Section A

- **1 (a)** The electrochemical epoxidation can be ran at ambient conditions, compared to the high T and P of the silver–based method.
 - The current methods may produce CO₂ due to overoxidation, leading to an increased carbon footprint
 - Water is an abundant / safe / sustainable oxygen source compared to flammable mCPBA
 - Generates useful H₂ (g) side–product
 - Higher atom efficiency compared to the mCPBA method that produces a large amount / stoichiometric amounts of RCOOH sideproduct.

(b) (i)
$$+ H_2O \longrightarrow O + 2H^+ + 2e^-$$

- (ii) No. of mol of cyclooctene oxide = $\frac{50}{126}$ = 0.3968 mol No. of mol of electrons req = 0.3968 mol × 2 × $\frac{100}{30}$ = 2.646 mol Total charge = 2.646 × 96500 = 2.55 × 10⁵ C
- (c) (i) The M_r of the product epoxide can be determined using <u>mass spectrometry</u>. The molecular ion peak is expected to <u>increase from 126 to 128</u> if the oxygen source was $H_2^{18}O$.
 - (ii) Use renewable electricity/ development of renewable energy sources/ low cost technology that generate electricity e.g. solar cells
 - Use renewable chemical feedstock e.g. CO₂ / create renewable ethene instead of fossil–fuel derived ethene
 - Optimising conditions to improve yield of epoxide over ketone
 - Understanding mechanism for ketone formation
 - Increase the yield of epoxide by increasing the selectivity to epoxide with which it's created.
 - Changing a catalyst to improve selectivity for epoxide over ketone
 - Modify the electrolyte to improve the interaction between ethene and the anode.
- (d) Since water is in large excess, the reaction is pseudo-zero order with respect to $[H_2O]$.

Let n be the order of reaction with respect to [cyclooctene]. rate = k'[cyclooctene]ⁿ

Taking logarithms on both sides of the equation,

 $\lg rate = \lg k' + n \lg [cyclooctene]$



$$n = gradient = \frac{-2.56 - (-3.52)}{-0.8 - (-2.16)} = 0.7059$$

Hence the order of reaction with respect to [cyclooctene] is 0.7.

(e) (i) <u>Ring strain</u> in a 3–membered ring, where the bond angle is constrained to <u>60°</u> <u>instead of 109.5°</u> for the sp³–hybridised atoms / <u>additional repulsion</u> <u>between bond pairs</u> destabilises the ring

(ii)

$$CH_2=CH_2(g) + H_2O(l) \rightarrow H_2(g) + \bigtriangleup^O(g)$$

 $\Delta H = \sum BE_{\text{reactants}} - \sum BE_{\text{products}}$ = BE(C=C) + 2(O-H) + ΔH_{vap} - [BE(H-H) + BE (C-C) + 2BE(C-O) - 105] = 610 + 2(460) + 40.8 - [436 + 350 + 2(360) - 105] = **+169.8 kJ mol**⁻¹

(iii) $\Delta S > 0$ as the number of gaseous particles increases from 1 to 2 mol as the reaction proceeds. Since $\Delta G = \Delta H - T\Delta S$ and $|T\Delta S|$ increases as temperature increases, ΔG becomes less positive /more negative, reaction becomes more spontaneous.

[Total: 16]

- 2 (a) (i) Compare the <u>angles of rotation of plane-polarised light</u> by the enantiomerically pure reactant and the stereochemical products using a polarimeter.
 - (ii) <u>S_N1 / Unimolecular nucleophilic substitution</u>

Compound X forms a **stable carbocation** that is **resonance stabilised** as the positive charge can delocalise into the benzene ring. For S_N2 , the **bulky phenyl** ring provides **steric hindrance** to the approach of the nucleophile from the side opposite the leaving group.

Moreover for $S_N 1$, <u>ratio of % retention to % inversion is about 1:1</u> / there is only a slight excess of inversion. There is equal probability of the nucleophile approach either face of the trigonal planar carbocation intermediate.

- (iii) This <u>minimises the formation of side–products</u> as a result of the attack by the polar solvent molecules which could potentially <u>act as nucleophiles</u>.
- (iv) The negatively charged N_3^- is a <u>stronger/better nucleophile</u> than the uncharged CH₃OH molecule so there is a <u>greater extent of S_N2</u>.

OR

The <u>linear</u> N_3^- anion can approach the side opposite the leaving group with <u>less steric hindrance</u> than the CH₃OH molecule so there is a <u>greater extent</u> of S_N2.

OR

The <u>negatively charged N_3^- is repelled</u> by the <u>negatively charged leaving</u> <u>group</u> so there is lower probability of attack from the same side where the leaving group leaves.

(v)



----- ion-dipole interaction



Formation of ion–dipole interactions between water molecules and the OPNB⁻ anion/ leaving group could facilitate the <u>capture of water molecules/ correct</u> <u>orientation of water molecules</u> for attack at the <u>same side of the</u> <u>carbocation</u>, which results in retention of configuration.



- Axes
- E_{a1}, E_{a2} and $E_{a1} > E_{a2}$
- ΔH < 0
- Reactants, products and intermediate
- (ii) Yes. Since the first step has a <u>higher activation energy</u> than the second step / the <u>first step is slow</u> while the second step is fast, the <u>carbocation is</u> <u>consumed in the second step as quickly as it is generated</u>.

Thus, the <u>concentration of the carbocation intermediate is low and</u> <u>constant</u> for most of the reaction, and the <u>rate of change of concentration</u> of the <u>carbocation intermediate</u> can be approximated to be <u>zero</u>.

(iii) The <u>carbocation</u> formed from compound Y is <u>more stable</u> than that formed from compound X due to the presence of the <u>electron-donating methyl</u> <u>group on the phenyl ring</u> which helps to <u>disperse the positive charge</u>.

Remark: While both carbocation intermediates are resonance stabilised, the carbocation intermediate formed from Y has the positively charged carbon in one of its resonance structures adjacent to the electron–donating methyl group.



Using Hammond's Postulate, since the first step is endothermic, the transition state is **product-like**. The **late transition state for the first step will be of lower energy** since it should be **similar in energy / geometry to the carbocation** intermediate. Hence the rate of reaction is <u>faster</u> with a <u>lower</u> **activation energy**.

(b) In the gaseous phase, <u>solvent effects can be ignored</u>, so the reaction mechanism is only affected by structure of alkyl chloride and the nucleophile.



Note: stereochemistry needed

- (ii) S_N2: the transition state <u>does not involve breaking the C-H or C-D bond</u>, so the <u>strength of bond has minimal effect</u> on the overall rate of reaction, so k_H ≈ k_D → deuterium KIE ≈ 1.
 E2: rate determining step involves breaking the C-D bond which is stronger than C-H bond, so k_H > k_D → deuterium KIE > 1.
- (iii) As the <u>alkyl chlorides become more substituted</u> from primary to secondary to tertiary, the <u>deuterium KIE increases</u>, implies that <u>E2 reaction becomes</u> the dominant mechanism over $S_N 2$.

This is because as the <u>alkyl chlorides becomes more sterically hindered</u> around the electrophilic C, it becomes <u>increasingly difficult for the</u> <u>nucleophile to approach and attack the electron deficient carbon</u> and <u>subsequently easier for the base to abstract a H from the adjacent C</u>. Hence the probability of the alkyl chloride undergoing S_N2 decreases and E2 increases.

- (d) With CH₃COO⁻, deuterium KIE will be <u>lower than 1.71</u>. Since the <u>acid strength of ethanoic acid is higher than HCIO, CH₃COO⁻ is weaker conjugate base than CIO⁻.</u> CH₃COO⁻ will have a <u>lower tendency to abstract H</u> than CIO⁻, so <u>S_N2 reaction would be favoured over E2</u> OR <u>the extent of E2</u> reaction would be less favoured over S_N2 with CH₃COO⁻.
- (e) (i)

(C)



Note: Formation of **A** involves a nucleophilic attack on the less sterically hindered epoxide carbon.

(ii) O OH

(f) (i) correct S configuration anti-staggered Newman projection



(ii) Optical purity = ee% = $\frac{[\alpha]_{sample}}{[\alpha]_{pure enantiomer}}$ = $\frac{25}{168}$ = 14.9% Let x be the % of (+)-phenylsuccinic and y be the % of (-)-phenylsuccinic acid. x + y = 100 y - x = 14.9 (since the overall optical rotation is negative, y > x) Solving, y = 57.5% x = 42.5%[Total: 18] **4 (a)** A chromophore is a system containing the electrons responsible for the absorption of (electromagnetic) radiation.



(iii) The λ_{max} value for penta-1,3-diene is around 215 nm (accept any value from 180 - 250)

Due to <u>conjugation</u>, the <u>energy gap between the HOMO and the LUMO</u> of penta-1,3-diene is <u>in between</u> that of ethene and hexa-1,3,5-triene. The <u>energy requred to excite an electron</u> from the HOMO and the LUMO for penta-1,3-diene <u>between that needed for ethene and hexa-1,3,5-triene</u>, hence λ_{max} is larger than that needed for ethene, but smaller than that for hexa-1,3,5-triene.



The product mixture is formed as 1,2-addition and 1,4 addition occur with two nucleophiles present in the reaction mixture – bromide anion and ethanol.



8

2 of them are the enantiomers of A_2 and B_2 .

(ii)

[Total: 12]

Section B



(ii) The <u>tertiary carbocation</u> formed is <u>stabilised</u> due to the <u>positive charge on</u> <u>the carbocation being dispersed</u> by the <u>delocalisation over two phenyl</u> <u>rings</u>, as well as the presence of an <u>electron donating alkyl group</u>.

OR

Lack of strong base for E2

OR

Protonation of –OH group forms a good leaving group.

(b) (i) The nucleophile has <u>equal probability</u> of attacking the <u>trigonal planar</u> carbonyl carbon from <u>top or bottom</u> of the plane.



(iii)



acid



base

Note:



(c) (i) Acid catalyst is required to <u>protonate the O atom</u> on the carbinolamine intermediate, to convert the –OH group into a <u>better leaving group</u> to obtain the iminium ion intermediate.

OR

Protonation of carbonyl group makes it a stronger electrophile.

(ii)





10

(d) (i) diastereomer (or E-Z isomer, **B** is the E isomer)



(ii)



Drawing of each chair conformers

The conformer with **<u>bulky</u>** isopropyl substituent on the <u>**equatorial position**</u> will be favoured so that this conformation <u>**minimises unfavourable 1,3-diaxial**</u> <u>**interactions**</u>.

(iii) The rate of reaction of <u>isomer B</u> is much <u>slower</u>. A and B undergoes <u>E2</u> in sodium ethoxide.

The <u>proton</u> of **B** is in the <u>anti-periplanar</u> arrangement only when <u>all three</u> <u>substituents are in the axial positions</u>. Ring-flip must first occur and <u>very</u> <u>small proportion</u> of **B** will be in this higher-energy conformation.

No C-H bonds antiperiplanar to the C-CI bond: no E2

Cl

favoured conformation with bulky iPr group in the equatorial position

One C-H bond is antiperiplanar to the C-CI bond: E2 occurs



disfavoured conformation with bulky iPr group in the axial position

: OEt

OR

The rate of reaction of **isomer A** is much **faster**. A and B undergoes **E2** in sodium ethoxide.

The **proton** of **A** is in the **anti-periplanar** arrangement when **the bulky isopropyl substituent are in the equatorial position**. **A large proportion** of **A** will be in this lower-energy conformation.



Note: The negatively-charged intermediate that forms **B** will be more stabilised as the $-NO_2$ group is ortho to the -OH group. In one mesomeric form, the negative charge resides on the C atom bonded to the strongly electron-withdrawing $-NO_2$ group. This is not possible for the other negatively-charged intermediate.



(b) (i) Concentration of transferrin = $\frac{0.463}{4170 \times 1.00}$ = 1.11×10^{-4} mol dm⁻³ 12

Concentration of transferrin $=\frac{1.11\times10^{-4}\ mol}{\times}\times\frac{81000\ g}{1.11\times10^{-4}\ mol}$ dm³ mol = <u>8.99 g</u> dm⁻³

 $0.424 = 4170 \times C_T + 2290 \times C_D$ (ii) $0.401 = 3540 \times C_T + 2730 \times C_D$

Solvina.

Concentration of T-Fe₂ = 7.299×10^{-5} M = 7.30×10^{-5} mol dm⁻³ Concentration of **D**-Fe = 5.224×10^{-5} M = 5.22×10^{-5} mol dm⁻³

Percentage of Fe(III) that is bound to transferrin $2\times7.299\times10^{-5}$ $\frac{--}{2 \times 7.299 \times 10^{-5} + 5.224 \times 10^{-5}} \times 100\%$ = 73.6 %

The π electrons in benzene ring are delocalised and free to move. (c) (i)

In the presence of a magnetic field, the delocalised π electrons will circulate/ (move in a direction) to generate a magnetic field to oppose the applied magnetic field.

As a result, the benzylic protons (outside ring) lie in a region where induced magnetic field reinforces the applied magnetic field. This increases the energy gap between the parallel and anti-parallel spin and hence the protons are deshielded and resonate at a higher chemical shift value.



- (ii) Molecular ion peak occurs at 164. It is an even number / no isotope pattern (absence of M+2 peak) for C/ and Br.
 - ⇒ No C/ or Br present.

IR Significant absorptions at 1720 cm⁻¹ due to C=O stretch 1600 cm⁻¹ due to aromatic C=C stretch, 1275 and 1100cm⁻¹ due to C-O (possible) $2800 - 3000 \text{ cm}^{-1}$ due to C–H stretch Absence of 3000 – 3400 cm⁻¹ signals: absence of amide N–H stretch and carboxylic acid O-H stretch

δ/ppm	multiplicity	integration	deduction
7.8	doublet	2	Ar-H, a pair of doublets, most likely 1,4-disubstitued
7.3	doublet	2	
4.3	quartet	2	CH ₂ coupled to 3H/ 3 adjacent protons, deshielded by <u>electronegative</u> O
2.4	singlet	3	-CH ₃ next to benzene ring, with no adjacent H, deshielded due to close proximity with anisotropic effect from benzene ring
1.4	triplet	3	$-CH_2CH_3$ coupled to 2H / 2 adjacent protons

Checking the molecular formula of $C_{10}H_{12}O_2$ Molar mass = 10 × 12 + 12 × 1 + 1 × 16 = 164 g mol⁻¹

Structure of **C**:







The 12 H in TMS has the same chemical environment and gives an intense peak in a ¹H NMR spectrum.

Its δ (ppm) value is unique and does not coincide the ppm values of other organic compounds. / Si is less EN than C, hence shields the TMS protons so they resonate at a lower chemical shift value.

[Total: 20]

7 (a) P is a <u>di-substituted alkene</u> whereas R is a <u>mono-substituted</u> alkene. / P is a <u>more</u> <u>substituted alkene</u> compared to R. Hence P is <u>thermodynamically more stable</u> / <u>lower in energy</u> than R.

Note: the E2 reaction occurs under reversible conditions, hence favours the thermodynamic product.

Due to <u>steric reasons</u>, **P** (and the transition state leading to **P**) is <u>lower in energy</u> than **Q** (and the transition state leading to **Q**. Hence formation of **P** is <u>thermodynamically and kinetically favoured</u> over **Q**.

- (b) (i) The signal was due to the coupling between an alkene (vinyl) proton and the neighbouring non-equivalent alkene proton. Further splitting of the signal occurs owing to the coupling with the neighbouring three equivalent methyl protons.
 - (ii) $10 = \frac{100}{1.1} \times \frac{A_{(M+1)}}{A_M}$ $\Rightarrow A_M : A_{M+1}$ 100 : 11
 - (iii) Loss of m/z (148-117) = 31 \Rightarrow loss of $-OCH_3$ (C–O bond cleavage of ether)



- (c) (i) Degree of unsaturation = $0.5 \times (2 + 2 \times 10 10 + 2) = 7$
 - (ii) S lacks two alkene protons that existed in P.

OR

P has an alkene or carbon–carbon double bond.

(iii)



Comment: doublet at 1.80 ppm of P has been changed to singlet at 2.40 ppm in **S**. This suggest that the same methyl group does not have an adjacent proton and is experiencing an environment that causes it to be more deshielded.

- (d) (i) IR spectroscopy involves absorption of infra-red radiation that matches the vibrational energy levels of a molecule. These vibrations must also result in a change in the dipole moment of the molecule.
 - (ii) **Bent** around the central oxygen atom.

No. of vibrational modes = 3(3)-6 = 3Vibrations are due to **stretching** and **bending** of the molecule.



Students not required to draw the vibrational modes

(e) (i)

(ii)



ACCEPT



(iii) The use of ozone can selectively afford aldehyde.

[Total: 20]