacent Br on each ring [1]  
 [3]

[Total: 16]

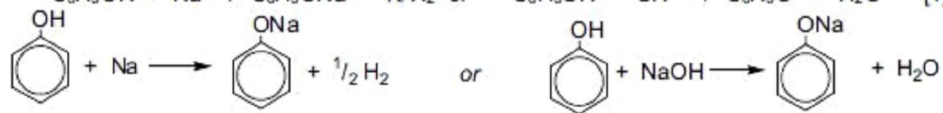
Q16.

5 (a) (i)



[1]

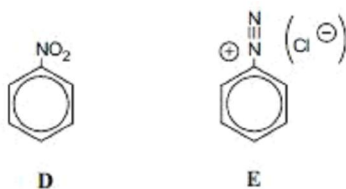
(ii) Na metal or NaOH [1]  
 Fizzes/gas given off with phenol or phenol dissolves (anisole doesn't) [1]  
 $C_6H_5OH + Na \rightarrow C_6H_5ONa + \frac{1}{2} H_2$  or  $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$  [1]



(neutral) iron(III) chloride [1]  
 Solution goes purple/violet [1]  
 $3C_6H_5OH + FeCl_3 \rightarrow Fe(OC_6H_5)_3 + 3HCl$  [1]

[4]

(b) (i)



[1] + [1]

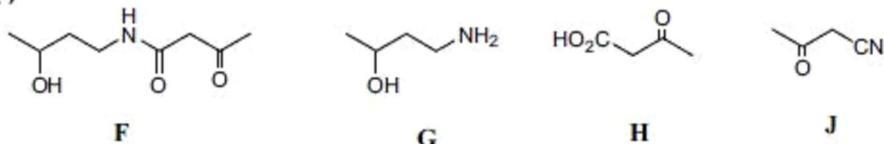
(ii) step 2: Sn + HCl **NOT** LiAlH<sub>4</sub>, NaBH<sub>4</sub> [1]  
 conc. + reflux *(warm is insufficient)* [1]

**step 4 is conditional of structure E**

step 4: warm + in H<sub>2</sub>O [1]

[5 max 4]

(c) (i)



F must be an **amide**

[4]

(ii) reaction 1: H<sub>2</sub> + Ni *or* LiAlH<sub>4</sub> [1]  
 reaction 2: heat + aqueous HCl [1]  
[6]

[Total: 14]

**Q17.**

**3 (a) (i)** ketone, alcohol, alkene, arene/aryl/benzene/phenyl. any three [2]  
(if more than 3 are given, mark the first 3 the candidate has written)

<b>(ii)</b> (2,4-)DNPH/Brady's Lawsone $\Rightarrow$ orange/red, (not yellow) ppt <b>and A</b> $\Rightarrow$ nothing	or $\text{FeCl}_3$ (aq or neutral) or purple/violet with <b>A</b> , or <b>and</b> nothing with Lawsone	or $\text{Br}_2(\text{aq})$ or white ppt with <b>A</b> , or <b>and</b> decolourises with Lawsone	[1] [1]
---	--	---	------------

**(iii)**  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  or  $\text{SnCl}_2$  or  $\text{Na} + \text{ethanol}$  or any suitable reducing agents with  $E^\ominus < 0.2\text{V}$ , e.g.  $\text{SO}_2$ . **NOT**  $\text{H}_2 + \text{Ni}$  etc. [1]

**(iv)**

or

(One of the Br atoms in either formula could be an OH group instead. Br on the benzene ring negates this mark)

[1]  
[6]

**(b) (i)**  $E_{\text{cell}} = 1.33 - 0.36 = \text{(+)}0.97\text{ (V)}$  [1]

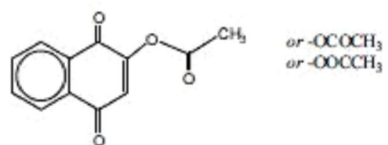
**(ii)**  $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{C}_{10}\text{H}_8\text{O}_3 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{C}_{10}\text{H}_8\text{O}_3$

3:1 ratio [1]  
balancing [1]

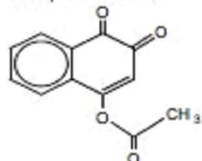
**(iii)**  $= 0.05 \times 7.5/1000 = 3.75 \times 10^{-4}$  mol [1]  
 $n(\text{A}) = 3 \times 3.75 \times 10^{-4}$   
 $= 1.125 \times 10^{-3}$  in  $20\text{ cm}^3$   
**[A] =  $5.63 \times 10^{-2}$  mol dm $^{-3}$**  (allow 5.6, 5.62, 5.625 etc.) [1]  
**[5]**



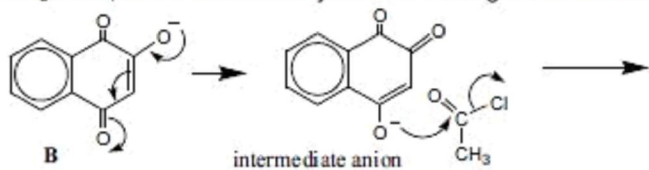
(c) (i) compound **C** is [1]



(ii) compound **D** is [1]



(iii) mechanism: 3 curly arrows in **B** or correct intermediate anion [1]  
a curly arrow from an O<sup>-</sup> or an oxygen with a lone pair to the carbon of the C=O group in CH<sub>3</sub>COCl, and a second curly arrow breaking the C-Cl bond [1]

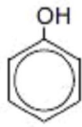
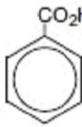
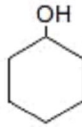


[4 max 3]

[Total: 14]

Q18.

5 (a)

	H <sub>2</sub> O			
Na	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>
KOH(aq)	X	X	X	X
Na <sub>2</sub> CO <sub>3</sub> (aq)	X	X	CO <sub>2</sub>	X

[5]

(b) (i) (CH<sub>3</sub>)<sub>3</sub>C-Cl (any unambiguous structure or name)

[1]

(ii) reduction or hydrogenation

[1]

(iii) either CH<sub>3</sub>CO<sub>2</sub>H and heat with (conc) H<sub>2</sub>SO<sub>4</sub>  
or  
CH<sub>3</sub>COCl

[1]

(iv) reflux

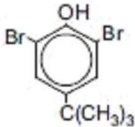
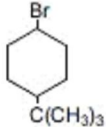
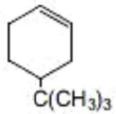
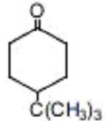
[1]

dilute HCl

[1]

[5]

(c) (i)

reagent and conditions	product with <b>A</b>	product with <b>B</b>
$\text{Br}_2(\text{aq})$		no reaction
heat with HBr	no reaction	
pass vapour over heated $\text{Al}_2\text{O}_3$	no reaction	
heat with acidified $\text{K}_2\text{Cr}_2\text{O}_7$	no reaction	

[6]

(ii) either:  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ : no observation with **A** and goes from orange to green with **B**.

or:

$\text{Br}_2(\text{aq})$ : white ppt. with **A** and no observation/ppt with **B**

[1]

[7]

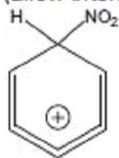
[Total: 17]

Q19.

3 (a) (i)  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]  
conc (both acids) and  $30^\circ\text{C} < T < 60^\circ\text{C}$  or warm [1]

(ii) dilute  $\text{HNO}_3$  or  $\text{HNO}_3(\text{aq})$  [1]  
and room temp. (allow  $T \leq 30^\circ\text{C}$ ) [3]

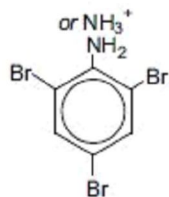
(b) (allow intermediate from methylbenzene)



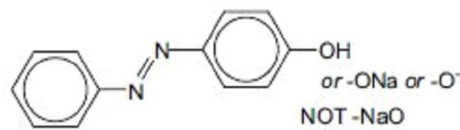
[1]  
[1]

(c) Sn/tin (or  $\text{SnCl}_2$ , Fe) + HCl (NOT  $\text{H}_2\text{SO}_4$  or  $\text{H}^+$ , Zn, or  $\text{LiAlH}_4$ ) [1]  
[1]

(d) (i)



A



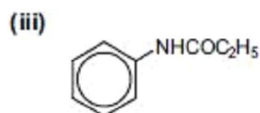
B

[1] + [1]

(ii)  $\text{NaNO}_2 + \text{HCl}$  or  $\text{H}_2\text{SO}_4$  or  $\text{H}^+$  or  $\text{HNO}_2$  [1]  
 $T \leq 10^\circ\text{C}$  [1]  
[4 max 3]

(e) (i) amide [1]

(ii)  $M_r = 108 + 11 + 14 + 16 = 149$   
 $\%N = (14 \times 100) / 149 = 9.4\%$  [1]



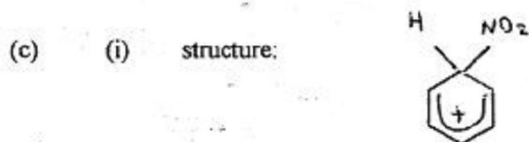
[1]  
[3]

[Total: 11]

**Q20.**

5 (a)  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]  
 conc acids (aq negates) **and** T between 50 - 60° C [1]  
 2

(b) electrophilic substitution [1]  
 1



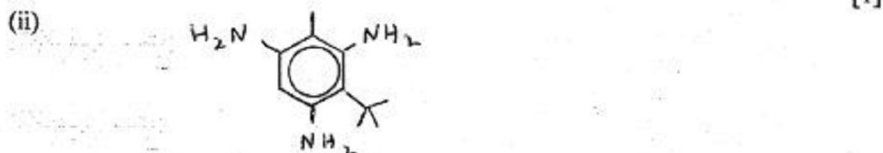
look for the "horseshoe" of delocalised electrons (somewhere around the rest of the ring, away from the  $\text{sp}^3$  carbon atom) and the (+) charge somewhere on/near the horseshoe (NOT on the  $\text{sp}^3$  carbon. A (+) charge on H or  $\text{NO}_2$  negates [1]

(ii)  $\text{X}^+ = \text{NO}_2^+$  [1]

(iii)  $\text{Z}^+ = \text{H}^+$  (NOT  $\text{H}_3\text{O}^+$ ) (penalise once only for absence of (+) signs) [1]

(iv)  $2 \text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$  [2]  
 ([1] for species, [1] for balancing. Allow [1] for: the acids  $\longrightarrow \text{NO}_2^+ + \text{HSO}_4^- (+\text{H}_2\text{O})$ )

5



Ignore alkyl groups – these can be "R" or even incorrect.  
 Allow  $\text{NH}_3^+$  or  $\text{NH}_3\text{Cl}$  instead of one or more  $\text{NH}_2$  groups

[1]

2

**Total: 10**

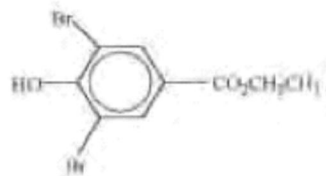
**Q21.**

4 (a) phenol, ester, arene/benzene ring any two (1) + (1) [2]

(b) (i)  $\text{Na}^+ \text{O}-\text{C}_6\text{H}_4-\text{CO}_2\text{C}_2\text{H}_5$  (1)

(ii)  $\text{Na}^+ \text{O}-\text{C}_6\text{H}_4-\text{CO}_2^- \text{Na}^+$  ✓  $\text{C}_2\text{H}_5\text{OH}$  ✓ (2)

(iii)



(1) [4]

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Page 3	Mark Scheme	Syllabus	Paper
	A/AS LEVEL EXAMINATIONS – NOVEMBER 2003	9701	4

(c) (i) acidity:  $G > E > F$  (1)

(ii) only G reacts/gives off  $\text{CO}_2$  with  $\text{Na}_2\text{CO}_3$  (1)

E and G both dissolve in  $\text{NaOH}(\text{aq})$  (1) [3]

**Total: 9**

Q22.

- 7 (a) orange colour disappears/bromine is decolourised (NOT discoloured, or goes clear) [1]  
 (white) precipitate/solid/crystals is formed [1] 2

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Page 5	Mark Scheme	Syllabus	Paper
	A LEVEL – NOVEMBER 2004	9701	4

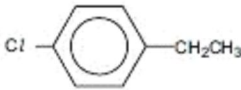
- (b) e.g. add neutral  $\text{FeCl}_3$  (aq) – violet colour with phenol  
 or add universal indicator – red/orange colour with phenol  
 or add Na metal – fizzing/ $\text{H}_2$  evolved with phenol  
 or add  $\text{NaOH}$ (aq) to the pure compound – phenol would dissolve  
 or add  $\text{H}^+$  (aq) to the pure compound – phenylamine would dissolve  
 or add  $\text{HNO}_2$  at room temperature – phenylamine would produce gaseous  $\text{N}_2$ .  
 or add  $\text{HNO}_2$  at  $5^\circ\text{C}$ , followed by an alkaline solution of phenol – phenylamine would produce a coloured (orange) dye [1] 1
- (c) IV  $\text{KMnO}_4$  + heat [1]
- V  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1] (both) conc<sup>d</sup> and at  $50^\circ\text{C} < T < 60^\circ\text{C}$  [1]
- VI  $\text{Sn} + \text{HCl}$  (NOT  $\text{LiAlH}_4$ ) [1] 4

Q23.

- 4 (a)  $\text{HO-C}_6\text{H}_4\text{-NH}_2 + 2\text{AgBr} + 2\text{OH}^- \rightarrow \text{O=C}_6\text{H}_4\text{=O} + \text{H}_2\text{O} + \text{NH}_3 + 2\text{Ag} + 2\text{Br}^-$  [1]  
 (or  $\text{C}_6\text{H}_7\text{NO}$ ) (or  $\text{C}_6\text{H}_4\text{O}_2$ ) **1**
- (b) rodinol should be **less basic** than  $\text{NH}_3$  [1]  
 because the lone pair on N is delocalised over/overlaps with the aryl ring [1]  
**2**
- (c) E is  $\text{H}_2\text{N-C}_6\text{H}_4\text{-O}^- \text{Na}^+$  or  $\text{H}_2\text{N-C}_6\text{H}_4\text{-ONa}$  [1]  
 F is  $\text{HO-C}_6\text{H}_4\text{NH}_3^+ \text{Cl}^-$  or  $\text{HO-C}_6\text{H}_4\text{NH}_3\text{Cl}$  [1]  
 G is  $\text{HO-C}_6\text{H}_2\text{Br}_2\text{-NH}_2$  up to  $\text{HO-C}_6\text{Br}_4\text{-NH}_2$  (ignore orientation) [1]  
**3**
- (d) (i)  $\text{HNO}_3(\text{aq})$  or dil  $\text{HNO}_3$  (**NOT** conc., and **NOT** + conc.  $\text{H}_2\text{SO}_4$ ) [1]  
 (ii) reduction [1]  
 (iii)  $\text{Sn} + \text{HCl}(\text{aq})$  [1]  
**3**
- (e) (i) phenol, amide [1] + [1]  
 (ii)  $\text{CH}_3\text{COCl}$  or  $(\text{CH}_3\text{CO})_2\text{O}$  [1]  
**3**
- total: 12**

Q24.

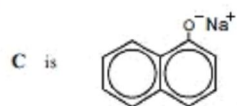


- 4 (a) (i) light or heat [aq or  $\text{AlCl}_3$  negates] (1)
- (ii)  $\text{NaOH/KOH/alkali/OH}^-$  (1)  
in alcohol/ethanol + heat [aq negates] (1)
- (iii)  $[-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-]$  [C-C not needed, but C=C is wrong] (1)
- (iv)  $\text{CH}_2=\text{CHCN}$  [C=C is needed here] (1) [5]
- (b) (i)  $^-/\text{OH}^-(\text{aq})/\text{NaOH}(\text{aq})/\text{aqueous alkali/}$  + heat [aq or solution or dil etc. needed] (1)
- (ii) (pale) yellow ppt/crystals (NOT orange or orange-yellow) (1)
- (iii) C/D is  $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$  ✓ D/C is  $\text{CHI}_3$  ✓ (1) + (1) [4]
- (c) (i)
- 

(1)
- (ii) needs  $\text{AlCl}_3$  or similar [light or aq negates] (1)
- (iii) (hot)  $\text{KMnO}_4(\text{aq}) + \text{OH}^-$  or  $\text{H}^+$  [NOT  $\text{Cr}_2\text{O}_7^{2-}$ ] (1) [3]
- [Total: 12]

Q25.

6 (a) (i)



allow ONa but no covalent O-Na bond

[1]

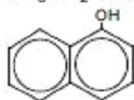
(ii) amide, ester

2 x [1]

(iii)  $\text{CO}_2$  or  $\text{H}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$   
 $\text{CH}_3\text{NH}_2$  or  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$

[1]

[1]



[1]

(iv)  $\text{H}_3\text{O}^+$  and heat  $>80^\circ$  or  $\text{OH}^-$ (aq) and heat  $>80^\circ$

[1]

[7]

(b) (i)  $\text{Br}_2$ (aq) (or other suitable solvent)

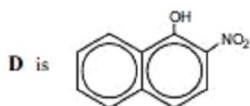
[1]

(ii) dilute/aqueous  $\text{HNO}_3$

[1]

[2]

(c) (i)

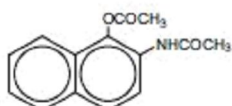


[1]

(ii) tin/Fe + HCl NOT  $\text{LiAlH}_4$

[1]

(iii)

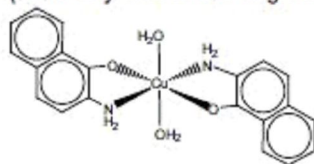


mark each side chain separately

2 x [1]

[4]

(d) (i) (allow any orientation of groups)



penalise missing H on  $\text{NH}_2$

[1]

(ii)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  or  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  NOT  $[\text{Cu}(\text{NH}_3)_6]^{2+}$

[1]

(iii) ligand substitution/exchange

[1]

[3]

[Total: max 15]

Q26.

- 5 (a) G is 4-nitromethylbenzene [1]  
 H is 4-nitrophenylethanoic acid [1]
- (b) step II:  $\text{Cl}_2 + \text{light or heat (T} \sim 100^\circ\text{C)}$  (AIC<sub>3</sub> or aq. negates) [1]  
 step III: KCN (in ethanol) + heat (T $\sim$ 75 °C) (HCN negates) [1]  
 step V: Sn or Fe + HCl (+ heat) [1]
- [Total: 5]**

## Q27.

- 4 (a) (cyclohexanol & phenol) hydrogen bonding to (solvent) water molecules [1]  
 due to OH group [1]  
**[2]**
- (b) phenoxide anion is more stable (than cyclohexoxide) / OH bond is weaker [1]  
 due to delocalisation of charge / lone pair over the ring [1]  
**[2]**

(c)

reagent	product with cyclohexanol	product with phenol
Na(s)	RONa or RO <sup>-</sup> Na <sup>+</sup>	ArONa or ArO <sup>-</sup> Na <sup>+</sup>
NaOH(aq)	<b>no reaction</b>	ArONa or ArO <sup>-</sup> Na <sup>+</sup>
Br <sub>2</sub> (aq)	<b>no reaction</b>	tribromophenol
I <sub>2</sub> (aq) + OH <sup>-</sup> (aq)	<b>no reaction</b>	<b>no reaction</b>
an excess of acidified Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq)	cyclohexanone	<b>no reaction</b>

five correct products 5 × [1]  
 five correct "no reaction"s [2]  
 (4 correct = [1]; 3 correct = [0])  
**[7]**

- (d) either Br<sub>2</sub>(aq): no reaction with cyclohexanol; decolourises or white ppt with phenol  
 or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + H<sup>+</sup>: turns from orange to green with cyclohexanol; no reaction with phenol
- correct reagent chosen **and** the correct "no reaction" specified [1]  
 correct positive observation [1]  
**[2]**

**[Total: 13]**

## Q28.

5 (a)

compound	all carbon atoms can be coplanar	not all carbon atoms coplanar
<b>A</b>	✓	
<b>B</b>		✓
<b>C</b>	✓	
<b>D</b>	✓	
<b>E</b>	✓	

all 5 correct [3]  
 (4 correct: [2], 3 correct: [1], <3 correct: [0])  
**[3]**

(b) reaction I:  $\text{Cl}_2 + \text{AlCl}_3 / \text{FeCl}_3 / \text{Fe} / \text{or bromides of Al or Fe}$  [1]  
 reaction II:  $\text{Cl}_2 + \text{heat} / \text{light} / \text{uv} / \text{hf}$  [1]  
**[2]**

(c) (i) **H** is  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  [1]

(ii) reaction III:  $\text{KMnO}_4 + \text{heat} (+ \text{OH}^-)$  [1]  
 reaction V:  $\text{NaOH}$  in water + heat [1]  
 reaction VI: conc  $\text{H}_2\text{SO}_4 + \text{heat}$  [1]

(iii) reaction III: oxidation [1]  
 reaction V: hydrolysis or nucleophilic substitution [1]  
**[6]**

**[Total: 11]**

Q29.

5 (a) (i) ester (1)

(ii) H is nitrobenzene – structure needed here (1)  
J is phenyldiazonium chloride – structure needed here (1)

(iii) step 2 Sn/Zn + HCl / H<sub>2</sub> + named cat / NaBH<sub>4</sub> / LiAlH<sub>4</sub> / Na + ethanol (1)  
step 3 HNO<sub>2</sub>/NaNO<sub>2</sub> + HCl at T = 10°C or less (1)  
step 4 heat/warm to T > 10°C (1)  
step 5 CH<sub>3</sub>COCl / CH<sub>3</sub>COCOCOCH<sub>3</sub> (1)

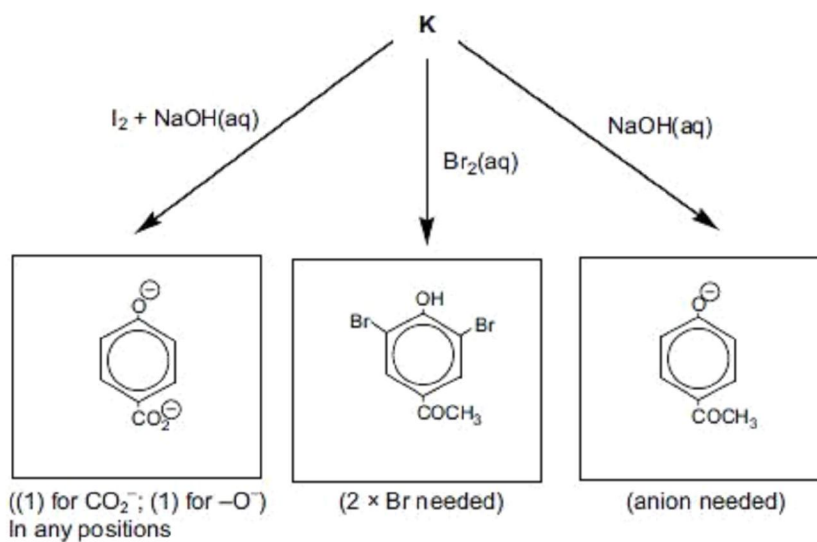
[7]

(b) (i) compounds that have the same molecular formula, but different structures (1)

(ii) phenol (NOT hydroxy) (1)  
(methyl) ketone or carbonyl (1)

(iii) K is 4-ethanoylphenol, HO-C<sub>6</sub>H<sub>4</sub>-COCH<sub>3</sub> (must be 1,4- disubstituted isomer) (1)

(iv)



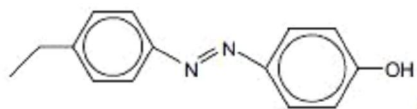
[4]  
[8 max 7]

[Total: 14]

Q30.

- 4 reaction I:  $\text{Cl}_2 + \text{light}$  (1) (not aq)  
 reaction II:  $\text{Br}_2 + \text{AlBr}_3$  or  $\text{Fe}$  or  $\text{FeBr}_3$  (1) (not aq)  
 reaction III:  $\text{NaOH}$ , heat in ethanol (1) (allow aqueous EtOH)  
 reaction IV:  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  (1) conc and  $< 60^\circ\text{C}$  (1) (2 marks)  
 reaction V:  $\text{KMnO}_4 + \text{H}^+/\text{OH}^- + \text{heat}$  (1)  
 reaction VI:  $\text{Sn} + \text{HCl}$  (1)  
 reaction VII:  $\text{HNO}_2 + \text{HCl}$ ,  $< 10^\circ\text{C}$  (1)

X is



(1) allow  $-\text{N}_2-$  and  $-\text{ONa}$

[max 8]

[Total: 8]

Q31.

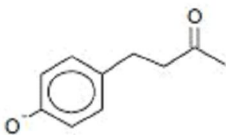
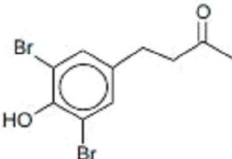
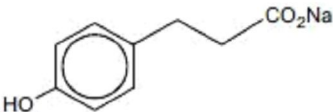
5 (a) phenol  
ketone

[1]

[1]

[2]

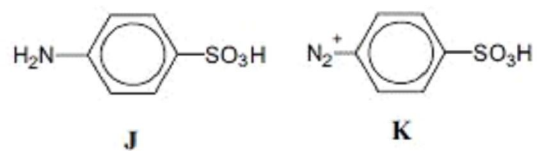
(b)

reagent	observation	structure of product	type of reaction
sodium metal	<b>effervescence /bubbles/fizzing</b>		<i>redox</i>
aqueous bromine	<b>decolourises or white ppt.</b>		<i>electrophilic substitution</i>
aqueous alkaline iodine	<b>yellow ppt.</b>		<i>oxidation</i>

[2]

[8]

(c) (i)



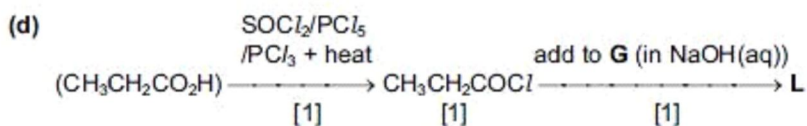
[1] + [1]

(ii) step 1:  $\text{NaNO}_2 + \text{HCl}$  or  $\text{HNO}_2$  [1]

at  $T < 10^\circ\text{C}$  [1]

step 2: (add **K** to a solution of **G**) in aqueous  $\text{NaOH}$  [1]

[5]

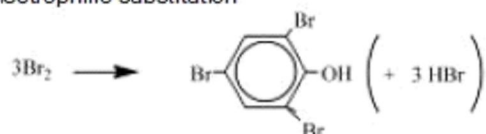


ecf from  $\text{CH}_3\text{COOH}$  [3]

[Total: 18]

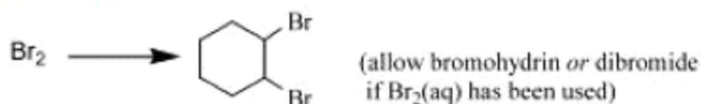
### Q32.

5 (a) (i)  $\text{Br}_2(\text{aq})$  [1]  
electrophilic substitution [1]



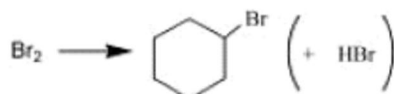
[1]

(ii) no special conditions [1]  
electrophilic addition [1]



product [1]

(iii) light/UV or heat [1]  
(free) radical substitution [1]



product [1]

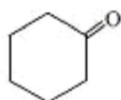
balanced equation in (i) (i.e.  $3\text{Br}_2$  and  $3\text{HBr}$ ) [1]

balanced equation in (iii) (i.e.  $\text{Br}_2$  and  $\text{HBr}$ ) [1]

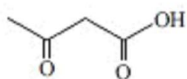
[11 max 10]



(b) (i)



**C**



**D**



**E**

3 correct structures (can be in any order) 3 × [1]

(ii) results of tests:

with 2,4-DNPH: **C and D** [1]

with I<sub>2</sub> + OH<sup>-</sup>: **D only** [1]

with NaOH: **D and E** [1]

(N.B. letters may be different – must refer to the candidate's formulae)

**[6]**

**[Total: 16]**



