

**Q1.**

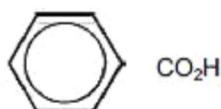
4 (a)  $\text{Cl}_2 + \text{light/heat}$  (aq negates) [1]

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  $\text{I}^- + \text{OCl}^- + \text{aq}$ ) [1]

C: (pale) yellow ppt.

D: no reaction (both) [1]

2

(e) mass of  $\text{CN}$  needed =  $0.03 \times 60 = 1.8\text{g}$  [1]

$M_r = 154.5, \therefore \text{amount} = 1.8/154.5 = 0.0117$  (mol) (allow 0.012) ecf [1]

2

(f) (i) increasing ease: H < D < 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.**

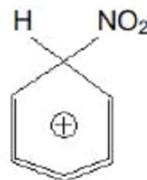
5 (a) (i)  $\text{Cl}_2$  +  $\text{AlCl}_3$  etc. (UV or aq negates) [1]

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

(iii)  $\text{HNO}_3$  +  $\text{H}_2\text{SO}_4$   
conc. +  $50^\circ < T < 60^\circ$  [1]  
[1]

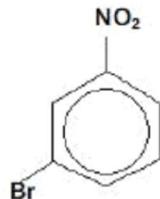
(b) (i)  $\text{A}^+ = \text{NO}_2^+$  or nitronium ion [1]

(ii) B is

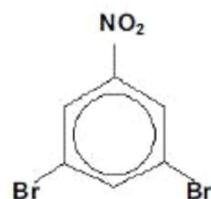


[1]

(c) (i)

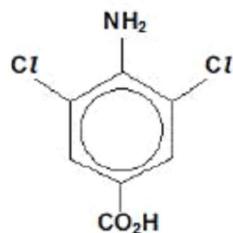
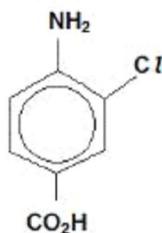


or



[1]

(ii)



[1]

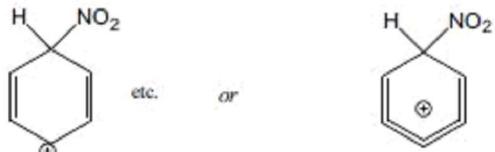
Total = [8]

Q3.

Test + reagents [1] Both observations [1]

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

Q4.

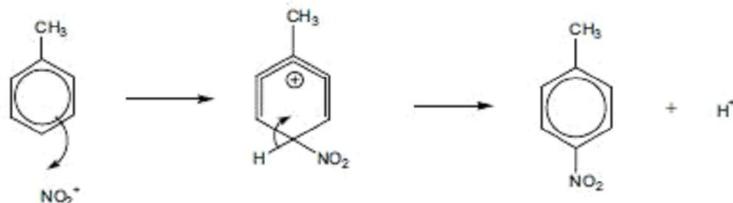
6	(a)	(i)	Electrophilic substitution <b>or</b> nitration	[1]
		(ii)	HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	[1]
			(both) conc., and at 50°C ≤ T ≤ 60°C	[1]
		(iii)	NO <sub>2</sub> <sup>+</sup>	[1]
				
			etc.      or	
			Any $\oplus$ on NO <sub>2</sub> or H negates	[1]
			H <sup>+</sup>	[1]
				Part (a): [6]
	(b)	(i)	Reduction	[1]
		(ii)	Sn/Fe/Zn/SnCl <sub>2</sub> + HCl/H <sup>+</sup> /H <sub>2</sub> SO <sub>4</sub> (but not conc. H <sub>2</sub> SO <sub>4</sub> ) <b>or</b> H <sub>2</sub> + Ni/Pt ( <b>not</b> LiAlH <sub>4</sub> )	[1]
				Part (b): [2]
	(c)		PCl <sub>5</sub> /PCl <sub>3</sub> /SOCl <sub>2</sub> /POCl <sub>3</sub> (+ heat) aq negates	[1]
				Part (c): [1]
	(d)	(i)	An amide, <b>not</b> peptide	[1]
		(ii)	Heat with H <sub>3</sub> O <sup>+</sup> <b>or</b> heat with OH <sup>-</sup> (aq)  Or warm ( <b>not</b> heat/reflux) with aqueous amidase/peptidase/protease <b>not</b> enzyme/trypsin/chymotrypsin/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:  $\text{KMnO}_4 (+\text{OH}^-)$  + heat [1]
- III:  $\text{Sn} + (\text{conc}) \text{ HCl}$  [1]
- IV:  $\text{CH}_3\text{CH}_2\text{OH}$  (or name) [1]  
 + c.  $\text{H}_2\text{SO}_4$  + heat [1]

[6]

(b)



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

[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.

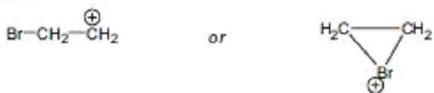
5	(a)	I:	$\text{Cl}_2 + \text{AlCl}_3/\text{Fe}/\text{etc}$	[1]														
		II:	$\text{Cl}_2 + hf$	[1]														
		III:	$\text{KMnO}_4 + \text{H}^+$	[1]														
		IV:	$\text{SOCl}_2$ or $\text{PCl}_3/\text{PCl}_5$ or $\text{P} + \text{Cl}_2$	[1]														
			(for I, II and IV, deduct a mark ([1] only) for one or more mentions of (aq))															
			(for I, mention of hf negates the mark)															
			(for I and II, if $\text{Cl}_2$ 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 $\text{C}_6\text{H}_5\text{-CH}_2\text{CN}$		[1]														
		step V: $\text{NaCN}/\text{KCN}$		[1]														
		heat (or 50-80°C) + ethanol/alcohol		[1]														
		step VI: $\text{LiAlH}_4$ or $\text{H}_2 + \text{Ni/Pt/Pd/Rh}$ or $\text{Na} + \text{ethanol}$		[1] [4]														
	(d)		<table border="1"> <thead> <tr> <th rowspan="2">compound</th> <th colspan="2">reagent</th> </tr> <tr> <th>cold water</th> <th>hot NaOH(aq)</th> </tr> </thead> <tbody> <tr> <td>E</td> <td><i>no reaction</i></td> <td><i>no reaction</i></td> </tr> <tr> <td>F</td> <td><i>no reaction</i></td> <td><math>\text{C}_6\text{H}_5\text{CH}_2\text{OH}</math></td> </tr> <tr> <td>G</td> <td><math>\text{C}_6\text{H}_5\text{CO}_2\text{H}</math></td> <td><math>\text{C}_6\text{H}_5\text{CO}_2^-\text{Na}^+</math></td> </tr> </tbody> </table>	compound	reagent		cold water	hot NaOH(aq)	E	<i>no reaction</i>	<i>no reaction</i>	F	<i>no reaction</i>	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	G	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	$\text{C}_6\text{H}_5\text{CO}_2^-\text{Na}^+$	
compound	reagent																	
	cold water	hot NaOH(aq)																
E	<i>no reaction</i>	<i>no reaction</i>																
F	<i>no reaction</i>	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$																
G	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	$\text{C}_6\text{H}_5\text{CO}_2^-\text{Na}^+$																
				6 x [1] [6]														
				[Total: 16]														

Q7.

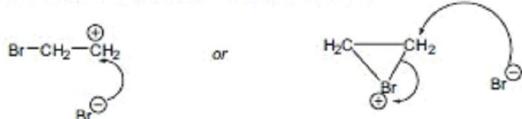
5 (a) reaction I electrophilic addition [1]

reaction II electrophilic substitution  
(salve: award [1] out of [2] for "addition" + "substitution", even if nucleophilic) [1] [2]

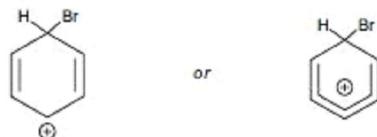
(b) reaction I: intermediate [1]



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

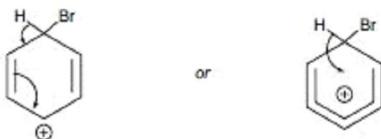


reaction II: intermediate [1]



(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]

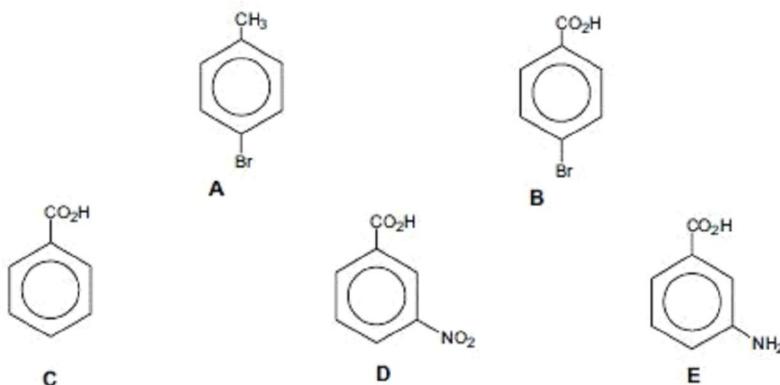
(c) Delocalised ring of electrons (in benzene) is stable, (so is re-formed in second step in benzene.)

or electrons in the ethene  $\pi$  bond are localised/more available for reaction with electrophiles

[1] [1]

Total: 71

Q8.



5 x [1]

[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]

[Total: 5]

**Q9.**

- 6 (a) (i) I:  $\text{SOCl}_2$  or  $\text{PCl}_5$  or  $\text{HCl} + \text{ZnCl}_2$  or  $\text{PCl}_3 + \text{heat}$  or  $\text{Cl}_2 + \text{P} + \text{heat}$   
[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  $S_N$  or  $S_N1$  or  $S_N2$  [1]

(iii) delocalisation of lone pair on C<sub>6</sub> of benzene ring produces a stronger C-C<sub>1</sub> 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: Sn + conc HCl [NOT LiAlH<sub>4</sub> or H<sub>2</sub> + Ni] [1]

(ii) III: electrophilic substitution [1]

IV: reduction or redox [1]

[5]

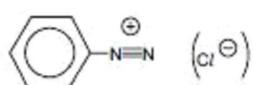
(c) e.g. add bromine water or  $\text{Br}_2(\text{aq})$  (a solvent is needed for the mark)  
or add  $\text{H}_2\text{O}_2$  solution

#### **phenylamine decolorization**

phenylamine decolorises the bromine or gives a white ppt; hexylamine does not or hexylamine turns UI blue, with phenylamine it stays green

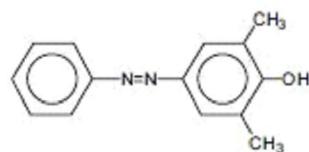
c. Hexylamine turns oil blue, with phenylamine it stays green.

(d)



(allow + charge on either N)  
(allow double or triple bond)

[1]



(phenylazo group must be at 4-position to -OH)  
(N=N must be double bond, not triple)

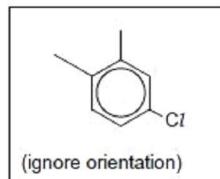
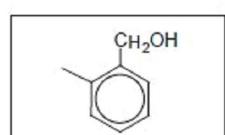
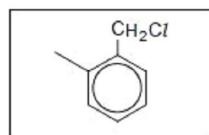
[1]

[2]

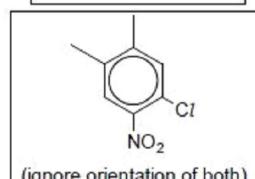
[Total: 13]

Q10.

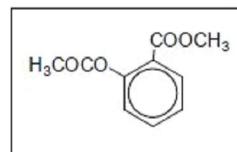
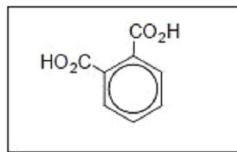
7



(ignore orientation)



(ignore orientation of both)

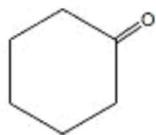


[6]

[Total: 6]

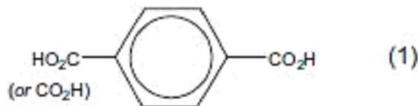
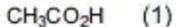
Q11.

(d)

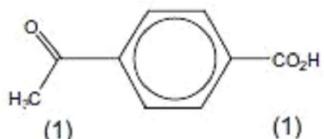


(1)

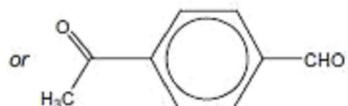
and



(1)



(1)



or

(1)

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

(1)

(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)

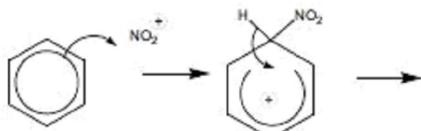
(ii) because the  $\pi$  electrons / double bonds are delocalised / in resonance or electrons are evenly distributed / spread out

(1) [2]

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

(1)

(ii) electrophilic substitution  
mechanism:



curly arrows from benzene to  $\text{NO}_2^+$ , and showing loss of  $\text{H}^+$   
correct intermediate (with "+" in the 'horse-shoe')

(1)

(1) [4]

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

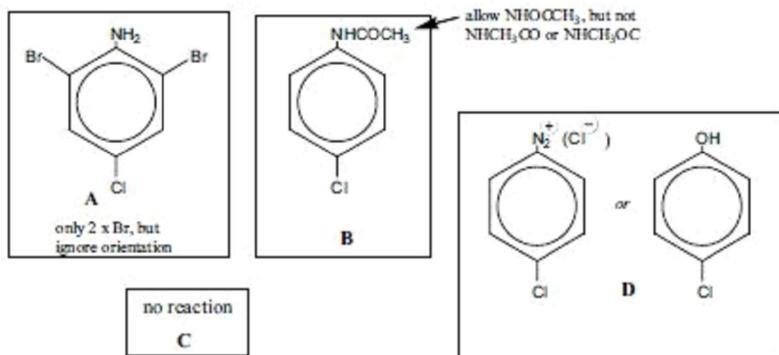
(1) [1]

(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]

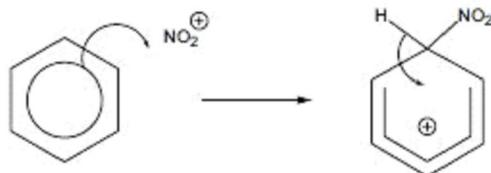
### Q13.

5 (a)

transformation	reagent + conditions
$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5\text{Cl}$	$\text{HCl}$ , no light or catalyst
$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{Cl}$	conc $\text{HCl}$ + $\text{ZnCl}_2$ or $\text{SOCl}_2$ or $\text{PCl}_5$ or $\text{PCl}_3$ and heat
$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Cl}$	$\text{Cl}_2$ + light
$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2$	$\text{Cl}_2$ , no light or catalyst
$\text{CH}_3\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{COCl}$	$\text{SOCl}_2$ or $\text{PCl}_5$ or $\text{PCl}_3$ and heat
$\text{H}_3\text{C}-\text{C}_6\text{H}_5 \rightarrow \text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{Cl}_2$ + $\text{AlCl}_3$
$\text{C}_6\text{H}_5-\text{CH}_3 \rightarrow \text{C}_6\text{H}_5-\text{CH}_2\text{Cl}$	$\text{Cl}_2$ + light or heat

[6]

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



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

- (ii) C is  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  [1]

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

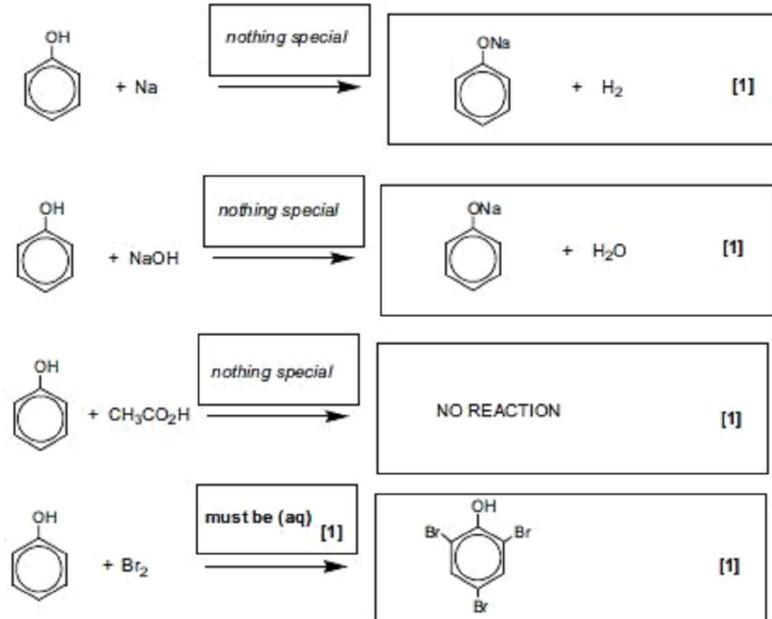
(If C is given as 3-bromotoluene, then allow the last [2] marks if steps 1 and 2 are reversed.)

[Total: 12]

## Q14.

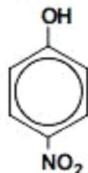
- 5 (a) acidity: ethanol < water [1]  
 due to +ve inductive effect of  $C_2H_5$  group or  $C_2H_5$  gives  $e^-$  to oxygen or intensifies  $e^-$  (in O-H bond) [1]  
 acidity: phenol > water [1]  
 due to stabilisation of the anion/anionic charge or makes the anion less basic [1]  
 [4]

(b)



[5]

(c) H is



[1]

reagents & conditions:

step 1 dilute  $HNO_3$  (dilute, not just 'aq'.  $H_2SO_4$  negates) [1]

step 2 Sn/ $SnCl_2$ /Fe +  $HCl$  or  $H_2$  + Ni/Pd (NOT  $H_2$  + Pt. NOT  $LiAlH_4$  or  $NaBH_4$ ) [1]

step 3  $CH_3COCl$  or  $(CH_3CO)_2O$  ('aq.' negates) [1]

[4]

[Total: 13]

Q15.

3. (a) (i) C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> [1]

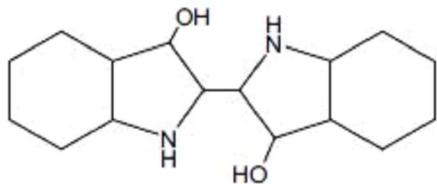
(ii) ketone, alkene, amine, aryl (benzene/arene/phenyl) (any 3) [2]  
[3]

(b) (i) reduction or redox [1]

(ii) NaBH<sub>4</sub> or LiAlH<sub>4</sub> (NOT H<sub>2</sub> + 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<sub>5</sub>/SOCl<sub>2</sub> [1] no reaction steamy fumes/fizzing [1]  
or PCl<sub>5</sub> + warm misty/white fumes  
2 x "no reaction" must be linked to "correct reagent" [1]  
[5]

(d) (i)



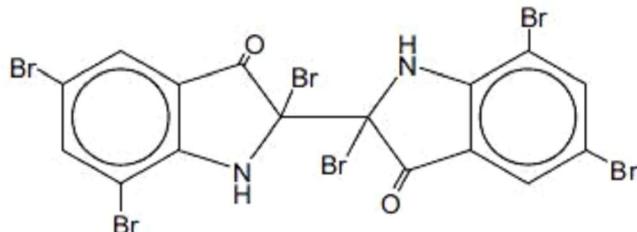
[1]

(ii) M<sub>r</sub> = 262, so 2.5 g = 2.5/262 = 9.54 × 10<sup>-3</sup> mol [1]  
(1 mol indigo absorbs 9 mol of H<sub>2</sub>)  
so volume of H<sub>2</sub> = 9 × 24 – 9.54 × 10<sup>-3</sup> = 2.06 dm<sup>3</sup> (2060 cm<sup>3</sup>)

[1]

[3]

(e)

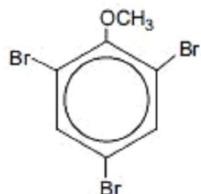


2 x Br on C=C [1]  
a Br on each ring [1]  
TWO non-adjacent Br on each ring [1]  
[3]

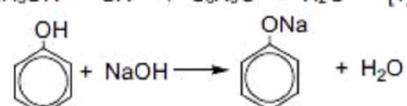
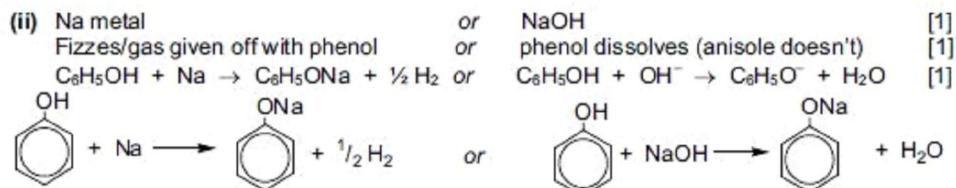
[Total: 16]

**Q16.**

5 (a) (i)

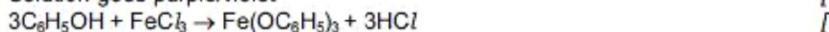


[1]



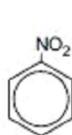
(neutral) iron(III) chloride      [1]

Solution goes purple/violet      [1]

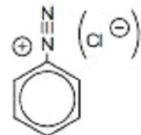


[4]

(b) (i)



D



E

[1] + [1]

(ii) step 2: Sn + HCl      NOT LiAlH4, NaBH4  
conc. + reflux      (warm is insufficient)      [1]  
[1]

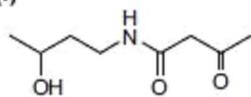
**step 4 is conditional of structure E**

step 4: warm + in H2O

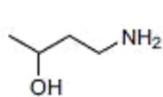
[1]

[5 max 4]

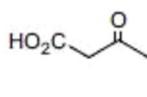
(c) (i)



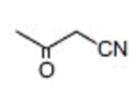
F



G



H



J

F must be an amide

[4]

(ii) reaction 1: H2 + Ni or LiAlH4  
reaction 2: heat + aqueous HCl

[1]

[1]

[6]

[Total: 14]

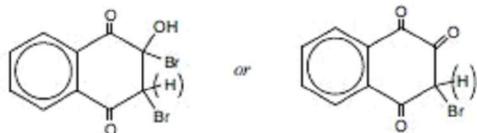
**Q17.**

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)

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

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

(iv)



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

[1]  
**[6]**

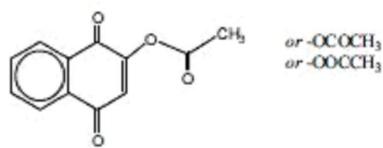
(b) (i)  $E_{\text{cell}} = 1.33 - 0.36 = (+)0.97 \text{ (V)}$  [1]

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

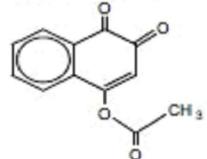
(c) (i) compound **C** is

[1]



(ii) compound **D** is

[1]

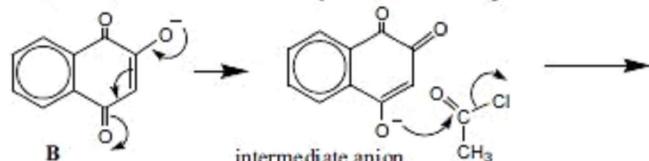


(iii) mechanism: 3 curly arrows in **B** or correct intermediate anion

[1]

a curly arrow from an  $\text{O}^-$  or an oxygen with a lone pair to the carbon of the  $\text{C=O}$  group in  $\text{CH}_3\text{COCl}$ , and a second curly arrow breaking the  $\text{C-Cl}$  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)  $(CH_3)_3C - Cl$  (any unambiguous structure or name) [1]
- (ii) reduction or hydrogenation [1]
- (iii) either  $CH_3CO_2H$  and heat with (conc)  $H_2SO_4$   
or  
 $CH_3COCl$  [1]
- (iv) reflux [1]
- dilute HCl [1]
- [5]

(c) (i)

reagent and conditions	product with A	product with B
Br <sub>2</sub> (aq)		no reaction
heat with HBr	no reaction	
pass vapour over heated Al <sub>2</sub> O <sub>3</sub>	no reaction	
heat with acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	no reaction	

[6]

(ii) either: Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/H<sup>+</sup>: no observation with A and goes from orange to green with B.

or:

Br<sub>2</sub>(aq): white ppt. with A and no observation/ppt with B

[1]

[7]

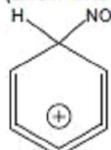
[Total: 17]

**Q19.**

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

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

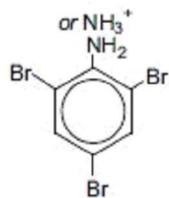
(b) (allow intermediate from methylbenzene)



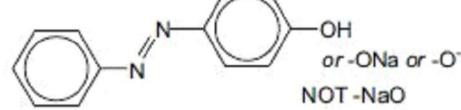
[1]  
[1]

(c) Sn/tin (or  $\text{SnCl}_2$ , Fe) +  $\text{HCl}$  (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]

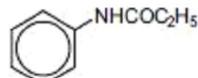
$T \leq 10^\circ\text{C}$  [1]  
[4 max 3]

(e) (i) amide [1]

(ii)  $M_r = 108+11+14+16 = 149$  [1]

%N =  $(14 \times 100)/149 = 9.4\%$  [1]

(iii)



[1]  
[3]

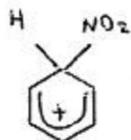
[Total: 11]

**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]

(c) (i) structure:



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]

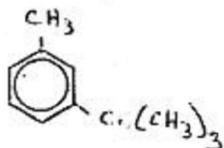
(ii)  $\text{X}^+ = \text{NO}_2^+$  [1]

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

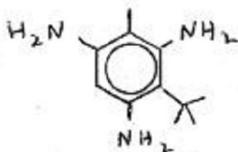
(iv)  $2 \text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$  [2]  
 ([1] for species, [1] for balancing. Allow [1] for: the acids  $\longrightarrow \text{NO}_2^+ + \text{HSO}_4^- (+\text{H}_2\text{O})$ )

**5**

(d) (i)



(ii)



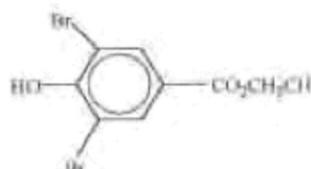
Ignore alkyl groups – these can be “R” or even incorrect.  
 Allow  $\text{NH}_3^+$  or  $\text{NH}_3\text{Cl}$  instead of one or more  $\text{NH}_2$  groups

[1]

**2**

**Total: 10**

**Q21.**

4	(a)	phenol, ester, arene/bezene ring	<i>any two</i>	(1) + (1)	[2]
(b)	(i)	$\text{Na}^+ - \text{O-C}_6\text{H}_4-\text{CO}_2\text{C}_2\text{H}_5$		(1)	
	(ii)	$\text{Na}^+ - \text{O-C}_6\text{H}_4-\text{CO}_2^- \text{Na}^+$	✓	$\text{C}_2\text{H}_5\text{OH}$	✓
	(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 $\text{NaOH(aq)}$			(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

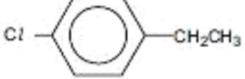
- (b) e.g. add neutral  $\text{FeCl}_3$  (aq) – violet colour with phenol  
or add universal indicator – red/orange colour with phenol  
or add Na metal – fizzing/ $\text{H}_2$  evolved with phenol  
or add  $\text{NaOH}$ (aq) to the pure compound – phenol would dissolve  
or add  $\text{H}^+$  (aq) 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)  $\text{HO-C}_6\text{H}_4\text{-NH}_2 + 2\text{AgBr} + 2\text{OH}^- \rightarrow \text{O=C}_6\text{H}_4=\text{O} + \text{H}_2\text{O} + \text{NH}_3 + 2\text{Ag} + 2\text{Br}^-$  (or  $\text{C}_6\text{H}_7\text{NO}$ ) (or  $\text{C}_6\text{H}_4\text{O}_2$ ) [1] 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

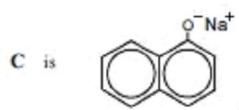
## Q24.

- 4 (a) (i) light or heat [aq or  $\text{AlCl}_3$  negates] (1)
- (ii)  $\text{NaOH}/\text{KOH}/\text{alkali}/\text{OH}^-$  (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)  $/\text{OH}^-(\text{aq})/\text{NaOH}(\text{aq})/\text{aqueous alkali} + \text{heat}$  [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

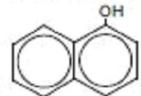
[1]

(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  $\text{OH}^-(\text{aq})$  and heat  $>80^\circ$

[1]  
[7]

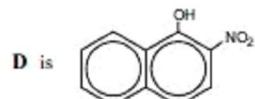
(b) (i)  $\text{Br}_2(\text{aq})$  (or other suitable solvent)

[1]

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

[1]  
[2]

(c) (i)

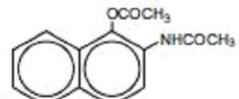


[1]

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

[1]

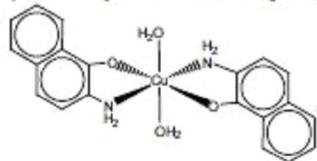
(iii)



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:  $\text{Cl}_2$  + light or heat ( $T \sim 100^\circ\text{C}$ ) (AICl<sub>3</sub> or aq. negates) [1]
- step III: KCN (in ethanol) + heat ( $T \sim 75^\circ\text{C}$ ) (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)	$\text{RONa}$ or $\text{RO}^-\text{Na}^+$	$\text{ArONa}$ or $\text{ArO}^-\text{Na}^+$
NaOH(aq)	<b>no reaction</b>	$\text{ArONa}$ or $\text{ArO}^-\text{Na}^+$
$\text{Br}_2$ (aq)	<b>no reaction</b>	tribromophenol
$\text{I}_2$ (aq) + $\text{OH}^-$ (aq)	<b>no reaction</b>	<b>no reaction</b>
an excess of acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq)	cyclohexanone	<b>no reaction</b>

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

- (d) either  $\text{Br}_2$ (aq): no reaction with cyclohexanol; decolourises or white ppt with phenol

or  $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+$ : 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
A	✓	
B		✓
C	✓	
D	✓	
E	✓	

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

- (b) reaction I:  $\text{Cl}_2 + \text{AlCl}_3 / \text{FeCl}_3 / \text{Fe} /$  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)

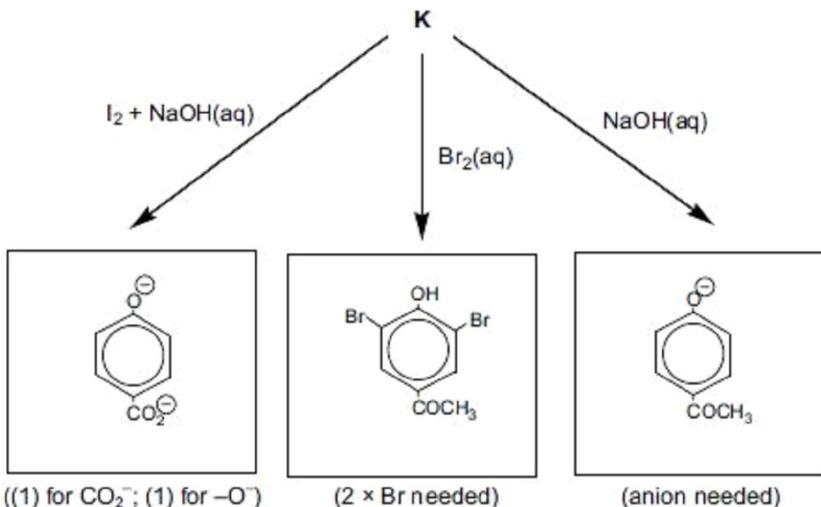
- (ii) H is nitrobenzene – structure needed here (1)  
J is phenyldiazonium chloride – structure needed here (1)
- (iii) step 2 Sn/Zn + HCl / H<sub>2</sub> + named cat / NaBH<sub>4</sub> / LiAlH<sub>4</sub> / Na + ethanol (1)  
step 3 HNO<sub>2</sub>/NaNO<sub>2</sub> + HCl at T = 10°C or less (1)  
step 4 heat/warm to T > 10°C (1)  
step 5 CH<sub>3</sub>COC<sub>2</sub> / CH<sub>3</sub>COCOCOCOCH<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)



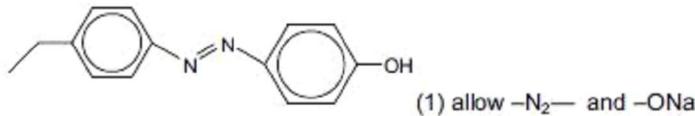
[4]  
[8 max 7]

[Total: 14]

Q30.

- 4 reaction I:  $\text{C}_6\text{H}_6 + \text{light}$  (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:  $\text{KMnO}_4 + \text{H}^+/\text{OH}^-$  + 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]

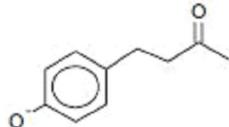
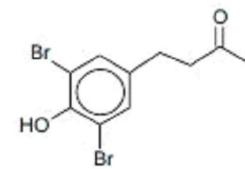
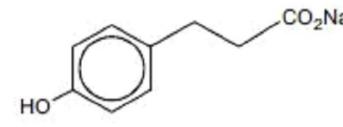
Q31.

5 (a) phenol  
ketone

[1]  
[1]

[2]

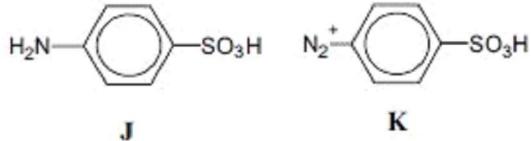
(b)

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

[2]

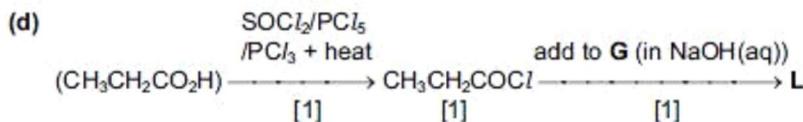
[8]

(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]**

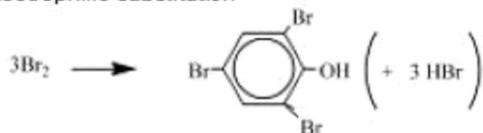


**ecf from  $\text{CH}_3\text{COOH}$**  [3]

**[Total: 18]**

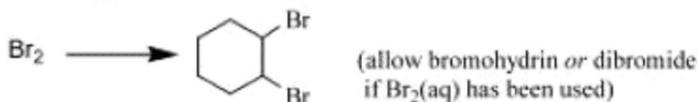
### Q32.

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



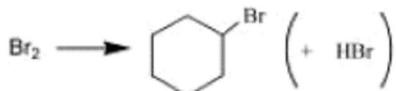
[1]

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



product [1]

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

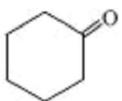


product [1]

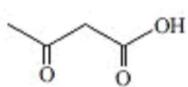
balanced equation in (i) (i.e.  $3\text{Br}_2$  and  $3\text{HBr}$ ) [1]  
 balanced equation in (iii) (i.e.  $\text{Br}_2$  and  $\text{HBr}$ ) [1]

**[11 max 10]**

(b) (i)



C



D



E

3 correct structures (can be in any order)  $3 \times [1]$

(ii) results of tests:

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

with  $\text{I}_2 + \text{OH}^-$ : 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]**



