# H3 Chemistry (9813/01) Preliminary Examination 2022 Suggested Solutions

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## Section A

**1** **(a)** **(i)** It is hard to prevent the formation of the carboxylic acid side product.

**(ii)** $K_2Cr_2O_7$(aq), $H_2SO_4$(aq), heat with immediate distillation.

It involves the use of toxic chromium reagents / wastes a lot of energy on heating and distillation / extremely low atom economy (anything sensible)

**(b)** **Steric**: The bulky methyl groups prevent TEMPO from dimerising as the 2 oxygen atoms cannot get close enough to form a bond.

**Electronic**: The p orbital on O containing the unpaired electron can overlap with the p orbital on N with the lone pair, resulting in delocalisation of the lone electron onto N / resonance stabilisation.

**(c)** (Oxygen is in excess as it is from the atmosphere.)

Amt of benzyl alcohol = $10^4$ / 108 = 92.59 mol

$$9.4 = \frac{n_{catalyst}}{n_{catalyst} + 92.59} \times 100$$

Amt of TEMPO = 9.606 mol

Mass of TEMPO

= (9.606)(9x12 + 18 + 14 + 16)

= 1.498 x $10^3$ g

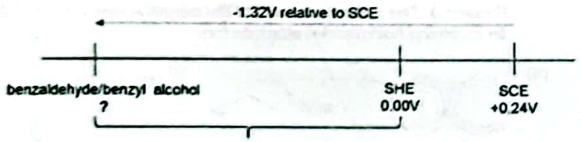
=1.50 x $10^3$ g or 1.50 kg

**(d)** **(i)** The SHE is not portable / practical as it requires a stream of $H_2$ gas at 1 bar.

(SCE is highly portable and commercially available.)

**(ii)** $C_6H_5CHO + 2H^+ + 2e^- \rightleftharpoons C_6H_5CH_2OH$

**(iii)**



−1.32 + 0.24 = −1.08V

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**(iv)** $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23V

$E_{cell} = E_R - E_O = +1.23 - (-1.08) = +2.31V$ [1]

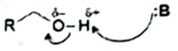
$\Delta G = -nFE = -(2)(96500)(2.31) = -446$ kJ mol$^{-1}$

**(e)** **(i)** A: +1

E: −1

incomplete ans

**(ii)**



→ $RCH_2O^- + BH^+$

D

**(f)** **(i)**

Process 1: $\frac{106}{106+18} \times 100\% = 85.5\%$

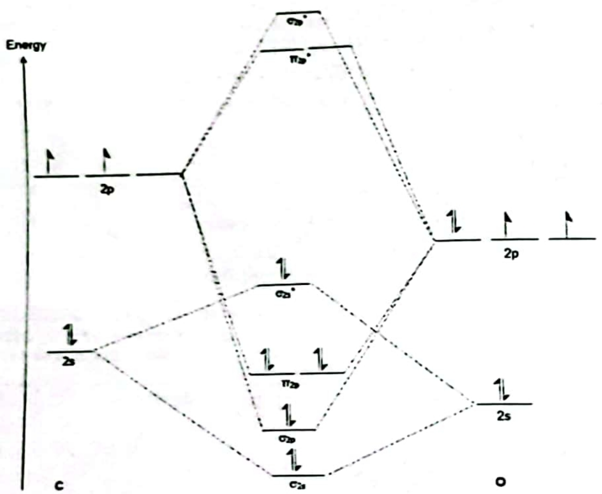
Process 2: $\frac{106}{106+58.5+18} \times 100\% = 58.1\%$

**(ii)**
- Most of the time, theoretical yield is not 100%
- Most of the time, reactants are not used in exactly stoichiometric amounts
- Disregards toxic solvents / catalysts as they are not included in the calculation
- Does not distinguish between toxic byproducts e.g. CO vs CO2 – CO as byproduct has better atom economy but it's more harmful than CO2 (anything sensible)

**(g)**
- Process 1. Award any relevant ideas.
- relies on molecular oxygen which is a readily available feedstock as compared to ClO– as an oxidising agent
- better atom economy
- utilises a naturally occurring enzyme instead of inorganic ClO– in stoichiometric amounts
- does not require CH2Cl2 chlorinated solvents
- does not require excess energy for cooling
- Can discuss from the perspective of process 2 being less green also.

**2** **(a)** **(i)** From carbon to oxygen, the number of protons increase and hence, nuclear charge increases. Successive electrons are added to the same outermost shell and so, the increase in shielding effecting is negligible / shielding effect remains approximately constant. Therefore, effective nuclear charge increases and the atomic orbitals of O will experience stronger nuclear attraction than those of C, resulting in the former to have lower energy.

(ii)



Bond order of CO = 3. This will cause the bond between C and O to be very strong.

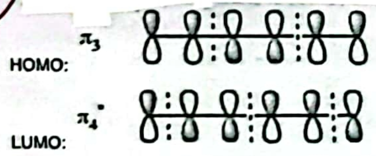
(iii) CO uses the lone pair of electrons from the HOMO ($\sigma_{2s}^*$) for donation.

Since the HOMO has more character from 2s of C than that from 2s of O / HOMO is closer in energy to the 2s of C, this means that C atom will donate the lone pair of electrons.

**(b)** (i) Organic molecules that contain atoms with lone pairs of electrons, π bonds or conjugated π bond systems can absorb energy in the UV-vis region of the spectrum. Their electrons can be excited from a bonding molecular orbital to an anti-bonding molecular orbital (or HOMO to LUMO).

For UV absorption, only the following transitions: $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ are allowed. Molecules with more conjugated π bond systems will give rise to a smaller energy gap between the HOMO and LUMO. Hence, electrons will absorb UV-vis at longer wavelengths.

(ii)



(iii) Benzene has a UV absorption peak which will <u>overlap</u> with the UV absorption peak of hexa-1,3,5-triene at 258nm.

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(iv) $A = \lg\left(\frac{I_o}{I}\right) = \varepsilon c l$

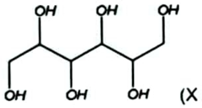
$\lg 5 = \varepsilon\,(1.8 \times 10^{-8})(1)$

$\varepsilon = 3.883 \times 10^{7}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{cm}^{-1}$

$\approx 3.88 \times 10^{7}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{cm}^{-1}$

(v) When light of 258 nm is shone, there is an electronic transition from π to π* and this breaks the π bond between C3-C4, allowing for rotation around the σ bond between C3 and C4.

(vi) X is

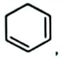


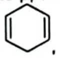
(X can also be alcohol with unreacted alkene(s)).

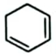
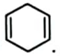
$KMnO_4(aq)$, $NaOH(aq)$, cold OR

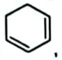
Concentrated $H_2SO_4$, 0 °C (or cold), followed by boiling water / steam

**(c)** (i) Heat each of these structures in the presence of $KMnO_4$ and $H_2SO_4(aq)$.

For , purple solution decolourises with effervescence observed. The gas forms white ppt in limewater and therefore is $CO_2$.

For , purple solution decolourises and no effervescence is observed.

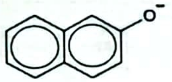
(ii)  will absorb at a longer wavelength than .

There is π conjugation for , resulting in smaller energy gap between π and π* orbitals, requiring less energy for electronic transition.

**3** **(a)** (i) Reason 1: $S_N2$ reaction cannot occur as the p orbital of Br atom will overlap with the π orbitals of benzene ring. The lone pair of electrons on the Br atom will delocalise into the benzene ring, strengthening the C–Br bond.

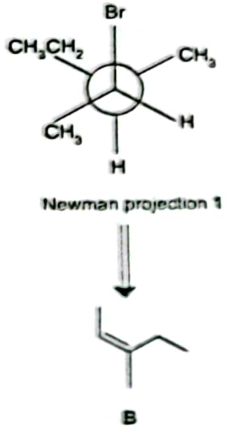
Reason 2: The backside of the C–Br bond is hindered by the bulky benzene ring for the nucleophile, ethoxide ion, to attack.

Reason 3: The π electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, ethoxide ion.

(ii) 

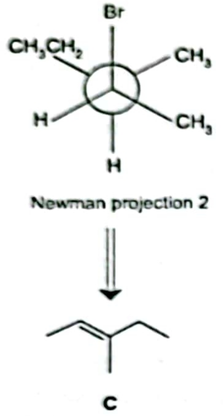
and 

**(b)** **(i)** If carbon 2 has an S-configuration, If carbon 2 has an R-configuration,



Newman projection 1

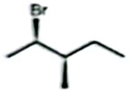
**B**



Newman projection 2

**C**

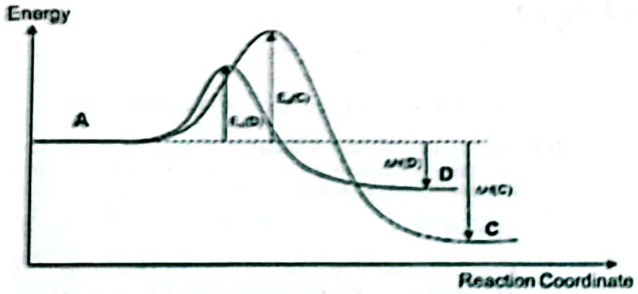
Since alkene **B** is not produced, **A** must have an R-configuration at carbon-2.



**A**

**(ii)** The bulky base, $(CH_3)_3COK$, cannot approach the H atom on carbon 3 as easily due to the steric hindrance caused by the bulky methyl and ethyl groups. Hence, the bulky base would preferentially approach the H atom of the methyl group at carbon 1 via E2 to form alkene **D**.

**(iii)**



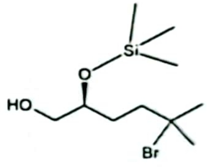
- The trisubstituted alkene **C** is more stable than the monosubstituted alkene **D**.

- The energy level of **C** will be lower than **D**. The enthalpy change for the formation of **C** is more exothermic than that of the formation of **D**.
- Hence, the $E_a$ of the formation of **C** will be higher than that of the formation of **D** as it is energetically unfavourable for the bulky base to attack the sterically hindered H atom on carbon 3.

**(iv)** When heat is involved, the formation of the more stable alkene **C** will be favoured as there are now more molecules of **A** having energy greater or equals to $E_a$ for reaction to proceed. Hence, the rate of formation of **C** will increase and the percentage yield of **C** will be higher than **D**.

**(v)** Percentage optical purity (e.e.) = $\frac{7.3}{66.9} \times 100\% = 10.9\%$

**(c)** **(i)** Step 2: $H_2$, Ni, heat or
$H_2$, Pt/Pd, room temperature or
$NaBH_4(aq)$, room temperature or
$LiAlH_4$ in dry ether, room temperature

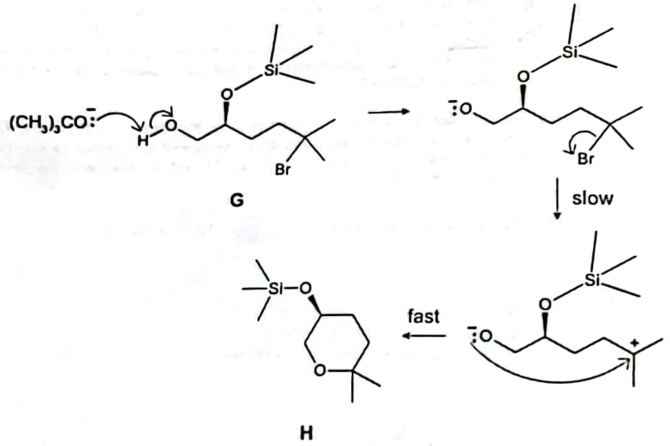


**G**

**(ii)** To protect the alcohol group in **E**. This is to prevent it from being deprotonated by the base in step 3 such that the alkoxide ion formed will undergo nucleophilic substitution with the electron deficient carbon of the C–Br bond. As such, a 5-membered ring ether will be produced instead of **H**.

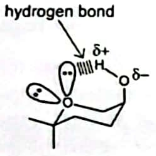
**(iii)** The $OH^-$ is a strong nucleophile and will undergo nucleophilic substitution with the electron deficient carbon of the C–Br bond to produce an alcohol instead of **H**.

**(iv)**



Note: Accept if Br$^-$ leaves first before deprotonation by (CH$_3$)$_3$CO$^-$.

**(v)**



conformation 1

The OH group occupying the axial position in conformation 1 is energetically more stable due to the formation of intramolecular hydrogen bonding between the OH group and the lone pair of electron on the O atom of ether. This outweighs the lower steric strain due to 1,3-diaxial interactions between the H and OH when the OH group occupies the equatorial position in conformation 2.

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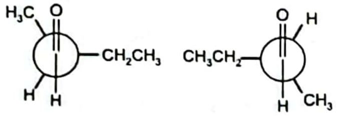
## Section B

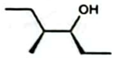
**4** **(a)** **(i)** The nucleophile in trajectory 1 approach with the smallest substituent nearby while the other three trajectories are closer to larger substituents. Hence, trajectory 1 is a less hindered attack while the nucleophile in other three trajectories passes the larger substituents and experience steric hindrance.

Therefore, trajectory 1 is the most reactive one, and it reacts to give the diastereoisomer major product.

**(ii)**

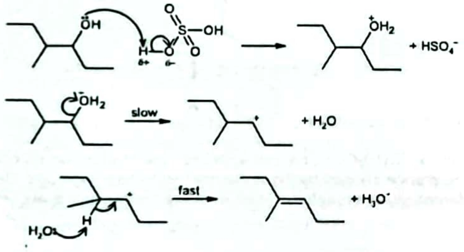


**(iii)**

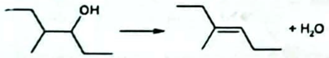


**(b)** **(i)**
- Overall order = 1
- Comparing the two experiments at 170 °C, when [$H_2SO_4$] increase, relative rate remain almost constant. Hence, the rate is independent of [$H_2SO_4$] or only dependent on compound **B**.
- E1 mechanism

**(ii)**



**(iii)**



$$\Delta H_r = (360 + 350 + 410) - (610 + 460) = +50 \text{ kJ mol}^{-1}$$

**(iv)** $\Delta S > 0$ as entropy of the system increases. There is an increase in the total number of particles in the system and more ways of arranging the particles in the system This results in a less disordered system to a more disordered system.

$\Delta G = \Delta H - T\Delta S$

Since $\Delta H$ is positive and $\Delta S$ is positive, $-T\Delta S$ is negative. At higher temperature, $\Delta G$ will be more negative and the reaction is more spontaneous.

**(c)** (i) Oxidation.

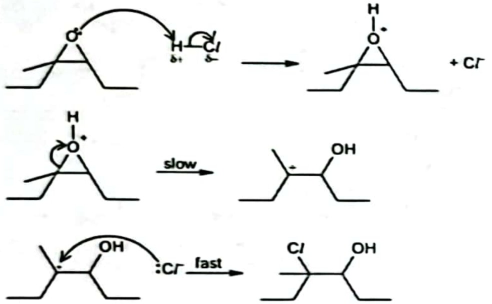
(ii) The bond energy is significantly lower as the C–O bonds in the 3-membered ring are weaker due to ring/angle strain.

**(d)** (i) The acid protonates the epoxide oxygen so as to make it a good leaving group.

(ii) When the tertiary carbocation is formed, the positive charge in the protonated epoxide is dispersed by the more electron donating alkyl groups.

However, $S_N2$ is not possible as the bulky alkyl groups bonded to the tertiary carbon provided more steric hindrance for the approaching $Cl^-$ nucleophile to attack the protonated epoxide.

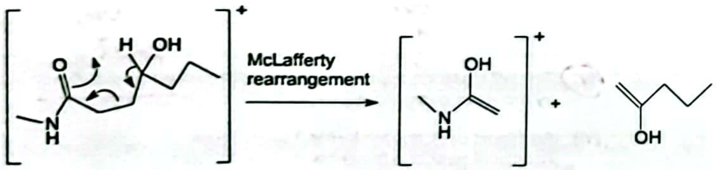
(iii)



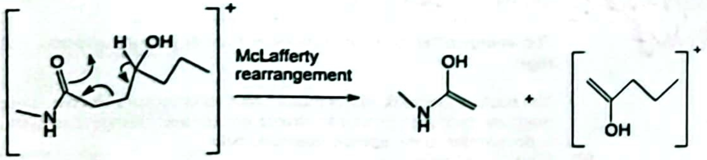
(iv) The leaving alcohol is being attracted to the carbocation even after cleavage, which prevent complete solvation and separation. The alcohol and carbocation recombines to give the original reactant is also known as *internal return (or ion-pair interaction)*. As a result, this causes steric hindrance on one face by the departing alcohol, favouring back-side attack by the $Cl^-$.

**5** **(a)** (i) $CH_3NH_2$

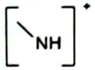
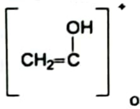
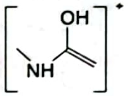
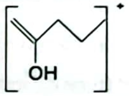
(ii)



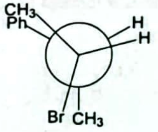
or



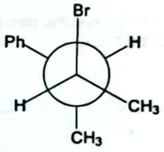
(iii)

| $m/z$ | Fragments |
|---|---|
| 30 |  |
| 43 |  $[CH_2{=}C(OH)]^+$<br>or<br>$[CH_3CH_2CH_2]^+$ |
| 73 |  |
| 86 |  |

**(b)** (i)

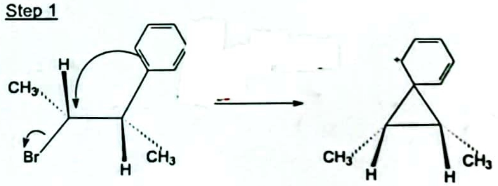


least stable

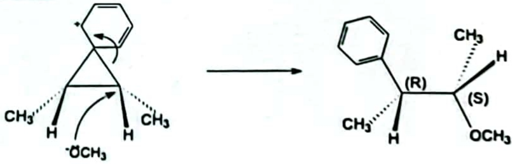


most stable

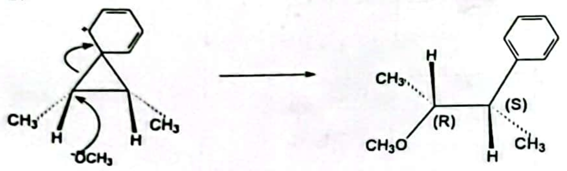
(ii) Step 1



Step 2



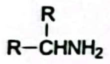
Or



(iii) The sulfide will react at a faster rate.

Since S is less electronegative than O, it can donate its lone pair of electrons more readily to the electron deficient carbon in the sulfide to form a three-membered ring intermediate.

(c) (i)



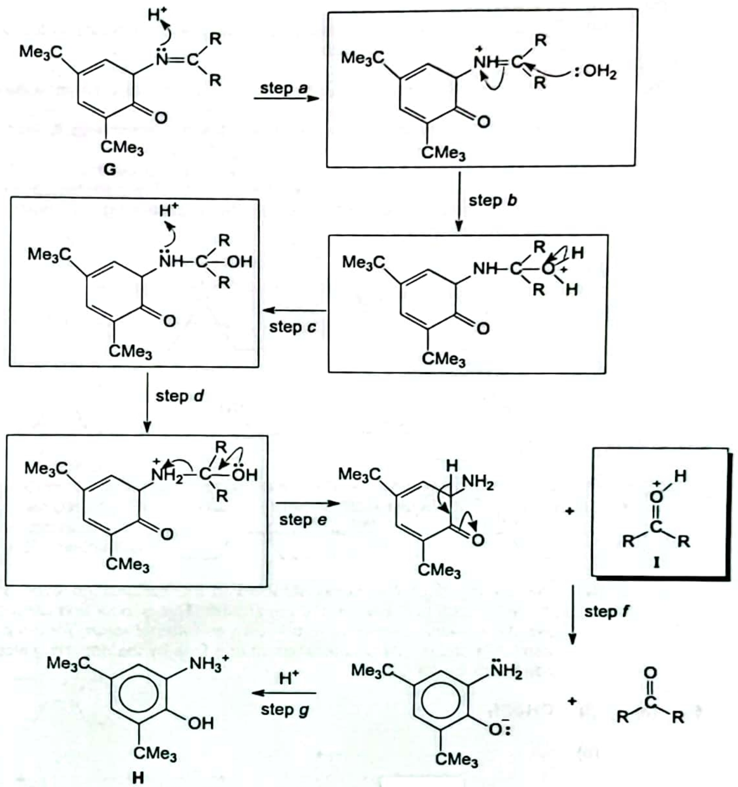
$\mathrm{R{-}\overset{R}{\overset{|}{C}}HNH_2}$

(ii) Step 1: nucleophilic addition followed by elimination of water / condensation

The presence of acid is required for the elimination of water. At lower pH, too much amine is protonated and slows down the preceding nucleophilic addition.

(iii) Constitutional isomers. They have the same molecular formula but different arrangement of atoms/different structural formula.

(iv)



(v) This will make the adjacent carbon atom more electron deficient and susceptible to attack by the water nucleophile.

(vi) Additional peak due to N–H at 3.0 – 6.0 ppm.
Additional peak due to phenol at 4.5 – 7.0 ppm

6 (a) (i) In an external applied magnetic field, all protons have their magnetic moments either parallel with the field or antiparallel to it. As a result, the degenerate spin states split into two states of unequal energy.

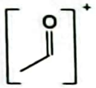
The energy difference between the two levels is small and falls within the radio frequency region.

The nuclear magnetic resonance phenomenon occurs when nuclei parallel with an applied magnetic field are induced to absorb energy and change their spin orientation such that it is antiparallel to the applied magnetic field.

(ii) From the IR spectrum

| Wavenumber of absorbance | Interpretation |
|---|---|
| Two strong absorptions at 1750 cm$^{-1}$ | C=O stretch in ketone and ester |
| Strong absorption at 1200 cm$^{-1}$ | C–O stretch in ester |

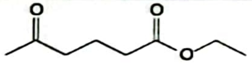
From the mass spectrum

| *m/z* | Deduction |
|---|---|
| 158 | M$_r$ of **A** = 158<br>Since **A** has 3 O atoms and 14 H atoms,<br>➢ no of C = $\frac{158-3(16)-14}{12}$ = 8<br>Molecular formula of **A** is $C_8H_{14}O_3$ |
| 43 | Presence of<br> |
| 113 | Loss of 158 – 113 = 45 ($C_2H_5O$)<br>$\underset{158}{[C_8H_{14}O_3]^{\bullet}} - \underset{45}{C_2H_5O} \rightarrow \underset{113}{[C_6H_9O_3]^{+}}$ |

From the NMR spectrum

| δ /ppm | Multiplicity | No. of adjacent protons | No of H | Deduction |
|---|---|---|---|---|
| 1.1 | triplet | 2 | 3 | $-C\underline{H_3}-CH_2$ |
| 1.8 | quintet | 4 | 2 | $CH_2-C\underline{H_2}-CH_2$ |
| 2.1 | singlet | 0 | 3 | $-C\underline{H_3}-C=O$ |
| 2.3 | triplet | 2 | 2 | $-C\underline{H_2}-CH_2$, next to C=O |
| 2.5 | triplet | 2 | 2 | $-C\underline{H_2}-CH_2$, next to C=O |
| 4.1 | quartet | 3 | 2 | $-C\underline{H_2}-CH_3$, next to electronegative O |

A:



(iii)

| Information | Deduction |
|---|---|
| **B** does not react with liquid bromine | **B** does not undergo electrophilic addition. **B** does not have C=C. |
| **B** forms an orange ppt with 2,4-DNPH | **B** undergoes condensation reaction. **B** contains aldehyde or ketone |
| **B** does not form ppt with Tollens' reagent | **B** does not undergo mild oxidation. Since **B** does not contain aldehyde, it contains ketone |

From the MS spectrum

$$n = \frac{100}{1.1}\left(\frac{1.8}{27}\right)$$
$$\approx 6$$

M$_r$ of **B** = 112

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Since **B** has 6 C atoms and 8 H atoms,
112 – 6(12) – 8 = 32
→ This indicates the presence of 2 O atoms

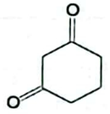
Molecular formula of **B** is $C_6H_8O_2$

Degree of unsaturation in **B** = $\frac{(2\times6)+2-8}{2}$
= 3
→ **B** is likely to have to 2 C=O bond and 1 ring

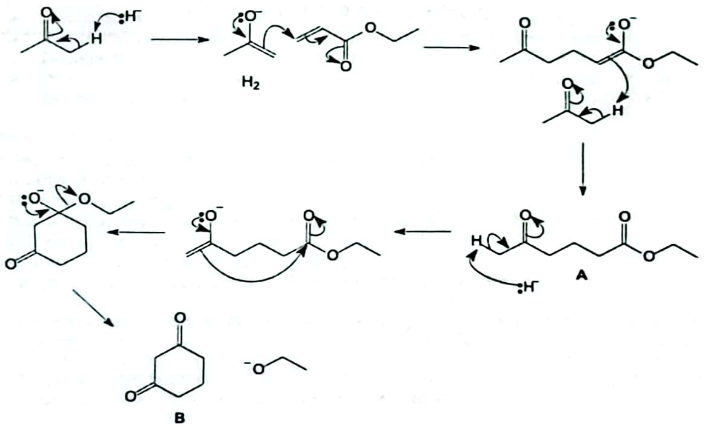
From the NMR spectrum

| δ /ppm | Multiplicity | No. of adjacent protons | No of H | Deduction |
|---|---|---|---|---|
| 2.1875 | multiplet | - | 2 | $-C\underline{H_2}-$ adjacent to more than 1 alkyl group |
| 2.625 | triplet / multiplet | 2 | 4 | 2 $C\underline{H_2}-CH_2$, next to C=O |
| 3.125 | singlet | 0 | 2 | $-C\underline{H_2}$ next to two C=O |

B:



(iv)

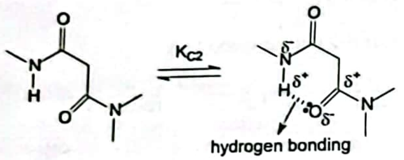


**(b)** **(i)** Since the deuterium nucleus does not absorb in the same frequency range as $^1H$, there will not be any appreciable signals from deuterated solvent in $^1H$ NMR spectrum which may mask the signals from the compound to be analysed.

Or

The solvent will not form unwanted hydrogen bonding with the amide proton.

**(ii)**



$CH_3NHCOCH_2CON(CH_3)_2$ can form a six-membered ring via intramolecular hydrogen bonding. The six-membered ring is more stable and favoured to be formed due to absence of angle and bond strain.

**(c)**

| m/z | Fragment | Probability | Relative intensity |
|---|---|---|---|
| 214 | $[^{79}BrCH_2CH^{35}ClCO_2CH_2CH_3]^+$ | $\frac{3}{4}\times\frac{1}{2}=\frac{3}{8}$ | 3 |
| 216 | $[^{81}BrCH_2CH^{35}ClCO_2CH_2CH_3]^+$<br>$[^{79}BrCH_2CH^{37}ClCO_2CH_2CH_3]^+$ | $\left(\frac{3}{4}\times\frac{1}{2}\right)+\left(\frac{1}{4}\times\frac{1}{2}\right)=\frac{4}{8}$ | 4 |
| 218 | $[^{81}BrCH_2CH^{37}ClCO_2CH_2CH_3]^+$ | $\frac{1}{4}\times\frac{1}{2}=\frac{1}{8}$ | 1 |

[Turn Over