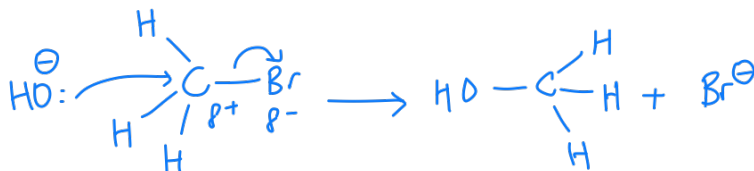


Question 1

Question 1(a)

(i) Draws an S_N2 mechanism [1] (Award 0 for other mechanisms)



Hence, the rate law is rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$. [1] (No e.c.f. given for wrong mechanism)

(ii) From X = F to I, the rate of reaction increases, and the leaving group X is better. The leaving group is better because the X⁻ ion is more stable [1] as seen in the decreasing pK_a values of HX. [1]

(iii) Concentrated sulfuric acid protonates the -OH group to form a -OH₂⁺ LG, which is a better LG than OH⁻ since H₂O is more stable than OH⁻ (or pK_a of H₂O is higher than H₃O⁺). [1]

(iv) Negatively charged nucleophiles will be more strongly attracted to an electron-deficient carbon, so water is the least nucleophilic. [0.5] The carboxylate ion is less nucleophilic because its nucleophilic lone pair is delocalised between 2 oxygen atoms, conferring it stability (through resonance/dispersal of negative charge), making it a weaker base. [0.5]

Hence, in Fig 1.2, a weaker base is a less nucleophilic one.

(v) Circles **Q**. [1]

Comment: S is less electronegative than O, so the lone pair on S is less attracted to its nucleus and more available for nucleophilic attack.

(vi) Disagree. Because although **P** is a stronger base than **Q**, **P** is less nucleophilic than **Q**. [1]

Question 1(b)

Appropriate substrate: 2-chloro-2-methylpropane (must be a tertiary halogenoalkane) [1]

Procedure to perform S_N1

In 2 separate flasks, place equal volume and concentration of substrate dissolved in water.

In 1 flask, add solid NaOH.

Heat both flasks, maintained at same temperature. [1]

Interpretation of results

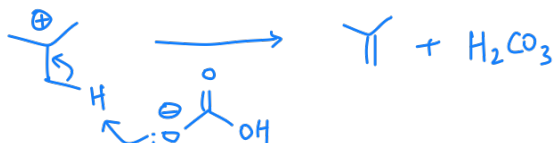
At frequent time intervals, monitor the concentration of substrate.

If the concentration of substrate is the same for both flasks at the same time, then the strength of the nucleophile does not affect the rate of substitution.

If the concentration of substrate is the lower for the flask with NaOH added in it as compared to the flask without NaOH added in it, measured at the same time, then the strength of the nucleophile does affect the rate of substitution. [1]

Question 1(c)

(i) Correct movement of electrons [1]



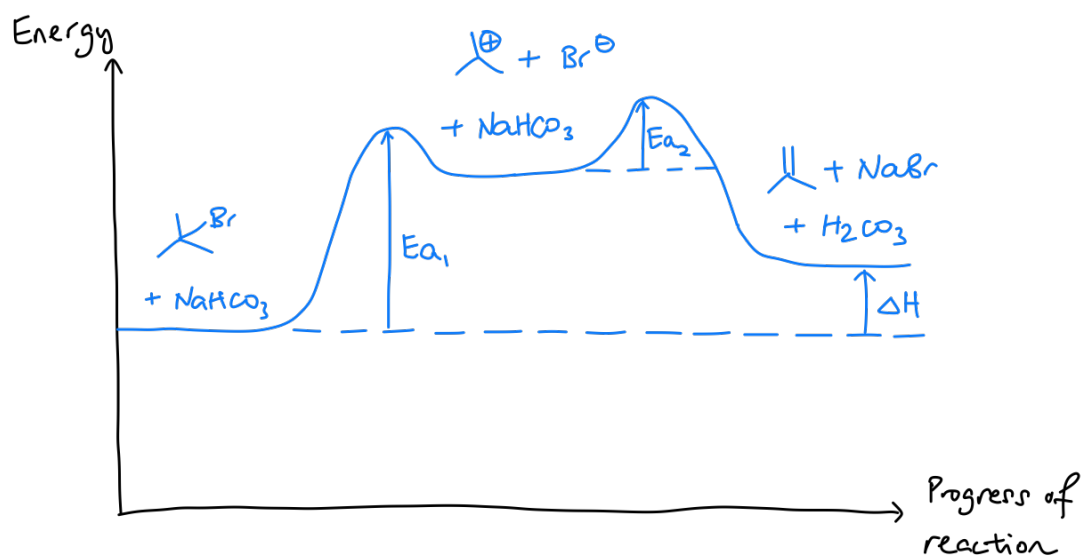
If the structure of the bicarbonate ion is not fully shown, the lone pair must originate from the O atom.

(ii) Correct reactants, intermediates and products [1.5]

Correct axes [0.5]

Endothermic reaction [1]

NaHCO₃ and NaBr may be dissociated into their ions.



Question 1(d)

(i) 2-bromo-2,3-dimethyl-butane [1]

Comment: 3-bromo-2,3-dimethyl-butane is NOT accepted.

(ii) **TS1** leads to 2,3-dimethylbut-2-ene being formed, while **TS2** leads to 2,3-dimethylbut-1-ene being formed. [1]

TS1 is higher in potential energy because the reaction pathway leading to the formation of 2,3-dimethylbut-2-ene must have a higher activation energy since it is the minor product, so its rate of formation is slower. [1]

(iii) The $-\text{C}(\text{CH}_3)_3$ group is closer to the bulky methyl groups in **TS1**, while in **TS2**, it's closer to the smaller H atoms. Hence, **TS1** is sterically disfavoured, more unstable, hence higher in potential energy, as the bulky methyl groups will repel the bulky base from approaching their side. [1]

Question 1(e)

Step 1: conc. H_2SO_4 , KCl , heat [1]

Step 2: $(\text{CH}_3)_3\text{CO}^-\text{K}^+$, heat [1]

Accept alternative reagents for step 1: PCl_3 , PCl_5 , SOCl_2 , conc. HCl

Comment: To form **Z** in high quantity, you need to use a bulky base. In **(d)**, you are hinted that the less substituted alkene resulting from an elimination of a halogenoalkane with a bulky base is favoured. Hence, you should convert the alcohol to a halogenoalkane, and then use a bulky base for elimination.

Answers with 1 step (e.g.): excess conc. H_2SO_4 , heat or Al_2O_3 , heat will not be accepted.

Step 2 must have a bulky base. The examiner reserves the right to exercise discretion to reject answers.

Question 2

Question 2(a)

(i) The carbon bonded to the bromine atom in bromoethane is electron-deficient and cannot perform a nucleophilic attack at the electron-deficient carbonyl carbon of propanone. [1]

(ii) Partial positive charge on Mg; partial negative charge on C [1]

(iii) Correct intermediate, accept with or without counter ions [1]



NH_4Cl contains a proton to protonate the intermediate to form the alcohol product. [1]

Question 2(b)

(i) Electrophilic (aromatic) substitution [1]

(ii) In Fig 2.1, the Grignard reagent's nucleophilic centre is on the carbon attached to Mg itself, not the aromatic ring. It undergoes a nucleophilic addition reaction only. [1] (As long as the candidates identify the nucleophilic site in their own way, the credit is awarded.)

In Fig 2.2, the nucleophilic centre is the pi-electrons on the aromatic rings. A nucleophilic addition onto CO_2 results in aromaticity being disrupted, creating an unstable intermediate. Hence much more energy needs to be supplied for the reaction to continue, which is why the conditions are harsher in Fig 2.2. [1]

(iii) The phenoxide ion's aromatic ring is activated (because the lone pair on O is delocalised into the aromatic ring which results in additional electron density in the aromatic ring) [1].

But the aromatic ring in benzene is not activated, so its not nucleophilic/electron-rich enough to attack CO_2 as a nucleophile. [1]

(iv) SOCl_2 [1]

Comment: The question states that sulfur analogues of carbonyl compounds and carboxylic acid derivatives are similar in their reactions. Since you use thionyl chloride to convert a carboxylic acid to an acyl chloride, you can do the same here too.

Question 2(c)

(i) Correct structure [1]



(ii) Any 1 of the following [1]

Add $\text{K}_2\text{Cr}_2\text{O}_7$ (aq), H_2SO_4 (aq), and heat. Solution will turn from orange to green.

Add KMnO_4 (aq), H_2SO_4 (aq), and heat. Purple solution decolourises.

(iii) Step 1 protects the aldehyde so it won't undergo an intramolecular addition reaction when the Grignard reagent is formed. Step 3 reforms the aldehyde. [1]

Comment: Candidates need to imply that Step 1 is a protecting step, or state the purpose of the protection: to prevent an intramolecular addition when the Grignard reagent is formed.

Question 2(d)

(i) The Grignard reagent will undergo an acid-base reaction with water, destroying the Grignard reagent. [1]

(ii) The reaction is highly exothermic, so adding a lot of propanone will generate too much heat which will cause the reaction to go out of control (or implied). [1] (or reaction mixture will boil off resulting in a poor yield)

Question 2(e)

(Fractional) Distillation. [1]

The ether and **A** have simple molecular structure. [0.5]

Stronger hydrogen bonds exist between molecules of **A** [0.5] while weaker permanent dipole-permanent-dipole or dispersion forces exist between molecule of **B**. [0.5]

Hence, they would have different boiling points [0.5], with the boiling point of **A** being higher than that of the ether.

Comment: We cannot use a separating funnel because the 2 compounds are miscible with one another.

Question 3

Question 3(a)

(i) The long carbon chains of cellulose interfere with the formation of hydrogen bonding with water. [1]

(ii) ΔG is positive and large in magnitude. [1] Cellulose is a weaker base than water because of the presence of an electron-donating alkyl group which intensifies the negative charge on the conjugate base, while the hydroxide ion does not have alkyl groups. [1] Hence, the formation of the conjugate base of cellulose is strongly disfavoured, and not spontaneous. [1]

(iii) The hypothetical carbocation intermediate has no electron-donating alkyl groups to stabilise the positive charge on the carbon. [1] Furthermore, the $-\text{CO}_2^-$ group (or carboxylate group) is electron-withdrawing which destabilises the already electron-deficient carbon holding the positive charge. [1]

(iv) A high concentration of hydroxide ions would shift the position of equilibrium 1 to the right, raising the concentration of $\text{R}-\text{O}^-$. [1] This hence increases the rate of formation of CMCNa since $\text{R}-\text{O}^-$ is involved in the rate determining step (of the $\text{S}_{\text{N}}2$ reaction). [1]

(v) $K_1 = [\text{R}-\text{O}^-] / [\text{OH}^-]$ and rate of formation of CMCNa = $k_2[\text{R}-\text{O}^-][\text{C}/\text{CH}_2\text{CO}_2\text{H}]$ [1 for both statements]

rate of formation of CMCNa = $K_1 k_2 [\text{OH}^-][\text{C}/\text{CH}_2\text{CO}_2\text{H}]$. [1] award ecf from previous expressions that are wrong

Comment: The question states that cellulose is insoluble in water, so the term $[\text{R}-\text{OH}]$ should not appear in the expression for K_1 .

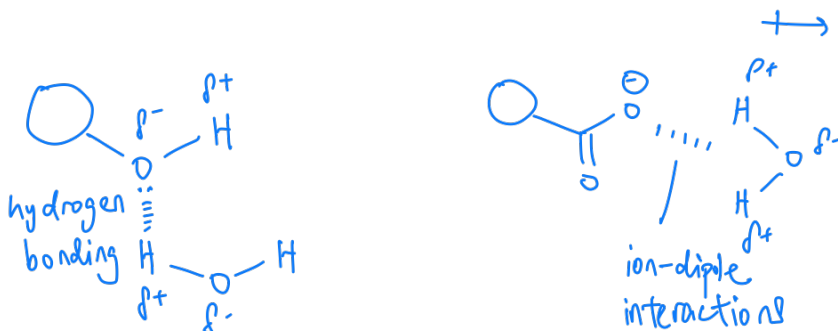
Question 3(b)

(i) Condensation [1]

(ii) A high temperature is selected to evaporate the water formed from cross-linking so that the reaction is driven forward. [1]

(iii) [2] each for hydrogen bonding and ion-dipole interactions

1 mark for type of interaction, 1 mark for diagram



Hydrogen bonding:

- Partial positive and negative charges
- Lone pair on oxygen atom

Ion-dipole interactions:

- Partial positive and negative charges
- CO_2^- explicitly shown (O^- is acceptable)
- Dipole moment on water shown

(iv) More extensive hydrogen bonding (and ion-dipole interactions) with the water molecules and the hydrogel. [1]

Question 3(c)

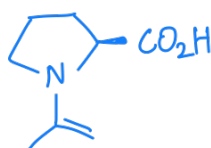
(i) NaCl dissociates in water into its aqueous ions which disrupts the formation of hydrogen bonds and ion-dipole interactions between water and hydrogel since the ion-dipole interactions between water and Na^+ and Cl^- ions are stronger due to their low ionic radii. [1]

(ii) Cu^{2+} has energetically accessible vacant d-orbitals to accept a lone pair of electrons from the hydrogel. [1] However, Na^+ does not have energetically accessible orbitals as its next vacant orbital is the 3s orbital, which is much higher in energy compared to the fully occupied 2p orbitals. [1]

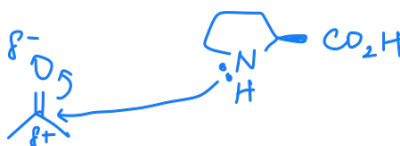
Question 4

Question 4(a)

(i) Correct structure [1]



(ii) A nucleophilic addition mechanism is drawn. [1] Deduct 0.5 per missing item up to 1 mark.



e.c.f. is awarded if the candidate uses benzaldehyde as the reacting species instead.

(iii) $\text{p}K_b$ value for the N atom of **A** is higher than that of proline. The lone pair of the N atom is delocalised into the adjacent alkene which makes it less available to abstract a proton [1], rendering the N atom to be a weaker base than that for proline. [1]

(iv) The OH^- nucleophile is not chiral. As chiral interactions only arise from chiral molecules, no enantiomer will be favoured over the other since no chiral interactions/reactions took place. [1]

Question 4(b)

(i) **21** is a Lewis base because it acts as a nucleophile in the first step when it attacks the carbonyl carbon. [1] At the end of the reaction, **21** is regenerated and chemically unmodified. [1] (The candidate does not need to explain why **21** speeds up the reaction.)

(ii) In the $\text{C}=\text{C}-\text{C}=\text{N}$ system, electrons from the $\text{C}=\text{C}$ pi bond can delocalise into the $\text{C}=\text{N}$ p orbitals. [0.5] Since N is more electronegative than C [0.5], the electron density at the $\text{C}=\text{C}$ pi bond

is lowered (or electrons are less available) [0.5], so the terminal C has a partial positive charge, which enables it to be an electrophilic centre [0.5 for partial positive charge OR electrophilic centre OWTTE] where a nucleophile (H_2O_2) can attack.

(iii) C1 is sterically hindered [0.5] as the bulky group of the chiral catalyst prevents a nucleophile from approaching it. C3 isn't as sterically hindered since the bulky group of the chiral catalyst is further. [0.5]

(iv) The H_2O_2 nucleophile preferentially attacks from the bottom of the plane [0.5] because the approach from the top of the plane is sterically hindered since majority of the bulky group is above the plane [0.5].

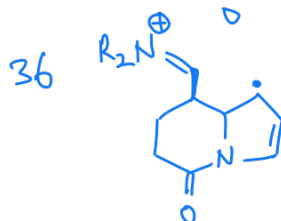
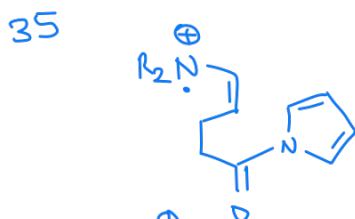
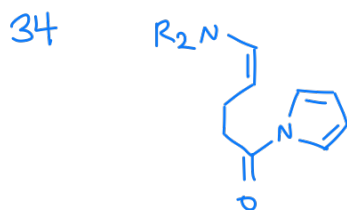
Question 4(c)

(i) +4 [0.5] $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ [0.5]

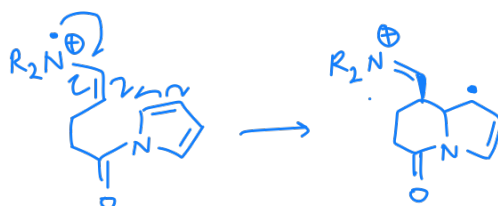
(ii) There are bulky groups in the catalyst [0.5], and the amine functional group can form an iminium ion [0.5].

(iii) Award [1] for each. Where stereochemistry is not included, deduct 0.5.

Award e.c.f. for **35** and **36** as long as the structures follow through from the previous intermediate.



(iv) Correct mechanism [1] This is either [1] or [0] marks awarded. e.c.f. is awarded only if the mechanism is correct, and **35** and **36** have the same structural features that arise from the mechanism.



Comment: 5 fish-hook arrows to be drawn in total. 2 new bonds were formed, while 1 was broken.

(v) H_2 [1] and $LiAlH_4$ [1]

Comment: The reduction of a double bond is done with hydrogen gas, while lithium aluminium hydride reduces the amide to an amine. The steps can be done either way.

Question 4(d)

The body is a chiral environment / chiral interactions take place in the body [1], so drugs must be enantiomerically pure for them to undergo reactions that are chiral in nature. Shine plane polarised light through a sample of a drug and check the direction and angle of rotation. [1]