2022 H3 Chemistry Preliminary Exam

This paper is a collaboration between RVHS, ACJC and JPJC

1 (a) (i) Assume ideal gas behaviour,

$$PV = \frac{m}{M_r}RT$$

$$PM_r = \frac{m}{V}RT$$

$35 \times 10^6 \times 2 = \text{density} \times 8.31 \times 298$

$\text{Density} = 2.827 \times 10^4 \text{ gm}^{-3}$

$= 28.3 \text{ kg m}^{-3}$ [2]

(ii) $\text{Volume of } NH_3 = \frac{1}{682} = 1.466 \times 10^{-3} \text{ m}^3$

$\text{Energy density} = 12.9 \times 10^9 \text{ J m}^{-3}$

Energy obtained = $1.466 \times 10^{-3} \times 12.9 \times 10^9 =$ <u>1.89×10^7 J</u> [1] [1]

(b)
- NH_3 has higher energy density than H_2
- Hydrogen's production is not environmentally friendly / produces CO_2 as a by-product while ammonia's production does not.
- NH_3 costs less / requires less energy to be liquefied and stored as a liquid.
- It is easier to transport / store NH_3 as a liquid than H_2 as a gas. [1]

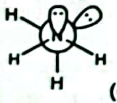
(c) (i) $CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$ [1]

(ii) Redox [1]

(d) (i) $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ [1]

(ii) $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$ [1]

(e) (i)



(gauche conformation) [2]

When in this <u>conformation</u>, lone pair of electrons on each nitrogen atom experience <u>some repulsion</u> but the <u>dipole of the N–H bonds do not cancel each other</u>. Molecule is <u>polar</u> in this conformation.

- Answer must highlight the compromise between the repulsion of lone pair of electrons and the overall polarity of the molecule.

(ii) N_2H_4 is <u>less basic</u> than NH_3. <u>$-NH_2$ is electron withdrawing</u> and reduces the availability of the lone pair of electrons on N to coordinate with H^+. [1]

(iii) $E_1: N_2 + 4e^- + 4H_2O \rightleftharpoons N_2H_4 + 4OH^-$

$E_2: N_2H_4 + 2e^- + 2H_2O \rightleftharpoons 2NH_3 + 2OH^-$

(iv) $4E_1 + 2E_2 = 6E_3$

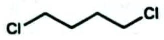
$E_1 = -1.21 \text{ V}$ [2]

(f) $H_2SO_4(aq)$ / $HCl(aq)$ / $HNO_3(aq)$ / $C(s)$ / any weak acid [1]

(g) (i)
- Eliminates the use of aqueous-based electrolytes / prevents water from being reduced at the cathode
- Allows for polar and non-polar species to be soluble in the electrolyte and transported to the electrodes.
- Polar species e.g. H_2O interact via ion-dipole interactions with the ions, while non-polar species e.g. N_2 interact via instantaneous dipole-induced dipole interactions with the hydrocarbon portion of the cation. [2]

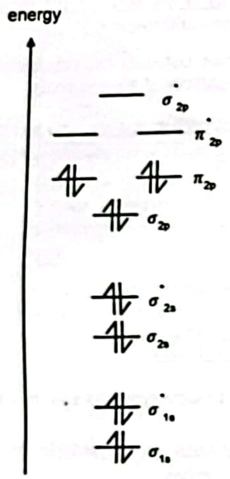
(ii) $P_{6,6,6,14}$ can be <u>used/operated at lower temperatures</u> than C_4mPyr due to its larger ionic size. [1]

(iii)



(bimolecular) nucleophilic substitution [2]

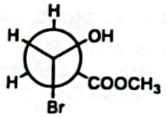
(h)



- Must show MO from 2s and 2p atomic orbitals (1s atomic orbitals are optional)
- Correct number of electrons in MO diagram
- σ_{2p} lower than π_{2p} in energy

[2]

2 (a) (i)



[1]

(ii) The mechanism occurs with the molecule adopting an antiperiplanar geometry as shown below.

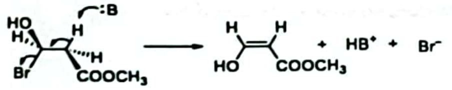
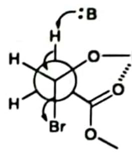


illustration of antiperiplanar

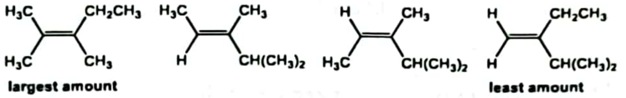
Due to the presence of hydrogen bonding between –OH group and –COOCH₃ group, the following conformation is obtained, resulting in the stereoisomer obtained at the end of the elimination process.

[2]



(iii) E2 is favoured by **strong bases** e.g. aqueous NaOH [1]

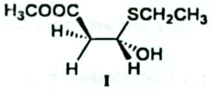
E1 mechanism



E1 reactions generally give the **more highly substituted alkene** which is **more stable** as the **major product**. Comparing the two tri-substituted alkenes, there is **less steric hindrance between –H and –CH(CH$_3$)$_2$** compared to –CH$_3$ and CH(CH$_3$)$_2$. [3]

(b) (i) **Nucleophilic substitution, S$_N$2** [1]

(ii)



I

[1]

(iii) S$_N$2 is favoured by **(CH$_3$)$_2$SO/ polar aprotic solvents**

These are solvents that are **polar enough to dissolve the substrate and nucleophile but do not participate in hydrogen bonding with the nucleophile**.

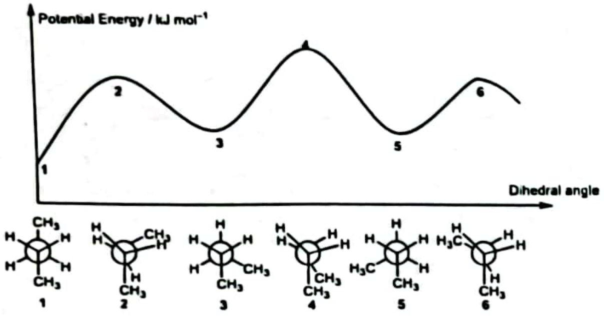
OR

CH$_3$OH stabilises the nucleophile through the formation of hydrogen bonds, which lower the energy level of nucleophile/ increases the activation energy of the reaction as compared to using (CH$_3$)$_2$SO as solvent [2]

(iv) **CH$_3$CH$_2$S$^-$ would have a higher reactivity** than CH$_2$C*l*CH$_2$S$^-$.

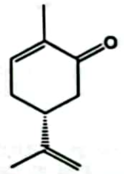
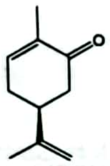
CH$_3$CH$_2$– group is more electron donating due to the lack of electronegative C*l* group. Hence, **S on CH$_3$CH$_2$S$^-$ has higher electron density and are more available for donation** compared to S on CH$_2$C*l*CH$_2$S$^-$ during reaction. [2]

(c)



[5]

3 (a) (i)

	
R	S

[2]

(ii) Let % (*R*)-carvone be X, %(*S*)-carvone be (1–X)

$X(-61) + (1-X)(+61) = -23$

$X = 0.6885$

$\% \text{ major enantiomer} = ee + \frac{100 - ee}{2}$

Enantiomeric excess = 37.7 [1]

(b) (i)

$$[\alpha]_D = \frac{10.07}{\left(\frac{5.97}{10}\right)(1.0)}$$

$= +16.87° = +16.9°$

[1]

(ii) Let % Y be n, % X be (1–n) [1]

$(1-n)(+41.7) + (n)(-13.5) = +16.87$

$n = 0.4498$

Percentage yield of Y is 44.98%

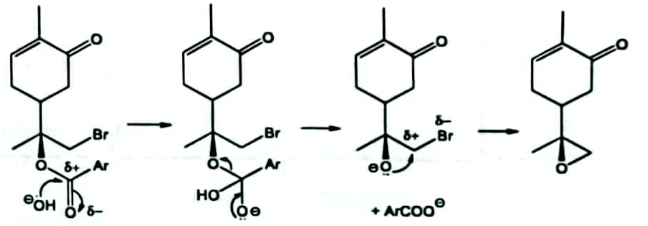
$\eta_{\cancel{X}Y\,\text{initial}}(1-0.4498)(350.9) + \eta_{\cancel{X}Y\,\text{initial}}(0.4498)(166) = 5.97$

$\eta_{\cancel{X}Y\,\text{initial}} = 0.02230 \text{ mol}$

Concentration of Y = 0.02230 (0.4498)(166) / 10

$= 0.1665 = 0.167 \text{ g cm}^{-3}$

(iii)



Addition-elimination followed by S$_N$ [2]

(iv) Due to conjugation with C=O/ delocalisation of π electrons in C=C into C=O, the C=C becomes less electron rich/ less nucleophilic. [1]

(c) (i) When a photon is absorbed by a molecule, an electron, residing in the bonding or non-bonding orbital, gains the energy and is promoted to a higher energy orbital, an anti-bonding orbital. Only π → π*, n → π* and n → σ* normally produce absorption in the uv/visible region and give the characteristic uv/visible spectra. add chromophores if qn is 3 m. [2]

(ii) 235 nm: π → π*

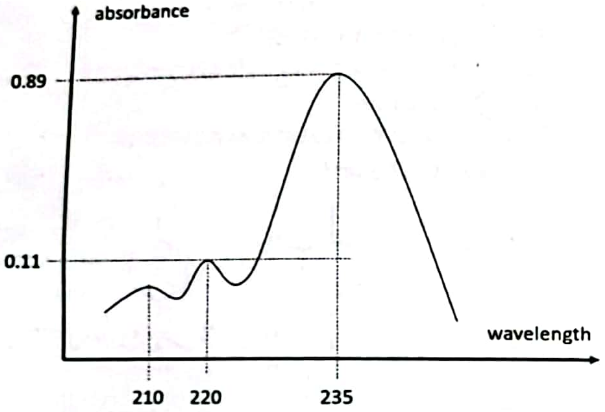
318 nm: n → π* [1]

(iii) Using A = εcl,

Relative amount of carvone : limonene

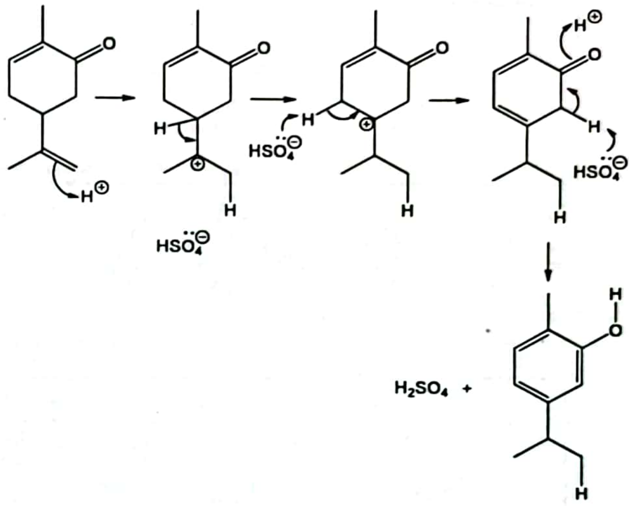
= (0.89 / 1513) / (0.11 / 251) = 1.34 [1]

(iv)



The maximum absorptions for both compounds appear at very similar wavelengths. There is significant overlap in the absorption spectra from 210 to 235 nm. For instance, the transition associated with π → π* limonene also adds to the energies absorbed for the π → π* transitions in carvone. Therefore, the individual amounts determined is inaccurate. [2]

(v)



[3]

(vi) Due to an increase in conjugation, the energy gap between the HOMO and LUMO is smaller in carvacrol than that in carvone. Thus, the wavelength of maximum absorption increases.

4 **(a)** CO and CO_2 [1]

(b) **(i)** **B**: E

C: Z [1]

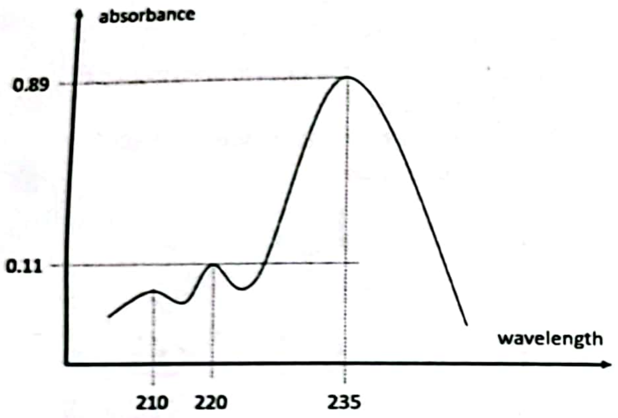
(ii) HC*l* adsorbs onto the aluminium oxide surface and adds across the weakened carbon-carbon triple bond in a syn fashion, giving rise to **B** only.

C will not be formed as the H and Cl atoms are on opposite sides of the C=C bond. [1]

(iii) $-8800 = -8.31 \times 298 \ln K_c$

$K_c = 34.9$ [2]

(iv)



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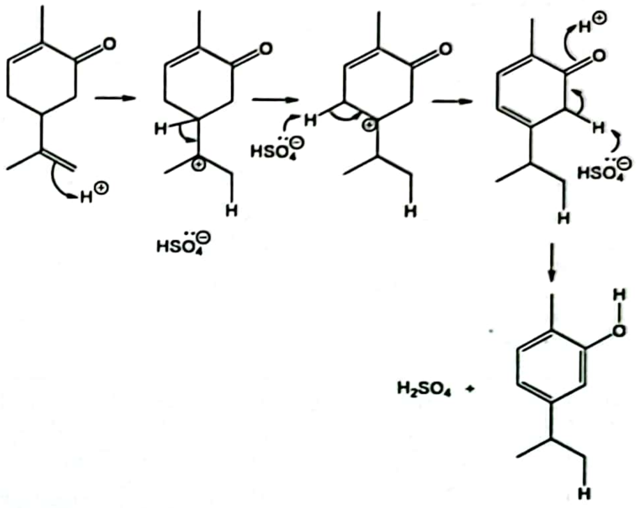

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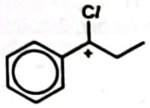
$K_c = 34.9$ [2]

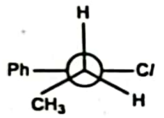
% of B = $\frac{1}{35.9} \times 100\% = 2.79\%$

(c) (i)

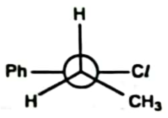


The positive charge is placed in a p orbital that overlaps sideways with the π electron cloud of the benzene ring. This allows for the delocalisation of electrons from the π electron cloud, stabilising the carbocation. [2]

(ii)



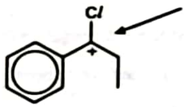
gives B



gives C

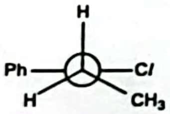
[2]

(iii)



Free rotation about the C–C single bond allows for Ph and methyl group to be trans to each other

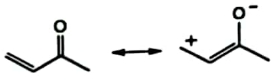
Steric repulsion between benzene ring and methyl group is greater than Cl atom and methyl group, as Ph is larger (has a larger electron cloud size) than Cl.



is lower in energy level and gives rise to a product of a lower energy level (thermodynamic product) [3]

(d) (i) (nucleophilic) Addition [1]

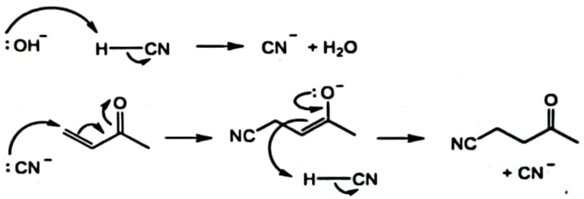
(ii) β – carbon atom is electron deficient because the π electron cloud of C=C bond / p orbitals of C in alkene overlaps with π electron cloud of C=O bond. Allows for electronegativity O to exert its electron-withdrawing effect on C=C bond via resonance. [3]



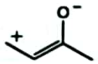
Inductive effect will cause α – carbon atom to be more electron deficient but the resonance effect is greater so β – carbon atom is more electron deficient.

The nucleophile attacks the β – carbon atom because it is less sterically hindered / more accessible / easier to approach than the carbonyl carbon.

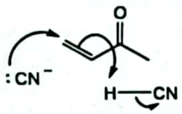
(iii)



- Ensure charge conservancy
- Mechanism can be drawn in individual steps
- CN⁻ must be regenerated in the mechanism
- Can use the resonance structure with formal charges



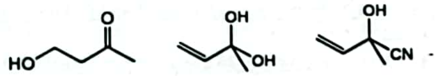
for the CN⁻ attack on β – carbon
- Do not draw CN⁻, enone and HCN in the same step, i.e.



as it is termolecular

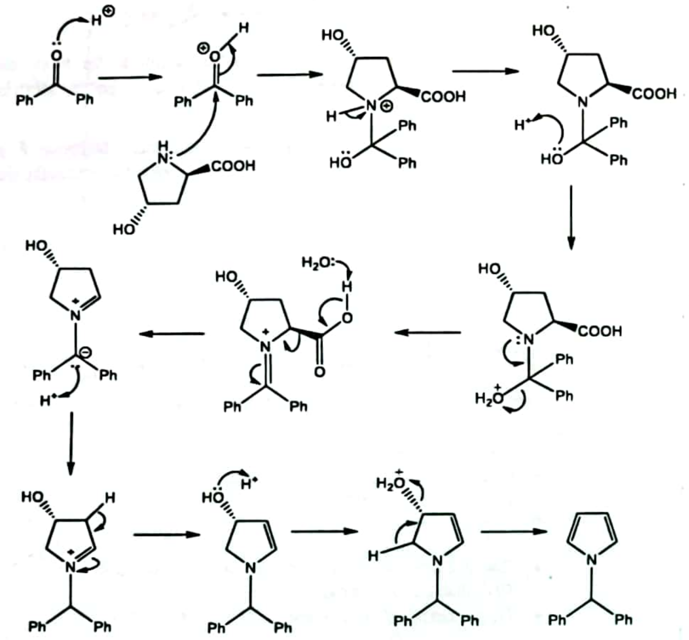
[2]

(iv)



Any two [2]

5 (a) (i)



[4]

(ii)

$(Ph)_2CO$	Final product
Strong C=O stretch 1670 – 1740 cm^{-1}	Weak C=C stretch 1635 – 1690 cm^{-1} / C-N stretch

[2]

(b) (i) For experiments 1 and 2, the major products (G2 and G4) has the labelled ^{13}C as its carbonyl carbon.

For experiment 3, the major product G5 does not have labelled ^{13}C. [2]

(ii) The reaction is likely to involve the reduction of CO_2 and oxidation of methanol.

The isotopically labelled methanol may be oxidised to ^{13}C labelled CO_2/CO and get inserted. The probability is low and that explains why G6 is the minor product. [1]

(c) (i) Tetramethylsilane (TMS)

TMS is used as the reference compound at 0.0 ppm as it gives a strong singlet signal even at low concentrations due to its twelve highly deshielded chemically equivalent protons. [2]

(ii) Mr of U = 218

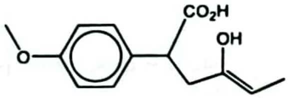
$$\text{No. of O atoms} = \frac{218 \times 0.220}{16} = \underline{3}$$

$$\text{No. of C atoms} = \frac{100}{1.1}\left(\frac{9.5}{67.1}\right) = \underline{13}$$

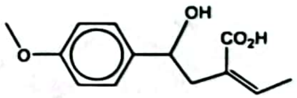
From NMR Spectrum:

δ	Splitting pattern	Integral	Deduction
1.54	doublet	3	$-CH_3$ next to CH
2.90	doublet	2	$-CH_2-$ next to CH
3.74	singlet	3	$-CH_3$ attached to electronegative O atom
3.90	triplet	1	-CH- next to CH_2, bonded to aromatic ring
5.57	quartet	1	-CH- next to CH_3, bonded to C=C
6.93	doublet	2	Protons on aromatic 1,4-disubstituted benzene ring
7.29	doublet	2	

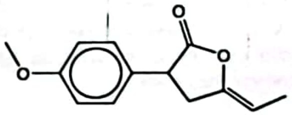
Structure of V:



OR



Structure of U:



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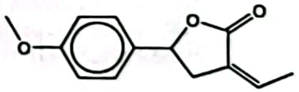
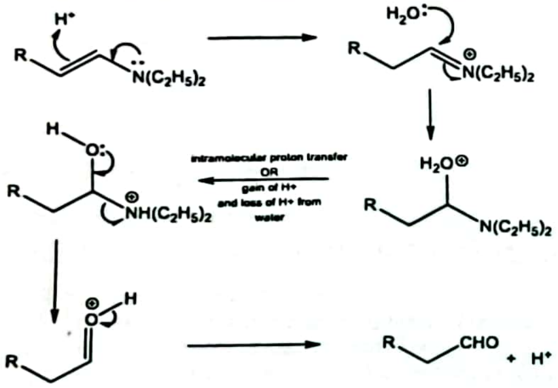


[9]

U undergoes <u>**acid hydrolysis**</u> to form **V**, which contains a <u>**carboxylic acid**</u>. **U** is an <u>**ester**</u>.

U, and **V** undergoes <u>**electrophilic addition**</u> with Br_2, indicating the presence of the <u>**alkene**</u> functional group in both compounds.

6 (a) (i)

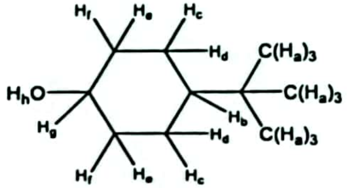


[3]

(ii) Absence of <u>strong C=O stretch (1670–1740 cm^{-1})</u>

Presence of <u>strong O–H stretch (3580–3650 cm^{-1})</u>

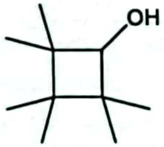
(iii)



Proton	δ/ ppm	Splitting pattern	Integration ratio
H_a		singlet	9
H_b	0.9 – 1.7	multiplet	1
H_c		multiplet	2
H_d		multiplet	2
H_e		multiplet	2
H_f		multiplet	2
H_g	3.2 – 4.7	multiplet	1
H_h	No signal, labile proton in deuterated solvent		

[4]

(iv)



[1]

(b) (i) $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$ [1]

(ii) No of moles of Br^- = 0.5950 / (39.1+79.9) = 5.00 × 10^{-3} mol (limiting)

No of moles of BrO_3^- = 0.3340 / (39.1+79.9+48) = 2.00 × 10^{-3} mol

No of moles of Br_2 produced = $\frac{3}{5}$ × 5.00 × 10^{-3} = 3.00 × 10^{-3} mol

No of moles of $NaAsO_2$

= No of moles of excess Br_2 in 250 cm^3 solution

= 9.93 × 10^{-3} × 0.0215 × 10 = 2.001 × 10^{-3} mol

No of moles of Br_2 used for bromination of salicylic acid

= (3.00 – 2.001) × 10^{-3} = 9.990 × 10^{-4} mol

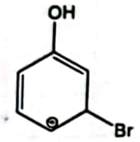
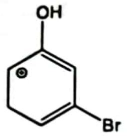
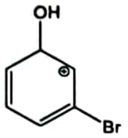
Mass of salicylic acid contaminant in 4.4035g of Aspirin tablets

= 9.990 × 10^{-4} × $\frac{1}{3}$ × 10 × 138 = 0.4595 g

% by mass of salicylic acid = (0.4595 / 4.4035) × 100 = 10.4% [3]

(iii) Does not meet. Exceed 0.3% [1]

(iv)

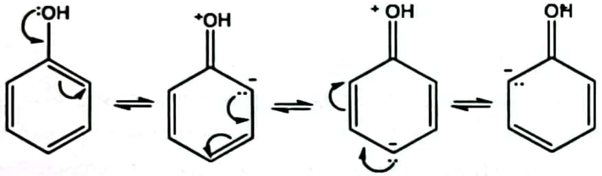
		
Delocalisation of lone pair diagrams		

Fewer resonance structures for carbocation means carbocation for 3–bromophenol is less stable.

OR

The positive charge is in **(iv)** resides on the carbon adjacent to an electron-donating OH group, hence the positive charge is reduced/stabilised through inductive effect.

OR



Through resonance, C2 and C4 are electron–rich. Hence, these 2 positions are more susceptible to electrophilic attack.

Lower yield for 3–bromophenol. [3]