

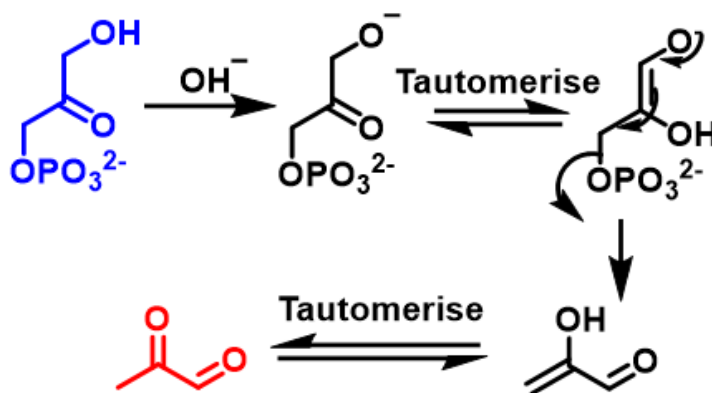
Sketches of Solutions

July 24, 2022

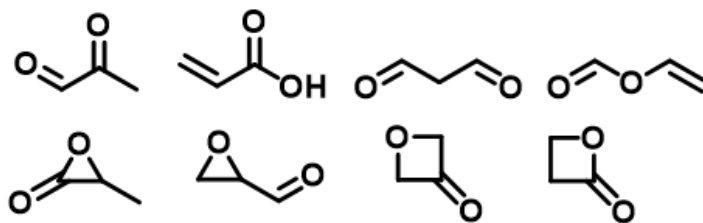
1 Short Answer Questions

1.1

- (a) The IUPAC name of the compound (A) is 2-oxopropanal, also known as methylglyoxal (MGO). The mechanism is as follows:



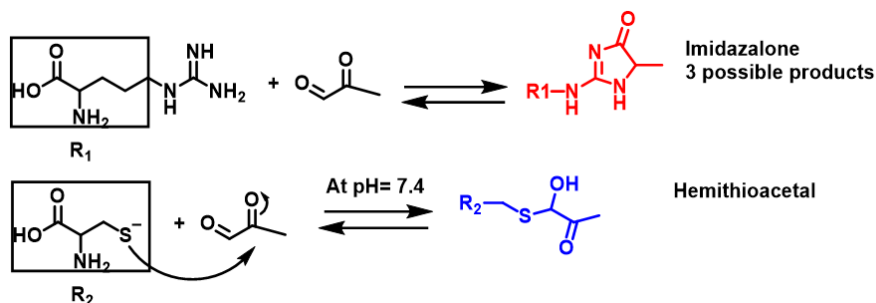
- (b) There are 8 structural isomers as shown:



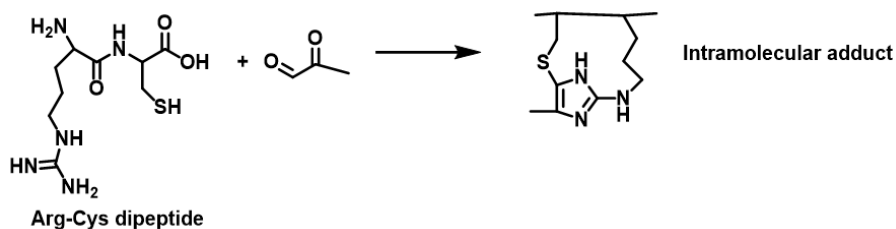
- (c) The nitrogenous analogue of carbonic acid is guanidine. Thiols are more reactive to MGO than guanidine because thiols are better nucleophiles at

physiological pH. Arginine (a guanidine) is protonated at this pH, thus being less nucleophilic. The attack of thiol is also sterically favored unlike guanidine.

- (d) Amino acid having guanidine group is arginine while the amino acid having thiol group is cysteine.



- (e) A molecule containing both guanidine and cysteine groups could be a Arg-Cys dipeptide



1.2



λ can be considered as an invariant with respect to time as λ ≫ A_o

Note: Do not consider H₂O_(g) since latent heat would have been provided or what gas approximation to consider

Since it is an isobaric and isochoric process

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV) \\ nC_v dT &= \Delta H dn_A \\ dn_A &= d(A_o(1-\xi)) = -A_o d\xi\end{aligned}$$

$$A_o C_v dT = \Delta H A_o d\xi$$

From Kirchoff's Law: $\Delta H = \Delta H^o + (C_{p2} - C_{p1} - C_{pw})(T - T_o)$

Here, even if $C_{p\text{mix}}$ instead of C_{pw} is considered, then marks were awarded

$$C_v dT = -(\Delta H^o + \Delta C_p(t - T_o)) d\xi$$

$$\frac{-C_v dT}{(\Delta H^o + \Delta C_p(t - T_o))} = d\xi$$

Differentiating with respect to time gives us

$$\frac{-C_v}{(\Delta H^o + \Delta C_p(t - T_o))} \frac{dT}{dt} = \frac{d\xi}{dt}$$

$$\frac{-d(A_o - A_o \xi)}{dt} = k A_o^n (1 - \xi)^n$$

$$\frac{d\xi}{dt} = k A_o^{n-1} (1 - \xi)^n$$

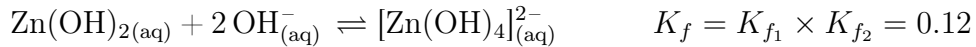
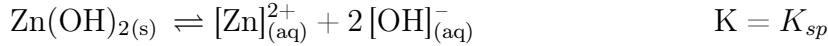
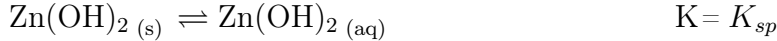
We know that

$$k = A e^{(E/RT)}$$

Thus, final answer is:

$$\frac{-C_v}{(\Delta H^o + \Delta C_p(t - T_o))} \frac{dT}{dt} = A_o^{n-1} A e^{(E/RT)} \left(1 + \int \frac{C_v dT}{(\Delta H^o + \Delta C_p(t - T_o))}\right)^n$$

1.3



Applying mass balance:

$$[\text{Zn(OH)}_2] = S = [\text{Zn}^{2+}] + [\text{Zn(OH)}^+] + [\text{Zn(OH)}_3^-] + [\text{Zn(OH)}_4^{2-}]$$

$$S = [\text{Zn}^{2+}] + [\text{Zn(OH)}_4^{2-}]$$

$$S = \frac{K_{sp}}{[\text{OH}^-]^2} + K_f [\text{OH}^-]^2$$

Differentiating it with respect to the hydroxyl ion concentration and equating it to 0 for minimum solubility gives us:

$$[\text{OH}^-] = \left[\frac{K_{sp}}{K_f}\right]^{1/4} = 10^{-4}$$

Thus, the pH of minimum solubility is 10. Thus,

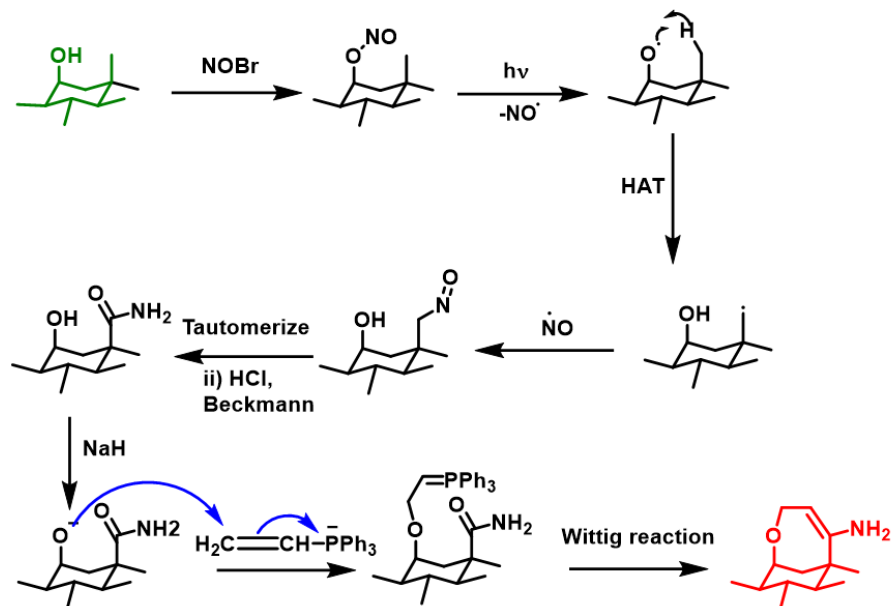
$$S = [\text{H}^+]^2 \frac{K_{sp}}{K_w^2} + \frac{K_f K_w^2}{[\text{H}^+]^2}$$

$$S = \frac{K_{sp}}{K_w^2} 10^{-2pH} + K_f K_w^2 \cdot 10^{2pH}$$

Thus, the graph is a parabola opening upwards with the minimum at $\text{pH} = 10$

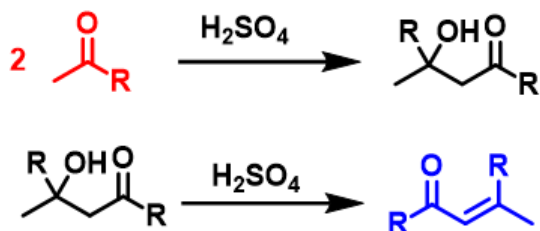
1.4

The mechanism is as shown below:



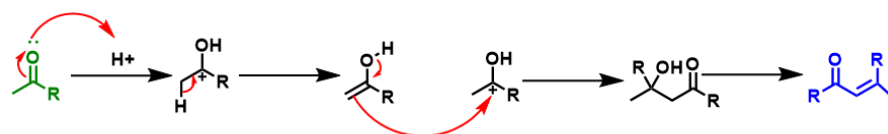
1.5

(a) It's the aldol condensation reaction.



But writing the two as a single reaction and going on till mesitylene are correct as well.

Assuming a specific methyl ketone attracted a light penalty.



(b)

Writing a correct mechanism for your answer to a) if it was one of the other correct answers has also been awarded marks.

Taking the H from the other side in step 2 attracted a light penalty since we don't know if that side has alpha hydrogen.

(c) The peaks that appear during the reaction are:

1. O-H peak around 3500 cm^{-1}
2. Aromatic C-H peak around 3010 cm^{-1}
3. Aliphatic C-H peak around 2900 cm^{-1}
4. C=O peak around 1700 cm^{-1}
5. Peaks in the fingerprint region.

(d) Reaction 1 is from ketone (A) to aldol (B). It's second order in A.
Reaction 2 is from aldol (B) to alpha beta unsaturated ketone (C). It's first order in B.

Assume rate constants k_1 and k_2 for the 2 reactions.

Then,

$$\begin{aligned}\frac{d[A]}{dt} &= -2k_1[A]^2 \\ \frac{d[B]}{dt} &= k_1[A]^2 - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B]\end{aligned}$$

This gives us the equations for concentrations of A, B, and C

$$[A](t) = \frac{[A]_0}{2k_1[A]_0 t + 1}$$

Where $[A]_0 = 0.1$. etc.

Then we see the height of the peaks in 1M sample of each of A, B, C.

A has C=O and aliphatic C-H. Let heights be A_{1700} and A_{2900}

Similarly, B_{1700} B_{2900} B_{3500}

Finally, we say that the height of the peak at, say 1700 is:

$$Peak_{1700}(t) = A_{1700} \cdot [A](t) + B_{1700} \cdot [B](t) + C_{1700} \cdot [C](t)$$

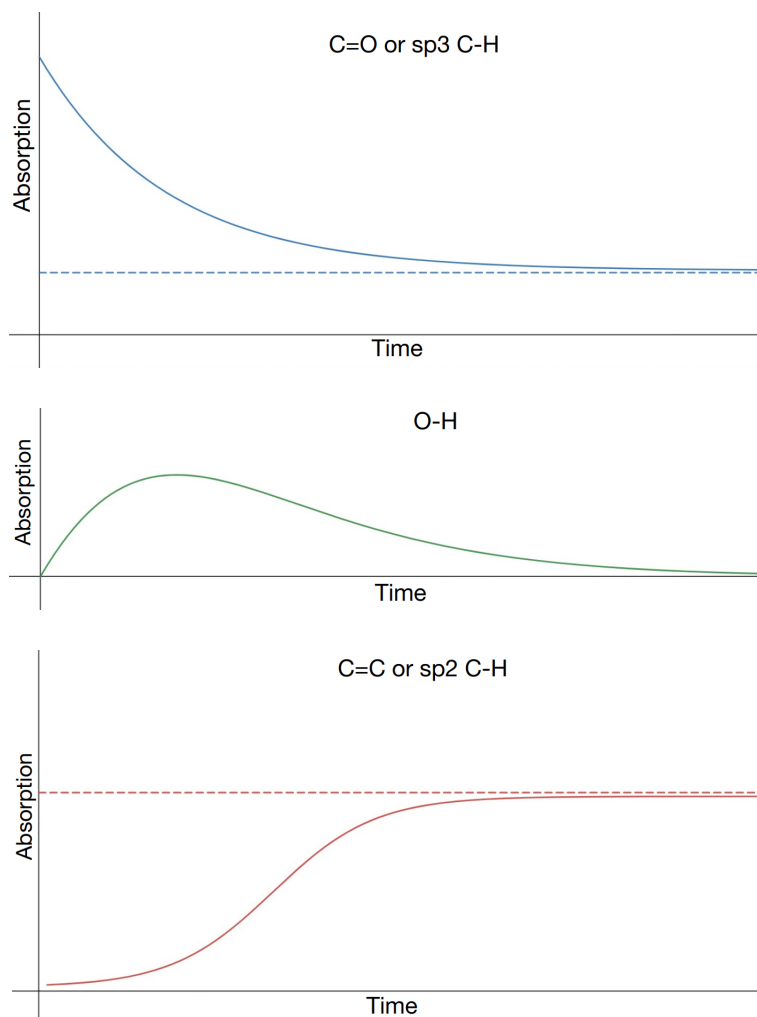
Logical simplifying assumptions made to calculate $[A]$, $[B]$, $[C]$ are accepted. A logically correct model for your answer to a) if it was one of the other correct answers has also been awarded marks.

Writing the funda as above and leaving them in differential form / integrating using Wolfram Alpha are also accepted.

(e) Concentration of ketone and sp³ C-H reduces over the reaction. Peak height decreases. Slope is $-2k_1[A]^2$, so is initially non-zero negative. and monotonically decreases till finally asymptotic to the peak height of 0.05M C. O-H peak is only observed in the Aldol intermediate, so peak height varies

only with $[B]$. It starts at 0 and finally goes back to 0. Slope is $k_1[A]^2 - k_2[B]$. Initially, $[A]$ is non zero and $[B]$ is zero. So slope is non zero positive. Finally, $[A]$ is 0 and $[B]$ exponentially goes to 0.

sp^2 C-H and C=C are only present in C. peak height increases with $[C]$. initially 0 and finally some non zero value. Slope is $k_2[B]$ so initially and finally slope is 0.



2 Long Answer Questions

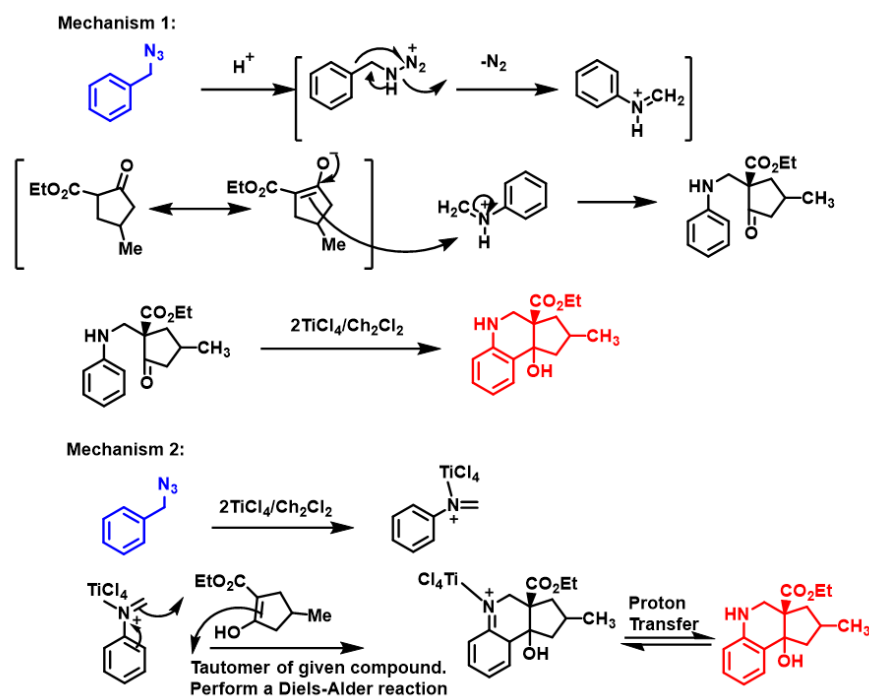
2.1 Azide - the Amide Bond Builder

2.1.1

The failure of alkyl azides to react with cyclohexanone in presence of protic conditions can be attributed to the unfavorable formation of the azidohydrin adduct. However, in the intramolecular case, the equilibrium is more favorable due to entropy considerations. The intermolecular reaction can be favored if we use more aggressive Lewis acids that increase the reactivity of the ketone. A possible Lewis acid is TiCl_4 .

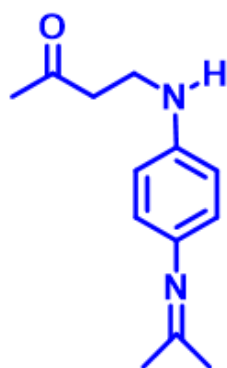
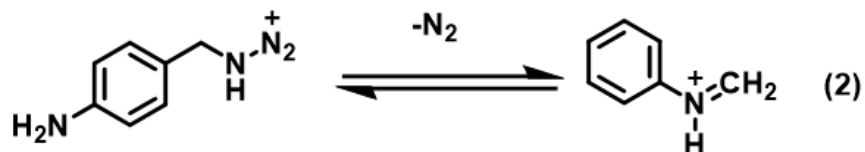
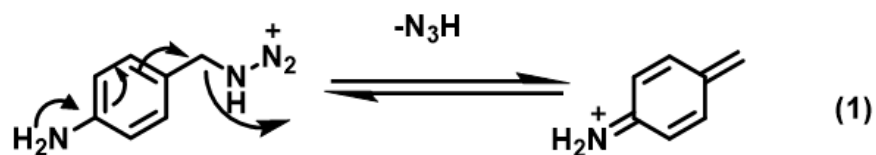
2.1.2

The first mechanism proceeds through a Mannich type mechanism followed by a Friedel Craft reaction, while the second reaction proceeds through a Diels-Alder reaction

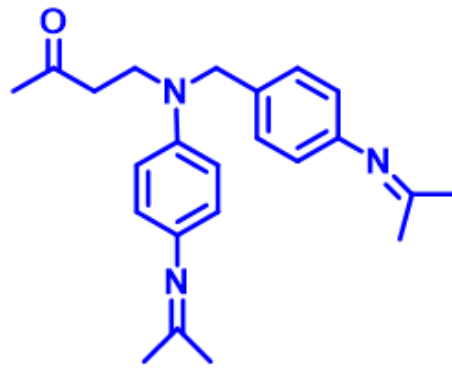


2.1.3

There are two leaving groups present that cause the difference in products to arise. A hydrazoic acid can leave, or nitrogen can leave. Upon reaction of (2) with the enolate followed by the imine formation with another molecule of acetone gives rise to Product A. Reaction of Product A with (1) followed by imine formation and proton transfer leads to formation of Product B



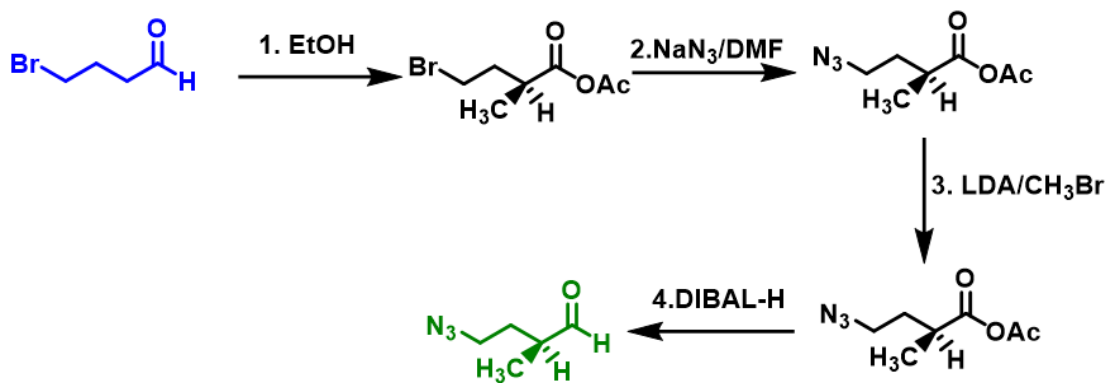
Product A



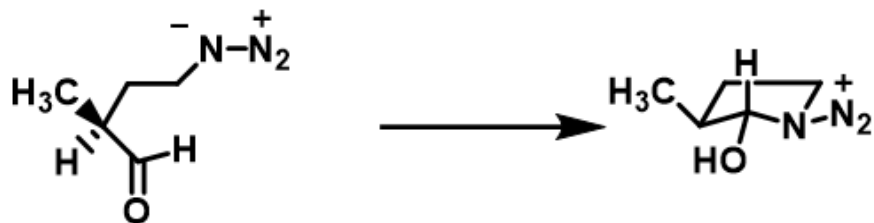
Product B

2.1.4

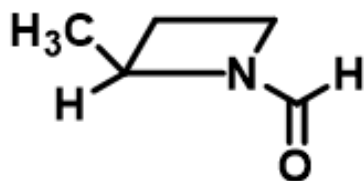
The following mechanism is one of the correct pathways. Alternative pathways that are logically consistent have been awarded marks. Now the nucleophilic nitrogen



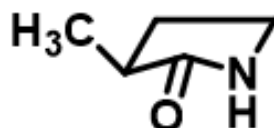
attacks the carbonyl carbon resulting in the formation of a 5-membered ring. Now, either the alkyl group or the hydride can migrate to give the final product.



We see that the alkyl group migration is disfavoured as it results in a four-membered ring.



Not observed



Observed

2.2 Mystery compound

2.2.1

(a) A = Sulphur

All Cl is located in NH_4Cl , and thus the weigh of Cl is found by:

$$\begin{aligned} 53.492 \text{ g } \text{NH}_4\text{Cl} &\rightarrow 35.453 \text{ g Cl} \\ 320.950 \text{ g } \text{NH}_4\text{Cl} &\rightarrow ? \text{ g Cl} \\ ? &= 212.717 \text{ g} \end{aligned}$$

Total amount of A present in the reaction is $405.108 \text{ g} - 212.717 \text{ g} = 192.391 \text{ g A}$.

128.26 g is free A and $(192.391 - 128.260) = 64.131 \text{ g A}$ in the nitride.

The amount of N bound in nitride is therefore, $92.144 \text{ g nitride} - 64.131 \text{ g A bound in nitride} = 27.980 \text{ g N bound in nitride}$.

The amount of Nitrogen bound in NH_4Cl is $320.950 - 212.717 = 108.233 \text{ g}$

Apply rule of multiple proportions,

Assuming proportionns of 1:1

Chloride:

$$\begin{aligned} 192.391 \text{ g A binds} &\rightarrow 212.717 \text{ g Cl} \\ ? \text{ g A binds} &\rightarrow 35.453 \text{ g Cl} \\ ? &= 32.065 \text{ g A} \end{aligned}$$

A could be Sulphur
Nitride:

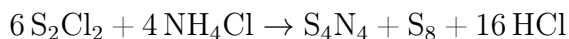
$$\begin{aligned} 64.131 \text{ g A binds} &\rightarrow 27.980 \text{ g N} \\ ? \text{ g A binds} &\rightarrow 14.007 \text{ g N} \\ ? &= 32.104 \text{ g A} \end{aligned}$$

Again, A could be Sulphur

Similarly taking 1:2 proportions for chloride and nitride it can be seen that around 64 g A of A is obtained. Thus, A can be Copper or Sulphur.

On seeing the overall reaction given, Sulphur is the most likely element A.

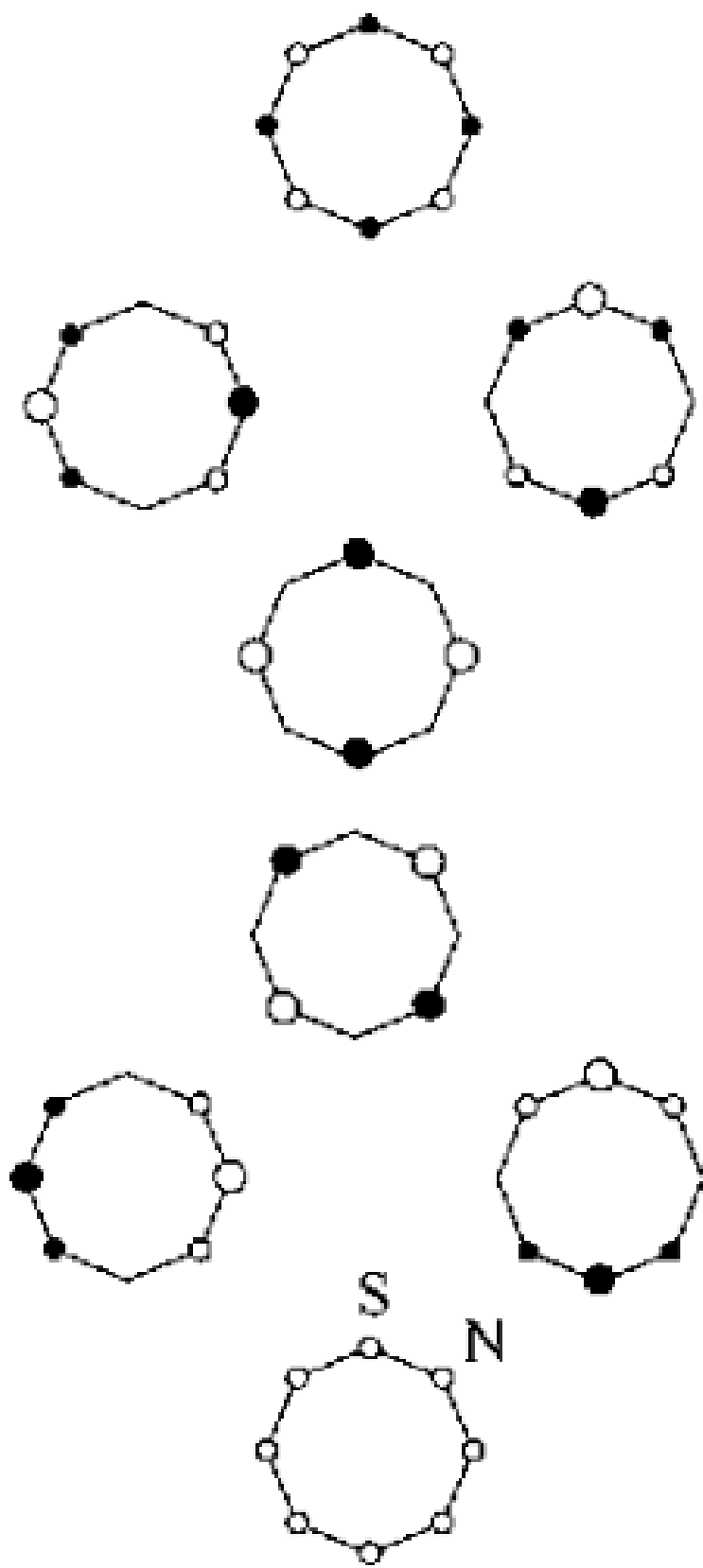
(b) The reaction with NH_4Cl is as follows:



The purple-brown colour of the solid is due to the various coloured substances present together such as S_4N_4 , S_8 and NH_4Cl . Trace amounts of $\text{S}_3\text{N}_3\text{O}_2$ and S_2N_2 were also found to be present. The sulphur generated is found to form a layer on the ammonium chloride resulting in lesser amount of ammonium chloride available for the reaction to proceed. Thus, a low yield is obtained.

2.2.2

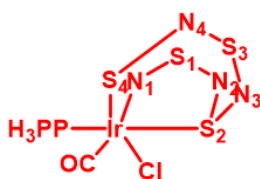
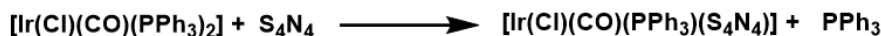
(a) The πMO scheme is as shown. The MO at the bottom signifies the lowest energy state. The sulphur and nitrogen atoms weren't specified but a lot of participants have given a good answer.



- (b) The planar state has a triplet configuration which undergoes a Jahn-teller distortion to give a cradle structure having strong transannular interaction between the p-orbitals. Now, when considering what element is planar and what is not, the bond distances ought to help. As the S-S bond was seen to be intermediate between bonding and non-bonding, we expect an interaction which indicates that the S-S p-orbital overlap exists and hence, the sulphur atoms are non-planar.
- (c) As explained above, since at R 2.4 Å (the distance at which the S-S overlap is the better than the 2p-2p overlap of N-N.), the relative p-p overlap integrals for As and P are larger than those for S and N. Thus, we expect that in P_4S_4 and As_4S_4 the sulphur atoms are planar and the phosphorus and arsenic atoms are non-planar.

2.2.3

Note: The changes in the distance of "Ir-A" was the intention of the examiner. Nonetheless, appropriate marks were given to those who attempted the question. The oxidative addition of S_4N_4 to the complex reduces the electron density on the metal and consequently a weakening of the $d_\pi - p_\pi$ backbonding to the carbonyl group. Thus, lowering the CO stretching frequency. Ir^-S_4 bond length is shorter than the $Ir-S_2$ bond length as the coordination number of the two sulphurs are different



Balanced Equation and the Structure of the adduct formed

2.2.4

- (a) resistance of the pellet is taken to be much lesser than the shunt resistor.

$$I = \frac{V}{R_{shunt}}$$

$$P_{pellet} = I^2 R_{pellet}$$

$$\frac{dQ}{dt} = I^2 \frac{\rho l}{A}$$

$$\begin{aligned}
C \frac{dT}{dt} &= \rho \frac{I^2 l}{A} \\
\rho &\propto \frac{dT}{dt} \\
T &\propto \frac{1}{1-t} \\
\Rightarrow \rho &\propto \frac{dT}{dt} \propto \frac{1}{(1-t)^2} \\
\Rightarrow \rho &\propto T^2
\end{aligned}$$

(b) Right after switching off, $T \approx 80K$

$$P = \sigma e A (40)^4 - \sigma e A T^4$$

$$-C \frac{dT}{dt} = \sigma e A (T^4 - 40^4)$$

Using Wolfram alpha to help with the integral, or making logical simplifying assumptions to calculate the integral are both allowed.

$T \propto t^{-\frac{1}{3}}$ is accepted.

Newton's law of cooling is NOT accepted, as the temperature of the pellet is twice the surrounding temperature.

(c)

$$\begin{aligned}
-C \frac{dT}{dt} &= \sigma e A (T^4 - 40^4) \\
\frac{dT}{T^4 - 40^4} &= -\frac{\sigma e A dt}{C}
\end{aligned}$$

Integrating,

$$\int_{80}^{70} \frac{1}{T^4 - 40^4} dT = - \int_0^t \frac{\sigma e A}{C} dt$$

Thus, we can solve the integral (With help from Wolfram Alpha if need be) to get the answer in terms of C, Since the dimensions of the pellet have been given. One more thing that can be done, but not expected, is since you know that the polymer is $(SN)_x$ by solving 2.2.1 to 2.2.3, after solving 2.2.4 a), refer literature to find proportionality constant. Then, since 5 seconds for 40 to 80 is given, you can solve that for C then get an actual number as the answer.

2.3 Fatty acid degradation

2.3.1

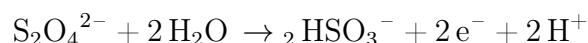
- (a) Since, the solution appears yellow, we expect the colour absorbed by the complex to be in the wavelength near violet. A close look at the plot given shows that Fe^{+3} is the metal present. Since, the metal was oxidised by air to obtain the solution, the ideal answer is Fe^{2+} . But since, the question did not

ask for what state the enzyme was present in, full marks have been awarded to those who got Fe correct.

- (b) The intracellular process that was being asked for was that of an "intracellular reduction" through pathways utilising molecules such as NADH or FAD.

2.3.2

The scientist was incorrect about his assumption as there must be two metal centres in the enzyme as is indicated by the plot.



Thus, two metal centres are present per enzyme as 1 mole of dithionite completely consumes 1 mole of X.

2.3.3

A bridging ligand is present, which upon mutation is unable to bridge the two centers, thereby, increasing the metal-metal distance. The suspected amino acid in literature is glutamic acid. Mention of a bridging amino acid has been awarded full marks.

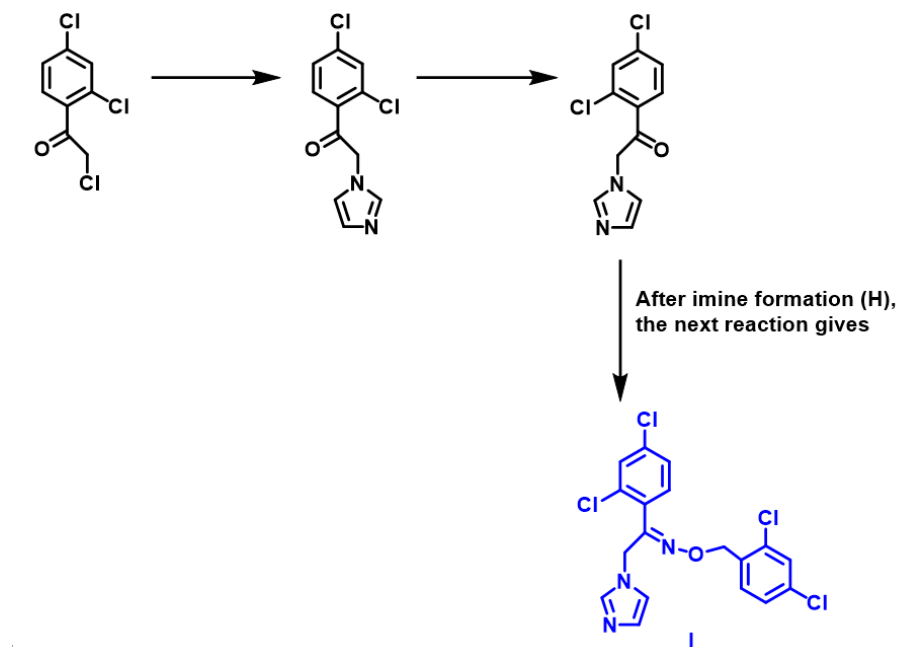
2.3.4

The mechanism that is suspected in literature is that of β hydrogen abstraction. The plausible mechanism that was expected was that the active site of the enzyme is such that small groups such as deuterium and hydrogen can be present in the β position and the reaction would occur. however, bulky groups hinder the formation of alkenes. Other plausible mechanisms have been also given marks.

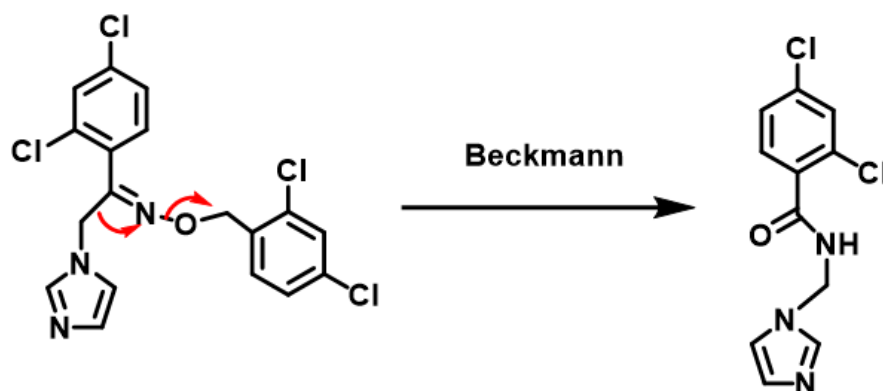
Note"For those interested, the enzyme X is "undA"

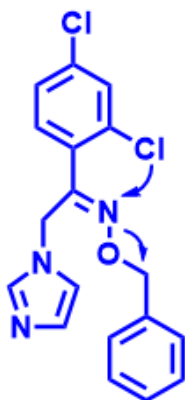
2.4 Pacman

The mechanism of obtaining I is shown. The rest of the steps are as follows: Benzene undergoes nitration followed by chlorination at meta position. This is followed by the diazonium salt formation and finally, 1,3-dichlorobenzene is obtained at step E. Step F is a Friedel-Craft acylation reaction. The steps that follow are as shown below:



Once, I is obtained, in the presence of an acid H^+ , oxygen will get protonated and Beckmann rearrangement occurs, giving us the final product as shown. If the oxime bond is towards the dichlorobenzene ring (E-isomer), normal Beckmann rearrangement will take place. However, if the oxime bond is away from the dichlorobenzene ring (Z-isomer), an intramolecular reaction will take place first where Chlorine of the dichlorobenzene ring will eliminate the protonated oxygen group (N.G.P.) forming a five membered cyclic ring and after this Beckmann rearrangement will take place. Hence, we will get same product irrespective of which isomer is reacted.

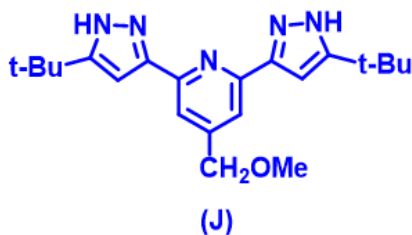
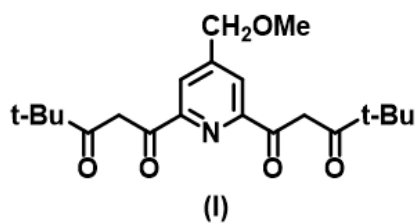
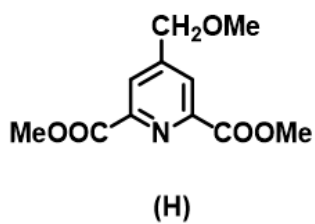
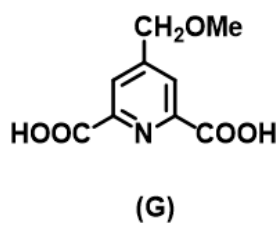
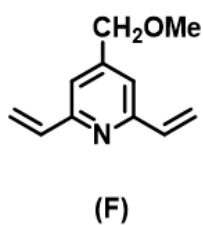
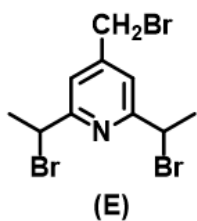
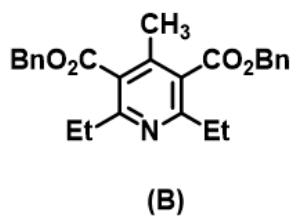
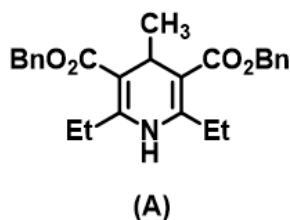




2.5 Tongs? Claws?

2.5.1

The formation of "A" is through the **Hantzsch pyridine synthesis**. The chalcone analogue intermediate formation was "K". The rest of the products are as follows:



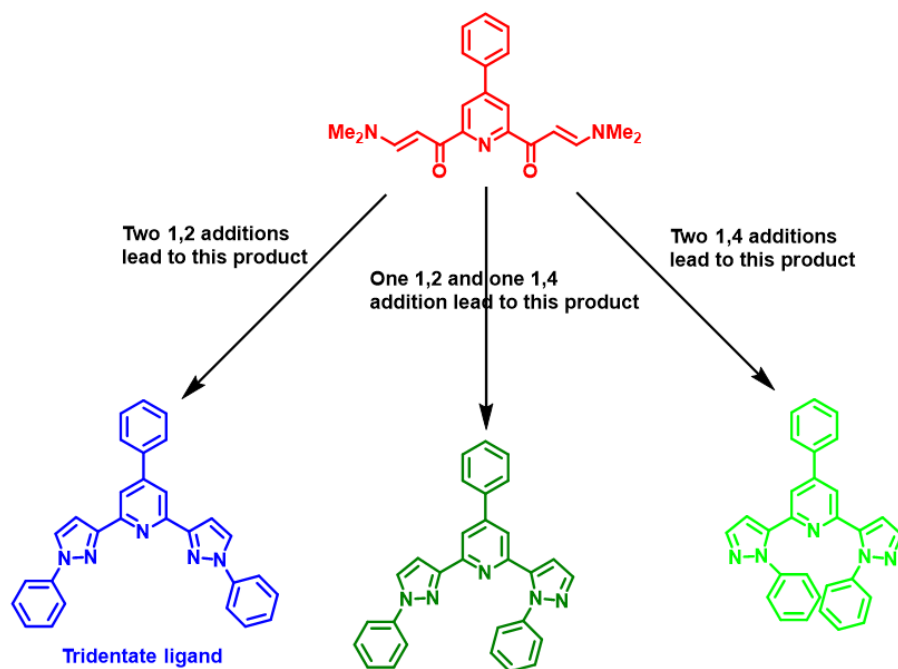
The "C" product is the deprotection of the benzyl groups to form carboxylic acid. It is followed by the decarboxylation, giving D.

2.5.2

HIO_3 is used as an oxidising agent where in it oxidises the dihydropyridine to pyridine. $\text{H}_2\text{-Pd/C}$ is used as a deprotecting agent, it deprotects the benzyl group.

2.5.3

The isomers and the method of their formation is listed below:



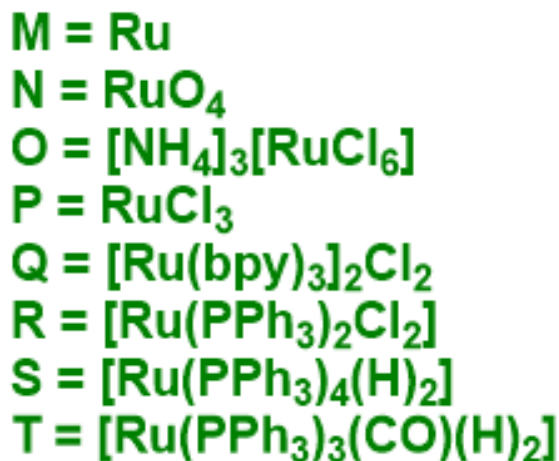
2.5.4

- (a) All the compounds are listed below. The metal "M" was supposed to be figured out to be Ruthenium by noting the following

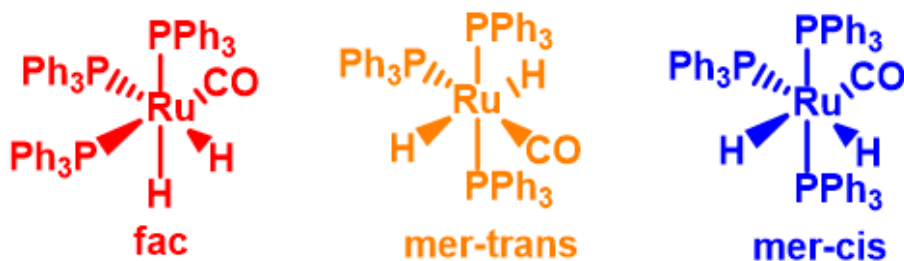
Note: We acknowledge that more information could have been provided to make the problem easier.

The fact that the percentage of the chlorine and element are approximately equal is a good clue. Suppose that it is a tetrahedral complex or an octahedral one. We obtain the masses of M to be approximately close to barium and a radioactive element respectively. However, these elements fail to satisfy some of the reactions or the conditions provided. Thus, we need to think of alternative stoichiometries. By means of trial and error, Ruthenium can be found out.

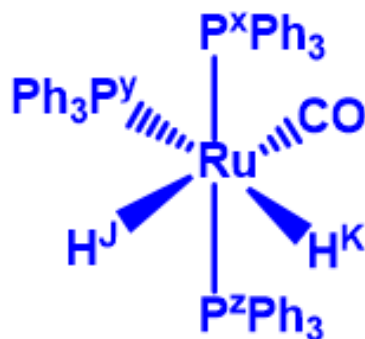
P.S Examiner's note: Since it was open internet, a simple google search for the reaction of 2,2' bipyridine along with a quick look at part (e) of this question would result in the correct answer. :p



- (b) The appearance of peaks on either side signifies that the reducing agent was PPh_3 . The two peaks were those of PPh_3 to Ph_3PO .
- (c) The stereoisomers of T are as shown below:



- The signal at 6.83 ppm is a 'triplet of doublets of doublets'. The signal at 8.3 ppm is a 'doublet of triplets of doublets'.
Note: Small typo here; should have been -8.3 ppm instead of -8.8 ppm
- The following is the mer-cis configuration.

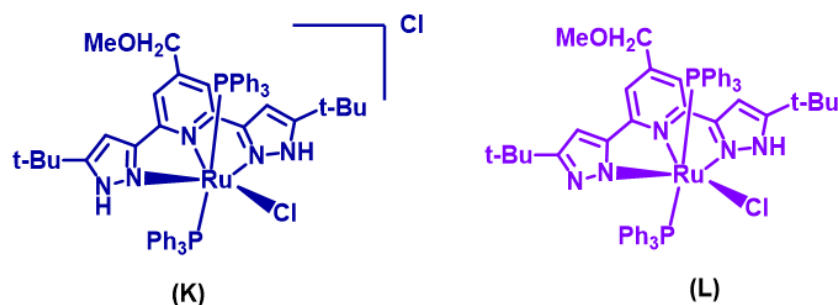


Now, note that H^k and P^y are trans to each other and hence must have the highest coupling constant. It must be followed by H^j and P^x and H^j and P^z since it is a triplet. Similar reasoning will give rise to the following table.

$H^k - P^y$	71 Hz
$H^j - P^x$	31 Hz
$H^j - P^z$	31 Hz
$H^k - P^x$	28 Hz
$H^k - P^z$	28 Hz
$H^j - P^y$	15 Hz
$H^k - H^y$	6 Hz

Note: If entries 2,3 and 4,5 were interchanged, marks were given.

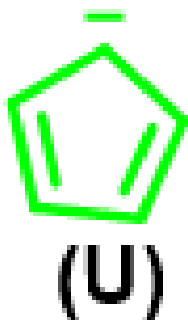
- (d) Since our ligand J is a tridentate ligand, the following product is formed. The addition of a weak base such as potassium carbonate leads to the deprotonation of the protic pincer ligand.



- (e) Q acts as a photocatalyst. It first absorbs blue light and gets excited to its triplet state. Now this excited photocatalyst has the unique property of acting as either an oxidant or reductant depending on a variety of factors. Here, it accepts an electron from the dye molecule to go to Ru^{1+} state which is a good

reductant and thus can reduce the electron acceptor by donating an electron, thus completing the catalytic cycle. Answers with reduction first and oxidation next are also acceptable as the order depends on the potential values

- (f) The given molecule is the dimer of cyclopentadiene and in the presence of heat, undergoes retro-Diels Alder reaction to give back cyclopentadiene and in the presence of NaH, cyclopentadienyl anion is formed. Thus, U is



Now, the reaction between cyclopentadienyl anion and ruthenium trichloride is well documented. However, we wanted to introduce you to the concept of Job's plot or the method of continuous variation. In this method, the stoichiometry of the resulting complex can be determined by taking the ratio of the moles of the individual compounds at the point of maximum absorbance. Calculate the molarity of P (RuCl_3)

$$x = \frac{0.83}{207} \times \frac{1000}{500}$$

$$x = 8mM$$

Observe that the maximum absorbance is obtained at a dilution of 260 μL . Thus, concentration of P when diluted to 260 μL is:

$$8mM \times 260\mu\text{L} = y \times 1mL$$

$$y = 2.08mM$$

Since, the total concentration is 6.24 mM, the amount of ligand present is 4.16 mM. Now, since the total volume of solution is 1mL, the number of moles of P and ligand present are 2.08 and 4.16 respectively. Thus, their ratio is 1:2 and therefore, the stoichiometry of the resulting compound is $\text{Ru}(\text{Cp})_2$

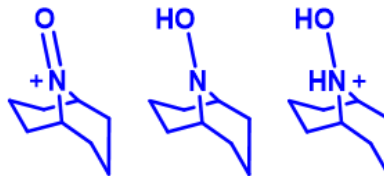
- (g) Upon oxidation of the ruthenocene molecule, Ru^{3+} disproportionates to form ruthenocene and Ru^{4+} . The reaction is as follows:



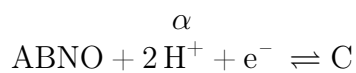
2.6 ABNO

2.6.1

(a) The structures of A,B and C are as follows:



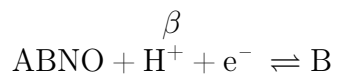
(b) Writing Nernst's equation for α, β



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{C}]}{[\text{ABNO}][\text{H}^+]^2}$$

$$E = E^\circ - \frac{RT}{nF} (-\ln[\text{H}^+])^2$$

$$E = E^\circ - 2 \frac{RT}{nF} \text{pH}$$



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{B}]}{[\text{ABNO}][\text{H}^+]}$$

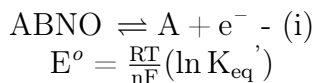
$$E = E^\circ - \frac{RT}{nF} \text{pH}$$

Thus, ratio of slopes is 2.

(c) It is a disproportionation reaction

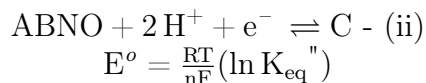


(d) For the following reaction,



Now, the potential is 0.75V and substituting the other variables, we get $\ln(K'_{\text{eq}} = 29.212)$

Now, for the following reaction:



Now, the potential is 0.95V (from y-intercept of α and substituting the other variables, we get $\ln(K''_{\text{eq}} = 37)$

Combining reactions (i) and (ii),

$$\begin{aligned} \text{ABNO} + 2\text{H}^+ &\rightleftharpoons \text{A} + \text{C} \\ K_{\text{eq}} &= K_{\text{eq}}' \times K_{\text{eq}}'' \\ K_{\text{eq}} &= 5.695 \times 10^{28} \end{aligned}$$

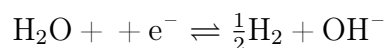
- (e) The question clearly states that one of the electrode reactions taking place is the oxidation of B to A.

So reaction at anode is:



Oxidation of alcohols to aldehydes/ ketones takes place within the electrolyte.
Reduction of A to B takes place in the electrolyte.

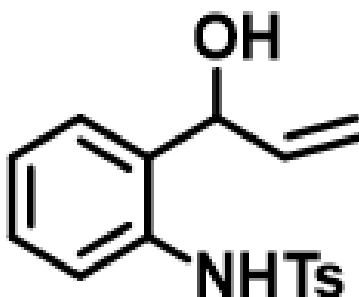
Reaction at cathode is:



2.7 An interesting synthesis

2.7.1

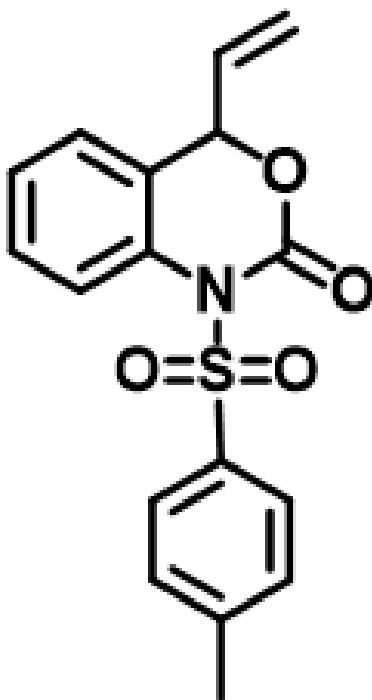
- (a) A is as shown below. since, the reaction is being performed at 0°C , cyclisation is not expected.



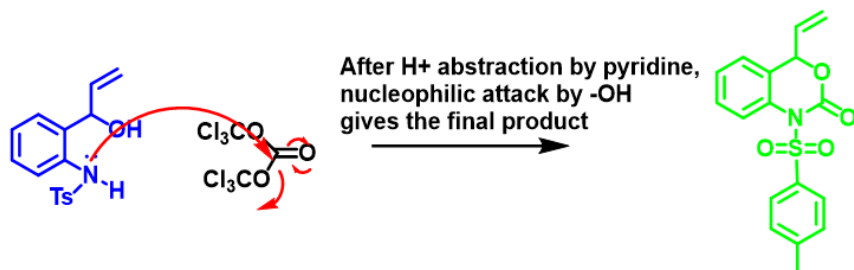
- (b) 1 equivalent is consumed by the active hydrogen attached to nitrogen. 1 equivalent is consumed by aldehyde. We take slightly more than this so that both sites of consumption of the reagent consume reagent fully.

2.7.2

- (a) **Note: A nitrogen was missing in the molecular formula given. Marks were appropriately assigned,**



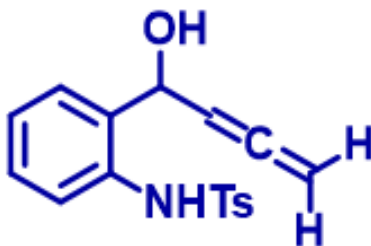
(b) A plausible mechanism is as shown below:



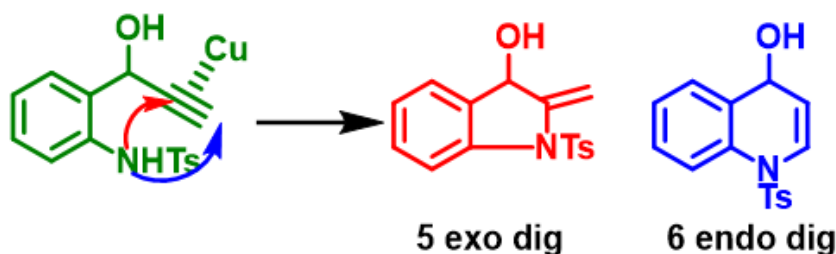
(c) Triphosgene loses a Cl^- and forms phosgene which gives further reaction. 2 equivalents of substrate react with 1 equivalent of phosgene. The role of pyridine is to abstract the acidic N-H proton.

2.7.3

- (a) The alkyne donates πe^- s and accepts an electron from the metal in its π^* ABMO. However, π donation tendency is more in alkynes than π^* accepting tendency. Thus, alkyne will pull the electron cloud towards it making the hydrogen in alkyne more acidic and can be immediately extracted.
- (b) The expected product is:



(c) The expected products are shown below along with the mechanism.



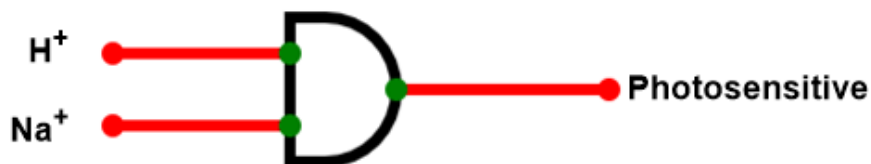
(d) Using Baldwin's rules, both 5 and 6 membered rings are equally favourable to form. But the exact product will not be known as the temperature and other conditions aren't given. TCP:KCP product cannot be predicted easily.

(e) Checked based on hypothesis.

2.8 Electron Transfer Mechanisms

2.8.1

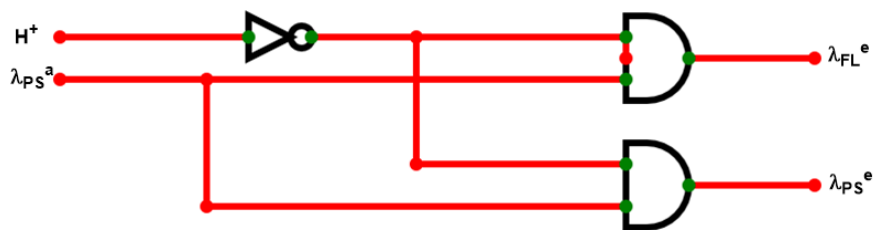
(a) Since the ether is 18-crown-6, it can coordinate to sodium and potassium. Any of the above metals were awarded marks. The type of logic gate is an AND gate.



(b) If other metals of the group such as lithium or rubidium are used, the output will always be zero as the atoms will not fit into the crown ether. Thus, the compound will not be photosensitive.

2.8.2

- (a) In acidic conditions, the N-N dimethyl amine and pyridine get protonated so the λ_{obs} of fluorophore and the emission wavelength of the photosensitizer do not match. The photosensitizer undergoes bathochromic shift and the fluorophore undergoes hypochromic shift and hence, colour is not seen.
- (b) The logic gate that is designed is as follows:

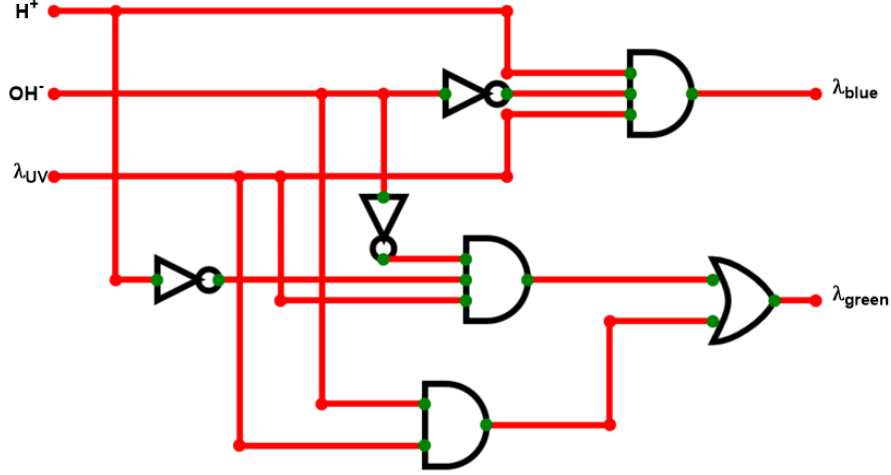


2.8.3

- (a) Region A is the fluorophore and region B is the linker. Region C is the photoreceptor. This is because region C has a pyrene and a carbonyl group so the chromophore attached to the pyrene isn't that well conjugated so we expect the absorbance of this region in UV. However, because A is well conjugated, it absorbs in the visible region.
- (b) In basic medium, the proton in the fluorophore is abstracted and thus, the photosensor and the fluorophore come in close proximity to show FRET and thus, display a blue colour

When Fe^{3+} is added, it coordinates between the ring such that the two rings are close together and cause FRET. However, some Dexter electron transfer can also occur leading to a decreased intensity. EDTA chelates the iron, restoring the green colour.

- (c) Number of units increases the distance between photosensitizer and fluorophore resulting in the colour remaining green.
- (d) The logic gate is as follows:



2.9 Hamiltonian

2.9.1

Using the given Schrodinger's equation for the multi-electron system, the Hamiltonian can be written as

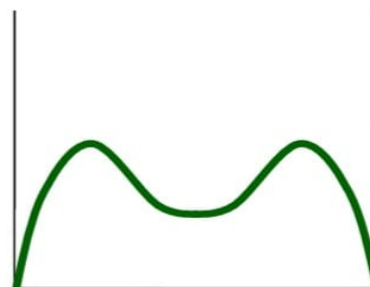
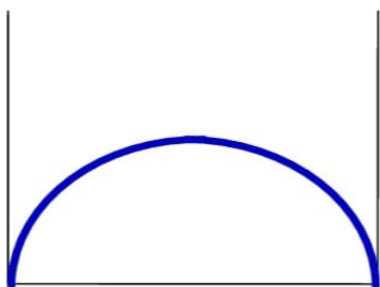
$$H = \left(\sum_{i=1}^n \left(-\frac{1}{2} \nabla_i^2 + v_{ext}(r_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right)$$

Substituting the above expression for Hamiltonian, the expectation energy can be calculated as shown below :

$$\begin{aligned}
 E &= \psi(r_1, r_2, \dots, r_n) | H | \psi(r_1, r_2, \dots, r_n) \\
 &= \phi_1(r_1), \phi(r_2), \dots, \phi(r_n) | H | \phi_1(r_1), \phi(r_2), \dots, \phi(r_n) \\
 &= \sum_{i=1}^n (\phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i + \phi_i | v_{ext}(r_i) | \phi_i) + \frac{1}{2} \sum_{i \neq j} \phi_i \phi_j | \frac{1}{r_{ij}} | \phi_i \phi_j \\
 &= \sum_{i=1}^n \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i + \sum_{i=1}^n \int \phi_i^*(r) v_{ext} \phi_i(r) + \frac{1}{2} \sum_{i \neq j} \int \frac{\phi_i^*(r) \phi_j^*(r') \phi_i(r) \phi_j(r')}{r - r'} dr dr' \\
 &= \sum_{i=1}^n \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i + \int v_{ext} \rho(r) dr + \frac{1}{2} \sum_{i,j} \int \frac{|\phi_i(r)|^2 |\phi_j^*(r')|^2 - |\phi_i(r)|^2 |\phi_i(r')|^2}{r - r'} dr dr' \\
 &= \sum_{i=1}^n \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i + \int v_{ext} \rho(r) dr + \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} dr dr' - \frac{1}{2} \sum_{i=1}^n \iint \frac{|\phi_i(r)|^2 |\phi_i(r')|^2}{|r - r'|} dr dr'
 \end{aligned}$$

2.9.2

The approach described does not consider instantaneous correlation between electrons into account since we treat interactions in an average way (mean-field approximation).



Distribution obtained using Mean Field Approximation

Expected Distribution

2.10 Spectroscopy and Green House Effect

- (a) Despite having no net dipole moment, due to the possibility of asymmetric stretching of CO_2 , it is IR active.
- (b) Energy absorbed by 1 molecule: $hc\bar{\nu}$
Energy absorbed by 1 mole: $N_A hc\bar{\nu}$

Case-1: Neglecting vibrational degree of freedom,

Degree of freedom of CO_2 : $3+2 = 5$

So, change in temperature, $\Delta T = \frac{2N_A hc\bar{\nu}}{5R}$

Final temperature, $T = 298\text{K} + \Delta T = 1286\text{K}$

Case-2: Considering vibrational degree of freedom as a constant

Degree of freedom of CO_2 : $3+2+3\times 3 - 5 = 9$

So, change in temperature, $\Delta T = \frac{2N_A hc\bar{\nu}}{9R}$

Final temperature, $T = 298\text{K} + \Delta T = 847\text{K}$

Note: In this question, the process conditions (constant volume) were missing, also the degree of freedom was supposed to be assumed constant. But marks were awarded if the participants had assumed any other conditions.

- (c) The temperature will be 0.03% of the change in part (b).
- (d) If the gas is van-der Waal, the heat capacity will change and the temperature change will depend on the process conditions. Eg: For an isochoric process the temperature change is same for both ideal as well as van der Waal gas. However, this is not the case for other thermodynamic processes.
- (e) Since humans are more relative to plants, one obvious solution is to plant more

trees. Along with that we should look for alternative methods to decrease the use of sources that emits too much CO₂. Moreover, steps should be taken to curb deforestation, etc. etc.

3 Tie breaker

Since Cobalt stabilises beer foam, it causes cardiomyopathy.
(rest of the answer was judged based on the answers given)