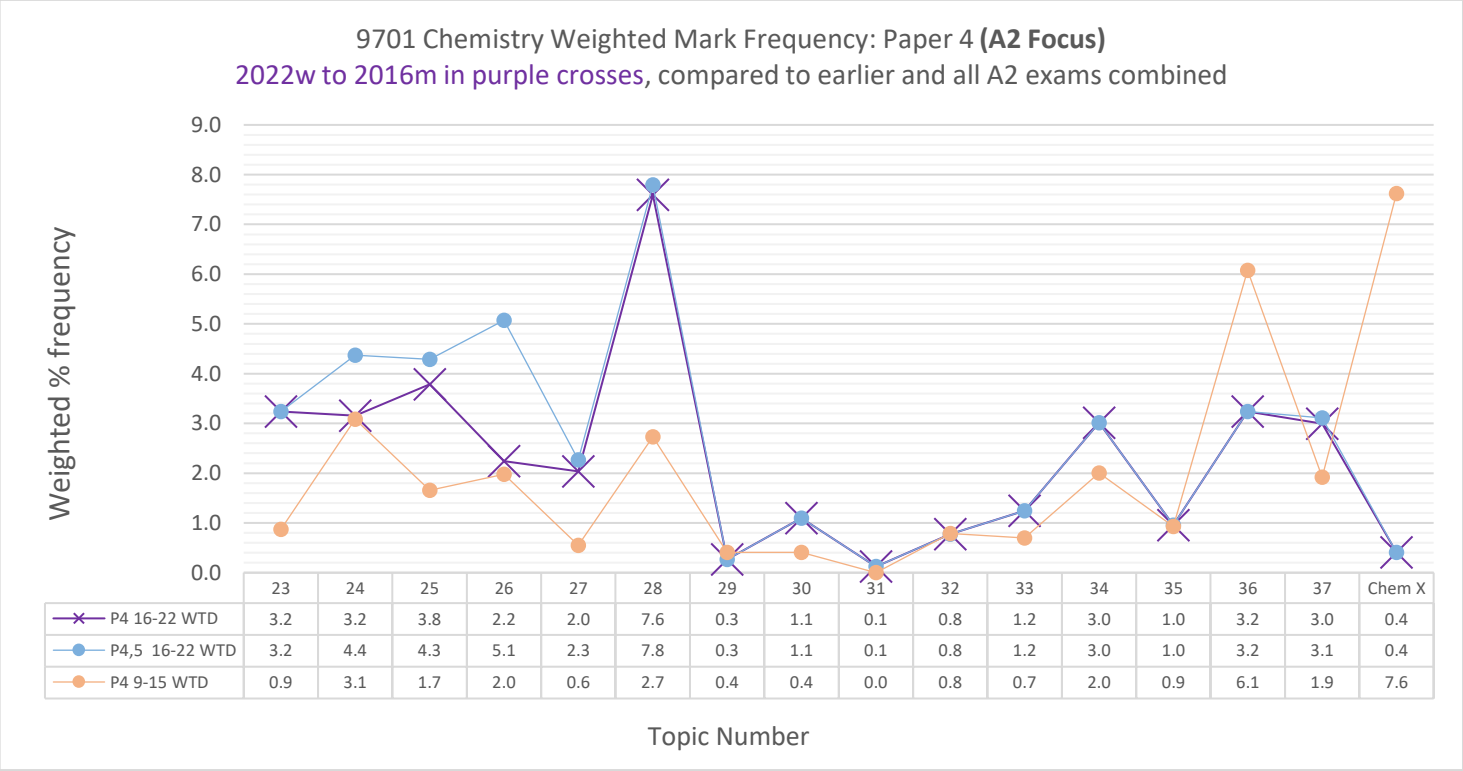
Name: Class: Date:

ALvl Chem 32 EQ 22m to 09w **Paper 4** Hydroxy compounds 79marks

As you start and work through this worksheet you can tick off your progress to show yourself how much you have done, and what you need to do next. The first task is just to read the first question and should take you less than 3 minutes to complete.

Paper 4 Topic Checklist Tick each task off as you go along	RANK:	P4 Noob	P4 Novice	P4 Bronze	P4 Silver	P4 Gold	P4[1] Winner	P4 Hero	P4 Legend
	Marks	1 Q Started	1 Q done	10% of marks	25% of marks	40% of marks	50% of marks	75% of marks	100% of marks
Topic 30 (marks)	68		5	7	17	27	34	51	68
Time - 72 seconds per mark (minutes)	83		6	8	21	33	41	62	83



	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
P4 16-22 WTD	3.2	3.2	3.8	2.2	2.0	7.6	0.3	1.1	0.1	0.8	1.2	3.0	1.0	3.2	3.0	0.4
P4,5 16-22 WTD	3.2	4.4	4.3	5.1	2.3	7.8	0.3	1.1	0.1	0.8	1.2	3.0	1.0	3.2	3.1	0.4
P4 9-15 WTD	0.9	3.1	1.7	2.0	0.6	2.7	0.4	0.4	0.0	0.8	0.7	2.0	0.9	6.1	1.9	7.6

What the most thoughtful students will get out of their extensive studying will be a capacity to do meaningful brain-based work even under stressful conditions, which is a part of the self-mastery skillset that will continue to deliver value for the whole of their lives. Outstanding grades will also happen, but the most important outcome from skillful action in study is being better at any important tasks even if circumstances are do not feel ideal.

Learning how to manage oneself so we can more reliably get ambitious and successful outcomes out of our challenges in a productive and positive way is one aspect of life's most valuable pursuit summarised and inscribed on the Temple of Apollo at Delphi: "know thyself".

1. To complete these questions, as important as your answer, is checking your answer against the mark scheme.
2. For each question, or page, convert your mark score into a percentage. This will allow you to see (and feel) your progress as you get more experience and understanding with each topic.
3. If you find you get a higher percentage answering short answer questions than multiple choice questions that often means you are using the marking scheme correctly; your correct answer might not be fully complete. The marks easiest to miss rely on providing more details fully described.

[1] **DO NOT** work on these higher levels of completion unless you have also achieved at least a "Silver" (25%) in the same topic in Paper 5, if it exists.

32 Hydroxy compounds

32.1 Alcohols

Learning outcomes

Candidates should be able to:

1 describe the reaction with acyl chlorides to form esters using ethyl ethanoate

32.2 Phenol

Learning outcomes

Candidates should be able to:

1 recall the reactions (reagents and conditions) by which phenol can be produced:
   (a) reaction of phenylamine with HNO_2 or $NaNO_2$ and dilute acid below 10 °C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol
2 recall the chemistry of phenol, as exemplified by the following reactions:
   (a) with bases, for example NaOH(aq) to produce sodium phenoxide
   (b) with Na(s) to produce sodium phenoxide and H_2(g)
   (c) in NaOH(aq) with diazonium salts, to give azo compounds
   (d) nitration of the aromatic ring with dilute HNO_3(aq) at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol
   (e) bromination of the aromatic ring with Br_2(aq) to form 2,4,6 tribromophenol
3 explain the acidity of phenol
4 describe and explain the relative acidities of water, phenol and ethanol
5 explain why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene
6 recall that the hydroxyl group of a phenol directs to the 2, 4 and 6 positions
7 apply knowledge of the reactions of phenol to those of other phenolic compounds, e.g. naphthol

Q# 1/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

(e) Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.

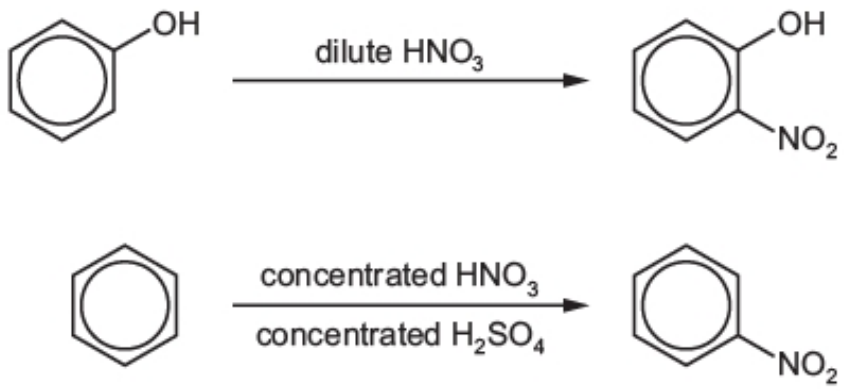


Fig. 4.5

Explain why the reagents and conditions for these two reactions are different.

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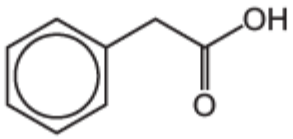
..... [3]

Q# 2/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 The structure of phenylethanoic acid is shown.



(b) Phenylethanoic acid, ethanol and phenol can all behave as acids.

Compare and explain the relative acidities of these three compounds.

..... > ..... > .....

most acidic least acidic

.....

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.....

.....

..... [4]

Q# 3/ ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 Phenol, C_6H_5OH, is a weak acid.

(a) Phenol can be made from phenylamine, $C_6H_5NH_2$.

Give the reagents and conditions for this reaction.

.....

..... [2]

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $C_6H_5NO_3$.

Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.

name .....

name .....

[2]

(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.

name .....

[2]

(ii) Describe **two** visual observations that can be made when phenol reacts with an excess of aqueous bromine.

observation 1 .....

observation 2 .....

[1]

(d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

(e) Water, phenol and ethanol can all behave as acids.

Place these three compounds in order of acidity, starting with the **most** acidic.
Explain your answer.

..... > ..... > .....

most acidic least acidic

.....

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.....

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.....

.....

[3]

Q# 4/ ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

5 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(b) Suggest why bromination of phenol occurs more readily than bromination of benzene.

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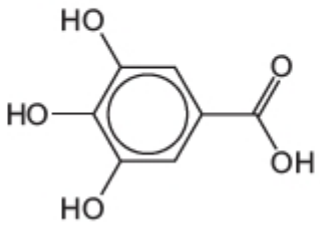
..... [2]

Q# 5/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5 /www.SmashingScience.org :o)

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(a) Gallic acid contains the carboxylic acid and phenol functional groups.

State and explain the relative acid strength of these two functional groups.

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..... [2]

Q# 6/ ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 **(a)** Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = C*l* or OH).

Explain why.

.....

.....

.....

.....

..... [3]

(b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, C_6H_4BrOH, are formed.

Suggest structures for these products. Name each compound.

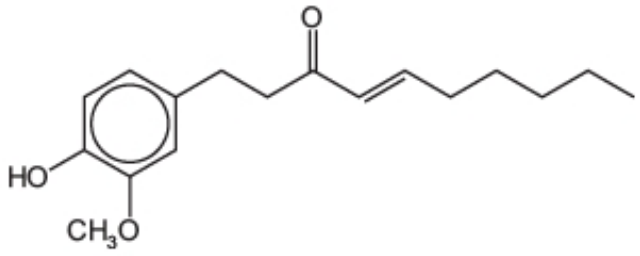
name: .....

name: .....

[2]

Q# 7/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8 /www.SmashingScience.org :o)

(b) The structure of shogaol is shown.



shogaol

(c) Zingerone is formed from gingerol.

Some reactions of zingerone are shown.

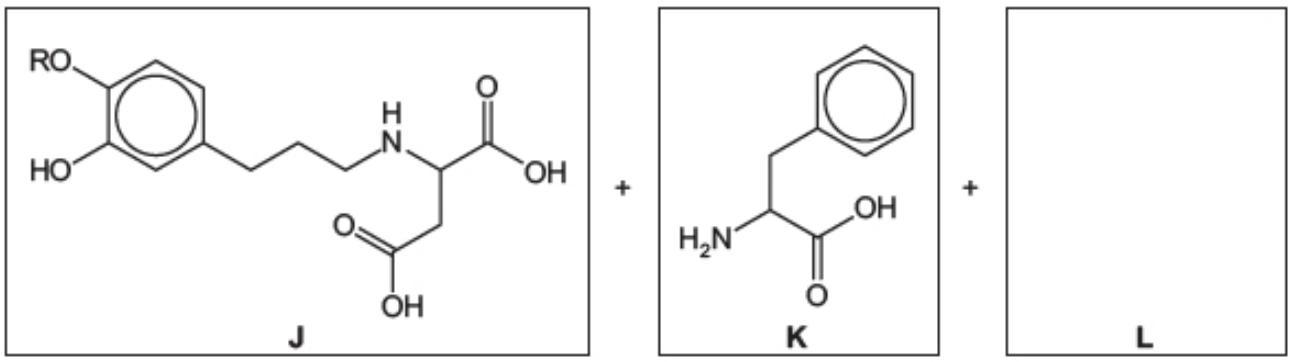
Complete the table to identify the functional groups in zingerone.

reagent and conditions	observation	functional group in zingerone indicated by the observation
benzenediazonium chloride, 5 °C, alkaline solution	red ppt.	
2,4-dinitrophenylhydrazine	orange ppt.	
warm with Tollens' reagent	no change	

[2]

Q# 8/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



(c) **(i)** Aqueous bromine was added dropwise to a solution of J until the bromine was in excess.

State what you would observe.

.....

..... [1]

(ii) J has the molecular formula $C_{14}H_{19}O_6N$.

Use this formula to write an equation for the reaction of excess aqueous sodium hydroxide with **one** mole of **J**.

..... [2]

Q# 9/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 **(a)** **(i)** State and explain the relative acidities of ethanol and phenol.

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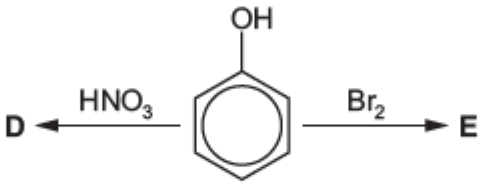
..... [2]

(ii) In the table below, give the reaction conditions for the formation of organic products **D** and **E** and draw their structures.



phenol

reagent	conditions	structure
HNO_3	dilute, 5 °C	**D**
Br_2		**E**

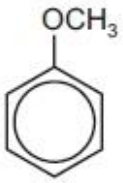
[3]

(iii) Name the mechanism of the reaction forming compound **E**.

..... [1]

Q# 10/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

5 **(a)** Methoxybenzene reacts with $Br_2(aq)$ in a similar manner to phenol.



methoxybenzene

(i) Draw the structural formula of the product of the reaction between methoxybenzene and an excess of bromine.

(ii) Suggest a chemical reaction you could use to distinguish between methoxybenzene and phenol. State the reagent, describe the observations you would make, and give an equation for the reaction.

reagent .....

observation .....

equation

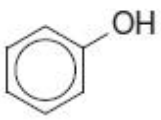
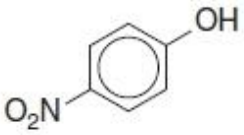
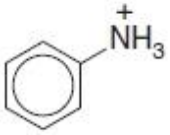
[4]

Q# 11/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

(b) **(i)** Write an equation for a reaction in which phenol, C_6H_5OH, acts as a Brønsted-Lowry acid.

.....

The pK_a values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

compound	pK_a
	10.0
	7.2
	4.6

(ii) Suggest an explanation for the difference in the pK_a values of phenol and nitrophenol.

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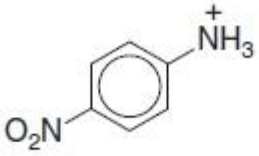
(iii) Using the information in the table opposite, predict which of the following pK_a values is the most likely for the 4-nitrophenylammonium ion.



Place a tick (✓) in the box beside the value you have chosen.

pK_a	
1.0	
4.5	
7.0	
10.0	

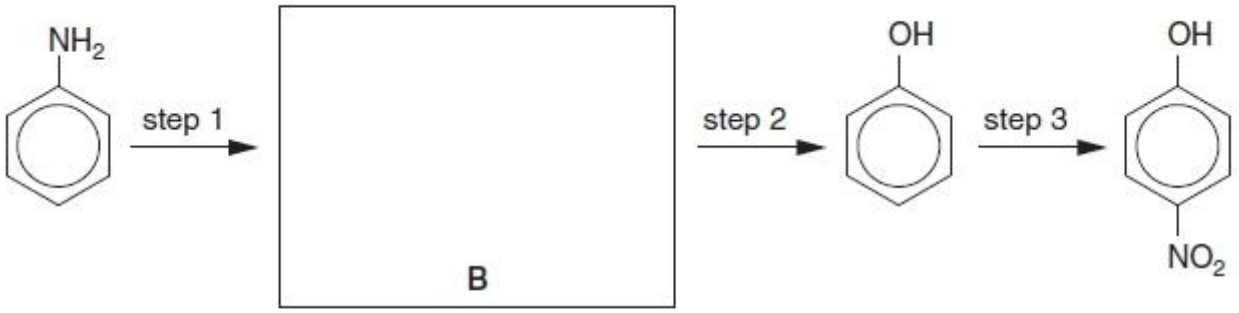
(iv) Explain your answer to part **(iii)**.

.....

.....

..... [5]

(c) Phenylamine can be converted to 4-nitrophenol by the following steps.



(i) Suggest the identity of intermediate **B** by drawing its structure in the box above.

(ii) Suggest reagents and conditions for the three steps in the above scheme.

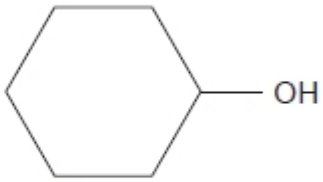
	reagent(s)	conditions
step 1		
step 2		
step 3		

[5]

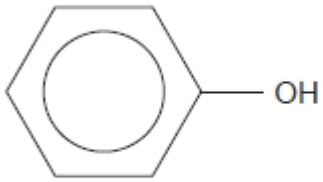
[Total: 14]

Q# 12/ ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4 Cyclohexanol and phenol are both solids with low melting points that are fairly soluble in water.



cyclohexanol



phenol

(a) Explain why these compounds are more soluble in water than their parent hydrocarbons cyclohexane and benzene.

.....

.....

..... [2]

(b) Explain why phenol is more acidic than cyclohexanol.

.....

.....

..... [2]

(c) For **each** of the following reagents, draw the structural formula of the product obtained for **each** of the two compounds. If no reaction occurs write ***no reaction*** in the box.

reagent	product with cyclohexanol	product with phenol
Na(s)		
NaOH(aq)		
$Br_2(aq)$		
$I_2(aq) + OH^-(aq)$		
an excess of acidified $Cr_2O_7^{2-}(aq)$		

[7]

(d) Choose **one** of the above five reagents that could be used to distinguish between cyclohexanol and phenol. Describe the observations you would make with each compound.

reagent .....

observation with cyclohexanol .....

observation with phenol .....

[2]

[Total: 13]

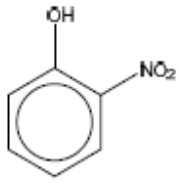
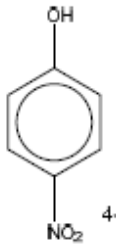
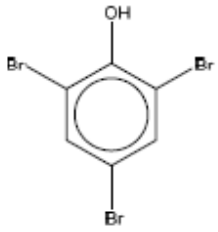
Q# 1/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4(e)	p-orbital on oxygen overlaps with ring / π system OR lone pair of e⁻ on oxygen is delocalised into the ring [1] electron density in ring increases [1] attracts/polarises electrophile better [1]	3

Q# 2/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(b)	M1: trend phenylethanoic acid > phenol > ethanol [1] M2: *why phenylethanoic acid is the strongest* • negative inductive electron withdrawing effect of C=O which weakens O-H bond / stabilises anion [1] M3: *why phenol is stronger than ethanol / weaker than phenylethanoic acid* • oxygen lone pair is delocalised into the ring system which weakens O-H bond / stabilises anion [1] M4: *why ethanol is the weakest* • electron donating alkyl / ethyl group which strengthens O-H bond / destabilises anion [1]	4

Q# 3/ ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(a)	**M1:** HNO_2 OR $NaNO_2$ + HCl [1] **M2:** T ⩾ 10 °C / warm **AND** water [1]	2
7(b)	 2-nitrophenol  4-nitrophenol 2 × [1]	2
7(c)(i)	 2,4,6-tribromophenol ✓ ✓ [2]	2
7(c)(ii)	bromine is decolourised **AND** white precipitate is formed **BOTH** [1]	1
7(d)	$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ [1] **ALLOW** any equation for phenol acting as an acid	1

7(e)	phenol>water>ethanol [1] • (phenol:) lone pair on oxygen is delocalised into the benzene ring • (ethanol:) positive inductive effect / electron donating effect of alkyl / ethyl group • correct statement about stabilisation of anion/ conjugate base OR weakening of O-H bonds once *in the context of phenol / ethanol* • correct statement about ease of proton/H^+ donation *in the context of phenol / ethanol* [2] Two correct statements = 1 mark	3

Q# 4/ ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

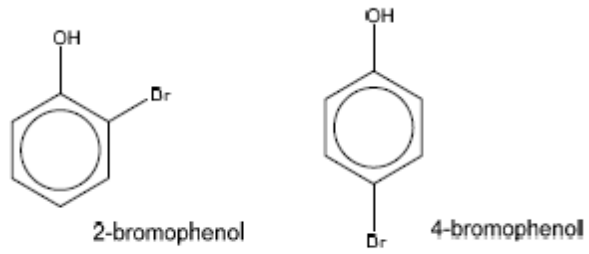
5(b)	lone pair of oxygen is delocalised into the ring any one from: • phenol has a higher electron density in the ring • phenol can polarise/induce a dipole in Br_2	2

Q# 5/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5 /www.SmashingScience.org :o)

5(a)	**M1** COOH is more acidic than phenol **AND** because the O-H bond in acid is weaker **OR** carboxylate ion is more stable **M2** O-H bond weakened / loses proton more easily **AND** by negative inductive effect of C=O / due to electronegative C=O **OR** carboxylate ion / anion is more stable **AND** due to delocalisation of minus charge by C=O / 2O	2

Q# 6/ ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(a)	**M1** C-X / C-Cl / C-O bond is stronger (in chlorobenzene / phenol) [1] **M2** p-orbital / lone pair on Cl / O(H) / X (in chlorobenzene / phenol) [1] **M3** electrons of the (Cl / O / electronegative atom) **AND** overlap / delocalise with π-electron cloud / delocalise into ring [1]	3

7(b)	 2-bromophenol 4-bromophenol structure and name correct [1]	2

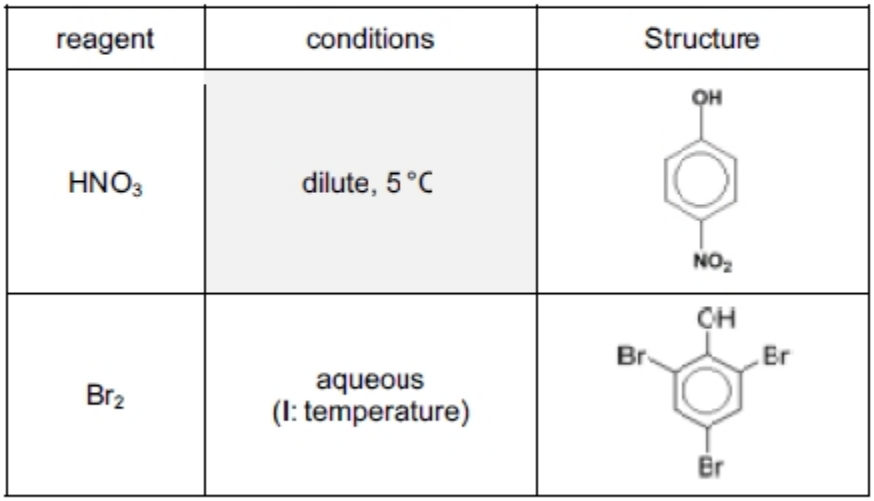
Q# 7/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8 /www.SmashingScience.org :o)

8(c)	phenol	1
	ketone	1

Q# 8/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

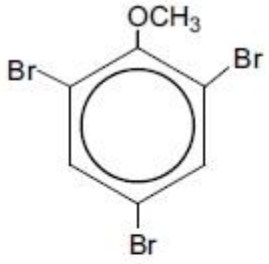
7(c)(i)	white precipitate	1
7(c)(ii)	$C_{14}H_{19}O_5N + 3NaOH \rightarrow C_{14}H_{15}O_5NNa_3 + 3H_2O$	2

Q# 9/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 (a) (i)	**M1**: phenol is **more acidic** than ethanol because the O–H bond in phenol is weakened / the phenoxide anion is stabilised / ethanol has an electron donating group **M2**: p orbital / lone pair of electrons on O can be delocalised over / overlaps with ring	1 1
(ii)	 	3
(iii)	electrophilic substitution	1

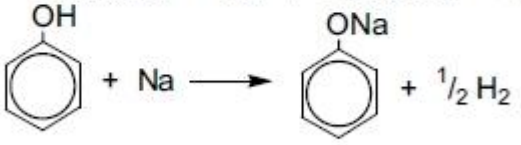
Q# 10/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

5 (a) (i)

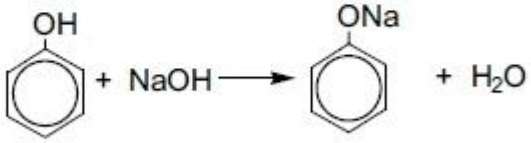


[1]

(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]



or



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

[4]

Q# 11/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

(b) (i) $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$ (*or* with $Na^+/H_2O/A^-$) [1]

(ii) pKa of nitrophenol is smaller/K_a is larger because it's a stronger acid/dissociates more than phenol [1]
stronger because the anionic charge is spread out moreover the NO_2 group *or* NO_2 is electron-withdrawing [1]

(iii) pKa = 1.0 [1]

(iv) Nitro group increases acidity / electron-withdrawing groups increase acidity [1]

[5]

(c) (i) **B** is phenyldiazonium cation, $C_6H_5–N^+\equiv N$ [1]

(ii)

reaction	reagent(s)	conditions
Step 1	**$NaNO_2$ + HCl or HNO_2** [1]	**T < 10°C** [1]
Step 2	**H_2O / aq**	**heat/boil/T > 10°** (both) [1]
Step 3	**HNO_3 NB HNO_3(aq) OK for both**	**dilute** (both) [1]

[4]

[5]

[Total: 14]

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^-Na^+	ArONa *or* ArO^-Na^+
NaOH(aq)	***no reaction***	ArONa *or* ArO^-Na^+
Br_2(aq)	***no reaction***	tribromophenol
I_2(aq) + OH^-(aq)	***no reaction***	***no reaction***
an excess of acidified $Cr_2O_7^{2-}$(aq)	cyclohexanone	***no reaction***

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

(d) *either* Br_2(aq): no reaction with cyclohexanol; decolourises *or* white ppt with phenol

or $Cr_2O_7^{2-}$ + 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]