# VICTORIA JUNIOR COLLEGE PRELIMINARY EXAMINATION 2021
# CHEMISTRY (Higher 3)
## Answers

**1** **(a)** **(i)** Gaseous particles exert negligible intermolecular forces on each other.
Volume of gas particles are negligible compared to the volume of the container.

[2]

**(ii)**

| | $H_2(g)$ | $\rightleftharpoons$ | $H_2(aq)$ |
|---|---|---|---|
| initial amount of $H_2$ / mol | 0 | | $6.96 \times 10^{-4}$ |
| change in amount of $H_2$ / mol | $x$ | | $-x$ |
| final amount of $H_2$ / mol | $x$ | | $6.96 \times 10^{-4} - x$ |

Using ideal gas equation,
$P_{H2}V_{gas} = xRT$
$P_{H2} = \dfrac{x \times 8.31 \times 298}{10^{-3} \times 1.01 \times 10^{5}}$ -----(1)
$= 24.5\,x$ ($P_{H2}$ is in atm)

Using equation 1.1,
$P_{H2} = \dfrac{[H_2]}{k_H}$
$= \dfrac{6.96 \times 10^{-4} - x}{7.82 \times 10^{-4}}$

$x = 6.96 \times 10^{-4} - 7.82 \times 10^{-4} \times P_{H2}$ -----(2)

sub eqn (2) into (1),

$P_{H2} = 24.5 \times (6.96 \times 10^{-4} - 7.82 \times 10^{-4} \times P_{H2})$
$1.019P_{H2} = 1.7052 \times 10^{-2}$
$P_{H2} = 1.67 \times 10^{-2}$ atm

[3]

**(iii)** **Partial pressure of $H_2$ will increase** as solubility of $H_2$ decreases with increasing temperature. As temperature increases, $\boldsymbol{k_H}$, which is similar to $K_c$, **decreases**. As temperature increases, **more energy is available to overcome the permanent dipole-induced dipole interactions between $H_2$ and $H_2O$**, allowing more gaseous $H_2$ molecules to form.

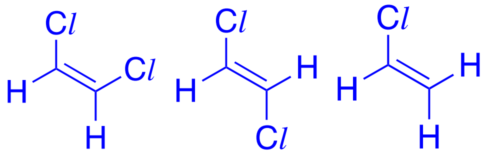
[2]

**(b)** **(i)**

TCE underwent reduction as the ON of C bonded to H decreases from 0 in TCE to –2 in the product.

[1]

**(ii)**



[2]

**(c)** **(i)** To allow time for equilibrium to be established between the aqueous phase and the headspace.

. [1]

**(ii)** From graph, concentration of $H_2$ = 5.9 ppm

Partial pressure of $H_2 = 5.9 \times 10^{-6} \times 1$ atm $= 5.9 \times 10^{-6}$ atm

Assuming temperature is constant throughout the experiment and any increase in pressure due to $H_2$ is negligible (assumption is valid since $5.9 \times 10^{-6} << 1$).

[3]

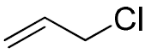
**(iii)** $S_{H2} = 5.9 \times 10^{-6} \div (6.87 \text{ x } 10^{4}) = \surd\surd 8.59 \times 10^{-11}$ (no units)

$[H_2]$ dissolved = no. of moles of $H_2$ ÷ volume of $H_2O$
$= 8.59 \times 10^{-11} \div (1 \times 18 \div (0.998)) \times 10^{3}$
$= 4.76 \times 10^{-9}$ mol dm$^{-3}$

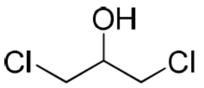
Since $4.76 \times 10^{-9}$ mol dm$^{-3}$ $> 1.0 \times 10^{-9}$ mol dm$^{-3}$, it is likely that anaerobic biodegradation was taking place in this sample.

[3]

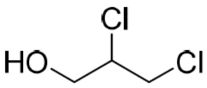
**2** **(a)** **(i)**



**A**



and / or **B**



[1]

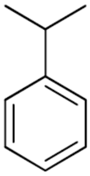
**(ii)** Ratio of M : M+2 : M+4 = ¾ x ¾ : 2 x ¾ x ¼ : ¼ x ¼
= 9 : 6 : 1

[1]

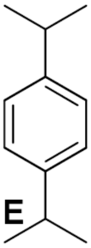
**(iii)** Na(s)

[1]

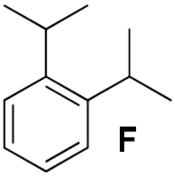
**(iv)**



**D**



**E**



**F**

[3]

**(v)** **E**: 6.6 and 7.1 ppm, 2 doublets, 2 protons each, aromatic protons
**F**: 7.1 ppm, complex multiplet, 4 protons, aromatic protons

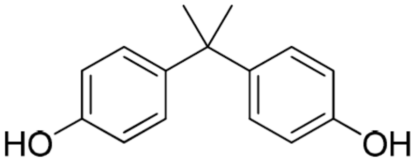
[1]

**(vi)**

| Chemical Shift / ppm | No. of Protons | Multiplicity | Deduction / Structural Features |
|---|---|---|---|
| 1.5 | 6 | s | -C(C**H**$_3$)$_2$ |
| 6.6 | 4 | d | Two **1,4-disubstituted benzene**, aromatic protons **deshielded** by **magnetic anisotropic effect** |
| 7.0 | 4 | d | |
| 9.1 | 2 | s | 2 **phenol** protons, they are **labile** and disappear in presence of $D_2O$<br>These protons **deshielded** by **electronegative oxygen** atom and **magnetic anisotropic effect** of benzene |

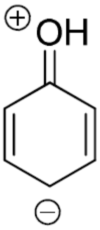
**G** is symmetrical (due to very simple $^1$H NMR spectrum)

**G**:



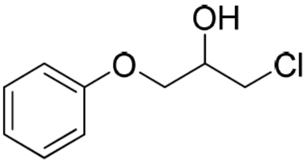
[3]

**(vii)**

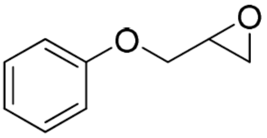


[1]

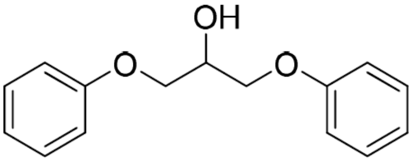
**(b)**



**H**



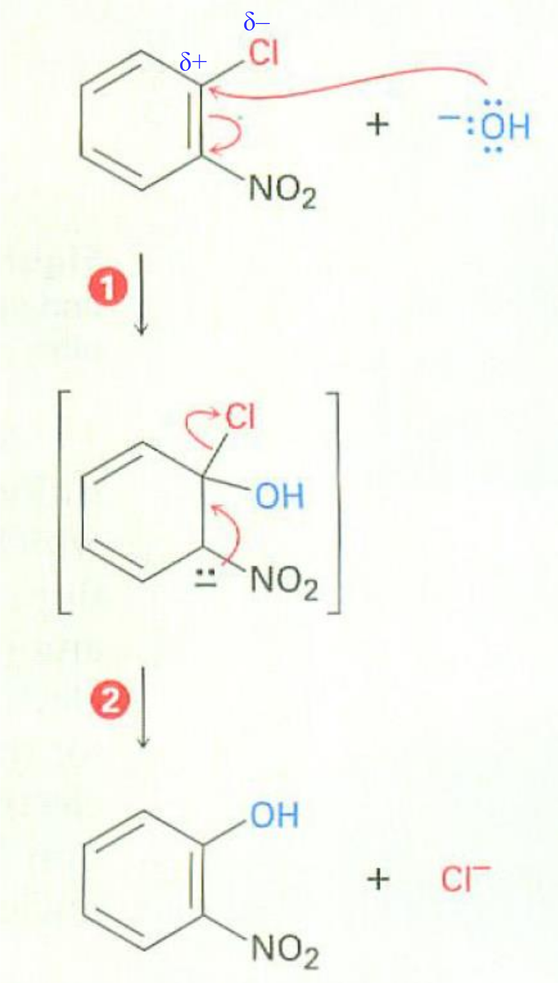
**J**



**K**

[3]

**(c)** **(i)**



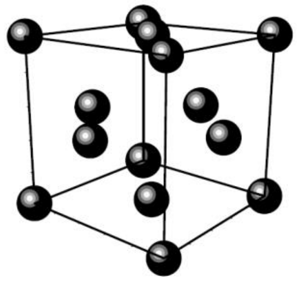
OH⁻ add to electron deficient carbon
partial charges
reform double bond and expel C*l*⁻

[2]

**(ii)** Through the appearance of **O-H stretch** of **phenol**, wavenumber range **3200 – 3600 cm$^{-1}$** in the organic product formed

[1]

(d) (i)



Number of Au gold atoms in unit cell = 8 x 1/8 + 6 x ½ = 4

[1]

(ii) Volume = $(0.408 \times 10^{-9})^3 = 6.79 \times 10^{-29}$ m$^3$

Mass = $1.93 \times 10^4 \times 6.79 \times 10^{-29} = 1.31 \times 10^{-24}$ kg

[1]

(iii) Mass of one Au atom = $1.31 \times 10^{-24} / 4 = 3.28 \times 10^{-25}$ kg

$N_A = 196.97 / (3.28 \times 10^{-22}) = 6.01 \times 10^{23}$

[2]

(iv) $\ln (n_h / n_{h0}) = -(E_h - E_{h0}) / RT = -mg\,(h - h_0) / RT$

$= -m^* N_A g\,(h - h_0) / RT$

$$\text{Gradient} = \frac{-m^* N_A g}{RT}$$

Numerical gradient = $-0.0235 \times 10^6$ m

$N_A = (\text{gradient} \times RT) / (-m^* g)$

$= (-0.0235 \times 10^6 \times 8.31 \times (15 + 273)) / (-8.3 \times 10^{-18} \times 9.81)$

$= 6.91 \times 10^{23}$

[4]

3 (a) (i)

When a photon is absorbed by a molecule, an electron gains the photon’s energy and is **promoted to a higher energy orbital**.

The electrons are **normally resident in the bonding orbitals**, or in the non-bonding orbitals if they are lone pairs on atoms such as nitrogen or oxygen.

The higher energy orbital to which **the electrons are promoted into is invariably an anti bonding orbital**. Only π → π*, n → π* and n → σ* symmetry allowed normally produce absorption in the uv/visible region and give the characteristic uv/visible spectra.

A system containing the electrons responsible for the absorption of radiation is called a **chromophore**. This system is usually a conjugated system of double bonds.

Different chromophores absorb at different wavelengths which allows some analysis of structure.

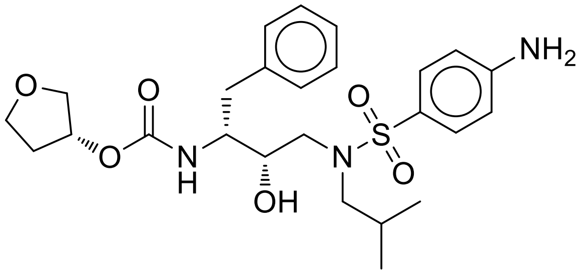
[2]

**(ii)** The π electrons in benzene can delocalise into $-NO_2$ or $–SO_2Cl$ which increases the extent of conjugation. Increased conjugation will decrease the energy gap between π and the π* orbitals (or HOMO and LUMO). Since $E = hc/\lambda$, the decrease in the energy gap will result in a longer wavelength of absorption for the reagent.

[1]

**(iii)** Chiral carbon at 5-membered ring: *S*
Chiral carbon joined to $–CH_2C_6H_5$: *S*
Chiral carbon joined to –OH: *R*

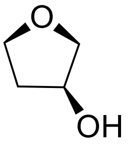
[2]

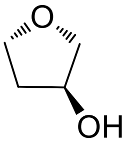


**(iv)** Enantiomer:
Maximum optical purity = 100 (+2) / (+8) = 25%

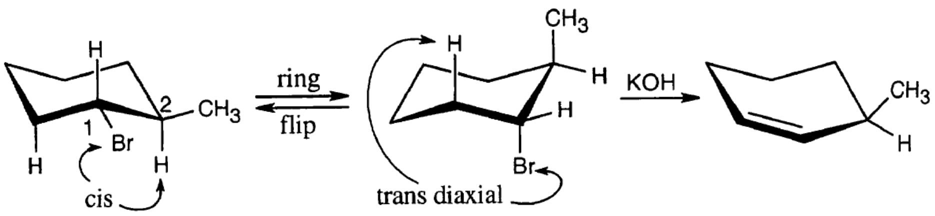
[1]

**(v)**





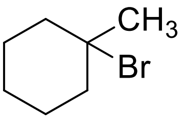
[1]



**(b)** **(i)**

conformation showing anti periplanar geometry
arrows for E2 mechanism
For **E2** mechanism to occur, the Br and H removed must be in the **anti periplanar** arrangement. To form the Zaitsev product, the Br and H cannot be in the required arrangement to form double bond across to the carbon containing $CH_3$ group.

[2]

**(ii)** Structural isomer: 

Thermodynamic product (Zaitsev product) will be formed when the reactions operate at **higher** temperatures. Although the reaction rate leading to the more stable product may be slower, because of higher temperature and equilibriation, eventually the lower energy product will be favoured to be formed.

Kinetic product (Hoffman product) arises (usually) from **steric hindrance** due to the **size of the attacking bulky base** (eg $(CH_3)_3CONa$) which would result in preferentially removal of H from the less substituted carbon. Another instance is when temperature of reaction is **lowered**, the activation energy leading to formation of less substituted alkene is lower and hence more favoured.

[2]

**(c)** **(i)** Multiplying the $K_c$ expressions for the four given reactions produces

$$\frac{[MoO_4^{2-}][H_2S]^4}{[MoS_4^{2-}]} = (1 \times 10^{-7})(1 \times 10^{-6})^4 / [MoS_4^{2-}] = 1.352 \times 10^{-20}$$

$[MoS_4^{2-}] = 7.40 \times 10^{-12}$ mol dm$^{-3}$

[1]

**(ii)** $0.365 = 11870 \times 10.0 \times [MoS_4^{2-}]$ (use of Beer's law)
$[MoS_4^{2-}] = 3.07 \times 10^{-6}$ mol dm$^{-3}$

Using $[MoO_2S_2^{2-}] + [MoOS_3^{2-}] + [MoS_4^{2-}] = 6.0 \times 10^{-6}$
$[MoO_2S_2^{2-}] + [MoOS_3^{2-}] = 2.93 \times 10^{-6}$

$[MoO_2S_2^{2-}] = 2.93 \cdot 10^{-6} - [MoOS_3^{2-}]$

$0.213 = 120 \times 10.0 \times 3.07 \times 10^{-6} + 9030 \times 10.0 \times [MoOS_3^{2-}] + 3230 \times 10.0 \times [MoO_2S_2^{2-}]$

Solving above two equations gives
$[MoOS_3^{2-}] = 2.00 \times 10^{-6}$ mol dm$^{-3}$
$[MoO_2S_2^{2-}] = 9.30 \times 10^{-7}$ mol dm$^{-3}$

[2]

**(iii)** Subtracting two equations given in the question gives
$[MoO_4^{2-}] = [H_2S] - 6.0 \times 10^{-7}$

$[MoO_3S^{2-}] = 8.0 \times 10^{-7} - [H_2S]$

Using $K_c$ expression for $K_4$:

$$6.5 \times 10^{-6} = \frac{[MoO_4^{2-}][H_2S]}{[MoO_3S^{2-}]}$$

$= ([H_2S] - 6.0 \times 10^{-7})[H_2S] / (8.0 \times 10^{-7} - [H_2S])$

Solving gives $[H_2S] = 7.8 \times 10^{-7}$ mol dm$^{-3}$

$[MoO_3S^{2-}] = 2.0 \times 10^{-8}$ mol dm$^{-3}$

$[MoO_4^{2-}] = 1.8 \times 10^{-7}$ mol dm$^{-3}$

Using $K_c$ expression for the other equilibria gives

$[MoO_2S_2^{2-}] = 9.8 \times 10^{-10}$ mol dm$^{-3}$

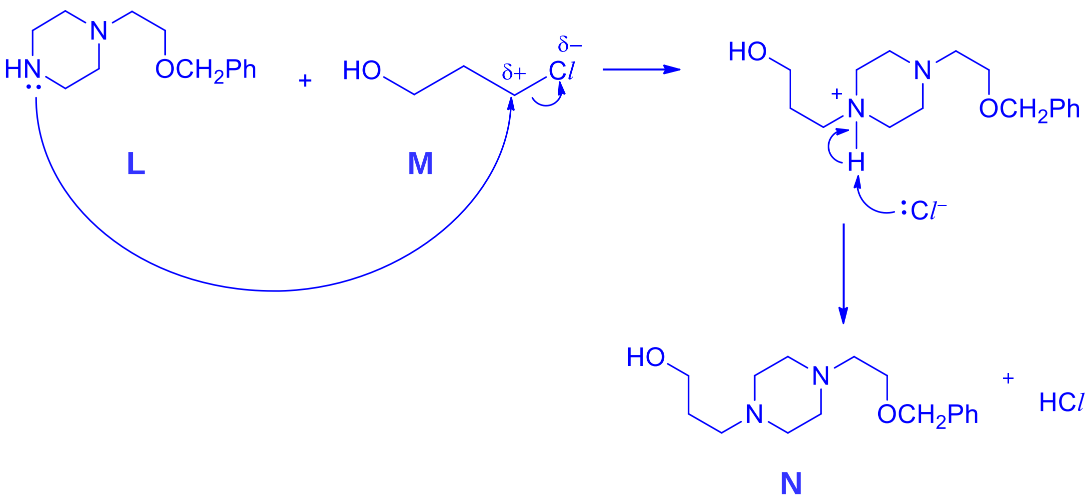
$[MoOS_3^{2-}] = 7.6 \times 10^{-11}$ mol dm$^{-3}$

$[MoS_4^{2-}] = 4.6 \times 10^{-12}$ mol dm$^{-3}$

relevant working

[4]

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



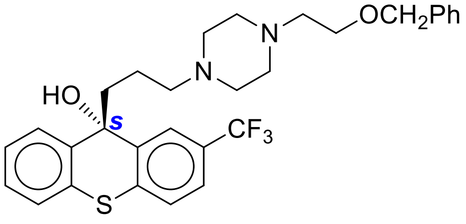
correct structure of **M**

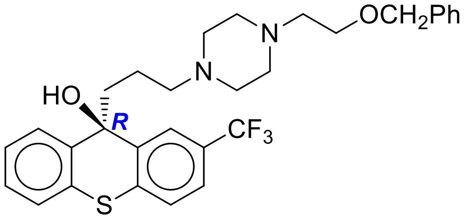
nucleophilic attack on C by N

Deprotonation by C*l*$^-$

[2]

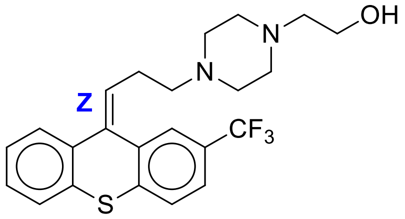
**(ii)**

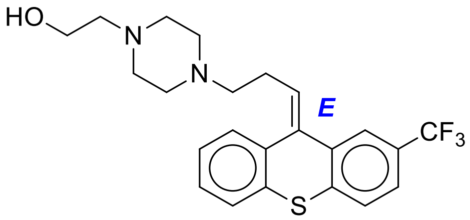




[1]

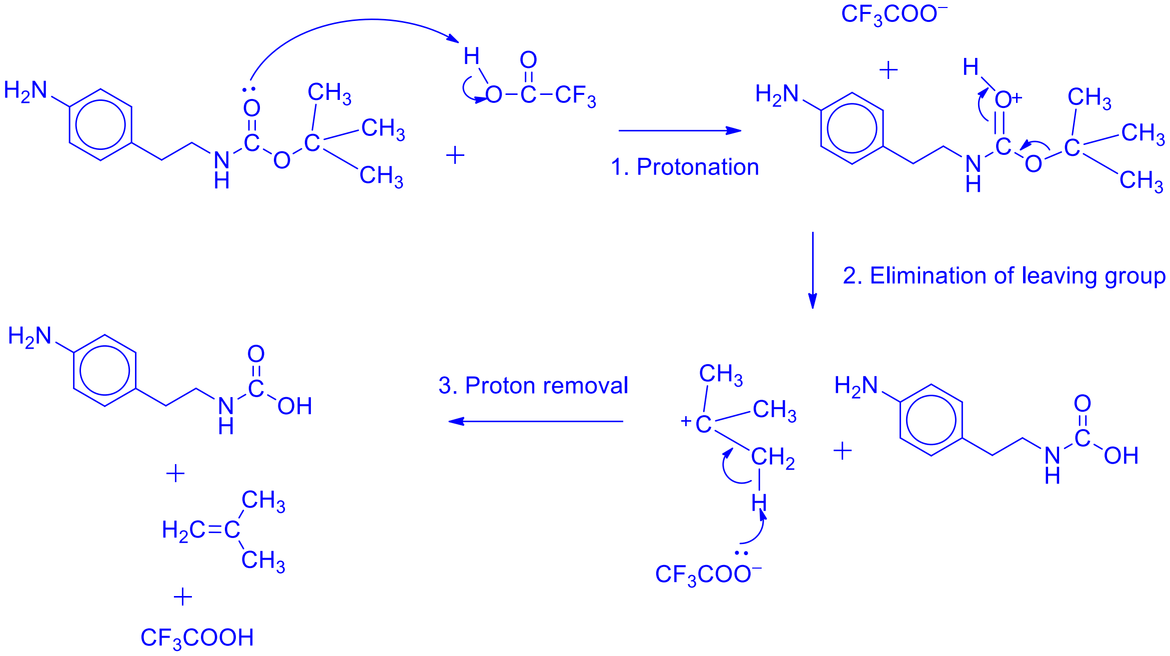
**(iii)** **Type of stereoisomerism: *E*, *Z* isomerism**





[2]

**(b)** **(i)**



protonation on O
elimination of leaving group
deprotonation by base
catalyst regenerated
correct arrow flow and lone pairs shown

[3]

**(ii)** **S** will result in a **faster** elimination reaction. The bromine and hydrogen to be eliminated in **S** has **similar geometry** to the example shown in the question. It will therefore undergo similar **E2** elimination with **syn periplanar geometry**. Based on the geometry of the corresponding bromine atom present in **T**, it will not be possible to undergo a syn nor anti periplanar E2 elimination. Therefore, **T** will under **an E1 elimination which is a slower route**.

[2]

**(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.**

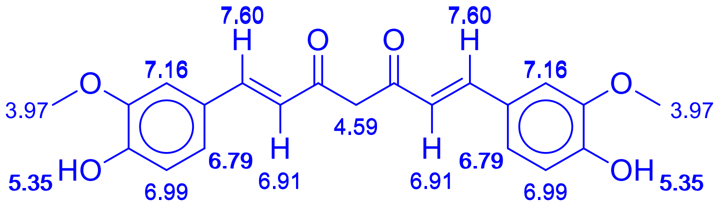
[2]

**(ii)** From information provided,
Trans-trans configuration, molecule has **two C=C**.
starting material (diketone) is $CH_3COCH_2COCH_3$.

From IR spectrum
**strong peak ~3400 cm$^{-1}$**, **–OH stretch** indicating presence of phenol
**strong peaks 1600 – 1700 cm$^{-1}$**, **C=O stretch** indicating presence of ketone
**strong peaks 1475 – 1625 cm$^{-1}$**, **C=C aromatic stretch** indicating presence of benzene ring
**weak peaks 1635 – 1690 cm$^{-1}$**, **C=C stretch** indicating alkenes present

| Chemical shift / ppm | Number of protons | Multiplicity | Deduction / Structural Features |
|---|---|---|---|
| 3.97 | 6 | singlet | 2 x $–OC\mathbf{H_3}$, |
| 4.59 | 2 | singlet | $–OCC\mathbf{H_2}CO–$ |
| 5.35 | 2 | singlet | 2 × –O**H**, highly **deshielded by proximity to electron withdrawing O atom**<br>**labile proton** (exchange with $D_2O$) |
| 6.8 - 7.2 | 6 | multiplet | **Aromatic C-H deshielded by magnetic anisotropic effect of phenyl ring**, split by |

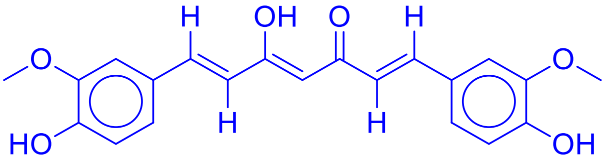
| | | | |
|---|---|---|---|
| | | | neighbouring proton. Since there are 6 H, **curcumin** is 2 × **trisubstituted benzene** |
| 6.91 | 2 | doublet | 2 × CH=C**H**C=O |
| 7.60 | 2 | doublet | 2 × Aromatic–C**H**=CH **alkene adjacent to aromatic ring** |



**Curcumin**

[6]

**(iii)**



tautomerized enol curcumin

**$2^3$ = 8 stereoisomers**

[2]

**5** **(a)** Amount of C = 92.3/12.0 = 7.69 mol
Amount of H = 7.7 / 1.0 = 7.70 mol
Empirical formula = CH
Since $M_r$ = 26, molecular formula of **U** is $C_2H_2$

[1]

**(b)** $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
Do not allow CaO as product.

[1]

**(c)** % by mass of N = 100 – 50 – 15 = 35%
Amount of Ca = 50/40.1 = 1.25 mol
Amount of C = 15/12.0 = 1.25 mol
Amount of N = 35/14.0 = 2.50 mol
**W** is $CaCN_2$

[1]

**(d)** Anion in **X**: $HCN_2^-$
$2CaCN_2 + 2H_2O \rightarrow Ca(OH)_2 + Ca(HCN_2)_2$

[1]

**(e)** **Y** is $H_2CN_2$.

$Ca(HCN_2)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2CN_2$

[2]

**(f)** Two possible structures for **Y**: H-N=C=N-H and $H_2N\text{-}C{\equiv}N$

Actual structure: $H_2N\text{-}C{\equiv}N$

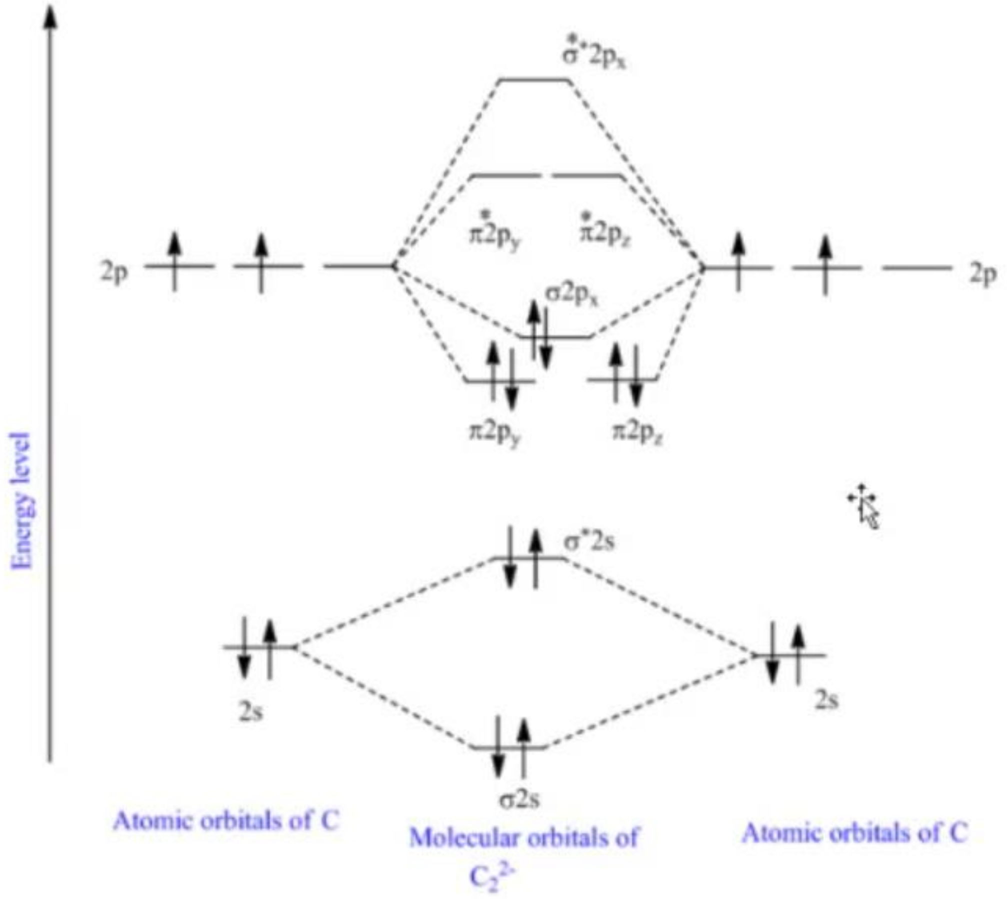
[2]

**(g)** **Z** is $H_2NCONH_2$.

$H_2NCONH_2 + H_2O \rightarrow 2NH_3 + CO_2$

[1]

**(h)** **(i)** Correct MO diagram with labelling.



Accept the $\sigma^*_{2px}$ and $\pi^*_{2py}$ and $\pi^*_{2pz}$ swopped around (if assuming symmetry).

Carbon has 4 valence electrons. In a $C_2$ molecule, a total of 8 valence electrons are present. In the formation of $C_2^{2-}$, 2 valence electrons will be added to σ bonding MO.

Bond order = (8 – 2)/2

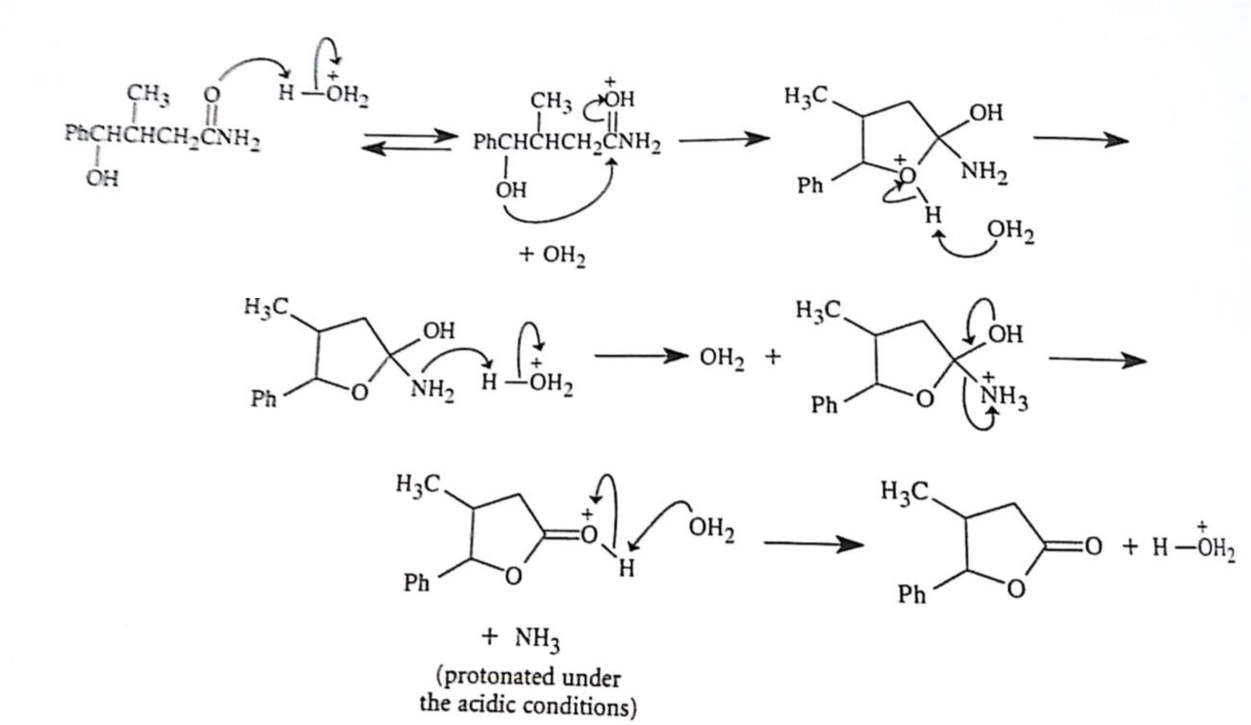
= 3

[2]

**(ii)** The **HOMO** of $C_2^{2-}$ is $\sigma_{2px}$, which **aligns with the C-C internuclear axis**. Hence, the acid-base adduct, $HC_2^-$, is expected to be **linear**.

[1]

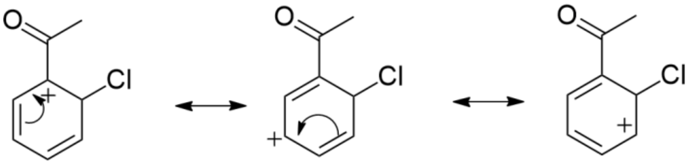
**(i)**



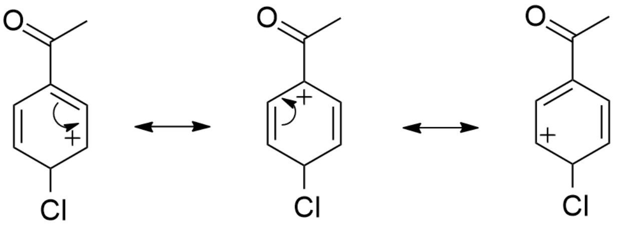
Lone pair on relevant atoms need to be shown. Ph = phenyl.

[3]

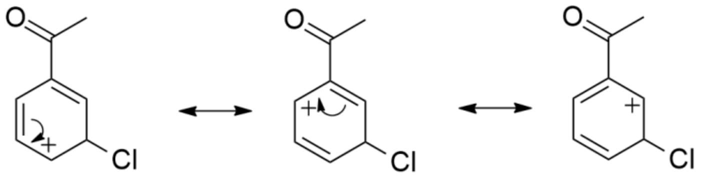
**(j)** Resonance forms for intermediate leading to 1,2 product:



Resonance forms for intermediate leading to 1,4 product:



Resonance forms for intermediate leading to 1,3 product:



For intermediate with the incoming electrophile C*l*$^+$ that attack the 2 and 4 position wrt –CO group, one of the resonance forms has the **positive charge in close proximity to the –CO group**, which exerts an **electron withdrawing inductive effect**. This will **destabilise the intermediate as the positive charge is intensified**.

The 3 positional isomer does not have such a resonance form, thus the intermediate leading to the formation is more stable and hence the 3-substitution is the major product.

[2]

**(k)** Only compound **IV** should have a proton NMR spectrum containing one 6-proton singlet in the alkyl region about δ1.5 corresponding to -C(C**H**$_3$)$_2$.

Only compound **V** should have a proton NMR spectrum that contains two closely spaced singlets in the integral ratio 2:1 in the benzylic region (C next to benzene) of the spectrum about δ2.5 corresponding to two -C**H**$_3$ groups that are at 2 position wrt C*l* and the other -C**H**$_3$ group respectively.

Only compound **VI** should have a proton NMR spectrum that contains two well-separated singlets in the integral ratio 3:1, the larger in the benzylic proton region (C next to benzene) at δ2.5 and the smaller at about δ3.5 corresponding to two C**H**$_3$ groups and the –C**H**$_2$C*l* group respectively.

Other plausible differences accepted.

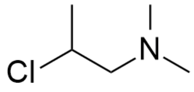
[3]

**6** **(a)** Acid-base or neutralisation

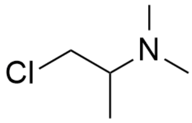
[1]

**(b)**

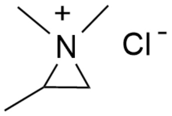
A:



**XI:**

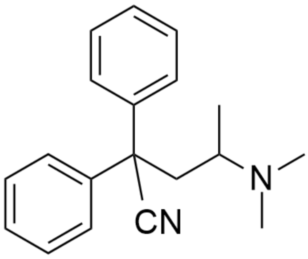


**XII:**

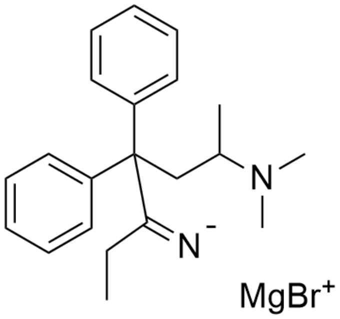


[2]

**(c)** **XIII:**



**IX:**



**X:**

[2]

**(d)** From $^1$H NMR spectrum

| Chemical shift / ppm | Number of protons | Multiplicity | Deduction / Structural features |
|---|---|---|---|
| 1.05 | 3 | triplet | $-CH_2C\mathbf{H}_3$ |

| | | | |
|---|---|---|---|
| 1.10 | 3 | doublet | $-CH(C\mathbf{H}_3)$ |
| 2.12 | 2 | doublet | $-C\mathbf{H}_2CH-$ |
| 2.26 | 6 | singlet | 2 x $-C\mathbf{H}_3$, next to **electron withdrawing N** atom |
| 2.49 | 2 | quartet | $-C\mathbf{H}_2CH_3$, next to **electron withdrawing C=O** |
| 2.78 | 1 | multiplet | $-C\mathbf{H}(CH_3)CH_2-$, next to **electron withdrawing N** atom |
| 7.35 | 10 | multiplet | 2 x **monosubstituted phenyl** rings. Aromatic C-**H** **deshielded** by **magnetic anisotropic effect** of phenyl ring |

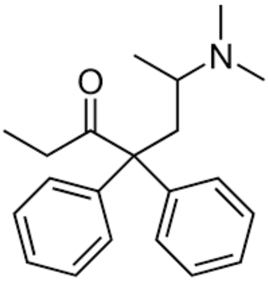
From IR spectrum

**Moderately strong peak near ~3000 cm$^{-1}$, aromatic C-H stretch indicating presence of sp$^2$ carbon in benzene ring**

**Moderately strong peaks near ~1500 cm$^{-1}$, aromatic C=C bond indicating presence of benzene ring**

**Strong sharp peak ~1700 cm$^{-1}$, C=O stretch indicating presence of ketone**

Methadone:



[5]

**(e)** **(i)** **Only one enantiomer will fit in receptor well enough to cause a physiological response.**

Other enantiomer, at best, represent a **waste of a valuable chemical** or could have a **deleterious, or even lethal, side effect on the metabolism of the patient.**

[1]

**(ii)** As the racemic mixture contains the basic amine, a **diastereomeric** salt will be obtained by reacting with (+)-tartaric acid, which is optically active.

The diastereomers will often have **different solubilities**, and so can be separated by **fractional crystallisation**. The free amines can then be liberated from the salts by reaction with aqueous sodium hydroxide.

[1]

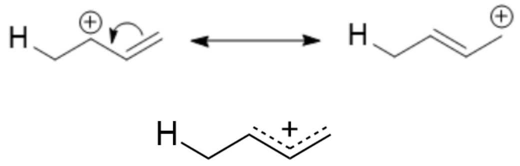
**(f)** **(i)** The **kinetic product is 3-chlorobut-1-ene and is favoured at low temperature**. The **transition state for 3-chlorobut-1-ene has positive charge on more substituted carbon and is more stable**, giving a lower activation energy and hence a higher rate of formation of the 1,2-addition product.

The **thermodynamic product is 4-chlorobut-2-ene and is favoured at a higher temperature**. The transition state for 4-chlorobut-2-ene has positive charge on less substituted carbon and is less stable, giving a higher activation energy and rate of formation of the 1,4-addition product is formed more slowly but the **product is more stable since it is a more substituted alkene**.

(accept if draw energy profile diagram with labelling)

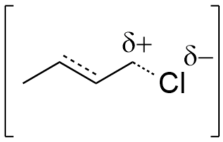
[1]

**(ii)** 1,4-addition product is formed due to the formation of carbocation stabilised by resonance.



By Hammond's postulate, as the formation of the carbocation is **endothermic,** the **transition state is close to energy of the carbocation**. Hence, its structure will resemble that of the carbocation:

Transition state:



[2]

**(g)** **(i)** In reaction **I**, **$S_N2$ is not favoured as $Br^-$ is not a strong nucleophile,** and also would not be able to displace the **poor leaving group, $CH_3CH_2O^-$**.

**$S_N1$ is also not possible as a primary carbocation** would have to be formed, which **is not favoured**.

In reaction **II**, **protonation of the (ether) oxygen** converts the ethoxide, a poor leaving group to **ethanol, a good leaving group**, and the reaction succeeds via the $S_N2$ mechanism..

(accept if draw mechanisms with relevant explanation)

[2]

**(ii)** Diethylamine is a **moderate nucleophile** and likely favors the **$S_N1$ mechanism**. The loss of optical activity most likely indicates that a **carbocation intermediate** is formed with a reactive carbon having a trigonal planar shape.
**Nucleophile attacks from top or bottom of the plane with equal probability to form equal amounts of the enantiomers** (racemic mixture).

(accept if draw mechanisms with relevant explanation)

[1]

**(iii)** $Cl^-$ is a relatively **poorer leaving group** than $Br^-$ leading to **increased ion-pair interactions between the carbocation and leaving group**.

The higher charge density of the chloride ion causes it to be attracted to the carbocation to a larger extent after cleavage. This causes **steric hindrance on one face**, **favouring backside attack**.

Furthermore, the **C–C*l* bond is stronger** than the C–Br bond and requires more energy to break. The **nucleophile can attack from the backside before the C–C*l* bond is completely broken**.

Resultant mixture contains **slightly more inversion product than product with retention of configuration**, resulting in a higher optical activity.

[2]