EXAM PAPERS PRACTICE

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Detailed mark scheme

Suitable for all boards

Designed to test your ability and thoroughly prepare you

Level: CIE AS and A Level (9701)
Subject: Chemistry
Topic: CIE Chemistry
Type: Mark Scheme

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+

CHEMISTRY AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful

Mark Scheme

Answer 1.

a) Benzene only has one peak in its ^{13}C NMR spectrum because:

- All the carbons are equivalent; [1 mark]

[Total: 1 mark]

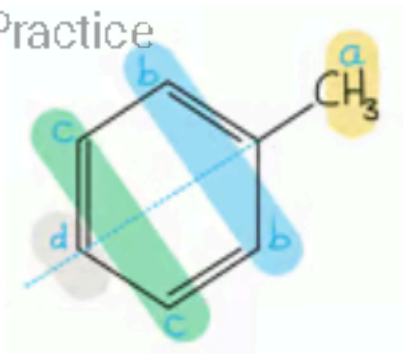
- This question highlights the need for you to be able to identify equivalent carbon environments
  - This is particularly relevant to symmetrical molecules, especially benzene and its derivatives

b) The number of ^{1}H peaks that would appear in the low resolution ^{1}H NMR spectrum of methylbenzene is:

- Four / 4; [1 mark]

[Total: 1 mark]

- To determine the number of ^{1}H peaks in a low resolution ^{1}H NMR spectrum, you have to decide how many different hydrogens there are in the compound
- This means identifying the ^{1}H nuclei that have different chemical environments



- The CH_3 group (labelled a) has no neighbouring hydrogens - this is one environment
- There are 5 C-H's in the methylbenzene ring
  - The two C-H groups directly adjacent to the methyl group carbon (labelled b) are equivalent (by symmetry) having one neighbouring hydrogen - this is a second chemical environment
  - The next two C-H groups around the ring (labelled c) are equivalent (by symmetry) having two neighbouring hydrogens, one on either side - this is a third chemical environment
  - The final C-H group directly opposite the methyl group carbon (labelled d) has two neighbouring hydrogens, one on either side - this is the fourth chemical environment

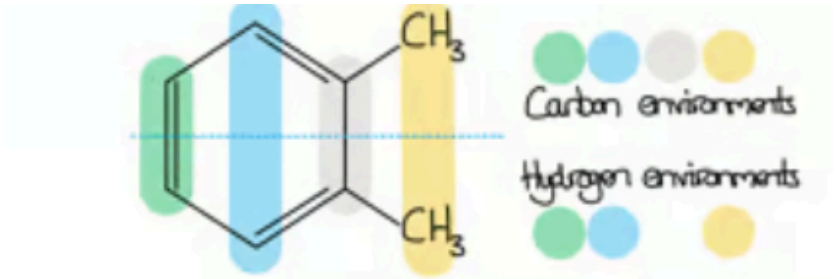
- The key to any NMR questions asking you to identify the number of peaks on a benzene derivative is spotting any symmetry in the molecule

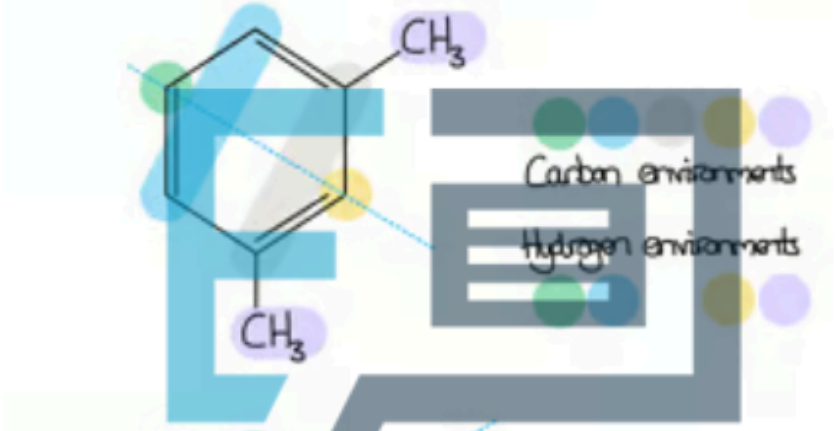
c) The number of expected peaks in the low resolution ^{1}H NMR and ^{13}C NMR spectra of the three dimethylbenzene isomers are:

Isomer	Number of peaks in ^{1}H NMR spectrum	Number of peaks in ^{13}C NMR spectrum	
1,2-dimethylbenzene	3	4	; [1 mark]
1,3-dimethylbenzene	4	5	; [1 mark]
1,4-dimethylbenzene	2	3	; [1 mark]

[Total: 3 marks]

- All three isomers will have at least one more ^{13}C peak due to the carbon with the methyl group that has no hydrogen attached - due to symmetry in the molecules, this only causes one extra peak





Answer 2.

a)

i) The structural formula of the standard reference chemical used in ^1H NMR is:

- $Si(CH_3)_4$; [1 mark]

ii) Tetramethylsilane is used as the standard reference chemical because:

Any **two** of the following:

- It is volatile / has a low boiling point ; [1 mark]
- It is non-toxic; [1 mark]
- It is inert ; [1 mark]
- It produces one single peak / signal; [1 mark]
- The peak it produces is far to the right / far away from other peaks; [1 mark]

[Total: 3 marks]

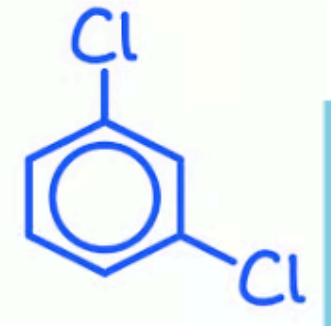
- The question is asking you to suggest the structural formula
  - **Remember:** Tetramethylsilane (TMS) is a silicon atom surrounded by four methyl groups
  - Therefore, its structural formula is $Si(CH_3)_4$
- TMS is used as the standard reference sample against which all other chemical shifts are measured
  - It has a value of 0 ppm
  - It will appear on the furthest right of an NMR spectrum
  - It does not interfere with the other peaks
  - It acts as a reference point to which the NMR spectrometer is tuned

b) The number of peaks in the compound 1,3–dichlorobenzene is;

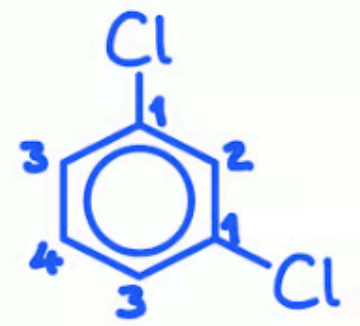
- 4 / Four; [1 mark]

[Total: 1 mark]

- The best way to determine the number of C-13 peaks / environments for 1,3–dichlorobenzene is to draw the displayed formula:



- You can then determine the number of peaks by looking at the different positions of the carbon atoms within the molecule:
  - Carbon atoms that are bonded to different atoms or groups of atoms have different environments and will have different chemical shifts
  - If two carbon atoms are positioned symmetrically within a molecule, then they are equivalent and have the same environment
  - They will absorb radiation at the same chemical shift and contribute to the same peak
- 1,3–dichlorobenzene has four different environments for the carbon atoms
  - It is much easier to see this once you have drawn out the structural formula of the molecule



c)

i) The number of peaks on the ^{13}C NMR of ethylbenzene is:

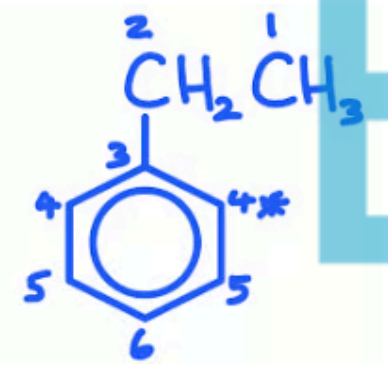
- 6 / six; [1 mark]

ii) The C-13 chemical shift range for the carbon with an * is:

- δ = 110 - 160 ppm; [1 mark]

[Total: 2 marks]

- The number of environments can be shown on the structural formula as shown:



- **Remember:** Look for carbon atoms that are bonded to different groups or positioned symmetrically within the molecule
  - Peaks 4 and 5 both show two sets of carbon atoms that are equivalent
  - This means that have the same chemical environment and will give the same chemical shift
- Looking at Table 1.1, the carbon with a * next to it will have a shift range of 110 - 160 ppm, for aromatic carbon atoms within ethylbenzene
  - The Kekule structure of benzene has been drawn here, which is unusual
  - If you are drawing benzene, while you will usually be allowed to use the Kekule structure, it would be better to use the delocalisation model using a circle to represent the delocalised ring of electrons

Answer 3.

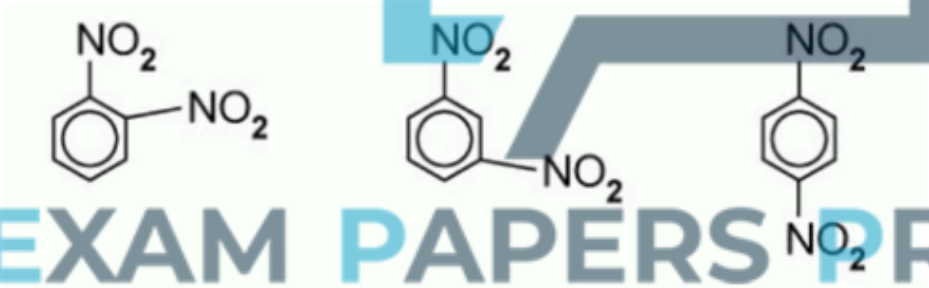
a) The identity of the molecular ions that gives rise to the peak at $m/e = 76$ is:

- $C_6H_4^+$; [1 mark]

[Total: 1 mark]

- **Remember:** The ion must have a positive charge
  - Without the positive charge, you could lose an exam mark
- The M_r of benzene = [(6 x 12.0) + (6 x 1.0)] = 78
  - So, a peak at 76 would be caused by $C_6H_4^+$

b) The **three** possible dinitrobenzene isomers of compound **A** containing a benzene ring are:



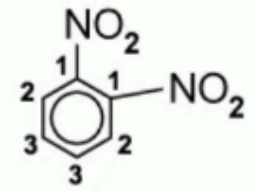
- Each correct structure; [1 mark]

[Total: 3 marks]

- The question tells you that you are looking for dinitro isomers
- This means that each isomer must have two nitro / NO_2 groups
- When you place one at the top of the ring / on carbon-1, the second nitro / NO_2 group can be placed:
  - On carbon-2
  - On carbon-3
  - On carbon-4

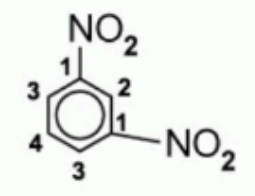
c) The labelled structures are:

- 1,2–dinitrobenzene:



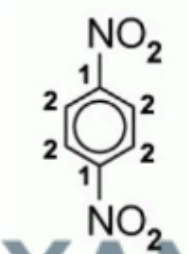
; [1 mark]

- 1,3–dinitrobenzene = compound **A**



; [1 mark]

- 1,4 - dinitrobenzene:



; [1 mark]

[Total: 3 marks]

- It said in the question compound **A** has four peaks
  - 1,3–dinitrobenzene has four different carbon environments
  - The two other isomers have 2 and 3 different carbon environments

Answer 4.

a) To determine the molecular formula of the unknown alcohol is:

- Percentage of oxygen = 21.6%; [1 mark]
- Moles of carbon = 5.41
  AND
  Moles of hydrogen = 13.5
  AND
  Moles of oxygen = 1.35; [1 mark]
- Ratio of carbon : hydrogen : oxygen is 4 : 10 : 1
  AND
  Therefore, the empirical formula is $C_4H_{10}O$; [1 mark]
- The mass of $C_4H_{10}O$ is 74.00
  AND
  Therefore, the molecular formula is $C_4H_{10}O$; [1 mark]

[Total: 4 marks]

- The important information in this question is that the unknown alcohol contains 64.9% carbon, 13.5% hydrogen and the rest oxygen
  - The amount of oxygen can be calculated by 100 - 64.9 - 13.5 = 21.6%
- The remainder of the question is a standard empirical formula calculation

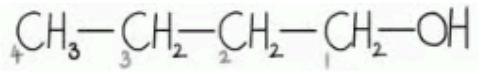
Element	C	H	O
Value from question	64.9	13.5	21.6
A_r	12.0	1.0	16.0
Moles	$\frac{64.9}{12.0} = 5.41$	$\frac{13.5}{1.0} = 13.5$	$\frac{21.6}{16.0} = 1.35$
Ratio	$\frac{5.41}{1.35} = 4.00$	$\frac{13.5}{1.35} = 10$	$\frac{1.35}{1.35} = 1$

- Therefore, the empirical formula is $C_4H_{10}O$
- $C_4H_{10}O$ has a mass of (4 x 12.0) + (10 x 1.0) + 16.0 = 74.00
- This is almost the same as the 74.12 g mol^{-1} given in the question, which means that the empirical formula is the molecular formula

b)

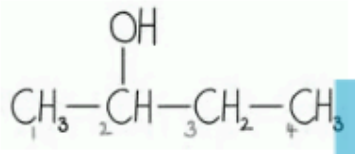
i) The four possible isomers of the unknown alcohol are:

- (Butan-1-ol)



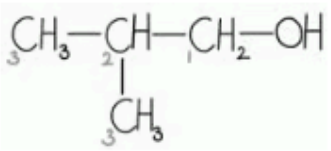
; [1 mark]

- (Butan-2-ol)



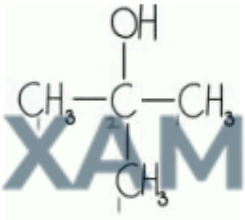
; [1 mark]

- (2-methylpropan-1-ol)



; [1 mark]

- (2-methylpropan-2-ol)



; [1 mark]

ii) The number of peaks for each isomer is:

- Butan-1-ol = 4 peaks
  AND
  Butan-2-ol = 4 peaks; [1 mark]
- 2-methylpropan-1-ol = 3 peaks
  AND
  2-methylpropan-2-ol = 2 peaks; [1 mark]

[Total: 6 marks]

- From part **(a)**, the unknown alcohol has a molecular formula of $C_4H_{10}O$
- Focussing on the carbon chain only, there are 2 possibilities:
  - A four carbon chain backbone
  - A three carbon chain backbone with a methyl group attached to carbon-2
- From here, you can consider the alcohol group
  - In both carbon chains, the alcohol group can be attached to carbon-1 or carbon-2
- This gives rise to the four possible isomers; butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol
- Butan-1-ol and butan-2-ol have no symmetry in their molecules, which means that they both have four different carbon environments resulting in 4 peaks on their carbon NMR spectra
- In 2-methylpropan-1-ol, the carbon environments are:
  - Carbon-1 with the alcohol group attached
  - Carbon-2
  - The remaining carbons (methyl groups) are both equivalent, which means that they give the same peak on the carbon NMR spectrum
- In 2-methylpropan-2-ol, the carbon environments are:
  - Carbon-2 with the alcohol group attached
  - The remaining carbons (methyl groups) are all equivalent, which means that they give the same peak on the carbon NMR spectrum

c) The isomer that has produced the chemical shift pattern shown is:

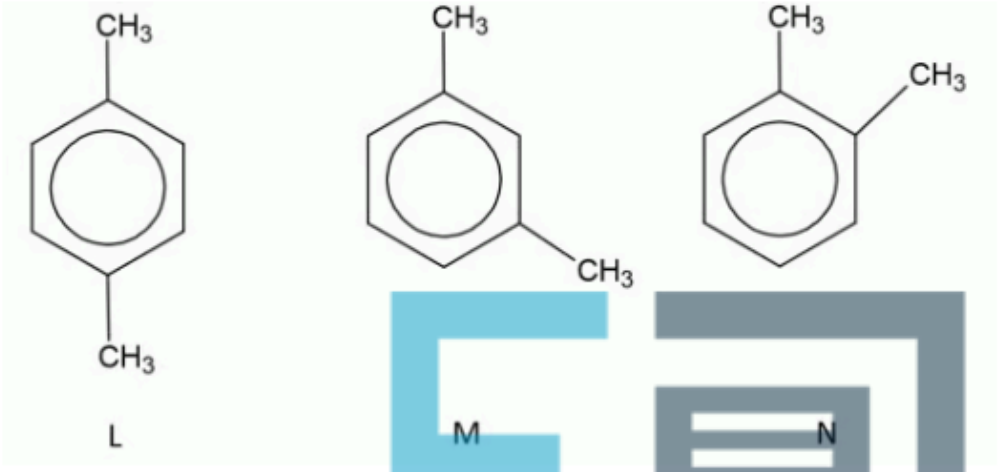
- 2-methylpropan-2-ol; [1 mark]
- 0 - 50 ppm = CH_3-CH_3 group; [1 mark]
- 50 - 70 ppm = C-OH group; [1 mark]

[Total: 3 marks]

- For determining which isomer produced the chemical shift pattern, you need to have determined that 2-methylpropan-2-ol forms two peaks (as shown in the spectrum)
- Then you can look at the data table and see that there will be 1 peak for 3 carbon atoms (of the methyl groups) which are all equivalent to one another and one peak for C-OH
- You then just need to quote the values for the shift pattern for the different carbon environments in your answer

Answer 5.

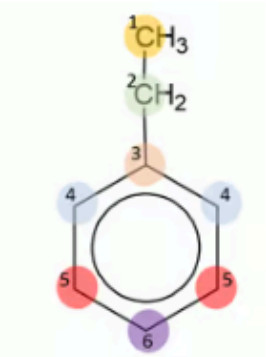
a) The structures of **L**, **M** and **N** are:



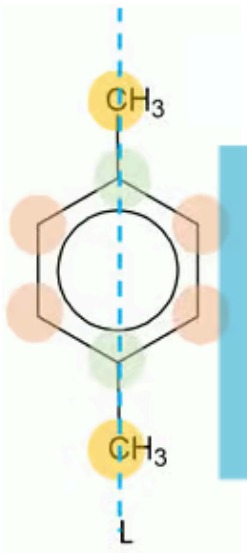
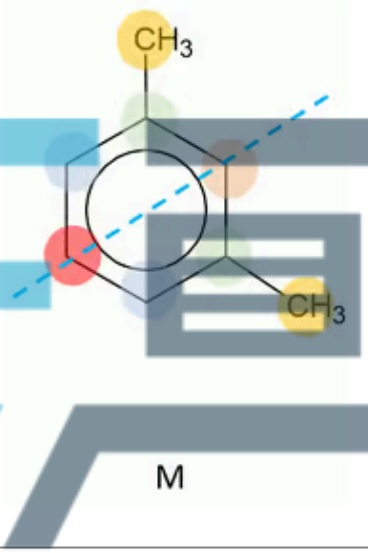
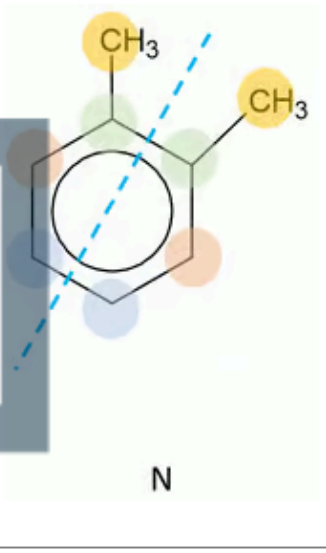
- Correct structure of **L**; [1 mark]
- Correct structure of **M**; [1 mark]
- Correct structure of **N**; [1 mark]

[Total: 3 marks]

- The low carbon-to-hydrogen ratio tells you it must be highly unsaturated or aromatic
  - Therefore, the benzene ring, C_6H_6 is a good starting point
- That leaves two carbons either together or separately joined on the ring
- Placing the two remaining carbons together would leave the ring as C_6H_5, so the five remaining hydrogens would make it an ethyl group side group, $-CH_2CH_3$
  - This option can be eliminated as it would have 6 unique environments due to symmetry:



- Placing the two remaining carbons apart, but joined on the ring separately would leave the ring as C_6H_4, making the two side groups both methyls, $-CH_3$
  - Next, assign the unique environments to the remaining structures, which have the formula $C_6H_4(CH_3)_2$
  - A line of symmetry through the structures helps to identify which are unique carbon environments:

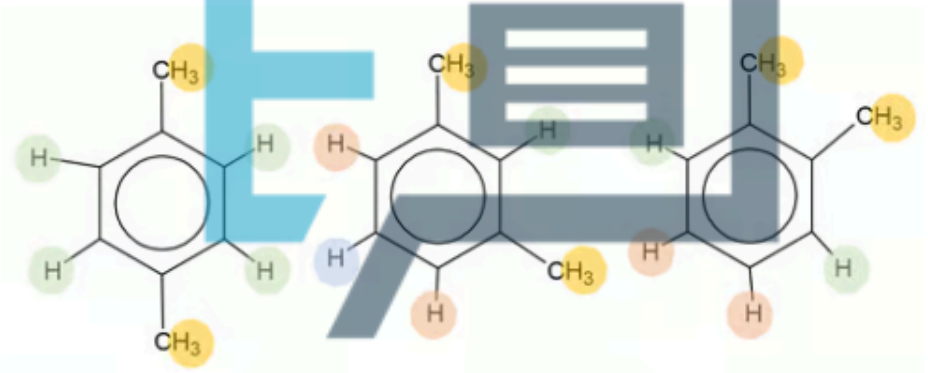
		
3 unique environments	5 unique environments	4 unique environments

b) The completed table of proton NMR for L, M and N is:

	Number of peaks	Relative Peak area	
L	2	3:2	; [1 mark]
M	4	6:1:2:1	; [1 mark]
N	3	3:1:1	; [1 mark]

[Total: 3 marks]

- Having deduced the structures of **L**, **M** and **N** in part (a), you can now assign proton environments to the structures
  - The protons have been added to the skeletal drawings to make them easier to see:



- **L** has two unique proton environments
  - The CH_3 groups which account for 6 protons in one environment
  - The benzene C-H accounts for 4 protons in one environment
  - This gives an overall ratio 6 : 4 which simplifies to 3 : 2
- **M** has four unique proton environments
  - The CH_3 groups which account for 6 protons in one environment
  - The benzene C-H accounts for 4 protons in three environments with a ratio of 1 : 2 : 1
  - This gives an overall ratio of 6 : 1 : 2 : 1
- **N** has three unique proton environments
  - The CH_3 groups which account for 6 protons in one environment
  - The benzene C-H accounts for 4 protons in two environments with a ratio of 2 : 2
  - This gives an overall ratio of 6 : 2 : 2, which simplifies to 3 : 1 : 1

c) The isomer with the highest melting point is:

- Isomer L; [1 mark]

Explanation:

- Linear molecule packs more easily / closely
  AND
  Have the strongest intermolecular forces / induced dipole-dipole attractions (as a result of this packing); [1 mark]

[2 marks]

- Molecular packing is the main criterion for determining melting point order
- 1,4- isomers / para-isomers (those with the side groups directly opposite) are symmetrical and fit more easily into a regular repeating structure (lattice)
  - This is similar to the idea of intermolecular forces in branched / non-branched compounds.

Answer 6.

a) The molecular formula of the compound **K** is:

- Mole ratio C : H : O = $\frac{70.58}{12.0}$: $\frac{5.92}{1.0}$: $\frac{23.50}{16.0}$

  OR

  Mole ratio C : H : O = 5.88 : 5.92 : 1.47; [1 mark]
- Empirical ratio C : H : O = $\frac{5.88}{1.47}$: $\frac{5.92}{1.47}$: $\frac{1.47}{1.47}$ **OR** = 4 : 4.03 : 1

  AND
- Empirical formula = C_4H_4O ; [1 mark]
- Mass of empirical formula = (4 x 12.0) + (4 x 1.0) + 16.0 = 68.0

  AND

  Evidence of *m / e* = 136 peak in the spectrum

  AND

  Molecular formula = $C_8H_8O_2$; [1 mark]

[Total: 3 marks]

- Use all the available information to solve the problem
  - Percentage composition by mass to determine the empirical formula
  - Mass spectrum to determine the molecular formula, in conjunction with your empirical formula calculation
- Showing your steps not only is good practice but also helps you pick up on errors more easily
  - You can then still receive some marks even if you make a mistake

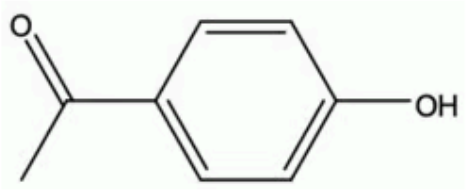
b) The functional groups present in compound **K** are:

- Phenol
  AND
  pH 5.0 represents a weak acid
  AND
  There is no reaction with sodium carbonate solution / Na_2CO_3 (aq); [1 mark]
- Ketone
  AND
  The reaction with 2,4–DNPH proves the presence of a carbonyl / C=O group
  AND
  The negative test with Tollens' reagent suggests it is a ketone / is not an aldehyde; [1 mark]

[Total: 2 marks]

- Qualitative tests / test-tube reactions are often used in conjunction with spectroscopic methods to determine the overall structure of a compound
- So, you need to know all of the functional group tests
  - **Careful:** The pH 5.0 / no reaction with sodium carbonate solution catches many students out

c) The structure of compound **K** is:

-  ; [1 mark]

Explanation:

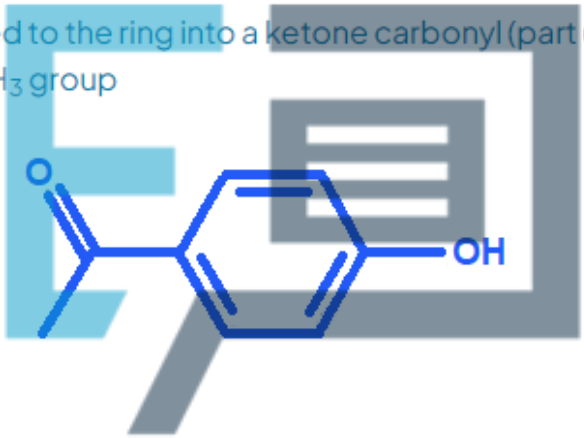
- There are four peaks between 110 - 160 ppm
  AND
  This means that there are 4 aromatic carbon environments / the molecule is 1,4–disubstituted; [1 mark]
- The peak at 190 - 220 for a carbonyl
  AND
  The peak at 25 - 60 for a carbon next to a benzene ring
  AND
  This means that there is a ketone group attached to the benzene ring; [1 mark]

[Total: 3 marks]

- There is a lot of useful information over all three parts of this question
  - Part (a)
    - Molecular formula $C_8H_8O_2$
  - Part (b)
    - Phenol group
    - Ketone group
  - Part (c)
    - Aromatic ring with 1,4 substitution
    - Ketone group attached to the aromatic ring
- Start with a phenol group with a carbon attached at the 4–position

- This accounts for 7 carbons, one oxygen and 5 hydrogens
- From the molecular formula, this leaves one carbon, one oxygen and three hydrogens to account for

- Make the carbon attached to the ring into a ketone carbonyl (part (c) information) by adding the C=O and a CH_3 group



- This structure now accounts for all of the atoms in the molecular formula