Outline of the solution to Problem 1: How to be a good host

10 marks

17 August, 2020

1 Trends

General trend – Down every column, the value of $\log K_{11}$ increases, reaches a peak value, then decreases. Other visible trends:

- Along each row the value of $\log K_{11}$ for potassium ion is the maximum.

- The changes in the values of $\log K_{11}$ are relatively abrupt for ammonium ion.

- The peak comes later as the size of the cation increases.

2 The host

It is an N-pivot <u>lariat</u> aza-crown ether (except for R = H, which is not a lariat ether)

3 Thermodynamic explanation of changes in the value of $\log K_{11}$

Enthalpic changes are caused due to:

- Electrostatic interactions between the cations and the O atoms of the crown ether and the arms (R groups) of the lariat ether.

- Hydrogen bonding between the H atoms of the ammonium ion and the O atoms of the ether.

- Solvation of the cations and the ether residues of the R group by the solvent methanol.

- Conformational changes due to complexation.

Entropic changes are caused due to:

- Desolvation upon complexation

- Conformational flexibility of the crown and loss of degrees of freedom on complexation

4 Explanation of trends

4.1 General trend-

When R=H, the only interaction is the ion-dipole interaction between the cations and the O atoms of the crown or H-bonding between the H atoms of ammonium ion with the O atoms of the crown. As the N of the aza-crown is substituted, the ether groups of the R interact with the cations and confer stability leading to negative enthalpy change. When R has three arms there are two possibilities: the first and second interact, and the third does not, which is not a problem. The second possibility is that the first and third arms interact, and the second one is bent, which is unstable due to steric hindrance. The two possibilities are probabilistic. So as the number of arms increase, the steric C-C or O-O repulsions increase leading to lower binding constant values.

4.2 Along each row the value of $\log K_{11}$ for potassium ion is the maximum-

The K^+ ion has just the optimum size for the 18 crown 6 ether. Thus, the complexation of potassium ions will have the lowest conformational strain (the sodium and calcium ions are smaller, and thus the conformational strain to ensure a good fit will be higher)

4.3 The changes in the values of $\log K_{11}$ are relatively abrupt for ammonium ion-

The tetrahedral shape of the ammonium ion leads to anisotropic interactions. Thus, the different orientations will have different energies, which leads to greater population variation in these microstates, and thus a decrease in entropy when compared to the metal cations which are isotropic as they are spherical charge distributions. Also, as the number of arms of the substituent increases, the number of ether groups increases which leads to a greater degree of hydrogen bonding with the hydrogens of the ammonium cation.

4.4 The peak comes later as the size of the cation increases-

The smaller cations (sodium and calcium) are able to move around slightly in the binding cavity for proper orientation with respect to the -R substitution, hence the optimum complex stabilization energy is maximized for a smaller -R group. K^+ and NH_4^+ ions have a better fit due to larger size and thus reach the peak value later.

Only explanations to **general trends** have been given. Certain specific trends require a more involved discussion.

Outline of the solution to Problem 2: Not a bed of roses
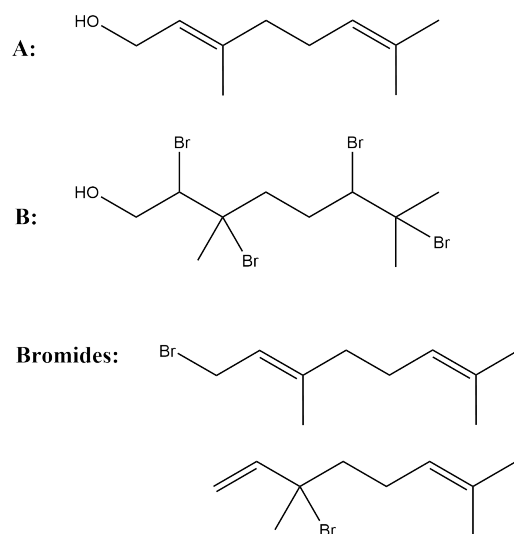
10 marks

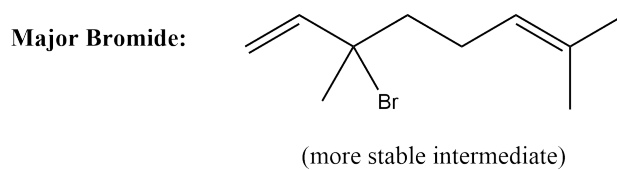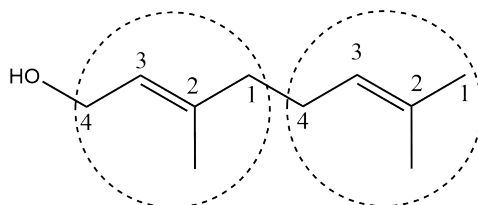## 21 August, 2020

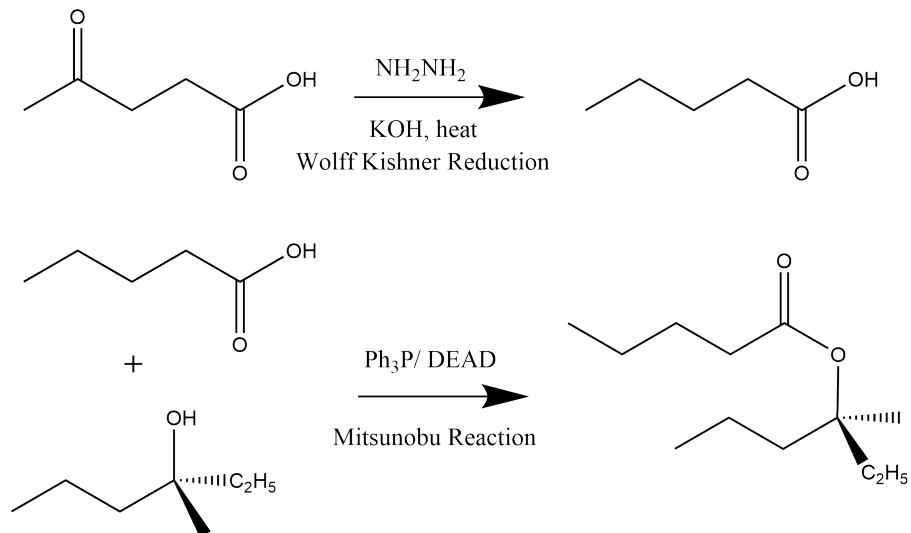Figure 1: Part a
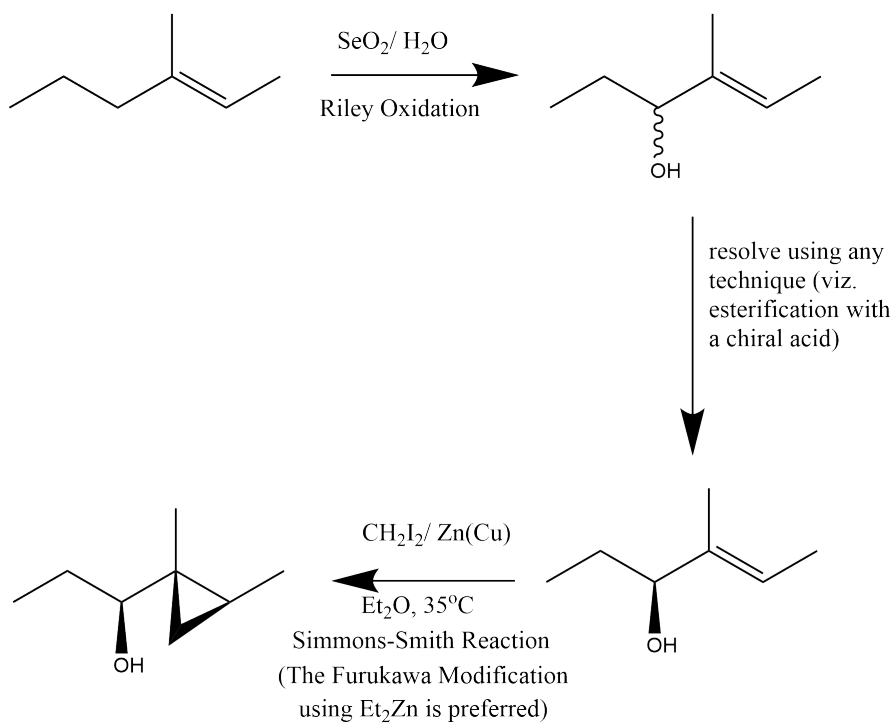

Figure 2: Part b

Figure 3: Part c

Figure 4: Part d

Figure 5: Part e

2

Outline of the solution to Problem 3: A case of catalysis

10 marks

24 August, 2020

Two main reasons for greater yield of (i) as compared with (iii) are suggested below:

1. The role of the dienophiles:
   (A) is a stronger dienophile due to presence of an electron withdraw group while (B) is a significantly weaker dienophile.

2. The role of MV:

   (a) The MV is involved in encapsulation of the two reactant molecules as guest and aids in achievement of proper orientation for the cycloaddition reaction. It further potentially stabilizes the transition state for the reaction.

   (b) The major contribution to the driving force for encapsulation is the stability provided to the guest molecules by $\pi - \pi$ interaction with the aromatic walls of the ligand. Thus, dienophile (A) is greatly stabilized by this interaction while (B) which does not have an aromatic substituent. Further, the non-planar cyclohexyl moiety which rotates freely about the C-N bond provides an additional orientational disorder which disallows proximity of the maleimide to the ligand walls in many orientations. Ultimately, incorporation of (B) inside MV is greatly affected.

To quantify the effect of dienophile strength on the yield, reactions (ii) and (iv) may be inspected –the yield ratio (ii) : (iv) is 1.25. So, the strength of the dienophile has quite a weak influence on the yield of the reaction (Reason 1 above).
In contrast, the yield ratio (i) : (iii) is 2. The dienophiles used are the same, so the much higher increment in yield must be attributed to the presence of MV and more stabilizing interactions with the substrates in reaction (i) (Reason 2 above). Another way to look at it would be to observe the yield ratios (i) : (ii) = 9 and (iii): (iv) = 5.6. This indicates that the increase in yield due to presence of the catalyst is much greater for reactant (A) than (B) (Reason 2 (b) above).
The above line of reasoning goes to establish that Reason 2 above plays a much stronger role than Reason 1 in the discrepancy in yields of reactions (i) and (iii).

Outline of the solution to Problem 4: It is in your blood

10 marks

3 September, 2020

1.

   (a) O_2^{2+} has high stability but low persistence.

   (b) (Fe(TPP)(2-MeIm) - TPP forms the porphyrin plane (albeit with a little doming which we can ignore) and 2-MeIm
   O_2^{2+} is expected to bind in <u>linear mode</u> to this complex

   (c) MO for the linear and perpendicular binding mode are as follows:
   For O_2^{2+} as there are no electrons in the antibonding orbitals of both linear and perpendicular
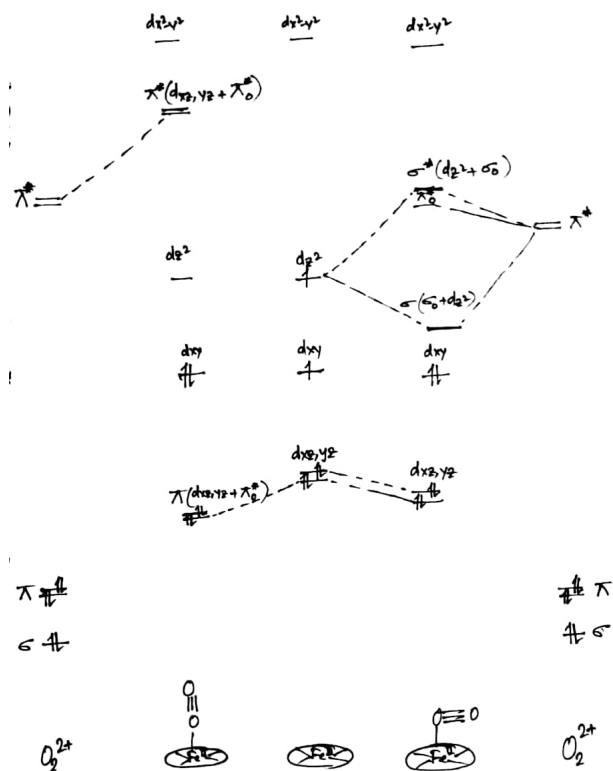

Figure 1: MO for the binding modes

   modes of binding, both may seem possible. But, since the linear mode maximizes metal to ligand
   pi bonding, the linear mode is the preferred mode of binding. This case is exactly analogous to the
   linear binding of CO to hemoglobin as CO is isoelectronic with O_2^{2+}.

2. No dimerization occurs forming $(FeP)_2$ O dimers.

In Fe-protoporphyrin complex IX the following reactions occur due to the absence of the steric bulk imposed by globin chain
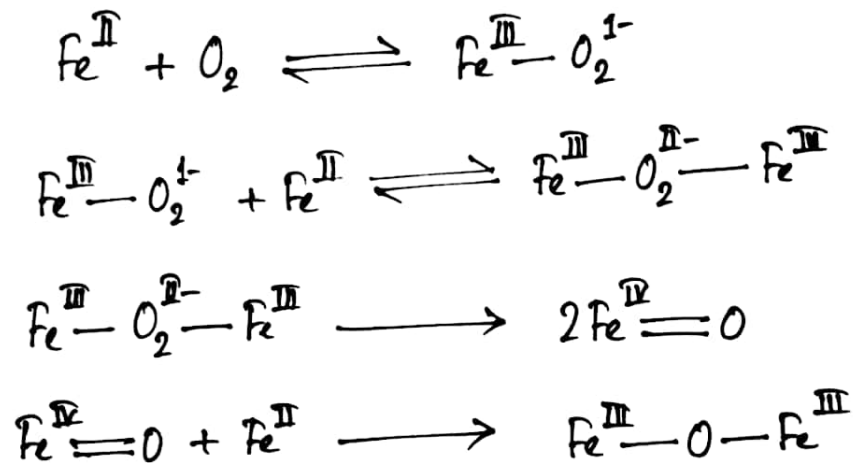
$$Fe^{II} + O_2 \rightleftharpoons Fe^{III} - O_2^{1-}$$

$$Fe^{III} - O_2^{1-} + Fe^{II} \rightleftharpoons Fe^{III} - O_2^{2-} - Fe^{III}$$

$$Fe^{III} - O_2^{2-} - Fe^{III} \longrightarrow 2Fe^{IV} = O$$

$$Fe^{IV} = O + Fe^{II} \longrightarrow Fe^{III} - O - Fe^{III}$$

Figure 2: Reaction sequence

3. Dimerization occurs through the double bonded oxenoid moiety obtained in reaction 3 above. In the case of Co-protoporphyrin complex, the doubled bonded oxenoid species will have one electron in the antibonding orbital as Co^{2+} is a d^7 species. Thus, the oxenoid species will be formed less due to
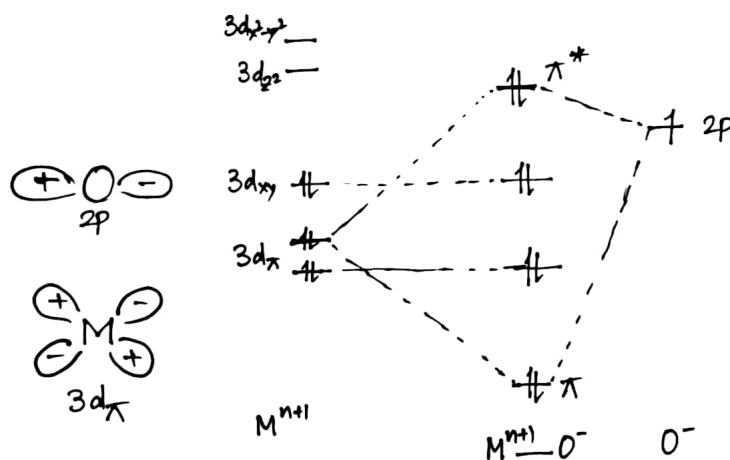

Figure 3: Orbital diagram showing stabilities of M–O species

instability and thus this complex is more likely to carry oxygen than iron protoporphyrin complex. The binding mode of NO to this complex will be perpendicular as the linear mode has an electron in the antibonding orbital. The bent mode may also be possible.
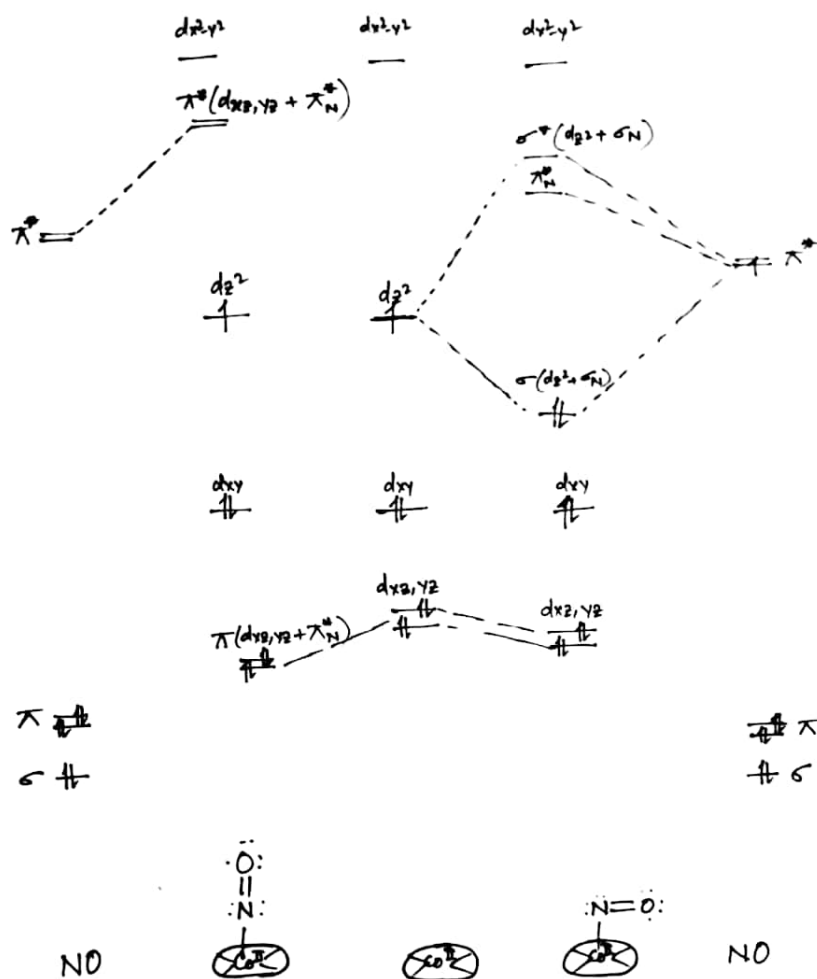
Figure 4: MO diagram for various modes in Co

Outline of the solution to Problem 5: A race to racemize
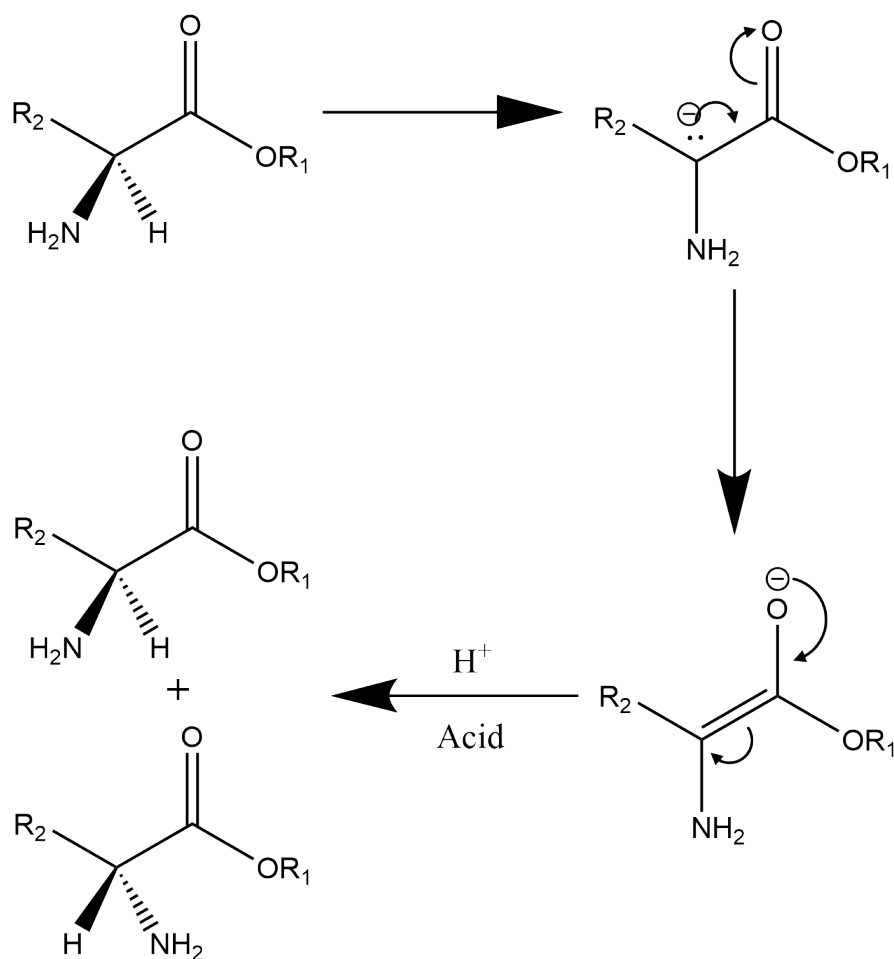
10 marks

5 September, 2020

Figure 1: Mechanism for racemization reaction

1.   i Serine has electron withdrawing -OH group which stabilizes the carbanion transition state

       ii When unsubstituted, the -COOH moiety loses the proton and has more cross conjugation. The substitution of the carboxylate moiety decreases cross conjugation and thus the carbanion transition state is stabilized.

2. $L \rightleftharpoons D$

   Rate constant for forward reaction $k_1 = 5.1 \times 10^3$

   Rate constant for forward reaction k_2

   $\frac{D}{L} = \gamma_0$ before boiling, γ_b after boiling, γ_{hK} after hydrolyzing the king, γ_{hQ} after hydrolyzing the queen. Then,

$$ln\left(\frac{1 + \gamma_{hK}}{1 - \gamma_{hK}}\right) = ln\left(\frac{1 + \gamma_{hQ}}{1 - \gamma_{hQ}}\right) + 2k_1 t_{boil}$$
$$= ln\left(\frac{1 + \gamma_{hQ}}{1 - \gamma_{hQ}}\right) + ln\left(\frac{1 + \gamma_b}{1 - \gamma_b}\right)$$

$$\therefore ln\left(\frac{1 + \gamma_b}{1 - \gamma_b}\right) = 2 \times 5.1 \times 10^3 \times t_{boil} \tag{1}$$

3. $L \rightleftharpoons D$

   $k_{conv} = 1.38$

   Rate constant for forward reaction $k_1 = 9.02 \times 10^{-5}$

   $\therefore$ Rate constant for forward reaction $k_2 = 6.536 \times 10^{-5}$

   $x_0 = [L]_0 - [L]_{eq} = 1 - [L]_{eq}$

   After boiling, $x_t = [L]_t - [L]_{eq} = x_0 e^{-(k_1 + k_2)t}$

   At equillibrium, $\frac{[D]_{eq}}{[L]_{eq}} = \frac{[L]_0 - [L]_{eq}}{[L]_{eq}} = k_{conv} = 1.38$

   $\Rightarrow L_{eq} = 0.42$

   $x = x_0 e^{-(k_1 + k_2)t} = 0.429$

   $d_e = 69.8\%$

4. $\frac{L_0}{L_t} = k_1 t; [L]_t = [L]_0 + [D]_t$

   d_e before boiling $= 100\%$

   d_e after boiling $= 67.8\%$

Outline of the solution to Problem 6: A shiver down the spine-l

10 marks

11 September, 2020

1. A^{2+} in Tetrahedral sites = xv
   B^{2+} in Tetrahedral sites = yv
   A^{2+} in Octahedral sites = (1-d-x)v
   A^{2+} in Octahedral sites = (d-y)v
   C^{3+} in Tetrahedral sites = (1-x-y)v
   C^{3+} in Octahedral sites = (1+x+y)v
   Thus,

$$W = \frac{[(1-d)v]!}{(xv)![(1-d-x)v]!} \times \frac{(dv)!}{(dv)![(d-y)v]!} \times \frac{(2v)!}{[(1-x-y)v]![(1+x+y)v]!}$$

2. (a) $A + (B) \rightleftharpoons (A) + B$
   $$K = \frac{x}{(1-x)(2-x)}$$

(b)

$$\Delta G^\circ = -RTlnK$$
$$lnK = -\frac{\Delta G^\circ}{RT}$$
$$= -\frac{(\Delta H^\circ - T\Delta S)}{RT}$$
$$lnK = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

From the graph, $\frac{\Delta S}{R} = 0$
Thus, entropy for non-configurational changes = 0

(c) $\Delta S = -R[xlnx + (1-x)ln(1-x) + xln(\frac{x}{2}) + (2-x)ln(\frac{1-x}{2})]$

3. Normal spinel structure
   $Co^{3+} \rightarrow$ Low spin in octahedral field and high spin in tetrahedral field. But low spin d^6 confers additional stabilization in octahedral site.
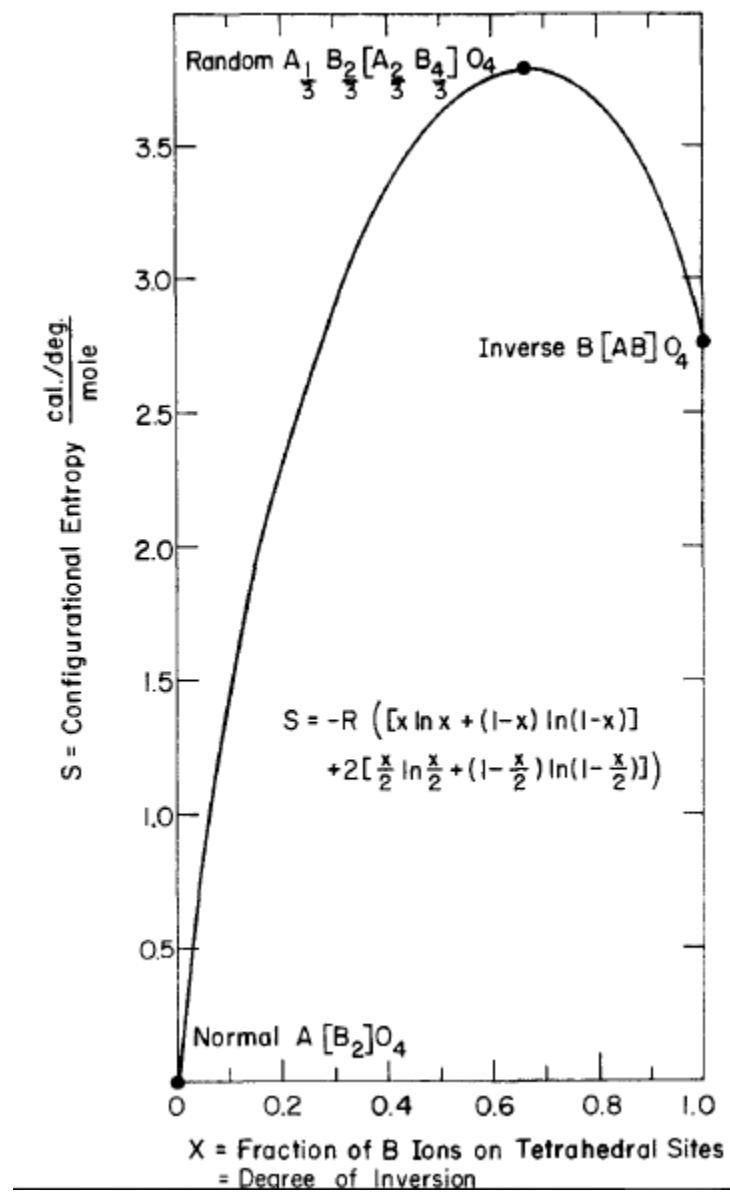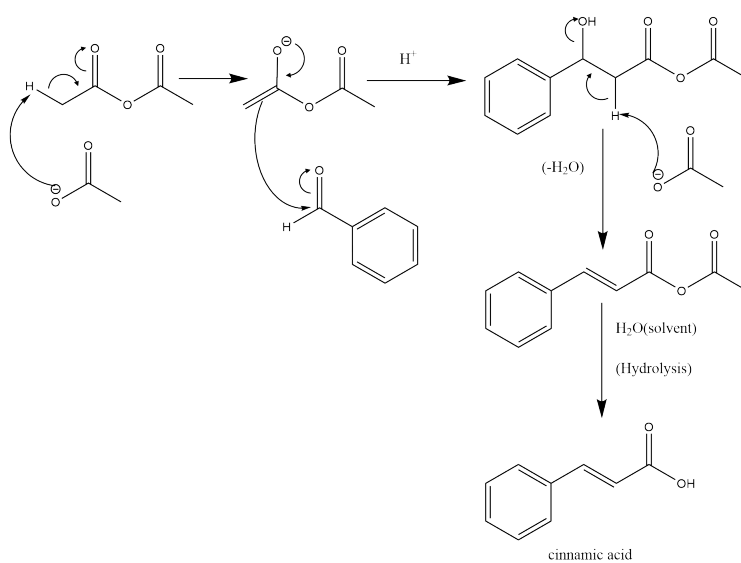
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Figure 1: Entropy v/s degree of inversion

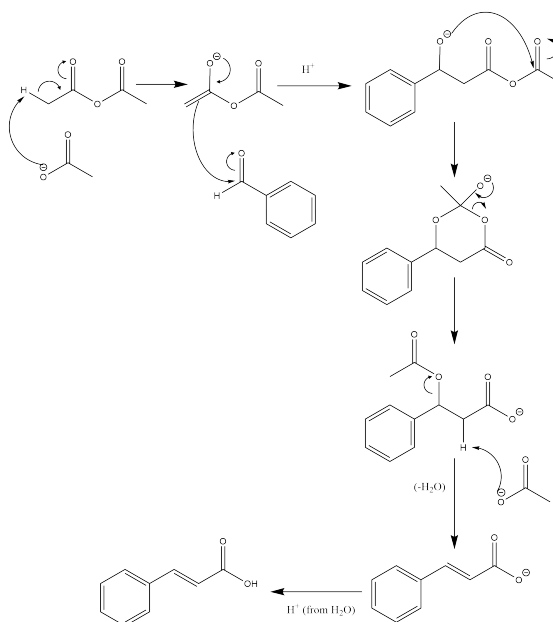# Outline of the solution to Problem 7: Almonds, Cinnamon, and everything in between
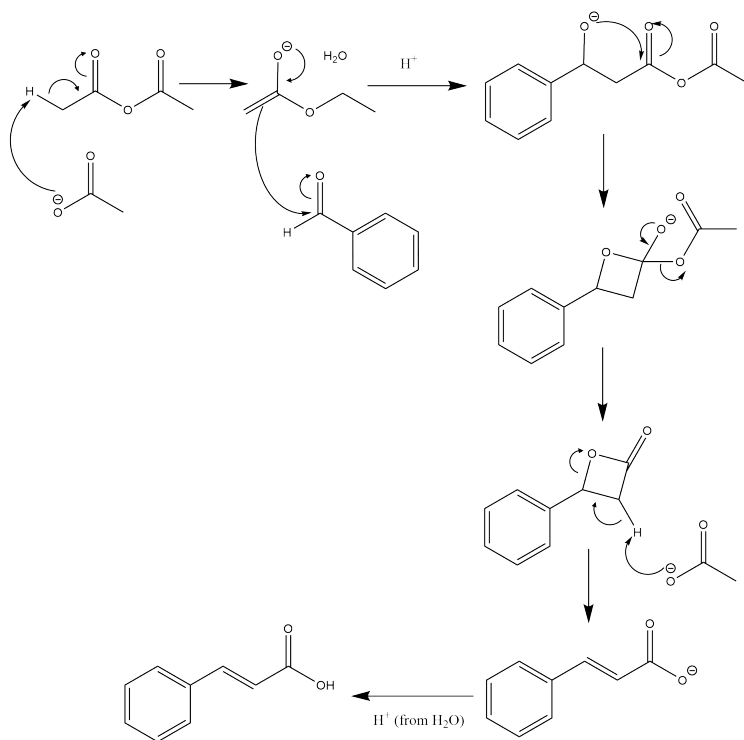
10 marks

14 September, 2020

1.
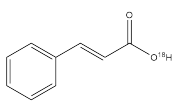

cinnamic acid
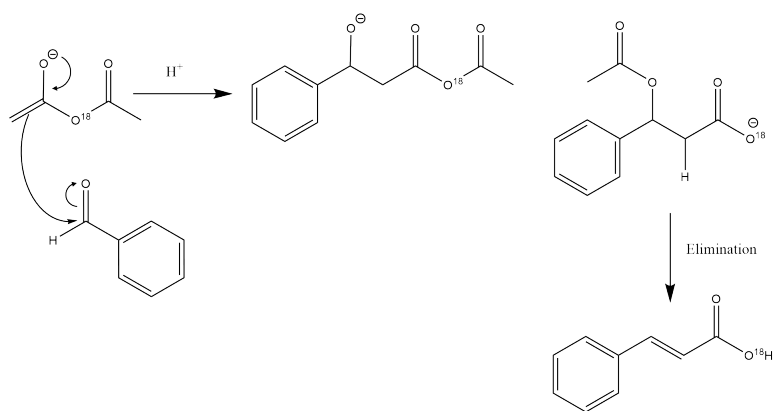
Mechanism A

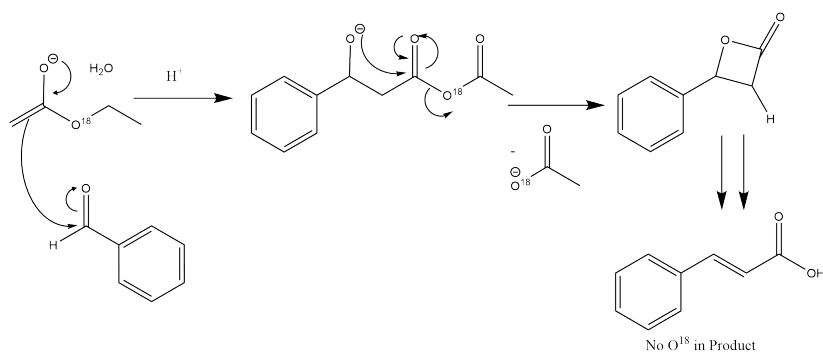Mechanism B

Mechanism   C

Now, in the first mechanism, we see the hydrolysis at the end that means if H_2O^{18} is

used as the solvent we'll get   as the product; as the H_2O^{18} attacks the anhydride to generate the acid in the proves of hydrolysis. So, Mechanism A can be rejected as no O^{18} was seen in the project

2.   Mechanism   B

Mechanism   C

Thus, Mechanism C can be rejected.

3. Combining these two, Mechanism B is the most suitable one. Step has been shown previously.

4. In this case, the reaction will stop after Acyl transfer since no elimination is possible due to   lack   of   hydrogen.