

Chemenigma 2021

Outline of Solutions

July 25, 2021

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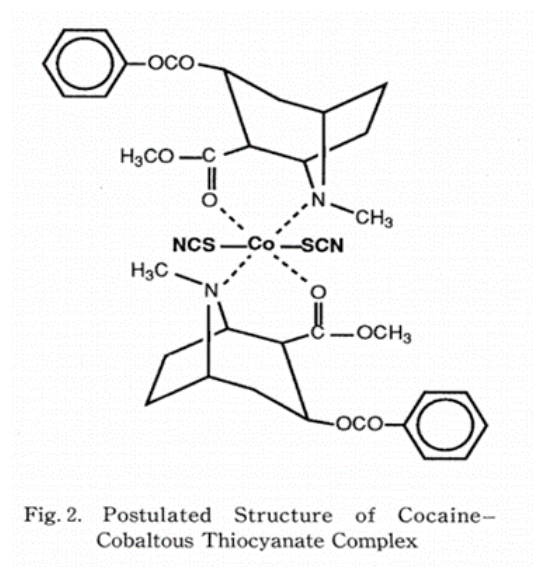
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1 Short Answer Questions

1.1

(a) Spoiler alert:Compound A is Cocaine,Test: Scott's Test



Easy to see that two SCN in cis will be sterically hindered due to large cocaine ligands. 6 - membered ring can only be formed with the ester carbonyl and not benzoxy group.

(b) Compound B can possibly form a similar complex acting as bidentate ligands forming 6 membered chelate rings using the two Nitrogen atoms (and similarly for C). Notably, there are several drugs that can give false positives in Step 1, but performing all 3 steps increases the specificity of the test.

Compound D lacks the methyl ester group present in cocaine and thus cannot form 6 membered chelate ring (Other carbonyl is too far away). This also shows that the methyl ester is necessary for complex formation whereas the role of benzoxy group is probably negligible.

(c) Adding hot aqueous NaOH would not only lead to neutralisation of the salt, but also saponification of the two ester groups. But since the carbonyl of the methyl ester group remains with the compound, we can predict that the resultant solution would still give a complex.

Reference : <https://doi.org/10.1248/jhs1956.41.274>

1.2

A is transplatin. The mass ratio suggests that molar ratio of A : $\text{H}_2\text{C}_2\text{O}_4$ is 1:2. X is $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$. If A was cisplatin, oxalato would act as bidentate ligand and only one molecule will be required. But since A is transplatin, it cannot form a chelate, it acts as monodentate ligand, and 2 molecules occupy trans positions.

B is cisplatin. On reaction with one molecule of $\text{S}_2\text{O}_2^{3-}$, the 2 cis Cl^- get replaced by bidentate $\text{S}_2\text{O}_2^{3-}$ ligand. The NH_3 groups are labilised by the strong trans-effect of the chelated $\text{S}_2\text{O}_2^{3-}$. $[\text{Pt}(\text{NH}_3)_2(\text{S}_2\text{O}_3)]$ readily reacts with the excess $\text{S}_2\text{O}_2^{3-}$ to produce $[\text{Pt}(\text{S}_2\text{O}_3)_2]^{2-}$ through the substitution of NH_3 groups. But in case of transplatin the NH_3 groups will be cis to the $\text{S}_2\text{O}_2^{3-}$ ligand and will not get easily substituted even on addition of excess $\text{S}_2\text{O}_2^{3-}$.

1.3

Solution:

Co^{2+} is d^7 system in high spin, 2 paired, 3 unpaired electrons in linear, tetrahedral, and octahedral.

Co^{3+} is d^6 system. 1 paired electron in linear (sp), 2 paired in square planar (dsp^2), and 3 paired in octahedral (d^2sp^3).

So Co^{2+} forms 3 complexes in 2:2:2 ratio and Co^{3+} forms in 6:3:2 ratio (inversely proportional, so $1 : \frac{1}{2} : \frac{1}{3}$).

1 mole of Co^{2+} binds with avg 4 mol water (2:2:2 ratio of 2, 4, and 6)

1 mole Co^{3+} binds with avg 3.3 mol water (6:3:2 ratio of 2, 4, and 6)

If there are x mole Co^{2+} and y mol Co^{3+} ,

$$\begin{aligned} x \times 4 + y \times 3.3 &= \frac{80.49}{18} \\ x \times (59 + 96) + y \times (59 + 1.5 \times 96) &= 182.84 \end{aligned}$$

Solve simultaneous equations to get x and y.

$$\begin{aligned} x &= 1.1052 \\ y &= 0.01255 \end{aligned}$$

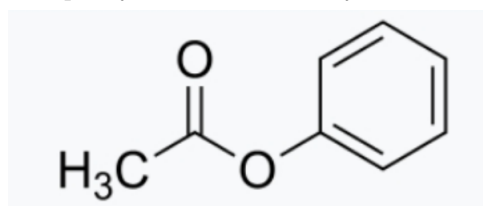
percentage Co^{2+} is $\frac{x}{x+y} \times 100\%$

Due to technical error leading to ambiguity in the term "spin energy", any reasonable interpretation of spin energy and calculations have been awarded marks

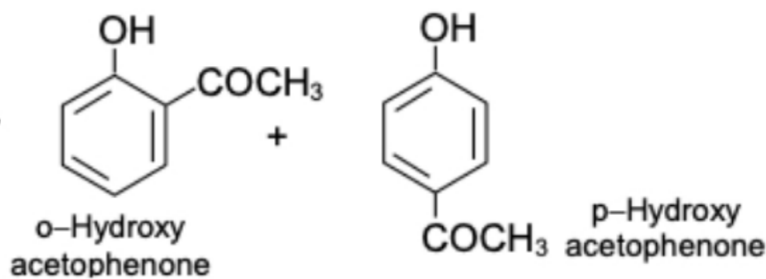
1.4

Since X gives violet colouration with FeCl_3 , we infer that it has a phenolic-OH group, and since Phenol itself has a MM of 94 u, X must be phenol.

Y is phenyl acetate formed by esterification.



The reaction mentioned then in the Fries rearrangement which uses Lewis acid catalysts like AlCl_3 and the products are:



Ortho - Intramolecular H bond

Para-Intermolecular H bond

The most downfield proton in both is the one in the -OH group. For dilute solutions, if we increase temperature, intermolecular H bonds are broken, and thus chemical shift of that proton is altered. (More H bonding generally causes peak to move downfield due to deshielding)

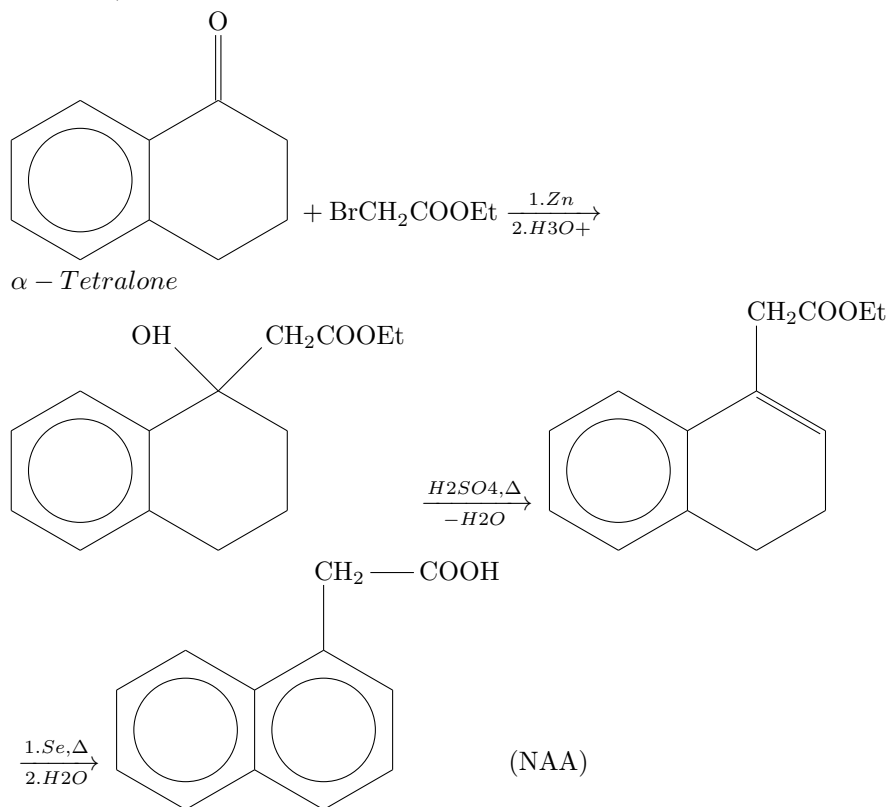
However, on the other hand, temperature won't have a significant impact on intramolecular H bonds, the chemical shift plot will be more stable. (Also the solvent is CCl_3 which doesn't form any H bond of its own). Thus both plots will have a negative slope and:

A -> small slope -> intramolecular H bonds -> ortho product

B -> large slope -> intermolecular H bonds -> para product

1.5

Option b)



1.6

(d) Dodecahedron

Notation - (Faces, Vertices, Edges)

(12,20,30) on capping becomes (60,32,90) on constructing pyramids, as there will be 5 faces in the new polyhedron on each pentagonal face (5xFaces) and one more vertex for each face (Faces + Vertices), which then becomes (32,60,90) on dualization. C_{60} has 60 vertices.

1.7

X, in its gaseous form, behaves ideally. Furthermore, we have a single mole of X, and compression is isothermal.

$$\text{So, } \Delta\mu_{(g)} = \int d\mu_T = \int_{p_1}^{p_2} V_{m(g)} dP = \int_{p_1}^{p_2} \frac{RT}{P} dP = RT \ln \left(\frac{p_2}{p_1} \right)$$

$$\Delta\mu_{(l)} = V_{m(l)} \Delta P = V_{m(l)} (p_2 - p_1)$$

$$\text{Now, } 10\Delta\mu_{(l)} = \Delta\mu_{(g)} \Rightarrow V_{m(l)} = \frac{RT \ln\left(\frac{p_2}{p_1}\right)}{10(p_2 - p_1)}$$

Answers, with or without substituting T, have been evaluated.

1.8

No. The Zero Point Energy is that of the entire molecule and not limited to a particular bond and the sum of energies of all the bonds in the molecule (here, hexane) is necessarily greater than the ZPE of the molecule. Further, the ZPE of the spectator vibrational modes are “inactive” in the dissociation reaction – only energy exceeding this may be converted from the vibrational motion to the motion along the reaction (here, dissociation) path.

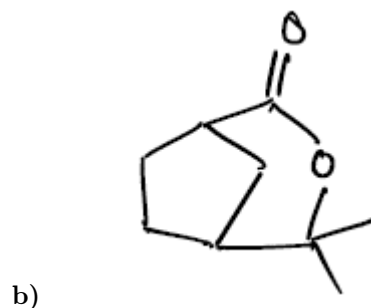
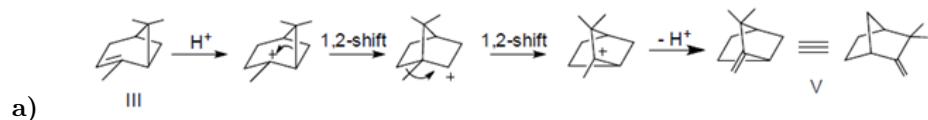
For more information, refer to:

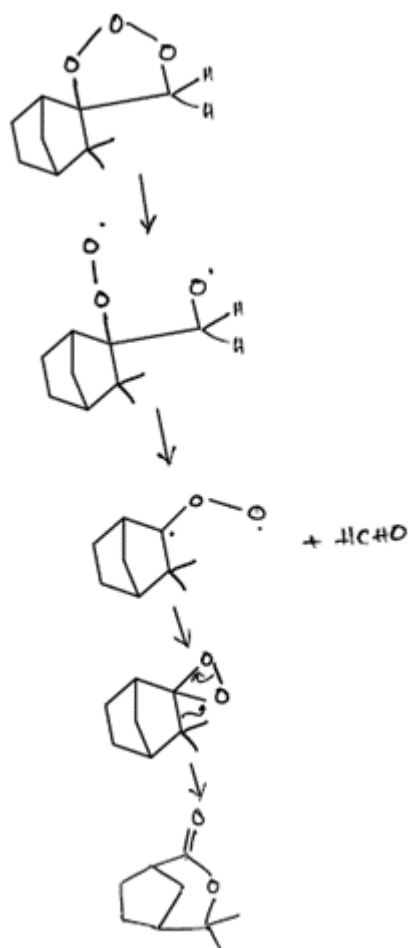
- Errol Lewars, Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics.
- György Lendvay, in Comprehensive Chemical Kinetics, 2019

2 Long Answer Questions

2.1 A Little Bit of Everything

2.1.1



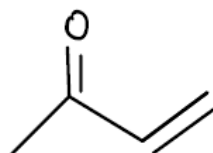


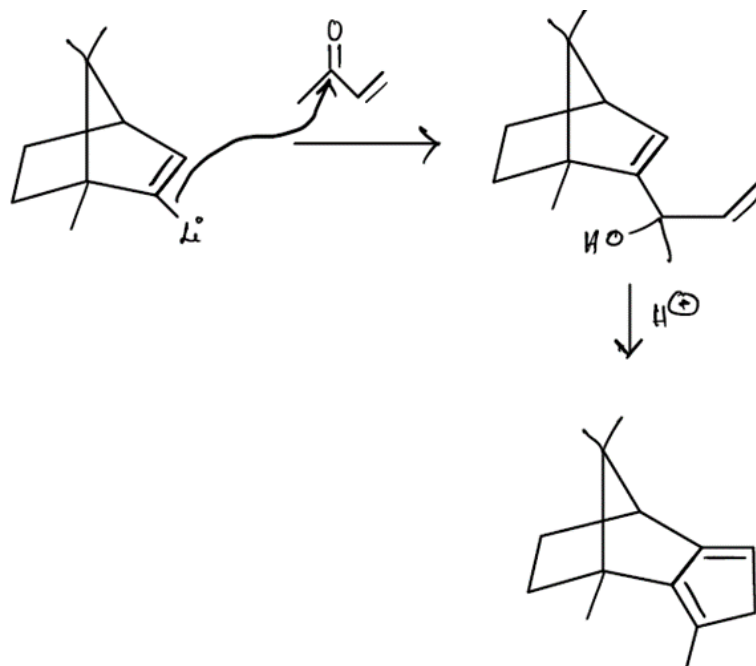
Mechanism:

So, camphor is not formed.

2.1.2

C_4H_6O -



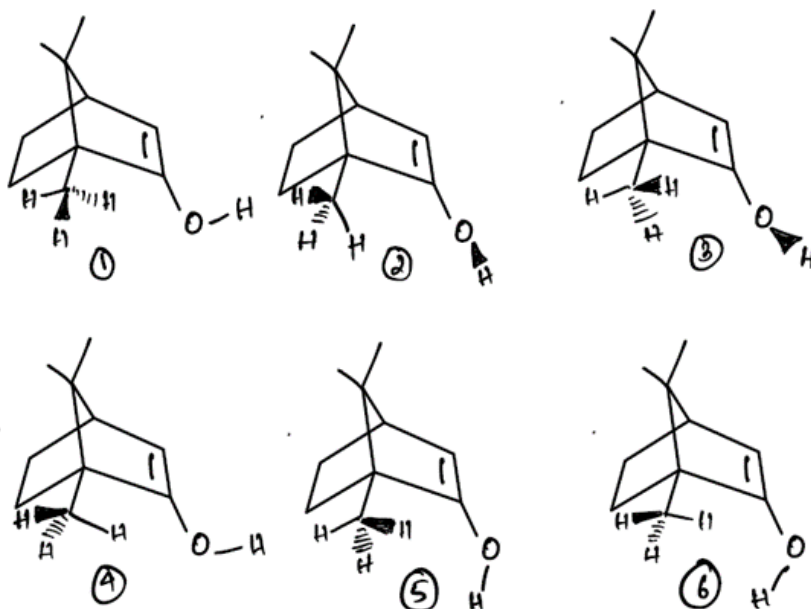


Mechanism:

2.1.3

Technique to be used - EPR spectroscopy $I_{Cl} = \frac{3}{2}$, let, I_x be x Calculate number of lines using the formula $\prod_{i=1}^3 (2NI + 1)$ where, N is the number of atoms of the species. The number of lines in the spectrum will be different for the two complexes.

2.1.4



Conformer 1 has the lowest energy.

2.2 Shine Bright Like a Pervoskite

2.2.1

(a) E: Ethylenesiaminetetraacetic acid (EDTA)

G: (reduced) L-Glutathionate

Function: They remove the uncoordinated Pb^{2+} from the crystal. In particular, they remove the ions from the surface which are not fully coordinated

(b) An essential point to note here is that E+G undergoes *intermolecular hydrogen bonding*. This improves its efficiency and hence promotes higher binding energy compared to application E or G alone.

2.2.2

(a) The type of Crystal defect is *Frenkel defect*. Note that ions migrate locally within the crystal. This is characteristic of Frenkel defects

(b) The uncoordinated Pb^{2+} ions promote the formation and stabilisation of Frenkel defects. With their removal, the formation of Frenkel defects is disfavoured and stability is improved. Any logical thermodynamic explanation based on crystal defect formation and stability also considered.

2.2.3

(a) Equation of Energy of 3 dimensional particle of given Cubical “box”: $\frac{3h^2}{8m_e L^2}$
Length of Box: Diameter of Iodide + Diameter of Lead anion (In essence it is I-Pb-I, so Radius of I^- + Diameter of Pb^{2+} + Radius of I^-) = 6.42\AA

Energy released: $E = \frac{hc}{\lambda} = 2 \times \frac{3h^2}{8m_e L^2}$. Factor of 2 appears due to electron-hole recombination, which by given assumption implies that twice the energy of an electron is released.

Hence: $\lambda = \frac{4cm_e L^2}{3h} = 225\text{ nm}$

This is a much higher wavelength as compared to the red wavelengths expected for MaPbI_3

Inaccuracies:

- Holes have different properties, for example different mobilities and hence different energies
- The central Methylammonium ion is not considered. This can lead to a larger L and hence longer wavelength
- Any other answer which fits in logically with the observed inaccuracy

(b) Radius of Bromide is lesser than Radius of Iodide

Now, $\lambda \propto L^2$, where $L = 2(R_{X^-} + R_{\text{Pb}^{2+}})$, a higher concentration of Bromine in the perovskite would lead to a decrease in the wavelength.

Hence, by controlling the parameter x , we can change the relative concentrations of the two halides, and consequently tune the bandgap

(c) An application is use in Solar Cells.

2.3 Curved Blinders

2.3.1

One of the possible ways :

Any reasonable model is considered

Rough Sketch :

Radius of curvature = r

$$\alpha = 180 - 2\theta$$

We see

$$r \sin \theta = r \sin (180 - 2\theta)$$

$$= 2r \sin \theta \cos \theta$$

$$r = \frac{x}{2 \cos \theta}$$

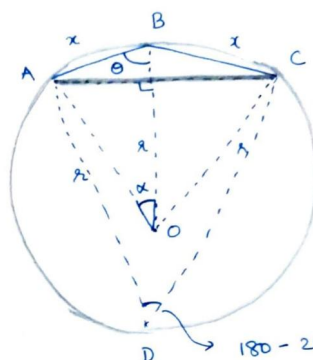
$$r = \frac{x}{2 \cos 72^\circ}$$

$$x \approx [C-C] + [C-C]_{\text{benz}} + 2[C-C]_{\text{benz}} \cos 60^\circ$$

$$\approx [C-C] + 2[C-C]_{\text{benz}}$$

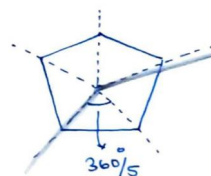
$$\approx 432 \text{ pm}$$

$$r \approx 699 \text{ pm}$$



$$OB = OA \\ = OC = r$$

Assume Furan == Pentagon



$$\text{Divergence angle} = 144^\circ$$

$$\Rightarrow \theta = 72^\circ$$

Rough Sketch: (refer to diagrams above)

Radius of Curvature = r

$$\alpha = 180 - 2\theta$$

We See:

$$x \sin(\theta) = r \sin(180 - 2\theta)$$

$$= 2r \sin(\theta) \cos(\theta)$$

$$r = \frac{x}{2 \cos(\theta)}$$

$$r = \frac{x}{2 \cos(72^\circ)}$$

$$x \approx [C - C] + [C - C]_{benzene} + 2[C - C]_{benzene} \cos(60^\circ)$$

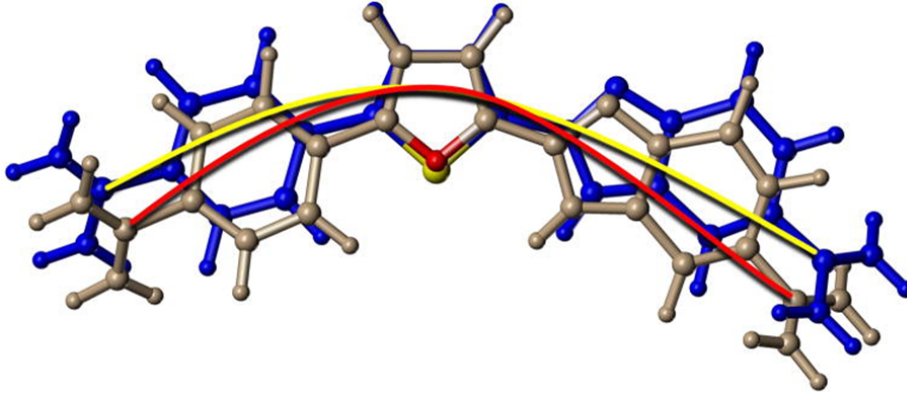
$$\approx [C - C] + 2[C - C]_{Benzene}$$

$$\approx 432 \text{ pm}$$

$$r \approx 699 \text{ pm}$$

2.3.2

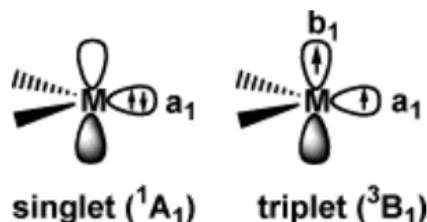
The larger size of sulfur and the resulting bond angle change from thiophene to phenyl, results in an increased radius of curvature for second case. This causes it to flatten slightly and less optimally fit the base pairs in the minor groove.



Reference : [Binding to the DNA Minor Groove by Heterocyclic Dications: From AT Specific Monomers to GC Recognition with Dimers \(nih.gov\)](#)

2.4 The 'p'-riodic Table

-
1. (a) On descending the p-block, the more radially expanded nature of the p-orbitals leads to a reduced overlap integral and weaker bonds, and σ bonds become substantially favored over π bonds. The heavier main-group compounds containing multiple bonds are expected to have much-enhanced reactivity (relative to their carbon analogs) arising from the inherent weakness of these multiple bonds. A common strategy to stabilize these multiply bonded species is the use of sterically demanding substituents to protect low-valent, reactive main-group centers. These bulky groups typically prevent the reactions that lead to formation of σ bond at the expense of π bond (e.g. polymerization or oligomerization of monomeric units; also, attack by nucleophiles or electrophiles). $-\text{Mes}$ group is much more bulkier than $-\text{Me}$ group, leading to kinetic stabilization of the disilene on the left.
 - (b) WLOG we can assume the substituents to be H (i.e. hypothetical scenario). Prior to bonding, we can think of $\text{H}_2\text{M}=\text{MH}_2$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{or Pb}$) to be composed of two MH_2 units. In all MH_2 species with six valence electrons the singlet state has two electrons in an orbital of σ -symmetry (a_1). In the triplet state this electron pair is unpaired and one electron resides in an orbital of π -symmetry (b_1).



A lower electronegativity of M and a higher principal quantum number increase the size of the AOs and lengthen the M–H bonds. This decreases the antibonding character of the $2\sigma_g$ orbital and thus lowers its energy. Since lower electronegativity of M also raises the energy of the $1\pi_{ux}$ orbital, the energy gap between these two MOs is reduced, causing greater mixing between the bent forms (owing to pseudo-JT effect) of the $2a_1$ and $3a_1$ orbitals. More effective mixing stabilizes the $2a_1$ orbital (it also destabilizes the $3a_1$ orbital, which however is empty).

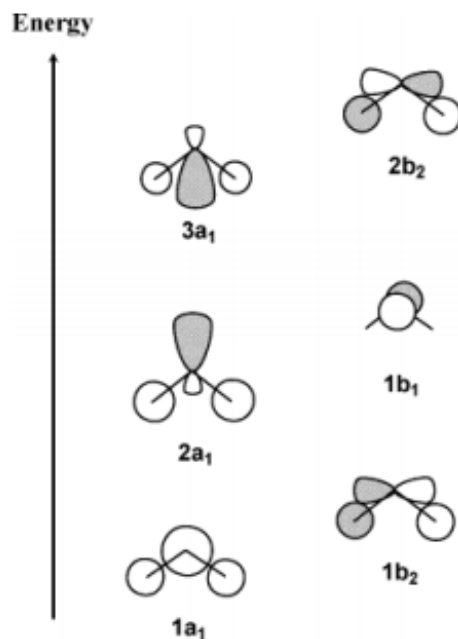


Figure 1. Schematic drawing of the molecular orbitals of MH_2 ($\text{M} = \text{C}, \text{Si}$) molecules.

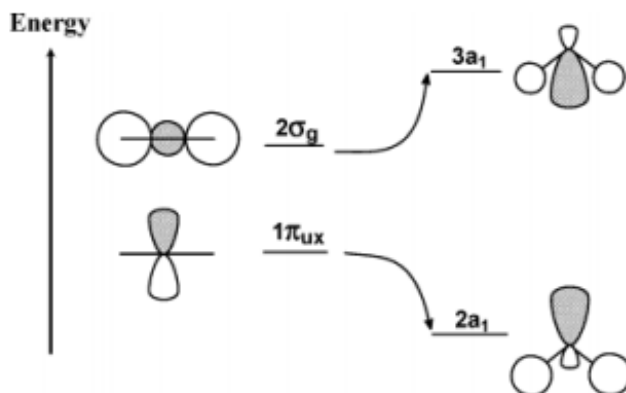
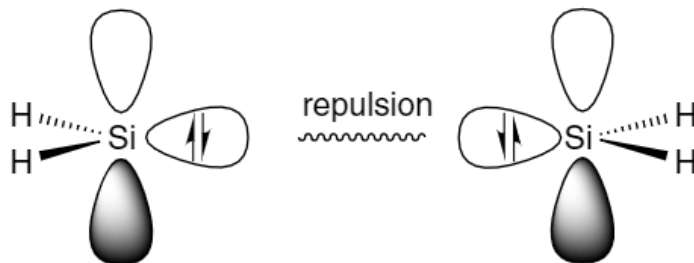


Figure 2. Energy change in the $1\pi_{ux}$ and $2\sigma_g$ orbitals of MH_2 ($\text{M} = \text{C}, \text{Si}$) on going from a linear to a bent geometry.

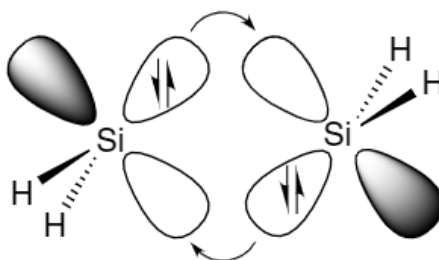
Now, the key point in dictating the energy gap between the $2a_1$ (HOMO) and the $1b_1$ (LUMO) orbitals is the degree of mixing between the occupied $2a_1$ orbital and the empty $3a_1$ orbital. The stronger the mixing between these orbitals, the lower the energy of the $2a_1$ orbital and the higher the $2a_1$ - $1b_1$ energy gap. The extent

of mixing between the $2a_1$ and $3a_1$ MOs is determined by the energy gap between the unmixable MOs of linear MH_2 to which they are related, i.e., the $1\pi_{ux}$ and $2\sigma_g$ orbitals. As $1\pi_{ux}$ and $2\sigma_g$ become closer together, more mixing occurs between $2a_1$ and $3a_1$ and their separation increases, thus stabilizing the $2a_1$ orbital.

This means: HOMO-LUMO gap of EH_2 ($E = \text{Si, Ge, Sn, or Pb}$) is more than that of CH_2 unit. Thus, ground state of the former is more likely to be singlet unlike that of the latter (which is a triplet). As a result, severe repulsion between the closed-shell orbitals of two $:EH_2$ units prevents dimerization, leading to $H_2E=EH_2$ in the planar form. However, the two $:EH_2$ units can form unique double bonds not only elongated to avoid the repulsion but also in trans-bent configuration, where each of $:EH_2$ units donates a lone pair of electrons to an empty p orbital of its bonding partner to form double donor-acceptor bonds:



(a) In-plane structure of $H_2Si=SiH_2$



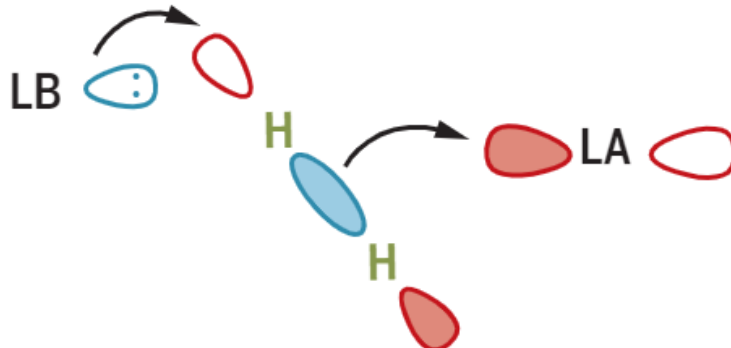
(b) Trans-bent structure of $H_2Si=SiH_2$

Note that single donor-acceptor bond would give a zwitterionic species similar to that in the left shown as hint.

- (c) When the substituents are N,N-difluoroamide groups, the alkene-analog would preferably assume a trans-bent zwitterionic structure because the positive as well as negative charges can be stabilized by delocalization over the mesomerically active substituent.

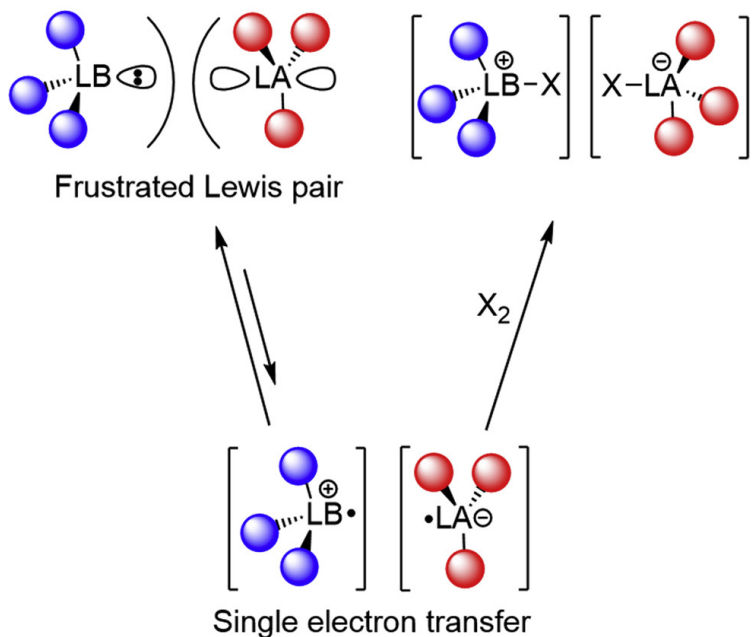
When the substituents are $\text{C}(\text{SiMe}_3)_3$ groups, the alkene-analog would prefer to exist as dialkyl monomeric species (i.e. $:\text{EH}_2$). This species is electron deficient, and the substituents in this case can exert +I effect, leading to stabilization.

2. (a) The activation of dihydrogen by FLP involves synergistic bonding and backbonding interactions of the frontier orbitals, whereby the σ orbital of H_2 donates to a low-lying vacant orbital on the p-block system (typically the LUMO of a Lewis acid), and the highest occupied molecular orbital (HOMO) of the Lewis base component of the p-block system donates to the σ^* orbital (LA = Lewis acid, which here is B; LB = Lewis base, which here is N):



The electron transfer (ET) model assumes that the LA/LB parts initially associate to form a weakly bound pair (also called “encounter complex”), which then interacts with H_2 , and polarizes it in a concerted manner. It is followed by two simultaneous electron transfer processes (as discussed earlier) in a push-pull manner. It results in weakening and subsequent heterolytic cleavage of the dihydrogen bond.

- (b) An alternative mechanism is a homolytic one via SET. The scheme is shown below ($\text{X} = \text{H}$):



- (c) (i) Electron paramagnetic resonance (EPR) spectroscopy may show the existence of unpaired electrons (validating the latter mechanism).
- (ii) Addition of quinones to reaction mixture gives rise to coloured charge transfer complexes if the reaction proceeds via the latter mechanism.
- (iii) If the reaction is driven by the latter mechanism, addition of Ph_3SnH to toluene solutions of the FLP results in an immediate colour change. ^{19}F , ^{11}B , and ^1H NMR spectroscopic data confirms the formation of the known salts $[\text{R}_3\text{NH}][\text{HBR}'_3]$ and $[\text{R}_3\text{NH}][(\mu\text{-H})(\text{BR}'_3)_2]$ respectively. Concurrent with this is the quantitative formation of the di-stannane $\text{Ph}_3\text{SnSnPh}_3$ as demonstrated by the observation of a singlet in the ^{119}Sn NMR spectra. The formation of these products is consistent with radical abstraction of H from the Sn species. This evidence for homolytic cleavage of the Sn-H bond stands in marked contrast to the corresponding reactions of $^t\text{Bu}_3\text{P}$ in which heterolytic cleavage of the Sn-H bond is observed.

- (d) Just like an FLP can perform H-H bond activation, it can also add to a C-C double bond. Thus, the olefin/paraffin mixture is first bubbled through some suitable organic solvent. Then, FLP is added to the resulting mixture. FLP reacts with olefin to form FLP/olefin zwitterionic adduct but paraffin fails to react with FLP. Now, solvent extraction is performed with water as the extracting solvent (note that the zwitterion would be soluble in aqueous phase unlike the paraffin). Later, the FLP/olefin adduct can be dissociated by various physical and/or chemical methods.
3. (a) The receptor (II) would chelate to chloride better. The H of the amino group participates in hydrogen bonding with X atom, mobilizing significant amount of electron density away from the distal end of the C-X bond. This enhances the partial positive charge density at the σ -hole, leading to stronger interaction with the anion.
This effect is more pronounced for iodine (i.e. $X = I$) because it is more polarizable than F, Cl, or Br.
- (b) Yes, the given statement is correct. Pearson's HSAB (i.e. hard-soft acid-base) principle is the key factor here. Both iodine and thiolate are soft moieties.
4. Owing to Se-N ChB, the effective reagent becomes conformationally rigid. In this case, it almost always attacks the substrate from the top face to generate a seleniranium ion (at the top face). Then, the backside nucleophilic attack generates the major product. In absence of the ChB, the crucial C-N bond present in the effective reagent can rotate and as a result, we do not get any impressive diastereomeric excess.
5. H-F bond is very polar and can induce strong dipole in a neighbouring Ne atom. This dipole-induced dipole interaction (which is a secondary chemical bond) gives rise to the entity HNeF. It is a Van der Waals compound, and not a true chemical compound.

2.5 This is 'Gibb'-erish

Solution is on the next page

2.5.1

This is solved using a reversible path:

263 K to 273 K – heat water (1)

273 K – freeze water (2)

273 K to 263 K – cool ice (3)

Now,

$$s_{water}^{273K} = \left[s_{ice}^0 + \int_0^{273} \frac{c_p}{T} dT \right] + \Delta s_{S \rightarrow L}^{273K}$$

$$\Delta \mu_1 = \int_{263}^{273} d\mu_1 = \int_{263}^{273} -s dT$$

(Note that in the above calculation, the vdP term is neglected since it is 10^5 times smaller in magnitude to the other term).

$$= - \int_{263}^{273} \left[s_{water}^{273K} + \int_{273}^T \frac{c_p}{T'} dT' \right] dT$$

$$= -[s_{water}^{273K}(10) + \{T c_p \ln T - T\}|_{263}^{273} - c_p \ln 273 \quad (10)]$$

A similar integral may be evaluated for $\Delta \mu_3$.

$\Delta \mu_2 = 0$ since ice and water are at equilibrium at 273K.

$$\Delta \mu = \Delta \mu_1 + \Delta \mu_2 + \Delta \mu_3 = - \left[10 \Delta s_{S \rightarrow L}^{273K} + 263 \ln \frac{273}{263} \{c_p^{water} - c_p^{ice}\} - 10 \{c_p^{water} - c_p^{ice}\} \right]$$

$$\approx 219 + 370 - 378 \approx -212 \text{ J/mol}$$

2.5.2

The above assertion is incorrect.

The Gibbs Energy of the mixture at any extent of the reaction is:

$$G = n_A \mu_A + n_B \mu_B$$

Let the reaction have started with 1 mole of A. Then, when the extent of reaction is ξ ,

$$n_A = 1 - \xi$$

$$n_B = \xi$$

$$\therefore G = (1 - \xi)\mu_A + \xi\mu_B$$

Now, assuming ideal behaviour of A and B,

$$\mu_A = \mu_A^0 + RT \ln \left(\frac{P_A}{P^0} \right) = \mu_A^0 + RT \ln(1 - \xi) + RT \ln \left(\frac{P}{P^0} \right)$$

$$\mu_B = \mu_B^0 + RT \ln \xi + RT \ln \left(\frac{P}{P^0} \right)$$

Where P is the net pressure at equilibrium.

$$\therefore G = \mu_A^0 - (\mu_A^0 - \mu_B^0)\xi + RT \ln \left(\frac{P}{P^0} \right) + RT [(1 - \xi) \ln(1 - \xi) + \xi \ln \xi]$$

The last term in the above expression may be referred to as $\Delta_{mix}G^0$, the Gibbs Energy of mixing. If this term were not present, the Gibbs Energy along a reaction path would be linear, and the equilibrium would lie on the side of the reactant with lower Gibbs Energy. However, due to the presence of the non-linear mixing term, an intermediate extent of reaction leads to the minimum Gibbs energy.

This may be rationalized physically using the idea of entropy. If a single component were present in the mixture, the entropy of the reaction mixture would be minimized, which is not the case in equilibrium.

2.5.3

We consider the P (or Al) in Si to be a dilute solution. Thus, the difference in chemical potential between the two doped layers is:

$$\begin{aligned} \Delta\mu &= \mu_P - \mu_{Al} \\ &= (\mu_{Si}^0 + RT \ln a_P) - (\mu_{Si}^0 + RT \ln a_{Al}) \\ &= RT \ln \left(\frac{a_P}{a_{Al}} \right) \\ &= RT \ln \left(\frac{\chi_P}{\chi_{Al}} \right) \end{aligned}$$

Where $a \rightarrow \chi$ for a dilute solution.

In case $\chi_P = \chi_{Al}$, $\Delta\mu = 0$. This indicates a neutral equilibrium, but equal concentrations are not achievable on a macroscale.

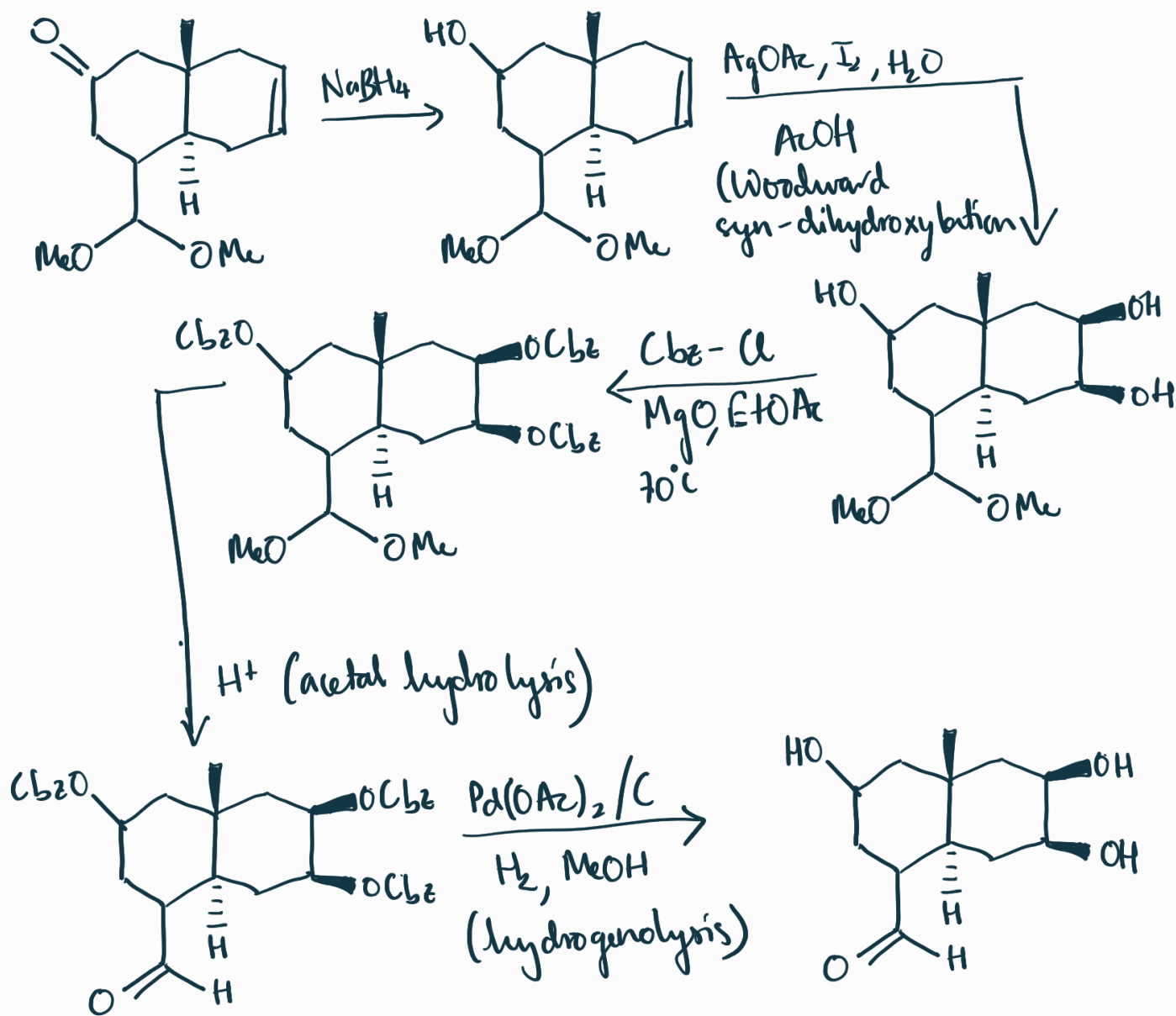
In case $\chi_P > \chi_{Al}$, $\Delta\mu > 0$. Thus, $\Delta G > 0$. This is a thermodynamically unstable system.

In case $\chi_P < \chi_{Al}$, we would have to take $\Delta\mu = \mu_{Al} - \mu_P$, thus, arriving at the same result.

2.6 The Stereochemical Demon

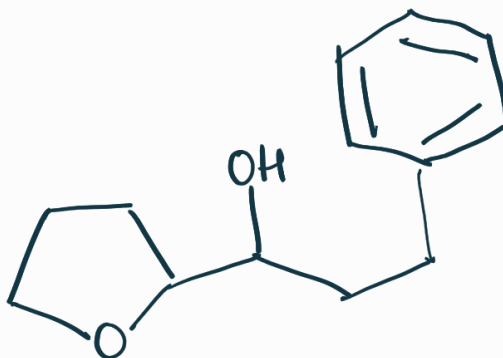
Solution is on the next page

2.6.1



2.6.2

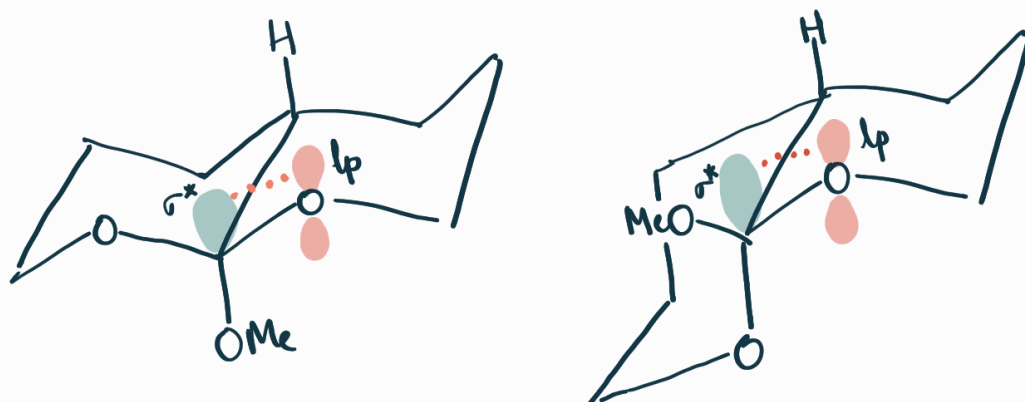
kinetic product :



reason : Baldwin's Rules (6-endo-tet disfavoured ; 5-exo-tet favoured)

2.6.3

reason: anomeric effect



refer to Deslongchamps et. al. (1985)

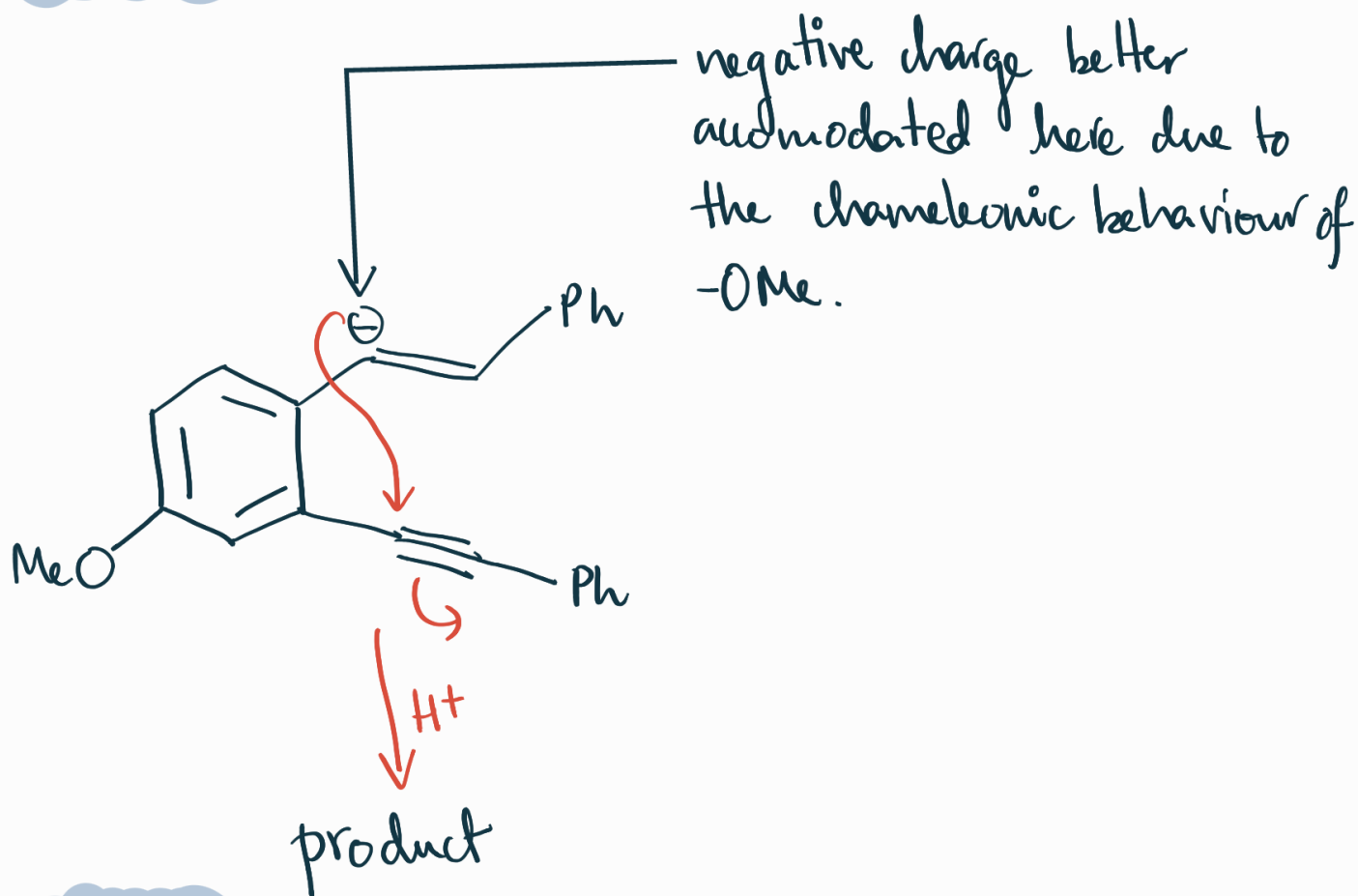
2.6.4

chelation control: $\text{Al}(\text{O}^i\text{Pr})_3$ coordinates to carbonyl oxygen and amide nitrogen.

subsequent stereochemistry determined by Cram's model.

chemoselectivity of reduction: $\text{C}=\text{O}$ of ketone more electrophilic than $\text{C}=\text{O}$ of amide/ester.

2.6.5



2.6.6

the reaction would yield the same product but would proceed faster since $-\text{OCF}_3$ σ^* is a better acceptor.

2.6.7

sterically encumbered substrate - non planar
Due to steric inhibition of resonance, $\text{C}=\text{O}$ group is unusually reactive. Hence, reaction is feasible.

2.7 Protonein

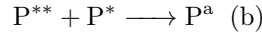
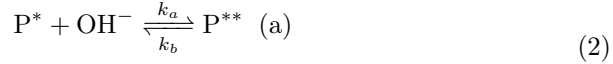
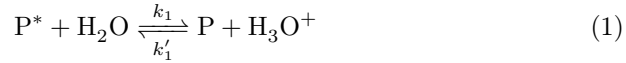
2.7.1

(a) Imine/schiff base formation won't happen. Leucine has an alkyl R group which won't react with aldehyde, so retinal won't be able to conjugate.

(b) pI of asparagine is 5.41 at 25 deg C compared to 2.98 of aspartic acid. Proton transfer would fail. (the H⁺ is in fact transported 100 times slower if 85th amino acid is substituted with asparagine; Ref - <https://doi.org/10.1073/pnas.87.3.1018>)

2.7.2

(a)



(2)(b) is the RDS. RDS can't be in Equilibrium

$$r_2 = k_c[P^{**}][P^*] \quad (3)$$

$$\frac{k_a}{k_b} = \frac{[P^{**}]}{[P^*][OH^-]} \quad (4)$$

$$\implies [P^{**}] = \frac{k_a}{k_b} [P^*][OH^-] \quad (5)$$

From (4) and (6)

$$r_2 = \frac{k_a k_c}{k_b} [P^*]^2 [OH^-] \quad (6)$$

$$\implies r_2 = k_2 [P^*]^2 [OH^-] \quad (7)$$

$$r_1 = k_2 [P^*][H_2O] - k'_1 [P][H_3O^+] \quad (8)$$

$$\implies \frac{-d[P^*]}{dt} = k_1 [P^*][H_2O] + k_2 [P^*]^2 [OH^-] - k'_1 [P][H_3O^+] \quad (9)$$

(b) Approximations when excess pH ≈ 14 solution is added,

1. reaction becomes pseudo-first order wrt [OH⁻] and [H₂O]
2. [H₃O⁺] tends to 0, so contribution of backward reaction (k'_1 term) is negligible

\therefore At pH ≈ 14

$$\frac{-d[P^*]}{dt} = k_1[P^*] + k_2[P^*]^2$$

$$\text{Solving, } t_{1/2} = \frac{1}{k_1} \ln \left(\frac{2k_1 + k_2[P^*]_0}{k_1 + k_2[P^*]_0} \right)$$

$$\text{Where } k_1 = k_1[\text{H}_2\text{O}] \text{ and } k_2 = k_2[\text{OH}^-]$$