VICTORIA JUNIOR COLLEGE PRELIMINARY EXAMINATION 2022
CHEMISTRY (Higher 3)
Suggested Answers

1 (a) Ratio = (–286/2)/(–394/12)
= **4.36**

[1]

(b)

This is to ensure that **$NaBO_2$** does **not precipitate** from the reaction mixture and coat the catalyst and reaction vessel, preventing further hydrolysis. [$NaBO_2$ has a lower solubility at 28 g per 100 g of water compared to $NaBH_4$ at 55 g per 100 g of water.]

[1]

(c)

$B(OH)_3$ is a **Lewis acid** since it **accepts** a **lone pair** of electrons from **water** to form $B(OH)_4^-$.

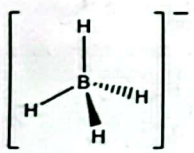
[1]

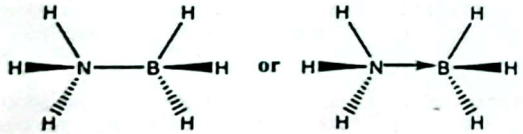
(d)

$$2NaBH_4 + (NH_4)_2SO_4 \rightarrow 2BNH_6 + 2H_2 + Na_2SO_4$$

[1]

(e)





[2]

(f)

The BH_4^- ions and water molecules are **adsorbed** onto the **active sites of the catalyst surface** by **forming weak bonds** between reactant molecules and the surface catalyst atoms.

This **increases the surface concentration of reactant** molecules and allows them to come into **proper orientation** for reaction.

The adsorption also **weakens the covalent bonds within the reactant molecules** and adjacent reactant molecules **react** to form products. The product molecule eventually **desorbs** from the catalyst surface.

[3]

(g) (i) In 1 min, amount of H_2 = $(1.0 \times 1.01 \times 10^5 \times 0.1 \times 10^{-3})/(8.31 \times 298)$
= 4.08×10^{-3} mol min^{-1}

Mass of Ru required = $(4.08 \times 10^{-3}/92) \times 101.1$
= 0.00448 g
= **4.48 mg**

[1]

(ii) Amount of $NaBH_4$ = 0.100 x 1.0
= 0.1 mol

Time taken = (0.1 x 4) / (4.08×10^{-3})
= **98.0 min**

[1]

(iii) Since reaction is first order wrt catalyst, halving the mass of Ru will half the rate (based on same volume of $NaBH_4$ used)

Using the Arrhenius equation, $(e^{-Ea/298R} / e^{-Ea/RT}) = ½$
$[-E_a/R(1/298 - 1/T)] = \ln ½$
$42000/8.31(1/298 - 1/T) = \ln 2$
T = **311 K**

[1]

(h) (i) $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid}$
$= E^\theta(O_2/OH^-) - E^\theta(H_2O/H_2)$
= 0.40 – (–0.83)
= +1.23 V

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

$\Delta G^\theta = -nFE^\theta_{cell}$

$= -4 \times 96500 \times 1.23$
$= -474780\ J\ mol^{-1}$
$= \mathbf{-475\ kJ\ mol^{-1}}$

[1]

(ii) Charge = 2.5 x 3.0 x 60 x 60 = 27000 C
Amount of e^- = 27000/96500 = 0.280 mol
Amount of O_2 = 0.280/4 = 0.0700 mol
Volume of air required at r.t.p. = 0.0700 x 24 x 100/20 = **8.40 dm^3**

[1]

(i) (i)

Anode: $BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall equation: $BH_4^- + 2O_2 \rightarrow B(OH)_4^-$

[2]

(ii) $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxd}$
$= E^\theta(O_2/OH^-) - E^\theta(B(OH)_4^-/BH_4^-)$

$1.64 = 0.40 - E^\theta(B(OH)_4^-/BH_4^-)$
$E^\theta(B(OH)_4^-/BH_4^-) = \mathbf{-1.24\ V}$

[1]

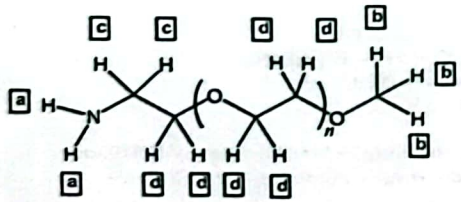
(iii)

The presence of H_2 due to **hydrolysis** of BH_4^- may result in its **oxidation** at the DBFC anode. Hence the anode potential observed is a "mixed" electrode potential of reactions between –1.24 and –0.83 V. (H_2 will likely be less than 1 bar.)

$B(OH)_4^- + 4H_2O + 8e^- \rightleftharpoons BH_4^- + 8OH^-$ –1.24V
$2H_2O(l) + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83V

[1]

2 (a) (I)



[2]

(ii) D_2O is added to identify compounds with **labile protons** - OH protons from alcohols and carboxylic acid and NH protons from amines and amides by **exchanging** their labile protons rapidly with D_2O to achieve **equilibrium**. **The deuterium nucleus does not absorb in the same frequency range as ^1H.** Thus, the signals corresponding to the labile protons will not be visible in the ^1H NMR spectrum when the NMR samples are shaken with D_2O.

$RNH_2 + D_2O \rightleftharpoons RNHD + HDO$

[1]

(iii) Peak area under each signal is directly proportional to the number of protons for that signal.

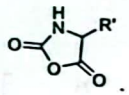
Hence peak area for **d** / peak area for **b** = number of **d** protons / number of **b** protons

133.7 / 0.9 = 4 x *n* / 3 (ignore the CH_2 group on the left of the repeating unit because CH_2 contributes only 2 protons which are negligible compared to all the protons in the repeating unit, accept if CH_2 protons are included in calculation)

n = **111** (nearest whole number)

[2]

(b) Let **A** be represented as RNH_2 and **C** as



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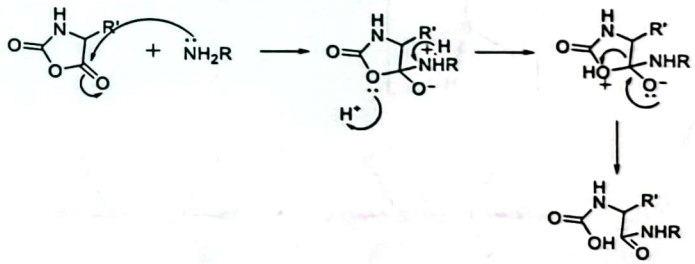


nucleophilic attack on C
deprotonation and protonation on O
elimination of leaving group
correct arrow flow and lone pairs shown

Gas is **CO_2**.

[3]

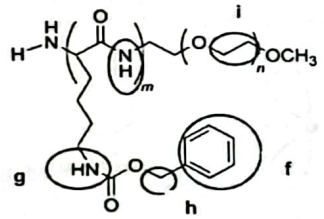
(c) Spectrum **3** is **A**. **A** does **not** have **C=O stretch** belonging to ester and amide, with wavenumber range of **1640 to 1750 cm^{-1}** unlike **C** and **D**.

Spectrum **1** is **C** and **2** is **D**. Both spectra have **N-H stretch** belonging to **amide**, with wavenumber range around **3250 to 3400 cm^{-1}**. **D** has many more amide N-H, hence has **more extensive intermolecular hydrogen bonding**. Thus N-H stretch in **D** is expected to be **broader** than in **C**.

correct assignment
plausible reasoning (other plausible reasoning accepted)

[2]

(d)



label the correct protons for calculations

Peak area under each signal is directly proportional to the number of protons for that signal.

We need to calculate a "conversion factor" that relates the peak areas of the protons to the actual number of protons for comparison. For example we choose the –(OCH_2CH_2)– protons.

Conversion factor = peak area of **i** / (*n* x 4) = 622 / (111 x 4) = 1.40
This means that one proton in spectrum of **(d)** corresponds to peak area of 1.40.

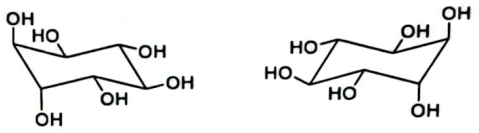
Choose another convenient signal to calculate *m*, for example
m = peak area of **f** / (5 x 1.40) = 119 / (5 x 1.40)
m = **17** (nearest whole number)

(No. of protons of **f** = 5 x no. of protons in –(CONH)– group)

(If we choose other signals, we will get slightly different answer for *m*.)

[3]

(e) **(i)**

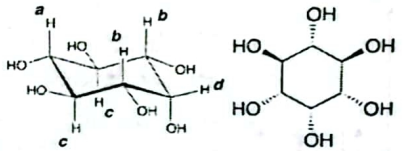


[2]

(ii) Enantiomeric excess = optical purity = 22 / 32 x 100 = **68.8 %**

[1]

(iii) *myo*-inositol:



Chemical Shift / ppm	No. of Protons	Multiplicity	Deduction / Structural Features
3.27	1	triplet	proton **a** (2 neighbouring **c**)
3.52	2	multiplet	proton **b** (one neighbouring **c** and one neighbouring **d**)
3.61	2	triplet	proton **c** (one neighbouring **a** and one neighbouring **b**)
4.05	1	triplet	proton **d** (2 neighbouring **b**)

(accept if assignment for **a** and **d**; **b** and **c** are swopped around)

myo-inositol is **symmetrical** / have an **internal plane of symmetry** due to being optically inactive.

the 6 alcohol protons are **labile** and disappear in presence of D_2O.

These protons are **deshielded** by **electronegative oxygen**.

[3]

(f) **(i)** **ZrO_2**, **ZnO**, **TiO_2** and **CdS**.
Photocatalytic water splitting is essentially electrolysis of water.

For the above semiconductors, the standard electrode potentials for reduction (at cathode) are **less positive / more negative** than $E^{\ominus}(H^+/H_2)$, hence reduction of water to H_2 is **favoured** at the cathode.

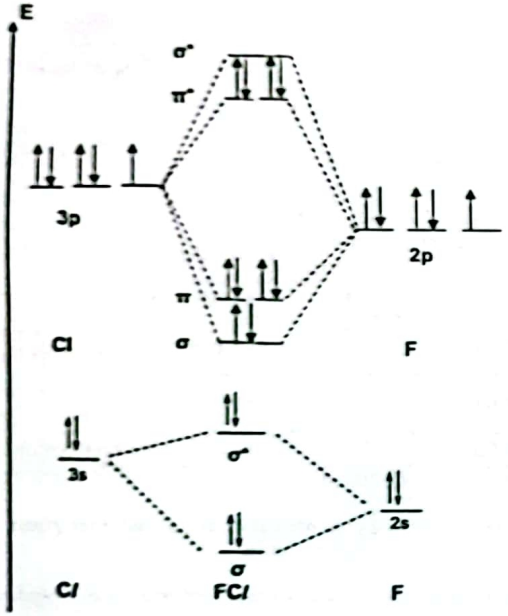
The standard electrode potentials for oxidation (at anode) are **more positive / less negative** than $E^{\ominus}(O_2/H_2O)$, hence oxidation of water to O_2 is **favoured** at the anode.

[2]

(ii) **CdS** as it requires the **least** amount of light energy to activate (2.4 eV).

[1]

3 (a) (i)



correct labelling of AO, bonding and antibonding MO
electrons placed in correct orbitals
F AO lower in energy than Cl AO

[2]

(ii) Bond order = ½ (number of electrons in bonding MO – number of electrons in anti-bonding MO)

MO energy level diagram for FCl and the three chlorine species are very similar.

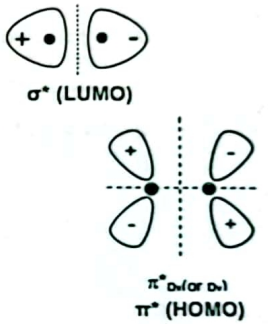
For Cl_2, bond order = ½ (8 – 6) = 1
For Cl_2^+, bond order = ½ (8 – 5) = 1.5
For Cl_2^-, bond order = ½ (8 – 7) = 0.5
calculation of bond orders

Since bond order of $Cl_2^+ > Cl_2 > Cl_2^-$ the electrons are less strongly attracted to each nuclei, leading to a **decreasing** bond strength, thus **decreasing** bond energy. Bond length **increases** as a result.

Assuming that the reactivity depends largely on overcoming the activation energy barrier involving **breaking** of covalent **bonds**, the reactivity order will be $Cl_2^+ < Cl_2 < Cl_2^-$.

[3]

(iii)



[1]

(b) (i) E_{a1}(using LDA) < E_{a1}(sodium ethoxide)
product formed using sodium ethoxide has lower energy than using LDA

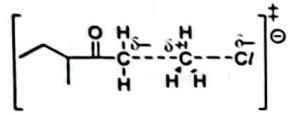
Formation of $(CH_3CH_2)CH_3CHCOCH_2CH_3$ is under **kinetic control**. When a reaction is under kinetic control, the ratio of two or more products is determined by the **relative energies** of the **transition states** leading to these products. *(The relative energies or stability of the products does not play a role under kinetic control.)* This arises from **steric hindrance due to the size of the attacking bulky base** (LDA), which would result in preferentially removal of proton from the less substituted carbon.

Formation of $CH_3CH_2C(CH_3)_2COCH_3$ is under **thermodynamic control / thermodynamically more stable** product. Although the

reaction rate leading to the more stable product may be slower, because of **equilibriation**, eventually the lower energy product will be favoured to be formed. Under thermodynamic control, the ratio of the products is determined solely by the **relative energies** (or thermodynamic stability) of the **products**.

[3]

(ii)

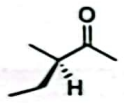


[1]

(iii) Pass a solution of the racemic mixture through a **column of a solid support** which is itself chiral, a **chiral stationary phase** (CSP). The process is called **enantioselective chromatography**, and works because the column will preferentially **retain/adsorb to one of the isomers** due to the formation of more favourable interactions (eg. instantaneous dipole-induced dipole interactions) with that isomer, while letting the other through at a quicker rate. They can thus be separated, and both can be recovered in good yield.

[1]

(iv)



[1]

(c) **(i)** The frequency of absorption should decrease as the mass of the atoms joined by the bonds increase.

Since S atom has **higher** atomic **mass** than O atom, C=S stretch (in both CH_3CSCH_3 and $CH_3CSCH{=}CH_2$) will have **lower** wavenumber as compared to C=O stretch (in CH_3COCH_3).

$CH_3CSCH{=}CH_2$ is a **conjugated** molecule, resulting in **delocalisation of π electrons**.

The C=S bond in $CH_3CSCH{=}CH_2$ is longer and **less stiff** than the isolated C=S bond in CH_3CSCH_3 because it **has more single bond character**, causing a shift to **lower frequency** and hence **lower wavenumber**.
Alternative: Draw resonance form of $CH_3CSCH{=}CH_2$

[2]

(ii) Chromophore is **$CSCH{=}CH_2$**.
Electronic transitions: $\pi \rightarrow \pi^*$ and $\mathbf{n} \rightarrow \pi^*$

[1]

(iii) CH_3COCH_3 gives **$[CH_3CO]^+$** (m/e 43) but CH_3CSCH_3 and $CH_3CSCH{=}CH_2$ give **$[CH_3CS]^+$** (m/e 59).
CH_3CSCH_3 gives **CH_3^+** (m/e 15) but $CH_3CSCH{=}CH_2$ give **$[CH_2{=}CH]^+$** (m/e 27).

[2]

(d) $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $\quad E^\theta = +0.40$ V
$E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = E^\theta(O_2/OH^-) - E^\theta(AgCl/Ag)$
$= +0.40 - (+0.22) = +0.18$ V

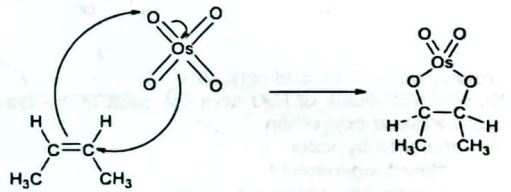
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Anode: $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$

$\Delta G^\theta = -nFE^\theta_{cell} = -4 \times 96500 \times (0.18) = -69480$ J mol^{-1}

$K_c = \exp(-\Delta G^\theta / (RT)) = \exp(69480 / (8.31 \times 298))$
$= \mathbf{1.53 \times 10^{12}}$ **mol^{-1} dm^3**

[3]

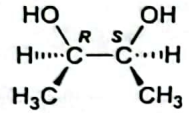
4 **(a)** **(i)**



oxidative addition
single full arrow movement on double bond of Os=O towards Os
single full arrow movement of adjacent double bond of Os=O toward carbon of C=C

[2]

(ii)

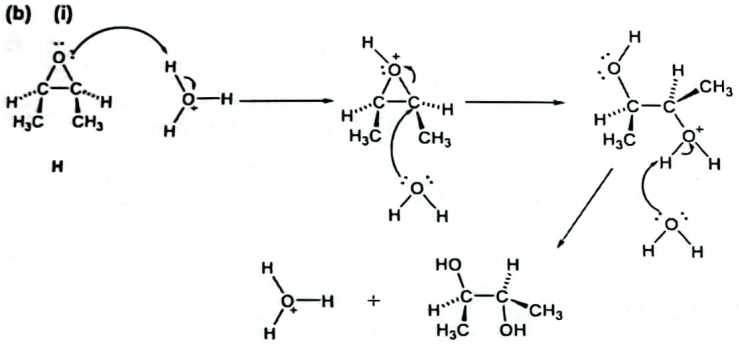


***meso*-2,3-Butanediol**

3D structure shown on both carbon atoms

[1]

(b) (i)



H

J

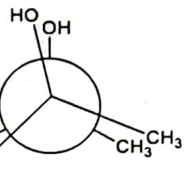
protonation on O by acid catalyst
Nucleophilic attack of H_2O from the back of the leaving group, the cyclic epoxide oxygen ion
deprotonation by water
acid catalyst regenerated
correct arrow flow and lone pairs shown

Assume the stereochemistry of H is as shown above. This follows S_N2, as the nucleophile H_2O attacks from the back of the leaving group, resulting in formation of J. One of the chiral centres in the intermediate has an inversion of configuration after attack by H_2O. The epoxide ring has a *cis* configuration / oxygen atom adds on same side of C=C bond in H.

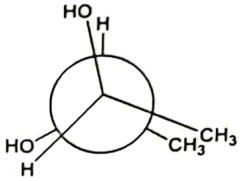
(If H_2O attack the chiral centre on the left, will form the enantiomer of J instead.)

[4]

(ii)



G



J

For each correct structure and labelling

G will be at a **higher** energy level than **J**. This is due to the **steric strain** caused by the **interaction** between the **two bulky CH_3 groups, two OH groups** in a ***syn* periplanar geometry** in **G**. **J** has only steric strain caused by interaction between **two bulky CH_3 groups**. (The activation energy to achieve the conformation in **G** through rotation of C-C bond has a higher energy.)

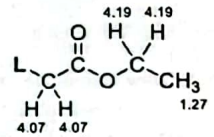
[3]

(c) From information provided,
Does not react with sodium carbonate, molecule does not have a **carboxylic acid functional group.**

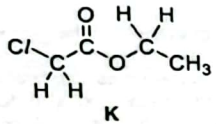
From IR spectrum,
strong peak at 1730 cm^{-1}, C=O stretch indicating presence of esters or ketone or aldehyde.

From ^1H NMR spectrum,

Chemical Shift / ppm	No. of protons	Multiplicity	Deduction / Structural Features
1.27	3	triplet	**$-CH_2-CH_3$**
4.07	2	singlet	**L–CH_2C=O, deshielded by electronegative oxygen.**
4.19	2	quartet	**–O–CH_2–CH_3, deshielded by electronegative oxygen.**



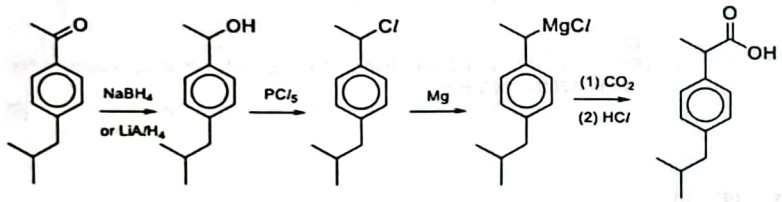
From the mass spectrum,
Ratio of the **peak** at m/z **77** and **79** is **3:1**. It implies that the halogen **L** is **chlorine.**
The fragment at m/z 77 must be $^{35}Cl/CH_2C{=}O^+$.



K
ethyl chloroacetate

[4]

(d) (i)

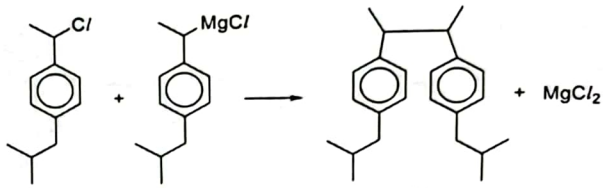


Reduction of ketone by $NaBH_4$ or $LiAlH_4$ in dry ether
Nucleophilic substitution using PCl_5 or PCl_3 with heat or $SOCl_2$ with heat
Addition of Magnesium metal
Nucleophilic attack on CO_2
Addition of HCl(aq) or H_2SO_4(aq)

for 3 correct intermediate structures

[4]

(ii)



N

[1]

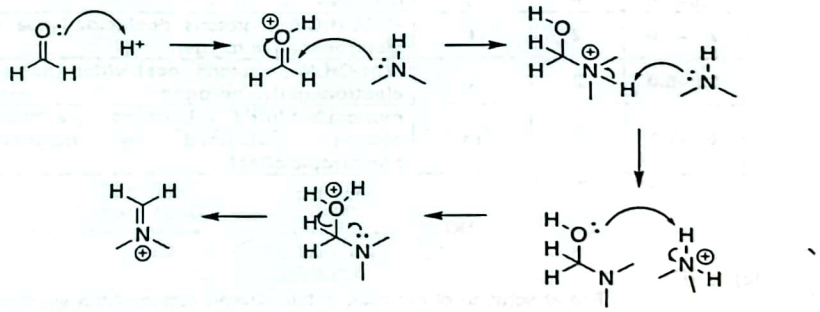
(iii) Since the dimer **N** is **non-polar** while ibuprofen is **polar, separating funnel** consisting of **Na_2CO_3(aq)** (or **NaOH(aq)**) and **hexane** (or any other non-polar solvent) can be used to obtain ibuprofen from the mixture.

Ibuprofen will dissolve in the **aqueous phase** while **N** will dissolve in the **organic phase**.

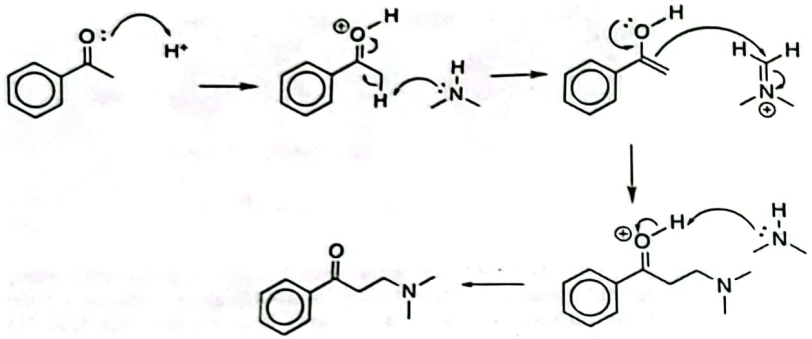
(Ibuprofen dissolved in aqueous phase will form the salt. To reform ibuprofen, add HCl(aq) till in excess. Then ibuprofen as an insoluble solid formed can be obtained by filtration.)

[1]

5 (a) Step 1a:

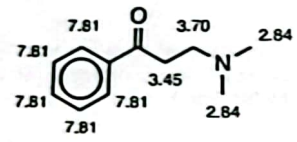


Step 1b:



[5]

(b)



Chemical Shift / ppm	No. of Protons	Multiplicity	Deduction / Structural Features
1.0–5.0	6	s	$(CH_3)_2N$–
2.2–3.0	2	t	–$COCH_2CH_2$–, protons **deshielded** due to **electronegative oxygen**
1.0–5.0	2	t	–CH_2CH_2N–, protons **deshielded** due to **electronegative nitrogen**
6.0-9.0	5	m	**monosubstituted benzene**, aromatic protons **deshielded** by **magnetic anisotropic effect**

[4]

(c) (i)

The absorption of radiation in the infrared region of the spectrum is usually associated with the vibrational energy levels within a molecule.

A non-linear molecule consisting of N atoms will have (3N – 6) independent modes of vibration (including stretching and bending). A linear molecule consisting of N atoms will have (3N – 5)

independent modes of vibration. These vibrations are the **stretching and bending modes of covalent bonds in molecules.**

For a vibrational mode to be **"active"** in the infra-red region, there must be a **change in the dipole moment** of the molecules when the vibration takes place.

The **frequencies** of the radiation absorbed by different **functional groups** are different. In general, the **frequency of absorption should increase as the "stiffness" of the bond between the two atoms increase and should decrease as the masses of the atoms joined by the bond increase.**

[2]

(ii) Acetophenone
Presence of **strong C=O stretch**, belonging to **ketone**, wavenumber range **1670–1740 cm^{-1}**

Q
Presence of **broad O–H stretch**, belonging to **alcohol**, wavenumber range **3200–3600 cm^{-1}**

[2]

(d) (i)

Interelectronic repulsion of the nucleophile with pi electron cloud of benzene leads to **high activation energy**

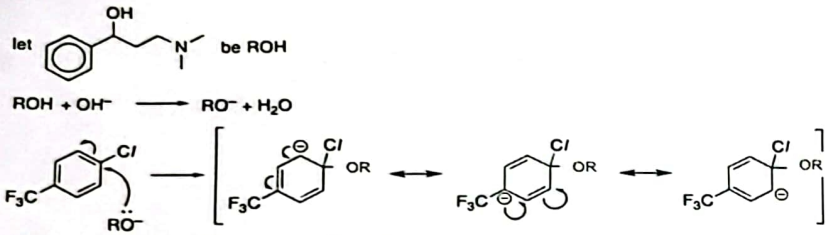
p orbital of halogen atom overlaps with that of benzene ring leading to **partial double bond character** in C–C*l* bond

The benzene ring poses **steric hindrance preventing rear attack of the nucleophile via an S_N2 mechanism**

(any 2 of 3 reasons)

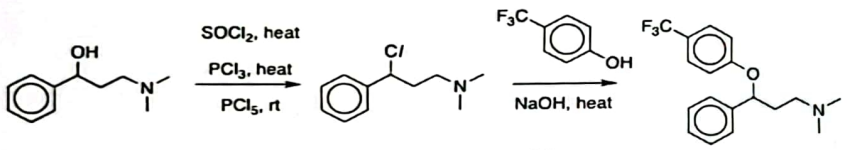
[2]

(ii)



[2]

(iii)



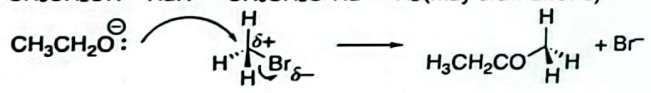
Each correct set of reagents and conditions
Correct structure of intermediate

[3]

6 (a) (i) These common bases are **much weaker than NaH** and are **not strong enough to deprotonate ethanol** to form a sufficiently strong *nucleophile* for the reaction.

[1]

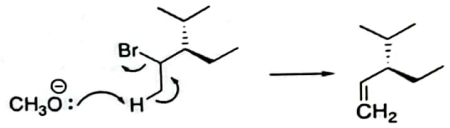
(ii) $CH_3CH_2OH + NaH \rightarrow CH_3CH_2O^-Na^+ + H_2$ (may draw arrows)



[2]

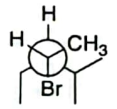
(b) (i) **The formation of T involves a nucleophilic attack of methoxide on a 2° alkyl halide. There is significant steric hindrance and the formation of the 5-membered transition state (via S_N2) is not favoured. Furthermore, methoxide is a very strong base and can extract a proton from carbon-1 very readily, leading to an elimination reaction.**

Elimination, E2

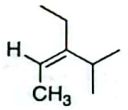


[3]

(ii) **Anti-periplanar elimination** in E2 mechanism, H and Br needs to be anti to one another.



Product formed is **Z-isomer**.

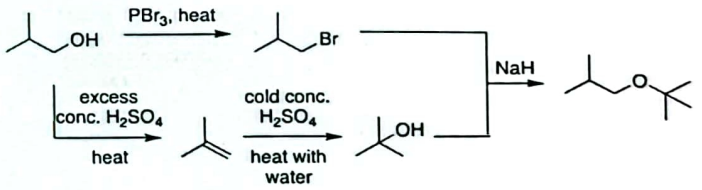


[3]

(iii) **V** is the major product as it is the **more substituted** alkene. (thermodynamic or Zaistev alkene)

[2]

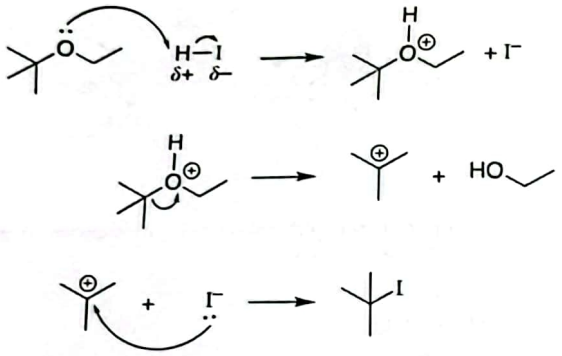
(c)



Note: cannot switch the alcohol and halogenoalkane due to competing elimination reaction

[4]

(d) (i)



protonation S_N1 partial charges curly arrows
The nucleophilic substitution involves a 3° alcohol. The formation of **a stable 3° carbocation** favours the S_N1 mechanism.

[3]

(ii) alcohol group in ethanol is also substituted to give 

[1]

(iii) HI is a stronger acid than CF_3COOH. CF_3COO^- is a **weaker nucleophile but a stronger base** than I^- and would instead act as a base to extract the proton.
(accept if draw mechanism)

[1]