

2021 Y6 H2 Chemistry Timed Practice – Suggested Solutions

Section B

B1 (a) $\frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_3(\text{org})]} \approx 25 \Rightarrow [\text{NH}_3(\text{aq})] = 25[\text{NH}_3(\text{org})]$

$$[\text{NH}_3(\text{aq})] + [\text{NH}_3(\text{org})] = 1.04$$

$$25[\text{NH}_3(\text{org})] + [\text{NH}_3(\text{org})] = 1.04$$

$$[\text{NH}_3(\text{org})] = 0.04 \text{ mol dm}^{-3}$$

$$[\text{NH}_3(\text{aq})] = 1.04 - 0.04 = 1.00 \text{ mol dm}^{-3}$$

$$\text{Amount of NH}_3 \text{ in } 25.0 \text{ cm}^3 \text{ sample of NH}_3(\text{aq}) = \frac{25.0}{1000} \times 1.00 = 0.0250 \text{ mol}$$

Since NH_3 and HCl react in a 1:1 ratio,

Amount of HCl required for titration = 0.0250 mol

$$\text{Volume of HCl} = \frac{0.0250}{0.100} = 0.250 \text{ dm}^3 = 250 \text{ cm}^3$$

Volume of HCl is unsuitable because it exceeds the burette capacity of 50.00 cm^3 , therefore it is tedious to refill the burette multiple times. This is a result of the concentration of ammonia being too high.

Examiners' Comments

- Some students did not read the question and failed to realise that there are two parts to the question – 1. To calculate the volume of HCl required; 2. To explain why $[\text{NH}_3]$ is unsuitable.
- Careful reading of the information provided will lead students to realise that the NH_3 is dissolved in both layers. Some students assumed that 1.04 mol dm^{-3} was the $[\text{NH}_3]$ in the aqueous layer.
- To calculate the volume of HCl required to titrate the aqueous layer, the concentration of NH_3 in the aqueous layer should be calculated first.
- Students need to elaborate beyond the fact that the volume of HCl required exceeds the burette capacity by explaining, for example, that there is thus a need to refill the burette, causing the experiment to become tedious.

(b) Ideally, 25.0 cm^3 of diluted ammonia would require 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ hydrochloric acid. Since 250 cm^3 of hydrochloric acid was required, a sample of the aqueous layer needs to be diluted 10 times i.e. obtain 25.0 cm^3 of aqueous ammonia and dilute to 250 cm^3 .

- Drain the bottom organic layer into a 100 cm^3 conical flask / beaker to discard. Pour/drain the remaining aqueous layer into another 100 cm^3 conical flask / beaker.
- Use a 25.0 cm^3 pipette to transfer 25.0 cm^3 of the aqueous layer solution into a 250 cm^3 volumetric flask.

3. Fill the graduated flask to the 250 cm³ mark with more deionised water. Use a dropping pipette (or teat pipette or dropper) to add the deionised water drop by drop when nearing the mark.
4. Stopper the graduated flask and shake the solution thoroughly to ensure that it is homogeneous. Label the solution FA 1.
5. Pipette 25.0 cm³ of FA 1 into a 250 cm³ conical flask. Add 2 drops of methyl orange indicator and swirl the conical flask.
6. Titrate the solution in the conical flask with the standard 0.100 mol dm⁻³ hydrochloric placed in the burette.
7. Stop the titration when the end-point of the titration is reached i.e. when one drop of the hydrochloric acid added changes the colour of the solution in the conical flask from yellow to orange.
8. Record the titration readings using an appropriate table.
9. Repeat the titration until at least two consistent results are obtained (i.e. the two titre volumes are within 0.10 cm³ of each other).

Examiners' Comments

Students should pay attention to the points to be included in their plan:

(1) Calculate a suitable volume of aq. layer to use for dilution

- Since the diluted aq. NH₃ will be titrated against HCl, an ideal titre volume of HCl would be 25.00 cm³ (with 25.0 cm³ NH₃ pipetted). However the undiluted aq. NH₃ requires a titre volume of 250 cm³ HCl – this means that the undiluted aq. NH₃ is 10 times too concentrated, or the dilution factor is 10.
- If a 250 cm³ graduated flask is used to prepare the diluted solution, the volume of aq. layer required = $\frac{250}{10} = 25 \text{ cm}^3$. This means 25 cm³ of aq. layer is transferred to the graduated flask, then the flask is topped up with water until a 250 cm³ diluted NH₃ solution is obtained.
- Most students were able to deduce the dilution factor, but some were unable to calculate the correct volume of aq. layer to use for dilution.
- A graduated flask must be used for the accurate dilution of solutions for titration. Many students were unable to recall the correct name of the flask and some used imprecise apparatus such as measuring cylinders.
- Graduated flasks of 100 cm³ or 250 cm³ capacity can be used but the correct corresponding volume of the aqueous layer needs to be used to achieve the 10-time dilution.

(2) Procedure to obtain the vol. of aqueous layer WITHOUT the organic layer

- An important clue is given in the diagram in the question which shows that the aqueous layer lies above the organic layer.
- One way to obtain the aqueous layer is to drain the organic layer first, then drain the aq. layer into a separate flask.
- Alternatively, a pipette can be used to withdraw the aqueous sample from the top of the funnel, but care must be taken not to disturb or stir the organic layer.

(3) Procedure to dilute the aq. layer to an appropriate volume

- The detailed procedure for using a graduated flask to dilute a solution should be given, including transferring the aqueous layer to the flask by suitable means, topping up to the mark with water, stopper and shaking the flask.

(4) Procedure for titration of diluted aq. NH₃ against HCl

- This is a strong acid-weak base titration, thus suitable indicators are methyl orange and screened methyl orange. Some students chose inappropriate indicators.
- The colour change at end-point must be stated correctly – for methyl orange, the colour change is from yellow to orange, since the indicator was added to basic NH₃ in the conical flask.
- For experiments involving titrations, the titration must be carried out until at least two consistent results are obtained.
- In writing procedures for planning questions, all apparatus used together with their capacities must be clearly stated, e.g. 25.0 cm³ pipette, 250 cm³ conical flask, 250 cm³ graduated flask.

(c)(i) When a small amount of acid is added,
NH₃(aq) + H⁺(aq) → NH₄⁺(aq)

When a small amount of base is added,
NH₄⁺(aq) + OH⁻(aq) → NH₃(aq) + H₂O(l)

Examiners' Comments

- The “→” should be used in this question to depict the response of the buffer to H⁺ or OH⁻ being added.
- Common incorrect answers show the ionisation of NH₃ and hydrolysis of NH₄⁺. These do not show how the buffer responds when its pH is being affected by the addition of acid or base i.e. how a buffer controls pH.

(c)(ii) pOH = 14 – 9.0 = 5.0

$$\text{pOH} = \text{pK}_b + \lg \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$5.0 = 4.75 + \lg \frac{[\text{NH}_4^+]}{0.80}$$

$$[\text{NH}_4^+] = 1.423 \text{ mol dm}^{-3}$$

Amount of ammonium chloride in 1 dm³ = 1.423 × 1 = 1.423 mol

Mass of ammonium chloride = 1.423 [14.0 + 4(1.0) + 35.5] = 76.1 g

Examiners' Comments

- Generally well answered.
- Common mistakes made involved:
 - Incorrectly remembering the formula to calculate the pH of buffer solution.
 - Incorrectly using 9 instead of 5 as pOH in the above equation.
 - Incorrectly using the *M_r* of NH₄⁺ instead of NH₄Cl as required by the question.

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- B2 (a)(i)** As phenol is a weak acid and dissociates to a very small extent (deduced from the very small K_a value), it can be assumed that equilibrium $[C_6H_5OH] \approx \text{initial } [C_6H_5OH]$.

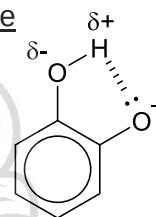
$$[H^+] \approx \sqrt{K_a[C_6H_5OH]} = \sqrt{10^{-10} \times 0.750} \\ = 8.660 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(8.660 \times 10^{-6}) = 5.06$$

Examiners' Comments

- Most students were able to first convert the $\text{p}K_a$ value given to K_a , and then correctly determined the $[H^+]$ and pH value. However, some candidates substituted 10.0 as K_a when it is the $\text{p}K_a$ value for phenol.
- Some candidates did not give the units for $[H^+]$. Appropriate units should always be associated with any part of a series of calculations, not just the final answer.

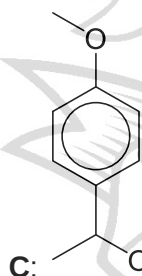
- (a)(ii)** The formation of intramolecular hydrogen bond stabilises the conjugate base formed from the first acid dissociation of catechol, hence catechol is a stronger acid than phenol.



Examiners' Comments

- Most students drew the correct structure of the monoanion.
- Few students correctly identified the intramolecular hydrogen bond as the factor which stabilised the conjugate base.
- Many students incorrectly suggested that the $-OH$ group was electron withdrawing which helped to disperse the negative charge on $-O^-$. The $-OH$ group on benzene is activating (information available from Data Booklet) and is actually electron-donating.
- Some students tried to argue that $-OH$ group on benzene is electron-donating and dispersed the negative charge on $-O^-$. These students did not realise that the $-OH$ group actually intensifies the negative charge on $-O^-$, which destabilises the conjugate base!

- (b)(i)**



C: OH

reaction 2 : NaBH_4 or LiAlH_4 in dry ether or H_2 , Ni, heat

reaction 3: PBr_3 or SOBr_2 or dry HBr(g) , heat

Examiners' Comments

- Reaction 2 is a reduction reaction and reaction 3 involves a nucleophilic substitution of alcohols. Some students are unfamiliar with or confused the reagents and conditions with other reactions.
- Note that no heating is required for reduction with NaBH_4 or LiAlH_4 in reaction 2.

(b)(ii) An electrophile is an electron-deficient species which can accept a pair of electrons.

Examiners' Comments

- Common mistakes observed were
 - "...accept an electron." – an electrophile accepts 2 electrons, not 1.
 - "...accept lone pair of electrons." – the pair of electrons which the electrophile accepts are not only from lone pairs of electrons. They can also come from bond pairs. For example, in the electrophilic addition of alkene, the electron pair comes from the pi bond of the C=C.

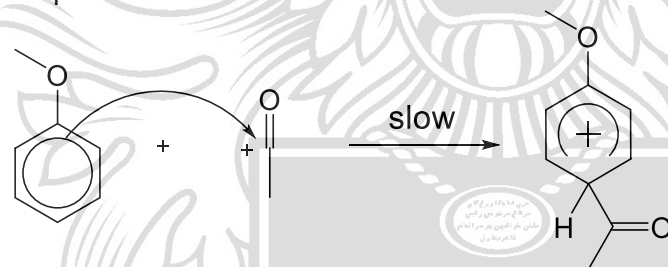
(b)(iii) $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightleftharpoons [\text{CH}_3\text{CO}]^+ + \text{AlCl}_4^-$

AlCl_3 acts as a Lewis acid.

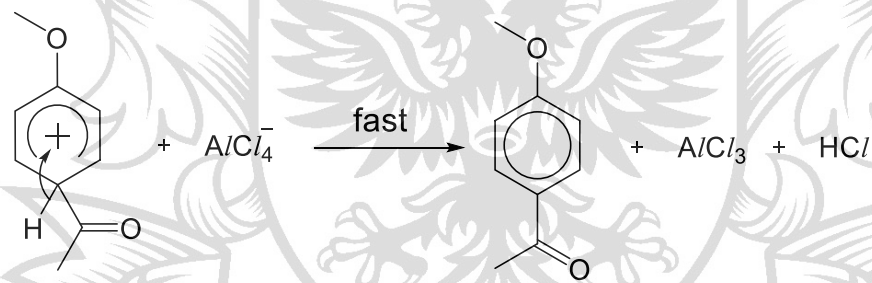
Examiners' Comments

- This question was generally well done.
- Many students included "catalyst" in their answer. Take note that the question asked for the role of AlCl_3 in the reaction above. Based on the equation, AlCl_3 is not a catalyst. Students must take care not to blindly write down what they have studied without understanding the specific situation they are answering.

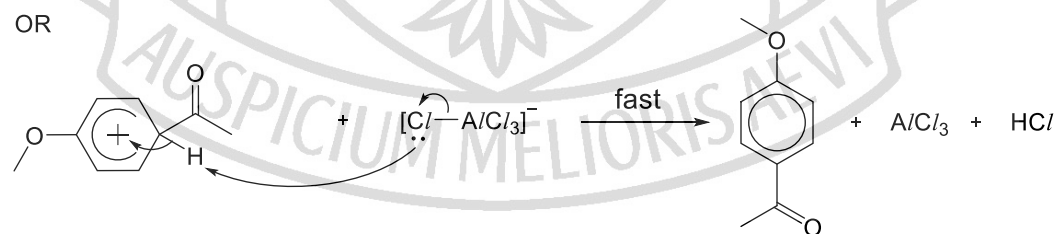
(b)(iv) Step 1:



Step 2:



OR



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Examiners' Comments

- Many students did not include AlCl_4^- or did not show the regeneration of AlCl_3 in the fast step.
- Some students drew the incorrect electrophile with an extra carbon  or with the electrophile still containing the Cl. The former could be due to a lack of familiarity with the use of skeletal formula – please practice using skeletal formula in your daily work.

- (b)(v) Compound J has 2 electron-donating / activating $-\text{OCH}_3$ groups compared to 1 in compound A. The benzene ring in J is more electron rich and J is more susceptible to electrophilic substitution.

Examiners' Comments

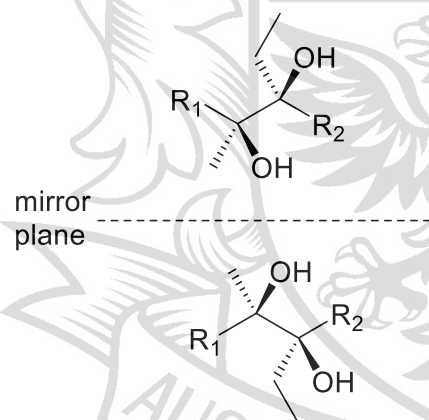
- In this comparison, it is important to clearly state that J has more $-\text{OCH}_3$ groups compared to A and hence the effect on J is greater than that in A.
- While many students recognised that there was one more $-\text{OCH}_3$ group attached to the benzene ring in J, some thought that this group was electron withdrawing. The activating and 2,4-directing effect of $-\text{OCH}_3$ can be found in the Data Booklet.

- (c)(i) $\text{KMnO}_4(\text{aq})$, $\text{NaOH}(\text{aq})$, cold

Examiners' Comments

- This question was generally well done.
- A few students incorrectly thought that the reaction was an electrophilic addition (of H_2O) rather than a mild oxidation. Take note that electrophilic addition of H_2O to a $\text{C}=\text{C}$ forms a mono-alcohol, but a diol was formed in this reaction.
- Students must specify the reagents used instead of just writing “alkaline” or “acidic”.

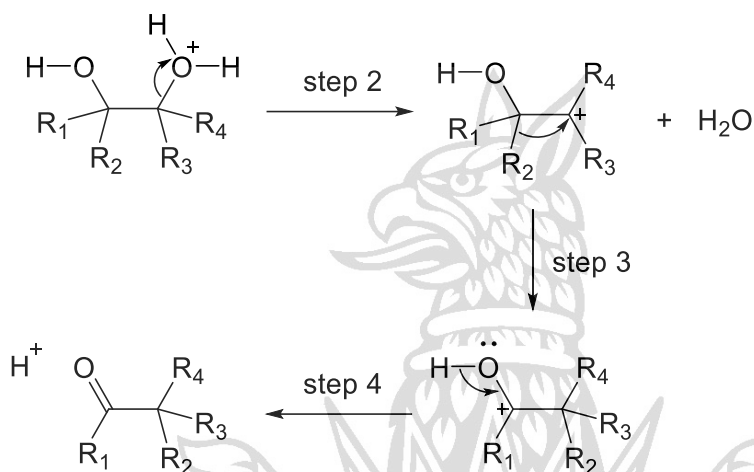
- (c)(ii) Enantiomerism



Examiners' Comments

- Some candidates only depicted the 3D configuration about one chiral carbon, when there are two chiral carbons in this compound. The 3D configuration about both chiral carbons must be shown.
- First, draw one 3D configuration of the compound to generate one enantiomer. To obtain the other enantiomer, draw the mirror image of the first structure.
- Students should note that there is no cis-trans isomerism in the compound as there is a lack of restricted rotation due to $\text{C}=\text{C}$ or ring structure.

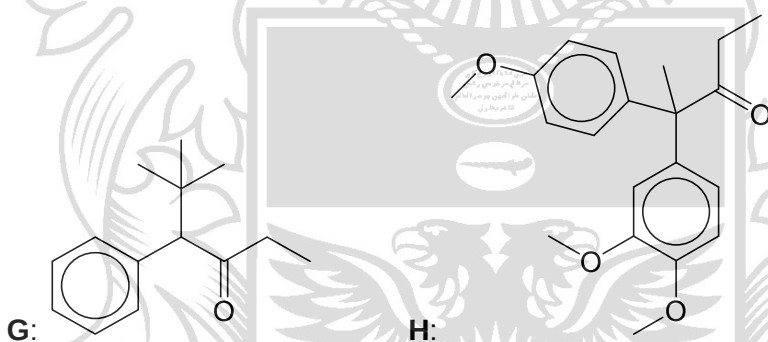
(d)(i)



Examiners' Comments

- Such a question tests students' actual understanding of arrow-pushing beyond memorising the required mechanisms. Such questions are not uncommon - please approach your tutors if you need help understanding arrow-pushing.
- In the formation of the $\text{C}=\text{O}$ bond (step 4), the arrowhead should point towards the $\text{C}-\text{O}$ bond rather than the '+'. The instructions given in the question were to draw only 1 curly arrow (instead of multiple arrows) and 1 positive charge (instead of partial positive/negative charges) for each step. Such clues were given to guide students towards the correct answer.

(d)(ii)



Examiners' Comments

- Many students found this part challenging but a good number of candidates successfully made use of the information provided to solve the problem.
- Students need to make use the list of priority of migration given to decide which group should migrate.
- Such questions are not uncommon and students should approach their tutors if they do not know how to approach such questions / make use of the clues.

Section C

C1 (a)(i) Rate is proportional to gradient of graph.

Order wrt [RCI]

$$\text{Gradient for [RCI]} = x \text{ mol dm}^{-3} = \frac{0.06 - 0.10}{8 - 0} = -0.005$$

$$\text{Gradient for [RCI]} = 2x \text{ mol dm}^{-3} = \frac{0.02 - 0.10}{8 - 0} = -0.01$$

Gradient for [RCI] = $x \text{ mol dm}^{-3}$ is **half** that for [RCI] = $2x \text{ mol dm}^{-3}$.

When [RCI] x 2, gradient x 2, rate x 2 i.e. reaction is **first order** with respect to **RCI**.

Order wrt [NaOH]

Both graphs are straight lines with a constant negative gradient, [NaOH] has no effect on the rate of the reaction, hence the reaction is **zero order** with respect to **NaOH**.

Examiners' Comments

- Some students believe that when half-life is not constant, then the reaction must be zero order w.r.t. the reactant – that is a misconception. The only accurate concept is that when half-life of a reactant is constant, the reaction is first order w.r.t that reactant. Thus, when the half-life of a reactant is NOT constant, we can only conclude that the reaction is NOT first order w.r.t. that reactant, i.e. the order of reaction can be any number e.g. 0, 1.5, 2, 3...
- Students should learn to use the shape of a [reactant]-time graph to deduce order w.r.t. the reactant.
- Students need to show clear working to determine the orders of reaction. In this case, calculating or comparing the gradients of the graphs is required.
- For the order w.r.t NaOH, students should demonstrate the understanding that $\text{gradient} \propto \text{rate}$ and not simply stating “rate is constant” with no reference to the data given, i.e. gradient of the lines.

(a)(ii) Rate = $k[\text{RCI}]$

The mechanism is S_N1

Examiners' Comments

- Students need to be specific in their answers. Some students simply stated “nucleophilic substitution” without specifying S_N1 or S_N2 . The kinetics data provided enough information for students to specifically deduce the S_N1 mechanism, and not S_N2 nor simply nucleophilic substitution.

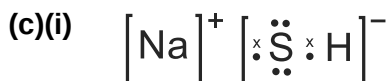
(b) $(\text{CH}_3)_3\text{CCl}$.

The C–Cl carbon is sterically hindered due to the presence of 3 bulky methyl groups which hinder the approach of the nucleophile, hence S_N2 does not take place.

The carbocation intermediate formed is stabilised by the presence of 3 electron donating alkyl groups.

Examiners' Comments

- Students are reminded to discuss both electronic and steric effects, as stated in the question.
- Students need to be clear and specific in their answer to the question – “3 methyl groups” instead of “3 alkyl groups”, and “hinder the approach of the nucleophile” instead of just using a generic answer like “there is steric hinderance”.



Examiners' Comments

- Some students thought that NaSH is a covalent compound when it is ionic.
- Some students forgot to include the sodium ion. Students are also reminded that the Na^+ ion should not have valence electrons shown.
- For the SH^- ion, a different symbol should be used to represent the electron from the negative charge. E.g. some answers used 7 dots (or 7 crosses) on S atom, which would mistakenly indicate that S has 7 valence electrons.

(c)(ii) **Validity of “ SH^- is a stronger nucleophile than OH^- ”**

Since S is less electronegative than O, the lone pairs of electrons on S are held less tightly compared to those of O and are more easily donated. Hence, SH^- is a stronger nucleophile than OH^- .

Validity of “reaction between SH^- and RCI will be faster”

The reaction between SH^- and RCI proceeds via the $\text{S}_{\text{N}}1$ mechanism where the SH^- nucleophile is not present in the rate determining step and hence has no effect on the rate of reaction i.e. the rate of reaction between SH^- and RCI will not be faster.

Examiners' Comments

- Students should focus their answers on the two underlined phrases, rather than the whole statement.
 - “Stronger nucleophile” – do you agree that SH^- is a stronger nucleophile? Why would it be stronger?
 - “Faster” – would a stronger nucleophile lead to a faster $\text{S}_{\text{N}}1$ reaction?
- Many students recognised that O is more electronegative than S but went on to draw the wrong conclusion that OH^- is therefore stronger than SH^- . This shows the lack of understanding of how nucleophiles work. Stronger nucleophiles are those that donate lone pairs more easily, and not those that hold on to lone pairs more tightly!
- In the $\text{S}_{\text{N}}1$ mechanism, the nucleophile is not involved in the rate determining step and therefore, the strength of the nucleophile will not affect the rate of the reaction.

(d) $\text{Cl}_2 < \text{P}_4 < \text{S}_8$ (or in words)

P_4 , S_8 and Cl_2 have simple molecular structures with instantaneous dipole–induced dipole interactions (id-id) exist between their respective molecules.

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Since the size of their electron clouds increase from Cl_2 to P_4 to S_8 , the strength of id-id interactions increase in the same order. The energy required to overcome the id-id interactions, and hence their melting points, increase from Cl_2 to P_4 to S_8 .

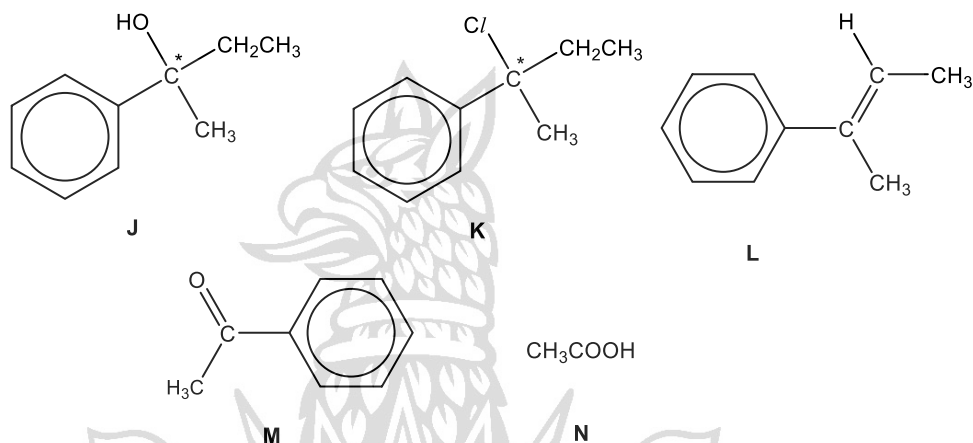
Examiners' Comments

- The order should be presented as how it should be read from left to right. Hence an increasing order of melting point should preferably not read like this: $\text{S}_8 > \text{P}_4 > \text{Cl}_2$ (which is actually how we would write for a *decreasing* order).
- The structure and bonding of the 3 elements must be explicitly stated especially since the question asked for it - simple molecular structures with instantaneous dipole-induced dipole interactions (id-id) exist between their respective molecules
- Please remember the structure of the elements in Period 3. Many students treated the three elements as atomic and simply compared the size of the atom's electron cloud ($\text{Cl} > \text{S} > \text{P}$) leading to a completely wrong melting point trend.
- Many students do not know the elemental form of phosphorus as P_4 , sulfur as S_8 , which is quite fundamental.
- Some students incorrectly thought that phosphorus and sulfur have giant molecular structures. They have simple covalent structures.
- Careful, detailed and deliberate study of your lecture notes is very helpful for this question.

(e)

Observations	Deductions
J reacts with PCl_5 to give K .	J undergoes nucleophilic substitution to give K • J is an aliphatic alcohol • K is a halogenoalkane.
J cannot be oxidised by acidified $\text{Na}_2\text{Cr}_2\text{O}_7$.	J is a tertiary alcohol.
Both J and K are optically active.	Both J and K have chiral carbon atoms.
K reacts with $\text{KOH}(\text{alc})$ to give L .	K undergoes elimination to give L , an alkene.
L exhibits cis-trans isomerism.	L has no chiral carbon atoms and different atoms or groups of atoms that are bonded to each of the doubly bonded carbon atoms.
L reacts with hot H^+/KMnO_4 to give M and N .	L undergoes strong / vigorous oxidation / oxidative cleavage
M gives positive iodoform test but not N .	M contains a $\text{CH}_3\text{CO}-$ group but not N .

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Examiners' Comments

- The performance for this question was highly polarised – many scored near full marks, while many did not get any. The only way to improve your handling of such questions is through a lot of practice, which can be found in your revision booklets!
- Most students were able to write sensible deductions based on the evidence given.
- Please remember to always state the **type of reaction** and the **functional group** involved. For example,
 - J** reacts with PCl_5 to give **K** – no credit.
 - J** undergoes **nucleophilic substitution** with PCl_5 to give **K**, therefore **K** is a **halogenoalkane** while **J** is an **alcohol**.
- The evidence that “**J** cannot be oxidised by acidified $\text{Na}_2\text{Cr}_2\text{O}_7$ ” was neglected by many students.
 - Some drew **J** as a secondary alcohol (which can be oxidised by $\text{Cr}_2\text{O}_7^{2-}$), instead of a tertiary alcohol (which cannot be oxidised by $\text{Cr}_2\text{O}_7^{2-}$).
 - Some treated a “negative” test as unimportant and ignored it. Negative tests can be used to positively identify the presence of functional groups.
- Many wrote that **M** contains a $-\text{CH}(\text{OH})\text{CH}_3$ group but that is not possible since **M** is the product of strong oxidation, and hence $-\text{CH}(\text{OH})\text{CH}_3$ should not be part of the deductions in this case.

C2 (a)

Similarity : Both Al_2O_3 and P_4O_{10} react with bases such as NaOH

Equations : $\text{Al}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Al}(\text{OH})_4^-(\text{aq})$

$\text{P}_4\text{O}_{10}(\text{s}) + 12\text{OH}^-(\text{aq}) \rightarrow 4\text{PO}_4^{3-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$

Difference: Al_2O_3 reacts with acids but P_4O_{10} does not.

Equations : $\text{Al}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

Examiners' Comments

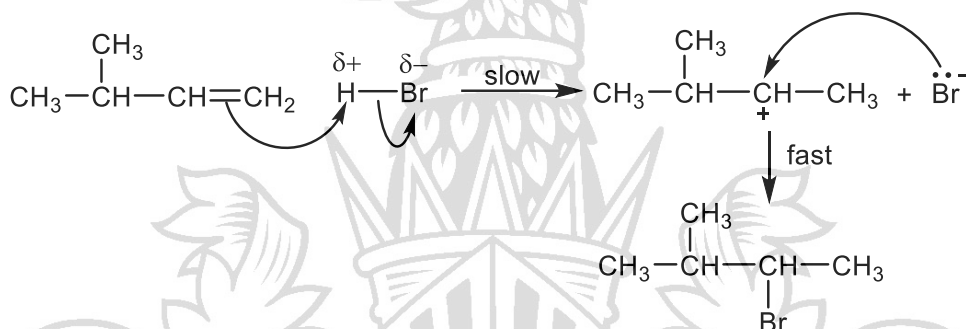
- There is no need to include spectator ions e.g. Na^+ here. Inclusion of these adds to the confusion in balancing the equations. Ensure that all chemical equations are balanced.
- It is clear that students find it challenging to write balanced equations for the topic of Periodic Table 1. So, more effort must be put in to pick up the skills to improve in this aspect.
- Some students misunderstood that Al_2O_3 reacts with OH^- to form $\text{Al}(\text{OH})_3$ instead of $\text{Al}(\text{OH})_4^-$.

(b)(i) Elimination (of water). Excess concentrated sulfuric acid, heat.

Examiners' Comments

- The type of reaction is elimination. The term “dehydration” is ambiguous and should not be used.

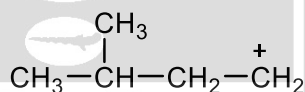
(b)(ii) Electrophilic addition



Examiners' Comments

- Some students forgot to state the name of the mechanism; others forgot to identify the slow and fast steps of the mechanism.
- Students are reminded to draw curly arrows with care, starting from a bond pair or lone pair of electrons and ending at an electron deficient centre.

(b)(iii) The following primary carbocation intermediate needs to be generated in step 1 of the mechanism in order for 1-bromo-3-methylbutane to form.



The primary carbocation is less stable than the secondary carbocation due to fewer electron-donating alkyl groups to disperse the positive charge.

Examiners' Comments

- A number of students thought that the carbocation formed on C1 has no R-groups. Note that a primary carbocation has 1 R-group.
- Some students used the observation that “the doubly-bonded carbon with more hydrogens would form a bond with the H from H-Br” as an explanation for this question. Students need to remember this is merely an observation and not the reason. The underlying reason is due to difference in stabilities of the carbocations formed.

(c)(i) Na(s)

Examiners' Comments

- The reaction requires the reagent chosen to react with both phenol and an aliphatic alcohol. Many students incorrectly used NaOH(aq) which will react with phenol, but not the aliphatic alcohol. Aliphatic alcohols are less acidic than phenols and hence require a strong reagent such as Na(s) for deprotonation.

(c)(ii) Compound **W** is formed from the attack of the O of the phenoxide.

Due to the overlap between the p-orbital on O containing the lone pair of electrons and the π cloud of benzene, the lone pairs on O are delocalised into the π cloud of benzene, making them less available for nucleophilic attack on 2-bromo-3-methylbutane.

Examiners' Comments

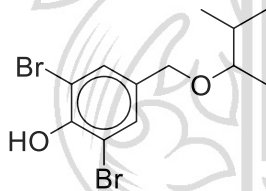
- Students need to be mindful of the terms they use in their explanations.
 - A p-orbital can overlap with the π cloud of benzene, but the orbital *does not* delocalise into the benzene ring.
 - A lone pair of electrons delocalises into the π cloud of benzene, but a lone pair of electrons cannot *overlap* with the benzene ring.
- Some students mentioned partial double bond character strengthening the C-O bond. This is irrelevant as we are not even considering the breaking of this bond when considering the nucleophilicity of phenoxide. Refer to the reaction scheme and you will notice that the C-O bond within phenoxide remains unbroken and the reaction involves forming a bond between the O of phenoxide and C of the halogenoalkane.

(c)(iii) The rate of reaction is faster with 2-iodo-3-methylbutane as the C-I bond is weaker than the C-Br bond.

Examiners' Comments

- Many candidates wrote too much – always decide how much to write based on the indicated marks.

(c)(iv)



Examiners' Comments

- Some students substituted only one Br onto the phenol. This can only be achieved if Br_2 in CCl_4 was used, not $\text{Br}_2(\text{aq})$.
- Others carelessly substituted the Br atoms at the 2,6- positions relative to the $-\text{CH}_2\text{OR}$ group.

(d)(i) Test: To each compound in separate test-tubes, add PCl_5 .
Observations: White fumes of HCl will be observed for geraniol, but not citral.

Test: To each compound in separate test-tubes, add 2,4-DNPH
Observations: Orange ppt observed for citral, but not geraniol.

Test: To each compound in separate test-tubes, add Tollens' reagent and heat.
Observations: Silver mirror observed for citral, but not geraniol.

Test: To each compound in separate test-tubes, add Fehling's reagent and heat.
Observations: Red-brown ppt of Cu_2O observed for citral, but not geraniol.

Test: To each compound in separate test-tubes, add SOCl_2 .

Observations: White fumes of HCl will be observed for geraniol, but not citral.

Test: To each compound in separate test-tubes, add Na .

Observations: Effervescence of H_2 gas which extinguished a lighted splint with a pop sound for geraniol, but not citral.

Examiners' Comments

- Generally well done.
- A common incorrect answer involved the use of $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$ and heat. Both the primary alcohol of geraniol and the aldehyde of citral will be oxidised i.e. the reaction does not distinguish the two compounds. This mistake probably arose from the lack of familiarity of the oxidation reactions of different oxidising agents and different functional groups.
- Effort needs to be invested in understanding the oxidation reactions.

(d)(ii) $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, heat with immediate distillation

Examiners' Comments

- Generally well done.
- As with the previous part, some students were unfamiliar with the different oxidising agents and incorrectly suggested using KMnO_4 or leaving out the need to heat with immediate distillation.

(d)(iii) NaBH_4 or LiAlH_4 in dry ether.

Examiners' Comments

- Generally well done.
- A common incorrect answer involved the use of H_2/Ni , heat. This is unsuitable because the $\text{C}=\text{C}$'s in citral will be reduced as well and geraniol will not be obtained as the product.

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