

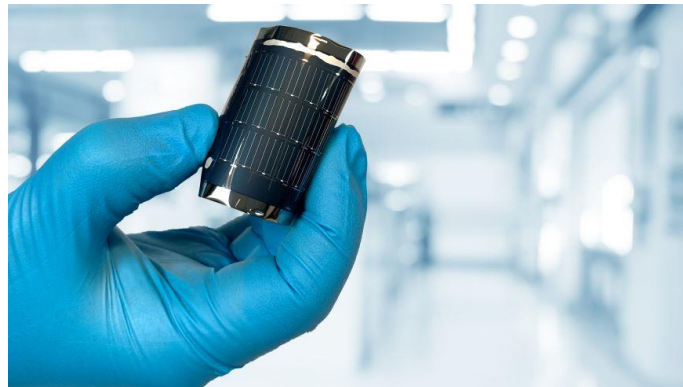
SwissChO 2022 Final Exam

Concept:

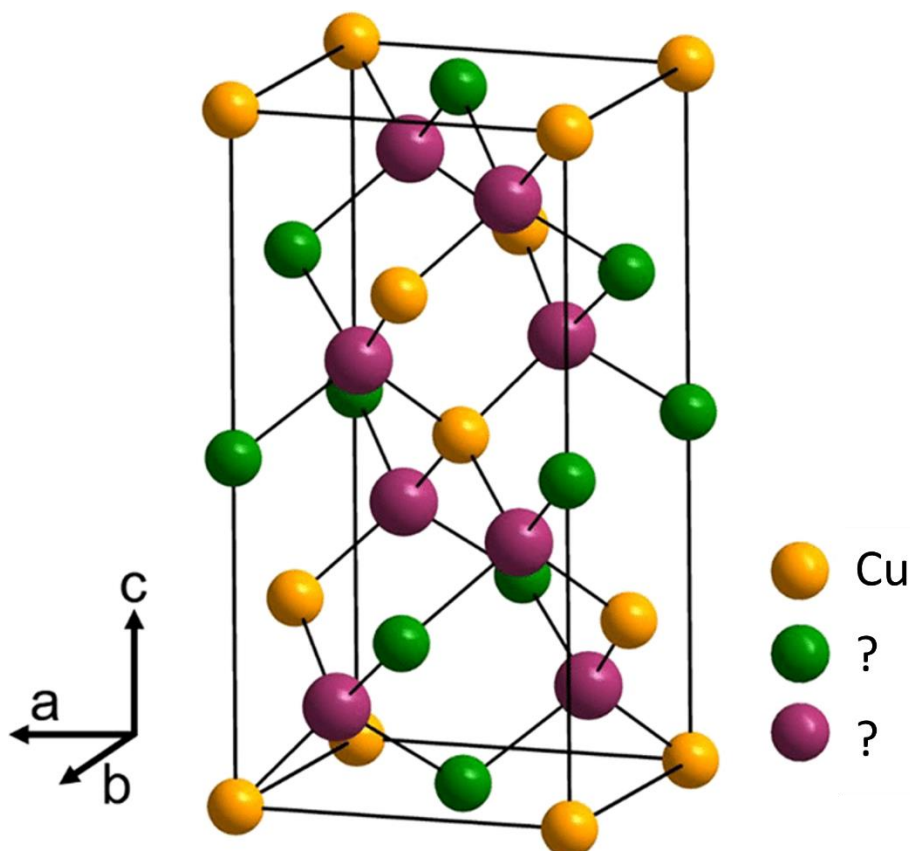
Task	(working) Title	Points	Author
1	Crystalline Solar Cells		Nina
2	Equilibria: Formation of Tartar in Wine		Thomas
3	Thermodynamics: Fuel of an Apogaeum Engine		Thomas
4	Electrochemistry of Gold		Nina
5	Kinetic Studies of the Formation of Nitryl Fluoride		Jasmin
6	Crystal Field and Complex Chemistry		Jasmin
7	Stereo- and Biochemistry of Lactic Acid		Nina
8	Structural Analysis	20	Daniel
9	Functional Group Interconversions		Luca
10	Total Synthesis		Luca
Total			

Problem 1 - Crystalline Solar Cells

Copper-indium-selenide crystals (CuInSe_2) are semiconductors and strongly absorb sunlight. Therefore, CuInSe_2 crystals have been studied for application in solar cells. Compared to other semiconductor materials, a much thinner CuInSe_2 film for light absorption is required because CuInSe_2 has a very high absorption coefficient. This also means CuInSe_2 -based solar cells are thin enough to be flexible. The record in efficiency for this type of solar cells is held by the Swiss Federal Laboratories for Materials Science and Technology (EMPA). In autumn 2021, the EMPA has claimed a 21.4 % efficiency to convert sunlight into electric power of this type of solar cell.



In the figure below the tetragonal unit cell of the CuInSe_2 crystal is depicted. The crystal structure type is like two zincblende unit cells (face-centered-cubic) stacked above each other. The angles of the unit cell are all $\alpha = \beta = \gamma = 90^\circ$. The lattice constants are $a = b = 5.8 \text{ \AA}$ and $c = 11.6 \text{ \AA}$.



1. The orange atom is copper. Which of the atoms (purple or green) is indium, which of the atoms (purple or green) is selenium?
Indium green ($6 \cdot \frac{1}{2} + 4 \cdot \frac{1}{4} = 4$), selenium purple ($8 \cdot 1 = 8$)

2. How many CuInSe₂ units make up a unit cell?

4

3. Calculate the density of CuInSe₂ in g cm⁻³!

MW = 336.32 g/mol

Per unit cell **4 times** the formula CuInSe₂

1345.28 g / mol per unit cell

1345.28 g / (6.022*10²³) = 2.23*10⁻²¹ g per unit cell

Volume of the cell

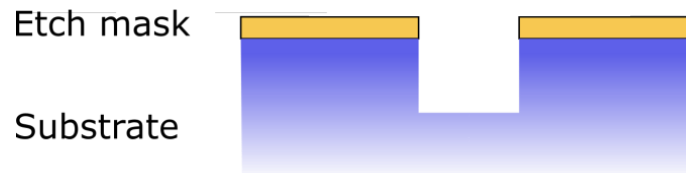
V = a * b * c = 5.8*5.8*11.6*10⁻²⁴cm³ = 3.9*10⁻²²cm³ per unit cell

$$\delta = \frac{m}{V} = \frac{2.23 * 10^{-21} \text{ g}}{3.9 * 10^{-22} \text{ cm}^3} = 5.7 \frac{\text{g}}{\text{cm}^3}$$

4. Copper, indium and selenium are applied to a surface by a method called “low temperature vapor deposition”. To perform this method, you need to know how much copper is needed in the final product. Calculate the metal content in wt% copper in CuInSe₂!

$$\text{wt\% Cu} = \frac{63.55 \frac{\text{g}}{\text{mol}}}{63.55 \frac{\text{g}}{\text{mol}} + 114.85 \frac{\text{g}}{\text{mol}} + 2 * 78.96 \frac{\text{g}}{\text{mol}}} = 18.9 \%$$

After the CuInSe₂ is applied as an even fine layer, you wish to take it away at certain spots. Therefore you use a method called “etching”. A mask is applied onto the CuInSe₂ surface and harsh reagents are applied to remove the CuInSe₂ crystals from the desired places.



5. Write down the balanced equation when CuInSe₂ is dissolved by etching solution (sulfuric acid H₂SO₄ and hydrogen peroxide H₂O₂). As products H₂SeO₄, In₂(SO₄)₃, CuSO₄ and H₂O are observed.



<https://www.nrel.gov/docs/fy01osti/30391.pdf>

<https://www.empa.ch/de/web/s604/cigs-efficiency-record-2021>

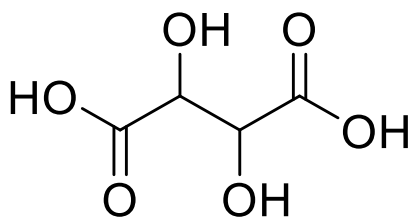
Problem 2 – Equilibria: Formation of Tartar in Wine

After a long time in storage, crystals can start to form in wine casks. Depending on the presence of colouring anthocyanins, these can be yellowish in white wine and pinkish in red wine. Famous German writer J.W. Goethe already documented this, and 100 years ago the chemical engineer W. Klapproth investigated the solubility of this mineral called “Weinstein” (literally, wine rock) or tartar. This tartar is the potassium salt of tartaric acid, a slightly tart tasting salt naturally occurring in grapes. Klapproth performed his investigations in pure water, which of course does not reflect the fact that wine contains a moderate amount of alcohol. Furthermore, he was not aware that the tartaric acid-alcohol-water system is made more difficult due to three facts: 1) solubility of tartrates in alcohol-water mixtures is lower than in pure water, 2) the solubility depends strongly on the temperature, and 3) tartaric acid can form other salts, e.g. with calcium.

Find some data on possible substances involved in the following compilation:

Tartaric acid, 2,3-Dihydroxybutanedioic acid: $C_4H_6O_6$ Solubility in water: $1'394\text{ g}\cdot\text{L}^{-1}$ at $20\text{ }^\circ\text{C}$

$pK_{a,1} = 2.89$ $pK_{a,2} = 4.34$



Tartar / Potassium hydrogen tartrate: $C_4H_5KO_6$ Solubility in water: $4.2\text{ g}\cdot\text{L}^{-1}$ at $20\text{ }^\circ\text{C}$

((R,R)-monopotassium tartrate) (W. Klapproth, Z.Analyt.Chemie 1922)

Limetartar / Calcium tartrate: $C_4H_4CaO_6$ Solubility in water: $1.2\text{ g}\cdot\text{L}^{-1}$ at $20\text{ }^\circ\text{C}$

((R,R)-Tartaric acid calcium salt) (handbook-of-chemistry-and-physics 2010)

- a) Tartaric acid has two stereogenic centres, in grape juice however, only the R,R-form occurs. Draw all possible stereoisomers of tartaric acid, determine if they are chiral and assign their absolute configurations.

0.5 for each determination of chirality:



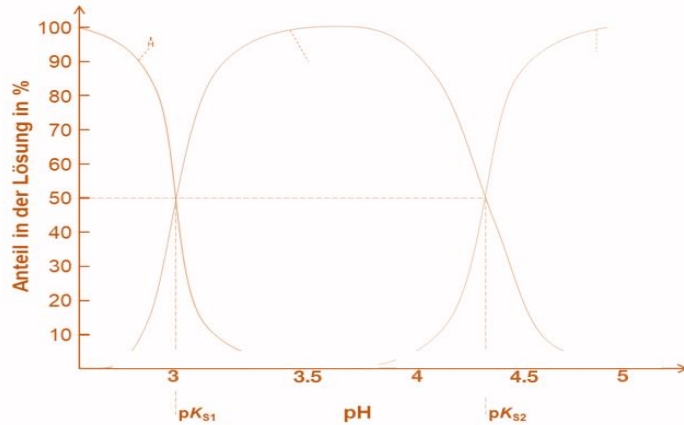
Tartaric acid is very soluble in water. You find the literature value in the table above. Give two reasons why this is the case.

Tartaric acid partially forms ionic forms and shows 6 positions where H bonds are possible (0.5 Pt)

- b) In which pH range will the formation of the classical tartar occur preferentially? And at what pH value exactly? Explain and draw a diagram showing the condition for the formation of tartrate as a function of pH.

Between the two buffer ranges, i.e. between 2.89 and 4.34 (0.5 Pt).

Since, according to the buffer equation, the proportions change after one pH interval from 1:1 to 1:10, the mean value, i.e. 3.6 would be ideal. (0.5 pt)



(1 Pt)

- c) In a white wine, the total tartaric acid content is $5.64 \text{ g} \cdot \text{L}^{-1}$ and the pH is 3.4. Which forms of tartaric acid are present in which molar concentrations? You can give the ratios slightly rounded for simplicity.

According to Henderson Hasselbalch at $\text{pH} = \text{pK}_{s1} + 0.51$ is...

$$[\text{H}_2\text{T}]/[\text{HT}^-] = 10^{-0.5} = 0.31 \approx 1:3 \quad (1:3.22)$$

And at $\text{pH} = \text{pK}_{s2} - 0.94$:

$$[\text{HT}^-]/[\text{T}^{2-}] = 10^{0.94} = 8.71 \approx 9:1 \quad (8.71:1)$$

With a total content of 5.64 g/l and a molar mass of 188.18 g/mol also

$[\text{Total}] = 0.03 \text{ mol/l}$, giving (simplified 3:9:1):

$$[\text{H}_2\text{T}] = 0.007 \text{ mol/l}; [\text{HT}^-] = 0.021 \text{ mol/l}; [\text{T}^{2-}] = 0.002 \text{ mol/l}$$

(more precise: 2.7:8.7:1)

$$[\text{H}_2\text{T}] = 0.0065 \text{ mol/l}; [\text{HT}^-] = 0.0211 \text{ mol/l}; [\text{T}^{2-}] = 0.0024 \text{ mol/l}$$

- d) The potassium content in grape juice varies depending on the soil conditions. In our white wine from c) it is determined to be 210 mg/L . What concentration in mol/L does this correspond to?
 $5.37 \text{ mmol/L} = 0.00537 \text{ mol/L} \quad (0.5 \text{ Pt})$

If the solubility of tartrate in a solution of 12% ethanol in water at 15°C is 2.25 g/L , does tartrate precipitate at this temperature? As a simplification, consider tartar as an insoluble salt and try to determine the solubility product at 15°C .

2.25 g/L corresponds to 0.012 mol/L dissolved K^+ - and HT^- ions, giving a solubility product of $1.4 \cdot 10^{-4}$
 (0.5 Pt)

[HT⁻] = 0.026 mol/l and [K⁺] = 0.00537 mol/L giving a product of $1.4 \cdot 10^{-4}$ => no precipitation!
(1 Pt)

- e) Now consider the following solubility table. At what temperature does tartrate (Weinstein) precipitate? ((What quantity at the next lower temperature?))

Precipitation at 15°C:

At 10 °C we find a solubility of 1.81 g/L giving only 0.0096 mol/L dissolved K⁺- and HT⁻ ions, corresponding to a solubility product of $9 \cdot 10^{-5}$ precipitation (1 Pt)

Solubility of tartrate (g/L) in alcohol-water model solutions					
Temperature (°C)	0% alcohol by volume (ABV)	10% ABV	11% ABV	12% ABV	13%ABV
-4	2.00	1.05	0.98	0.91	0.86
0	2.25	1.26	1.17	1.11	1.04
5	2.66	1.58	1.49	1.40	1.32
10	3.42	2.02	1.91	1.81	1.71
15	4.17	2.45	2.35	2.25	2.13
20	4.92	3.08	2.92	2.77	2.63

[Klapproth, W. (1922). *Zeitschrift für analytische Chemie*, 61(1), 1-19. (... Die mittlere Löslichkeit für Weinstein in 100ccm Wasser ergibt sich nach diesen Versuchen: bei 11° zu 0,376g, bei 12,5° zu 0,384g, bei 14° zu 0,422g...)]

Problem 3 – Thermodynamics: Fuel of an Apogaeum Engine

In order to bring a satellite into a stable orbit after shooting up from an initial parabolic flight curve or to bring it into a higher orbit, a special propulsion technique is used: the apogee engine.

In this process, two propellants are mixed and allowed to ignite in a combustion chamber. The thrust from the nozzle propels the remote-controlled satellite.

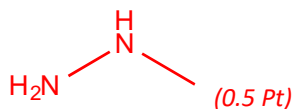
Often the components are so reactive that simple contact in the combustion chamber is sufficient! This is the case in this example, where, as often used, methylhydrazine (CH_6N_2 , liquid in the fuel tank) and dinitrogen tetroxide N_2O_4 (in fuel tank also liquid) are used as fuels without adding any other component.

You can find the thermodynamic data of all possible involved compounds in the following table:

thermodynamic data at $\approx 300\text{K}$ und 1 HPa

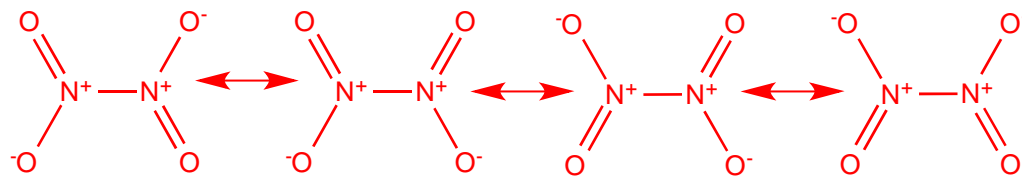
Stoff	ΔH_f° (g)	S° (g)	ΔH (l \rightarrow g)	Cp	\rightarrow convert:
CH_6N_2	54.2 kJ/mol	250 J/K·mol	40.3 kJ/mol	1.410 J/kg·K	0.065 J/mol·K
N_2O_4	9 kJ/mol	304 J/K·mol	2 kJ/mol	0.785 J/kg·K	0.072 J/mol·K
H_2O	-242 kJ/mol	189 J/K·mol	44 kJ/mol	1.858 J/kg·K	0.033 J/mol·K
N_2	0 kJ/mol	192 J/K·mol		1.039 J/kg·K	0.029 J/mol·K
CO_2	-393 kJ/mol	214 J/K·mol		0.817 J/kg·K	0.036 J/mol·K

a) Dinitrogen tetroxide, a dimer of nitrogen dioxide NO_2 is an extremely reactive substance, yet it is in equilibrium with nitrogen dioxide even at room temperature. How is this possible? Draw the skeletal formulae of the (asymmetrical) methyl hydrazine molecule and the (symmetrical) dinitrogen tetroxide molecule and explain why N_2O_4 is highly reactive and at the same time stable enough as not to disintegrate completely.



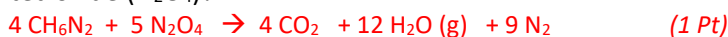
A N-O bond is extremely unstable because of the high electronegativities: very small bond enthalpy. (0.5 Pt)

On the other hand, dinitrogen tetroxide is mesomerically stabilised (0.5 Pt): 4 possible mesomeric boundary structures!



(0.5 Pt for the first and 0.5 Pt for 2 or 3 of the following)

b) Write down the stoichiometrically correct reaction equation: Calculate the required mass ratio used for an optimal stoichiometric mixture of methyl hydrazine (CH_6N_2) and dinitrogen tetroxide (N_2O_4)?



4 CH_6N_2 to 5 N_2O_4 calculate with corresponding molecular masses:

184.3 g to 460 g \Rightarrow mass ratio $\approx 1 : 2.5$ (1 Pt)

- c) Determine the heat of reaction per mole of one of the two reactants and also per gram of fuel mixture at standard conditions.

$$\Delta H = 4 \cdot -54.2 \text{ kJ/mol} + 5 \cdot -11.1 \text{ kJ/mol} + 4 \cdot -393 \text{ kJ/mol} + 12 \cdot -242 \text{ kJ/mol} = -4'748.3 \text{ kJ}$$

(1 Pt)

per 644.3 g fuel-mixture

Why 11.1 instead of 9 as given in the table?

If vaporization of the fuel is included in calculation: $+(4 \cdot -40.3 \text{ kJ/mol} + 5 \cdot 2 \text{ kJ/mol}) = +171.2 \text{ kJ/mol}$

+1 Pt

=> -4'577.1 kJ/mol per 644.3 g fuel-mixture

⇒ $\Delta H = \underline{27.5 \text{ kJ [or 25.8 kJ]}}$ per 1 g methyl hydrazine and 2.5 g dinitrogen tetroxide
(or 7.28 [or 7.37 kJ] per g fuel-mixture) (1 Pt for a recalculation)

The heat of reaction per mole is not answered

- d) Now the actual driving force is the free enthalpy. For this, however, the thermodynamic data of the substances would have to be available at the conditions in the nozzle; whereby the rocket technicians assume a temperature in the combustion chamber of about 3'400 K. So therefore, you have to convert: Adapt your heat of reaction from c) to the conditions:

$$\begin{aligned} \Delta C_p &= 4 C_p(\text{CO}_2) + 12 C_p(\text{H}_2\text{O}) + 9 C_p(\text{N}_2) - [C_p(\text{CH}_6\text{N}_2, \text{g}) + C_p(\text{N}_2\text{O}_4, \text{g})] \\ &= 4 \cdot 0.817 + 12 \cdot 1.858 + 9 \cdot 1.093 - [4 \cdot 1.410 + 5 \cdot 0.785] \text{ J/kg} \cdot \text{K} \quad (0.5 \text{ Pt}) \\ &= 4 \cdot 0.036 + 12 \cdot 0.033 + 9 \cdot 0.029 - [4 \cdot 0.065 + 5 \cdot 0.072] \text{ J/mol} \cdot \text{K} = 0.181 \text{ J/mol} \quad (1 \text{ Pt}) \end{aligned}$$

at $\Delta T = 3400 \text{ K}$, this means:

$$\Delta H = \underline{-4'577.1 \text{ kJ/mol}} + 3400 \text{ K} \cdot \Delta C_p = -4'577.1 + 0.615 \text{ kJ/mol} = \underline{-4576.5 \text{ kJ/mol}} \quad (0.5 \text{ Pt})$$

And now determine the driving force for the estimated temperature. Choose a reference (per mol or per g) in such a way that you can quickly give answers to loading questions from technology!

(If you do not know the procedure, then determine the driving force as a rough approximation at room temperature 300 K).

$$\begin{aligned} \Delta S &= 4 \cdot -250 \text{ J/K} \cdot \text{mol} + 5 \cdot -304 \text{ J/K} \cdot \text{mol} + 4 \cdot 214 \text{ J/K} \cdot \text{mol} + 12 \cdot 189 \text{ J/K} \cdot \text{mol} + 9 \cdot 192 \text{ J/K} \cdot \text{mol} \\ &= 2'440 \text{ J/K} \cdot \text{mol} = \underline{2.44 \text{ kJ/K} \cdot \text{mol}} \quad (0.5 \text{ Pt}) \end{aligned}$$

Using your numbers I get 2332 kJ/Kmol

$$\Delta G \approx -12'872 \text{ kJ per 644.3 g fuel mixture} \quad (1 \text{ Pt})$$

(at 300 K: 5'400 kJ) and this means

almost 70 kJ per g methyl hydrazine and 2.5 g dinitrogen tetroxide

in other words 20 kJ per g fuel mixture (1 Pt)

(at RT: 29 kJ pro g methyl hydrazine and, so 8.4 kJ per g fuel mixture (1 Pt))

- e) A smaller telecommunications satellite of 1'500 kg mass in a geostationary orbit at an altitude of 35'800 km should carry enough fuel to correct annual altitude errors of up to 100 km. How much energy is required for the transfer from a low-Earth orbit to an altitude of 1800 km until a stable geostationary orbit is reached, if the rule of thumb in technology is: the amount of fuel for this corresponds to the mass of the satellite?

20 kJ per g fuel mixture * $1.5 * 10^6$ g = $30 * 10^6$ kJ = 30 GJ (1 Pt)

What additional amount of fuel should be loaded if the satellite is to have thrust to correct an altitude difference of 100 km every year for at least 25 years?

Rough approximation: $30 * 10^6$ kJ / 34'000 km * 100 km/J * 25 J = $2.2 * 10^6$ kJ

Why 34 000 instead of 35 800?

This corresponds to additional 110 kg of fuel (1 Pt)

The actual required amount is smaller due to decreasing gravity!

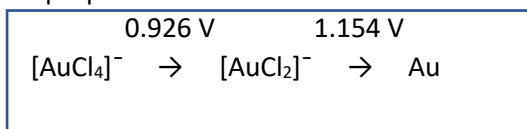
Check numbers and calculations again for final solutions (not relevant for translation)

Problem 4 – Electrochemistry of Gold

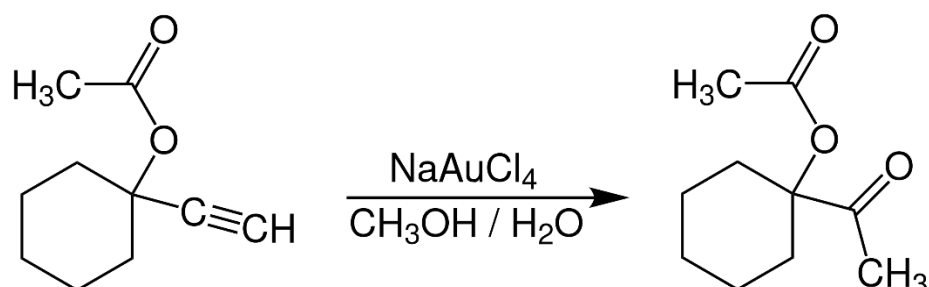
Gold is well known as a noble metal. However, some gold compounds exist such as the chloride coordination compounds $[\text{AuCl}_4]^-$ and $[\text{AuCl}_2]^-$.



1. What are the oxidation states of gold in $[\text{AuCl}_4]^-$, $[\text{AuCl}_2]^-$ and elementary Au?
2. Write down the half-cell reactions and the full redox reaction of the disproportionation reaction of $[\text{AuCl}_2]^-$.
3. Using the [Latimer diagram](#) at pH = 0 below, calculate if $[\text{AuCl}_2]^-$ would be stable to disproportionation.



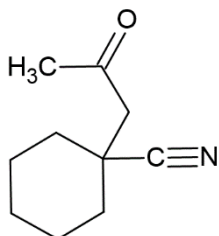
4. What is the electrochemical potential of the reaction going from $[\text{AuCl}_4]^-$ directly to elementary Au?
5. Is it possible to oxidize gold powder using pure oxygen? Provide a balanced redox reaction. Assume that the partial pressure of oxygen is $p(\text{O}_2) = 1 \text{ atm}$ and the gold is in aqueous solution in the presence of chloride ions. The electrode potential of the oxygen half-cell is given as $E_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 = 1.229 \text{ V}$.
6. At what pH interval is it possible to oxidize gold powder by hydrogen peroxide (H_2O_2 , $E_{\text{H}_2\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 = 1.763 \text{ V}$) in the presence of chloride-ions? Assume that the concentrations of all ions in the solution except H^+ are 1 mol/L and that the potential $E_{[\text{AuCl}_2]^-/\text{Au}}^0$ doesn't change its value with varying pH.
7. Gold salts, like NaAuCl_4 are used as catalysts in the oxidation of alkynes to methyl ketones. They can also be used in the formation of terminal amides. How would you change the reactant below to obtain an amide instead of a methyl ketone? Draw the revised reactant.



Solutions

- +III +I 0
 $[\text{AuCl}_4]^-$, $[\text{AuCl}_2]^-$ and elementary Au
- | | | | | |
|-----------|---|--|---|-----------|
| Oxidation | $[\text{AuCl}_2]^- + 2 \text{Cl}^-$ | $\rightarrow [\text{AuCl}_4]^- + 2 \text{e}^-$ | $\begin{array}{c} \\ \\ \end{array}$ | - 0.926 V |
| Reduction | $[\text{AuCl}_2]^- + \text{e}^-$ | $\rightarrow \text{Au} + 2 \text{Cl}^-$ | $\begin{array}{c} \\ \\ \end{array} \times 2$ | +1.154 V |
| <hr/> | | | | |
| Redox | $2 [\text{AuCl}_2]^- + [\text{AuCl}_2]^- + 2 \text{Cl}^-$ | $\rightarrow 2 \text{Au} + 4 \text{Cl}^- + [\text{AuCl}_4]^- + 2 \text{e}^-$ | | +0.228 V |
- The electrochemical potential is positive. Hence, $[\text{AuCl}_2]^-$ is unstable towards disproportionation. The right potential is bigger than the left \rightarrow hence it can disproportionate
- | | | | |
|------------------------------------|---|---------|--|
| $[\text{AuCl}_4]^- + 2 \text{e}^-$ | $\rightarrow [\text{AuCl}_2]^- + 2 \text{Cl}^-$ | 0.926 V | $\Delta G_1 = -z F E^\circ = -2 F E_1^\circ$ |
| $[\text{AuCl}_2]^- + \text{e}^-$ | $\rightarrow \text{Au} + 2 \text{Cl}^-$ | 1.154 V | $\Delta G_2 = -z F E^\circ = -1 F E_2^\circ$ |
| $[\text{AuCl}_4]^- + 3 \text{e}^-$ | $\rightarrow \text{Au} + 4 \text{Cl}^-$ | ??? V | $E^\circ = \frac{\Delta G_{\text{total}}}{-z F} = \frac{2 * E_1^\circ + 1 * E_2^\circ}{3 * F}$ |

$1/3 * (2 * 0.926 \text{ V} + 1 * 1.154 \text{ V}) = \underline{1.002 \text{ V}}$
- $4 \text{Au} + \text{O}_2 + 8 \text{Cl}^- + 4 \text{H}^+ \rightarrow 4 [\text{AuCl}_2]^- + 2 \text{H}_2\text{O}$ $E^\circ = 1.229 - 1.154 = 0.075 \text{ V}$.
 In the presence of chloride ions gold powder can be oxidized by pure oxygen, because $E^\circ(\text{O}_2/\text{H}_2\text{O})$ exceeds $E^\circ([\text{AuCl}_2]^-/\text{Au})$.
- The redox potential $E_{\text{H}_2\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0$ depends on pH (the Nernst equation):
 $\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$
 $E_{\text{H}_2\text{O}_2, \text{H}^+/\text{H}_2\text{O}} = E^\circ - \frac{0.059 \text{ V}}{2} \log \left(\frac{1}{[\text{H}^+]^2} \right) = 1.763 - 0.059 \text{ pH}$.
 The potential $E([\text{AuCl}_2]^- / \text{Au})$ doesn't change its value in acidic medium:
 $E_{[\text{AuCl}_2]^- / \text{Au}}^0 = 1.154 \text{ V}$.
 So, the reaction $2 \text{Au} + \text{H}_2\text{O}_2 + 4 \text{Cl}^- + 2 \text{H}^+ \rightarrow 2 [\text{AuCl}_2]^- + 2 \text{H}_2\text{O}$ is possible if
 $E_{\text{H}_2\text{O}_2, \text{H}^+/\text{H}_2\text{O}} > E_{[\text{AuCl}_2]^- / \text{Au}}^0$
 $1.763 - 0.059 \text{ pH} > 1.154$
 $\text{pH} < 10.3$
 (In fact, this pH interval is restricted to acidic medium as in basic solutions dichloroaurate(I) decomposes to gold(I) oxide.)
- <- using a nitrile compound instead



Citations

Picture

[https://de.wikipedia.org/wiki/Gold\(III\)-chlorid#cite_note-6](https://de.wikipedia.org/wiki/Gold(III)-chlorid#cite_note-6)

Idea for exercises and electrochemical potentials (Problem 13)

<https://50icho.eu/wp-content/uploads/2018/06/preparatory-problems-icho-2015.pdf>

[https://de.wikipedia.org/wiki/Gold\(III\)-chlorid#cite_note-6](https://de.wikipedia.org/wiki/Gold(III)-chlorid#cite_note-6)

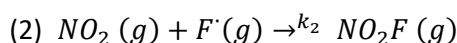
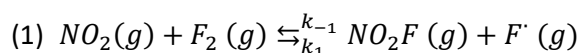
<https://pubs.acs.org/doi/pdf/10.1021/jo00011a058>

<https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.200901231>

Problem 5 – Kinetic studies of the formation of nitryl fluoride

Total Points: 12.5 Points

Nitryl fluoride can be formed through the reaction of fluorine gas with nitrogen dioxide according to the following steps:



- a. Formulate the overall stoichiometric equation for the formation of nitryl fluoride from the steps (1) and (2) above.



- b. Write down the rate law for the formation of nitryl fluoride:

$$\frac{d[\text{NO}_2\text{F}]}{dt} = \dots$$

$$\frac{d[\text{NO}_2\text{F}]}{dt} = k_1[\text{NO}_2][\text{F}_2] - k_{-1}[\text{F}^\cdot][\text{NO}_2\text{F}] + k_2[\text{F}^\cdot][\text{NO}_2] \quad (1\text{P})$$

- c. Which of the species in the steps (1) and (2) is highly reactive and therefore never present in a high concentration? (name only one)

The fluorine atom/radical F^\cdot . (1P)

- d. For the appropriate species, use a steady-state approximation to determine the concentration of this species.

As deduced above, the most reactive species is F^\cdot so we'll do a steady-state approximation for this species:

$$\frac{d[\text{F}^\cdot]}{dt} \approx 0 = k_1[\text{NO}_2][\text{F}_2] - k_{-1}[\text{F}^\cdot][\text{NO}_2\text{F}] - k_2[\text{F}^\cdot][\text{NO}_2] \quad (1 \text{ P})$$

$$[\text{F}^\cdot] = \frac{k_1[\text{NO}_2][\text{F}_2]}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]} \quad (1 \text{ P})$$

- e. With your results from c, write down the simplified rate law for the formation of nitryl fluoride.

$$\frac{d[\text{NO}_2\text{F}]}{dt} = k_1[\text{NO}_2][\text{F}_2] - \frac{k_{-1} \cdot k_1[\text{F}_2][\text{NO}_2]}{k_{-1} + k_2 \frac{[\text{NO}_2]}{[\text{NO}_2\text{F}]}} + \frac{k_2 \cdot k_1[\text{F}_2][\text{NO}_2]^2}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]} \text{ or}$$

$$\frac{d[\text{NO}_2\text{F}]}{dt} = k_1[\text{NO}_2][\text{F}_2] - \frac{k_{-1} \cdot k_1[\text{F}_2][\text{NO}_2]\text{NO}_2\text{F}}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]} + \frac{k_2 \cdot k_1[\text{F}_2][\text{NO}_2]^2}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]} \quad (2 \text{ P})$$

- f. Under the assumption that $k_2 \gg k_{-1}$, k_{-1} simplify the expression from d. The resulting equation is:

$$\frac{d[\text{NO}_2\text{F}]}{dt} = 2 \cdot k_1[\text{NO}_2][\text{F}_2] - \frac{k_{-1} \cdot k_1[\text{F}_2][\text{NO}_2\text{F}]}{k_2}$$

$$\frac{d[NO_2F]}{dt} = k_1[NO_2][F_2] - \frac{k_{-1} \cdot k_1[F_2][NO_2]}{k_{-1} + k_2 \frac{[NO_2]}{[NO_2F]}} + \frac{k_x \cdot k_1[F_2][NO_2]^2}{k_{-1}[NO_2F] + k_x[NO_2]}$$

$$\frac{d[NO_2F]}{dt} = 2 \cdot k_1[NO_2][F_2] - \frac{k_{-1} \cdot k_1[F_2][NO_2F]}{k_2} \quad (1 \text{ P})$$

- g. At very low concentrations of nitryl fluoride i.e., at the start of the reaction, the rate law gets very simple:

$$(3) \quad \frac{d[NO_2F]}{dt} = 2 \cdot k_1[F_2][NO_2]$$

Why is this the case?

At the beginning of the reaction, the concentration of NO_2F is zero, as no product has been formed yet. (1 P)

- h. From your result in task e, show in a few steps how you get to the simple rate law above (3).

$$\frac{d[NO_2F]}{dt} = 2 \cdot k_1[NO_2][F_2] - \frac{k_{-1} \cdot k_1[F_2][NO_2F]}{k_x}$$

You can simply cancel the whole second expression, as $[NO_2F]$ is very low and nearly zero right at the beginning of the reaction. (1 P)

In order to determine k_1 the initial reaction rate v_0 was determined for different concentration of fluorine and nitrogen dioxide.

Initial reaction rate v_0 (mol*m ⁻³ *s ⁻¹)	[F ₂] (mol*m ⁻³)	[NO ₂] (mol*m ⁻³)
0.004	5.2889*10 ⁻⁶	5.2889*10 ⁻⁶
0.008	5.3000 * 10 ⁻⁷	1.0555*10 ⁻⁴
0.006	9.3100*10 ⁻⁶	4.5068*10 ⁻⁶
0.002	4.5454*10 ⁻⁴	3.0770*10 ⁻⁸

- i. Considering all the data points, determine the rate constant k_1 with the corresponding units.

$$K_1 = 7.15 \cdot 10^7 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}; \text{ accepted range: } 7.00 - 7.3 \cdot 10^7 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

If it was determined by using all four values → full points

If it was determined by just calculating from one to three values → deduction of points

Missing or false units results also in a deduction of points. (2 P total)

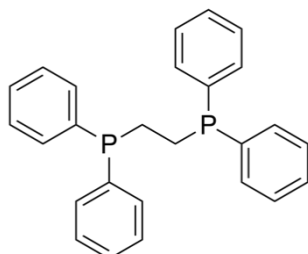
- j. After some time, the rate law from question g is no longer valid. Why is that? Hint: Think about which reactions take place.

The back-reaction of (1) will also take place now, as some nitryl fluoride has accumulated and its concentration can no longer be assumed to be very low. (0.5 P)

Problem 6 – Crystal field and complex chemistry

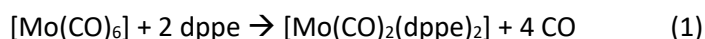
Total points: 11 P

Chelating ligands play a very important role in complex chemistry since they form very stable complexes, as they bind using more than one atom (hence their name, from Greek “chelé”, meaning a crab’s claws). One such chelating ligand is dppe (1,2-bis(diphenylphosphanyl)ethane). The structure of the Ligand dppe is given below:

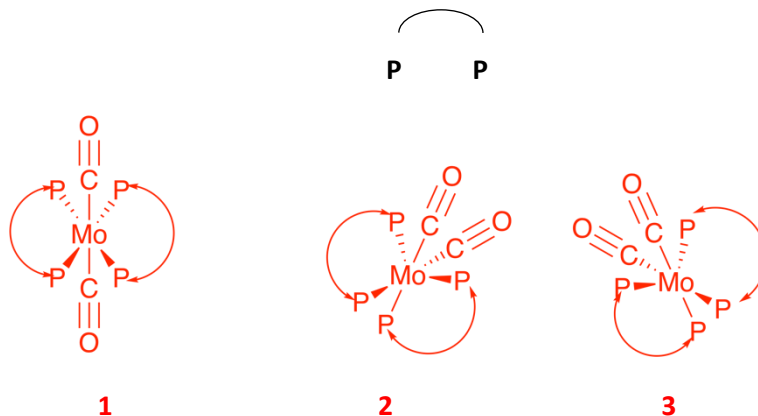


1,2-bis(diphenylphosphanyl)ethane

Consider the following reaction:



- What is the oxidation state of Molybdenum in the complexes above? What is its d-electron configuration?
The oxidation state of Molybdenum is in both complexes zero $\rightarrow 4d^6$ configuration. (1 P)
- As mentioned above, chelating ligands form very stable complexes, due to the binding of more than one donor atom. Considering reaction (1) what could be a major thermodynamic driving force for the formation of the product and why (consider the number of products and reactants)?
Entropy \rightarrow the “number of free molecules” after the reaction is higher, than before, which is entropically very favourable; further, CO is a gas, which is also very entropically favourable (already one of those two arguments will be awarded with full points) (1 P)
- Draw all possible stereoisomers of the product. To spare you a bit of time, you can draw the ligand dppe as follows:

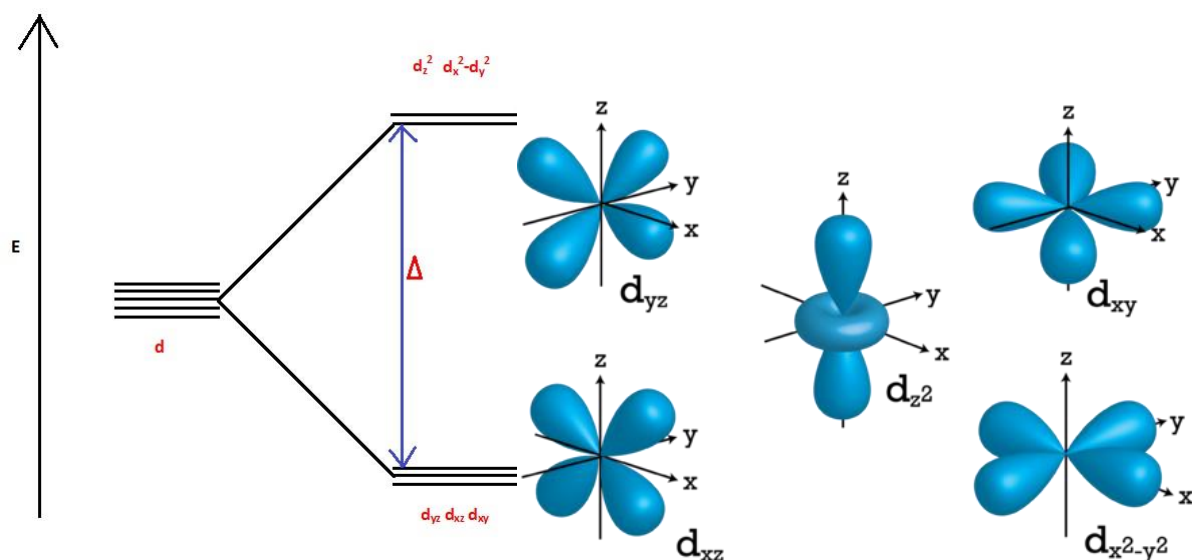


What is the relationship between the isomers? Are they diastereo- or enantiomers?

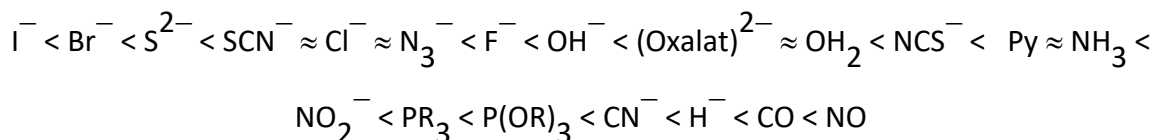
2 and 3 are enantiomers. 1 is not chiral.

(2.5 P)

A very valuable model for transition metal complexes is the crystal-field theory where the five d-orbitals get split up to different energies upon the influence of the ligands. This is shown for an octahedral complex below with the shape of the respective d-orbitals:



The splitting of the crystal-field increases according to the spectrochemical series for the ligands:



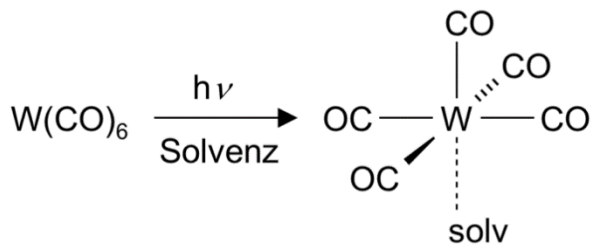
- d. Considering the provided spectrochemical series, what spin state do you expect for the complex $[\text{Mo}(\text{CO})_2(\text{dppe})_2]$, high-spin or low-spin and why?

Low-spin. CO is a very strong ligand and also dppe is rather strong, therefore we expect a large splitting, which results in a low-spin complex. (1 P)

- e. Draw the orbital diagram for an octahedron with the d-electrons of the metal centre according to your results from b and d. What is the magnetic property of the complex, paramagnetic or diamagnetic?

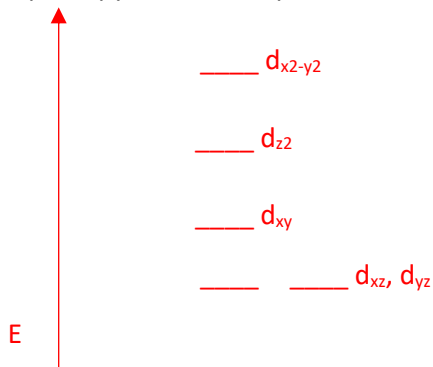
All six electrons are found in the three t_{2g} orbitals paired up. Hence the complex is diamagnetic. (0.5 P)

Tungsten hexacarbonyl, another example of an octahedral carbonyl complex has very interesting properties. Upon light exposure, one metal-carbon bond is broken and a square-pyramidal complex, which is stabilised by the solvent, is formed.



The crystal-field splitting for a square pyramidal complex is slightly different from the one of the octahedral complexes. The d_{z^2} orbital gets more stabilised and lies now between the energies of the d_{xy} and the $d_{x^2-y^2}$, further the d_{xz} and the d_{yz} are also slightly stabilised and now lie below the d_{xy} orbital.

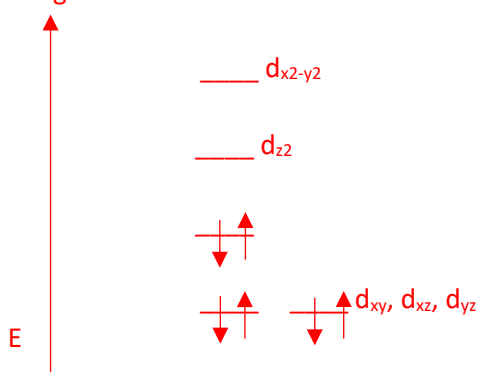
- f. According to the description above, draw a qualitative crystal field splitting diagram for a square-pyramidal complex and label the orbitals.



(2 P)

- g. Determine the d-electron configuration of the metal centre in $[\text{W(CO)}_5]$ and fill these electrons into the diagram obtained in f.

Tungsten is a $5d^6$ transition metal.



(2 P)

- h. What is the reactivity of the complex? Is it a Lewis-acid, a Lewis-base or none of those two? And why?

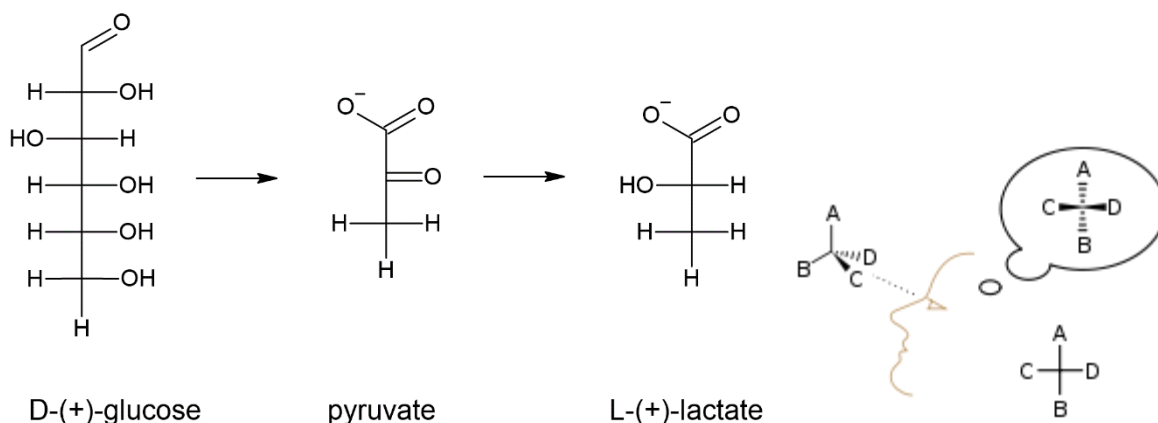
This complex reacts as a Lewis-acid due to an empty 5d-orbital (d_{z^2}) relatively low in energy. Another argument for its reactivity as a Lewis-acid could be the valence-electron configuration of the metal centre, which is 16 VE and through the coordination of another donor atom would become 18 VE, which is very stable \rightarrow empty binding site.

Points are also given, if the student argues that the complex is stabilised by coordination of a solvent molecule, which is characteristic for Lewis-acids.

(1 P)

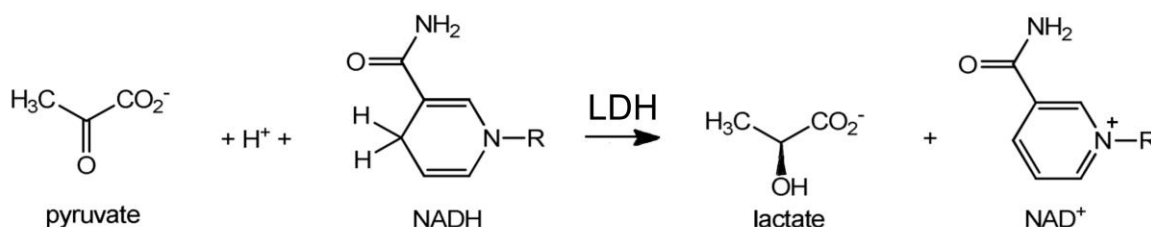
Problem 7 – Stereo- and Biochemistry of Lactic Acid

The human body needs energy to function. An effective means of energy production during short, intense exercise is *anaerobic glycolysis*. Anaerobic glycolysis is the transformation of *glucose* (sugar) via *pyruvate* to *lactate* when limited amounts of oxygen are available. The structures of glucose, pyruvate and lactate are shown below as Fischer projections.



- For the D-(+)-glucose, pyruvate and the L-(+)-lactic acid:
 - Indicate all chiral centres with a star.
 - Assign the absolute configuration ("R" or "S") to all chiral centres applying the Cahn-Ingold-Prelog (CIP) rules.
- Draw the enantiomer of D-(+)-glucose in the Fischer projection.

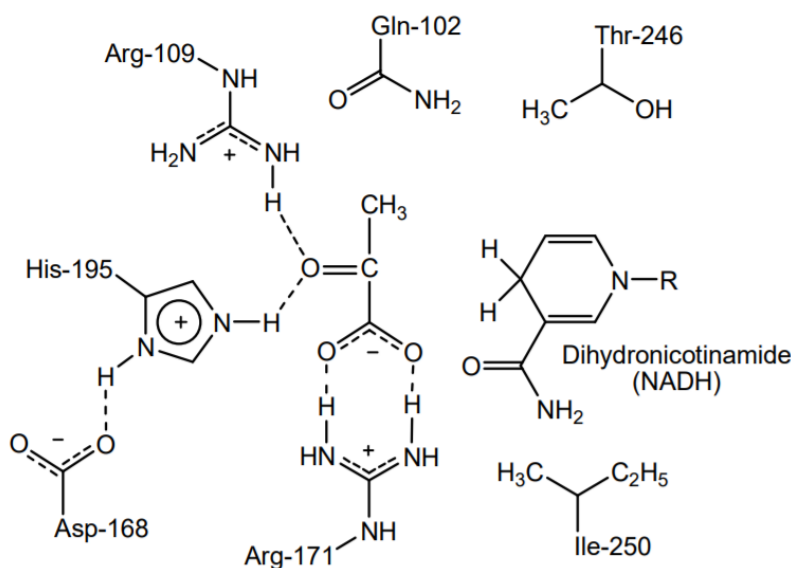
Let's have a closer look at the second step in the anaerobic glycolysis, i.e. the conversion of pyruvate to lactate:



NADH acts as the reducing agent in this reaction. The reaction is formally the transfer of hydride ion (H^-) from *NADH* to pyruvate. An enzyme called *lactate dehydrogenase (LDH)* catalyses this reaction. An enzyme is protein with a biocatalysis function. It has an active site to bind reactants.

The structure of the substrates pyruvate and *NADH* bound in the active site of *LDH* is shown schematically in Scheme 1. Several key amino acid residues in the active site of the enzyme *LDH* are indicated. They are abbreviated by their three-letter-code, sequence number in *LDH* and only the side chains of the respective amino acids are shown. The dotted lines between fragments of *LDH* indicate weak intermolecular interactions among groups in the active site.

Scheme 1



3. An achiral compound *pyruvate* is being converted to the chiral compound *L-(+)-lactate*. How is it possible that only one enantiomer, the *L-(+)-lactate*, arises?

The enzyme LDH has a **chiral** active site to bind the reactants, because it consists of chiral amino acids. So only one enantiomer (*L-(+)-lactic acid*) can be formed in this chiral environment.

4. What type of weak intermolecular interactions exists between Arg-109 and the carbonyl group of pyruvate, and between His-195 and the carbonyl group of pyruvate? Why does this interaction occur?

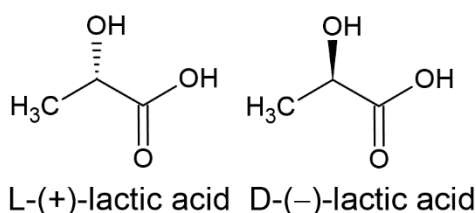
Hydrogen bonds. The carbonyl group is polarized, with a partial negative charge on the oxygen. The partial negative charge is attracted electrostatically to the positively charged His-195 and Arg-109.

Isoleucin has an alkyl (sec-butyl) side-chain. The side chain of Ile-250 lies directly below the plane of the dihydronicotinamide ring of NADH (Scheme 1).

5. What type of intermolecular interaction would the side chain of Ile-250 make with NADH?

Ile-250 can be involved in dispersion interactions (also called London forces or van-der-Waals interactions) with the dihydronicotinamide ring. The instantaneous dipole in Ile-250 that arises due to spontaneous fluctuations of electron density induces a dipole in the dihydronicotinamide, and the two dipoles interact.

You've tried to convert pyruvate to lactic acid in your lab by the reducing agent NaBH₄. You've been successful in your synthesis, however you obtain both enantiomers of lactic acid in equal amounts.



6. What is the name of a 50:50-mixture of both enantiomers?

Racemate or racemic mixture

7. You wish to separate the two enantiomers and find the following bases in your lab:

methylamine, dimethylamine, 1-amino-1-phenylethan and methylphenylamin

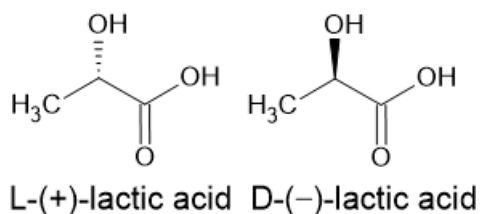
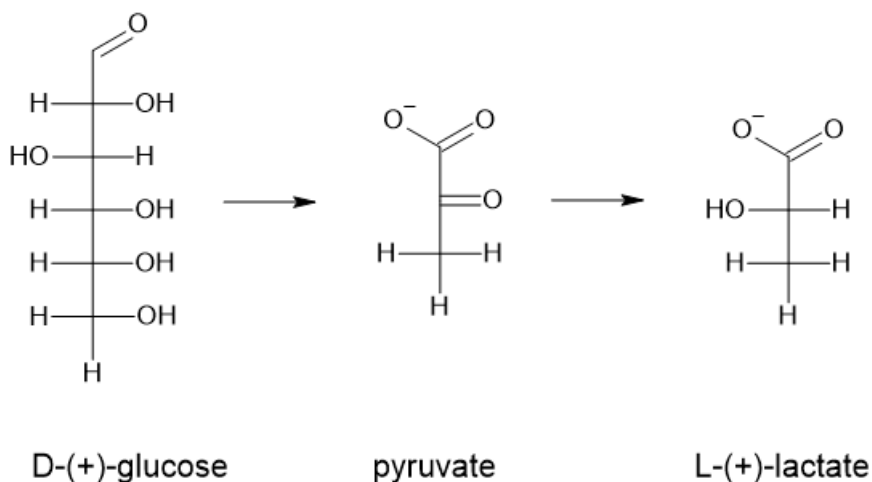
Which base is suited for enantiomer separation? How would you proceed?

Only **1-amino-1-phenylethan** is possible for enantiomeric separation as it is a chiral base (given it is enantiomerically pure). Let's assume you'd have the **R**-1-amino-1-phenylethan and you'd let it react in an acid base reaction with your enantiomeric lactic acid mixture. You'd obtain diastereomeric salts in RR resp. RS absolute configuration. This diastereomeric mixture is possible to separate by physical separation techniques like **fractional crystallisation**. After separation, the addition of an acid would yield the desired enantiomer of lactic acid.

Citation:

https://www.iuventa.sk/files/documents/5_icho/documents/preparatory%20problems%20icho%202012%20.pdf

molecules as png picture, (pdf or jpeg also possible or document in chemsketch)



Problem 8 – Structural Analysis

20 points

After staying (yet again) after hours in your laboratory, you come across some of your old lab partner's synthesis products. Strangely enough, you find a small vial marked only with the molecular formula of a compound which is still inside it. On the label you find: **C₁₅H₁₄O**.

Your interest being piqued, you decide to further investigate by running an IR and NMR spectrum of the compound to discover what it is.

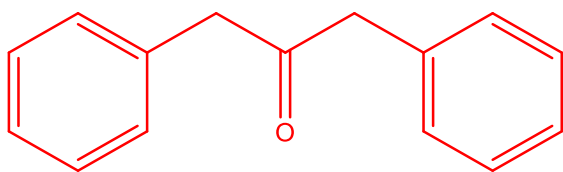
a) Using the molecular formula, determine the degree of unsaturation of the molecule.

$$DBE = \frac{2 \times C - H + N - X + 2}{2} = \frac{2 \times 15 - 14 + 2}{2} = 9 \quad (1pt)$$

b) Using the IR-Spectrum on the next page, identify the structural unit giving the peak with the highest intensity, which is not in the fingerprint area of the spectrum.

Peak : $\sim 1720\text{ cm}^{-1} \rightarrow$ carbonyl function (1pt) (if they say ketone 0.5pt)

c) Using both the IR- spectrum and the ¹H-NMR spectra of the compound given on the following pages, determine the structural formula of the compound and its IUPAC name.

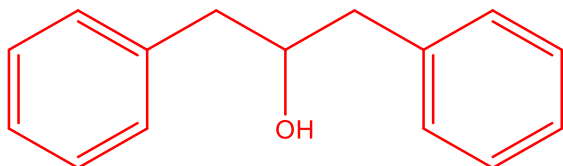


1,3-diphenylpropan-2-one (2pts for structure, 1pt for the name)

Whilst further rummaging through your partner's lab notes, you come across a paper, detailing which reactions led to the creation of compound C₁₅H₁₄O:

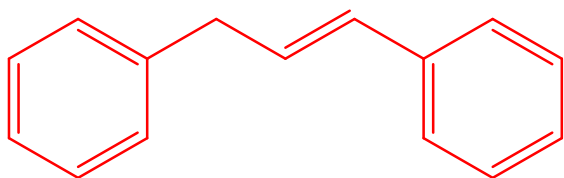
A reaction using BH₃, NaOH and H₂O was performed on compound **X** to create an intermediate molecule with the formula **C₁₅H₁₆O**. This compound was then oxidized using Al(OⁱPr)₃ to give the desired compound **C₁₅H₁₄O**.

d) Give the structural formula of the reaction intermediate C₁₅H₁₆O and its IUPAC name.



1,3-diphenylpropan-2-ol (1pt for structure, 1 pt for the name)

e) Give the structural formula of compound **X** and its IUPAC name. Can you name the reaction to get from compound **X** to the intermediate?



(1pt for the structure)

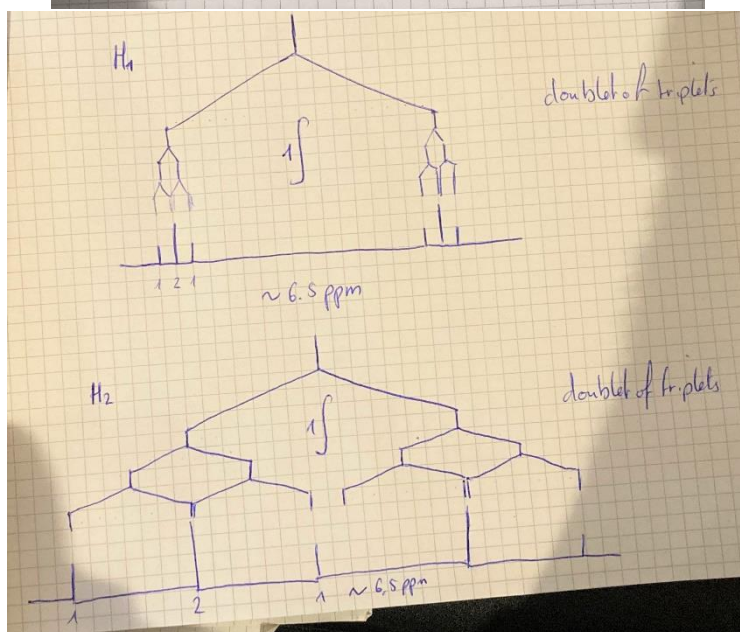
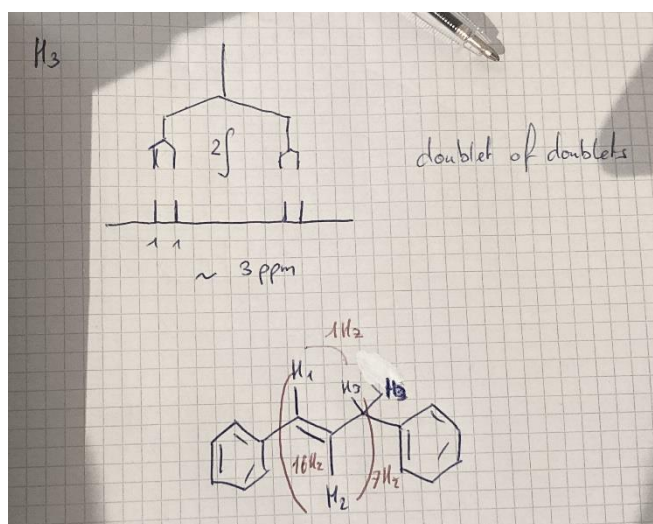
(E)-prop-1-ene-1,3-diyl dibenzene (1pt for the name, -0.25 if no stereo descriptor for double bond)

Hydroboration

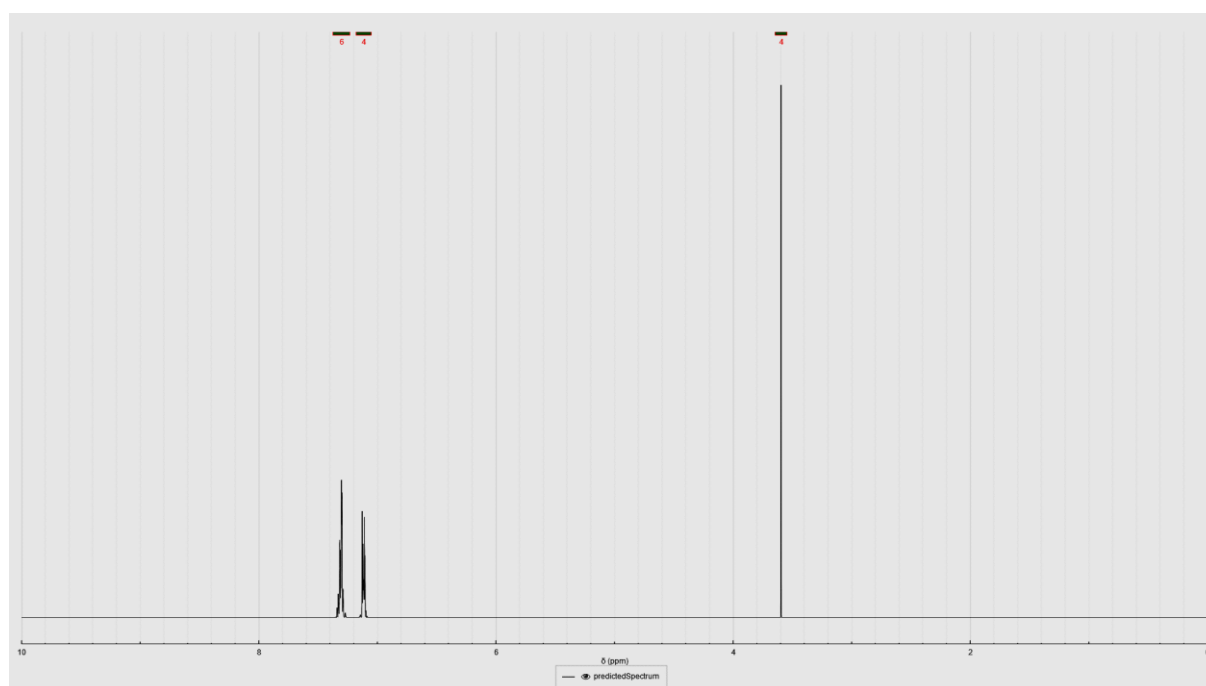
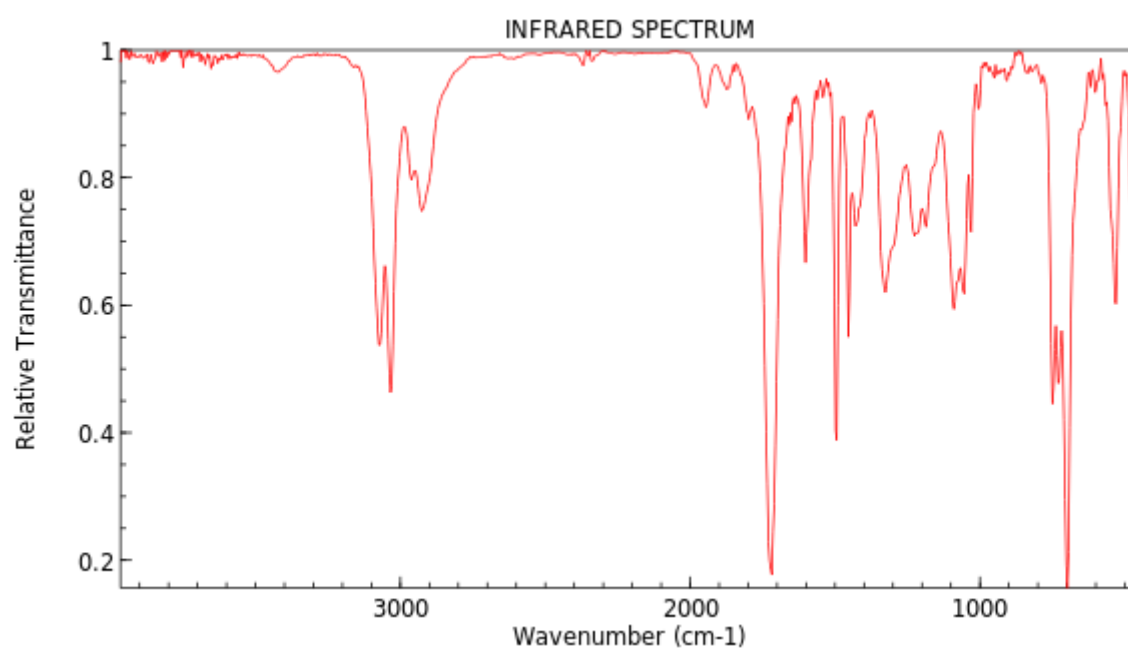
(1pt for reaction name)

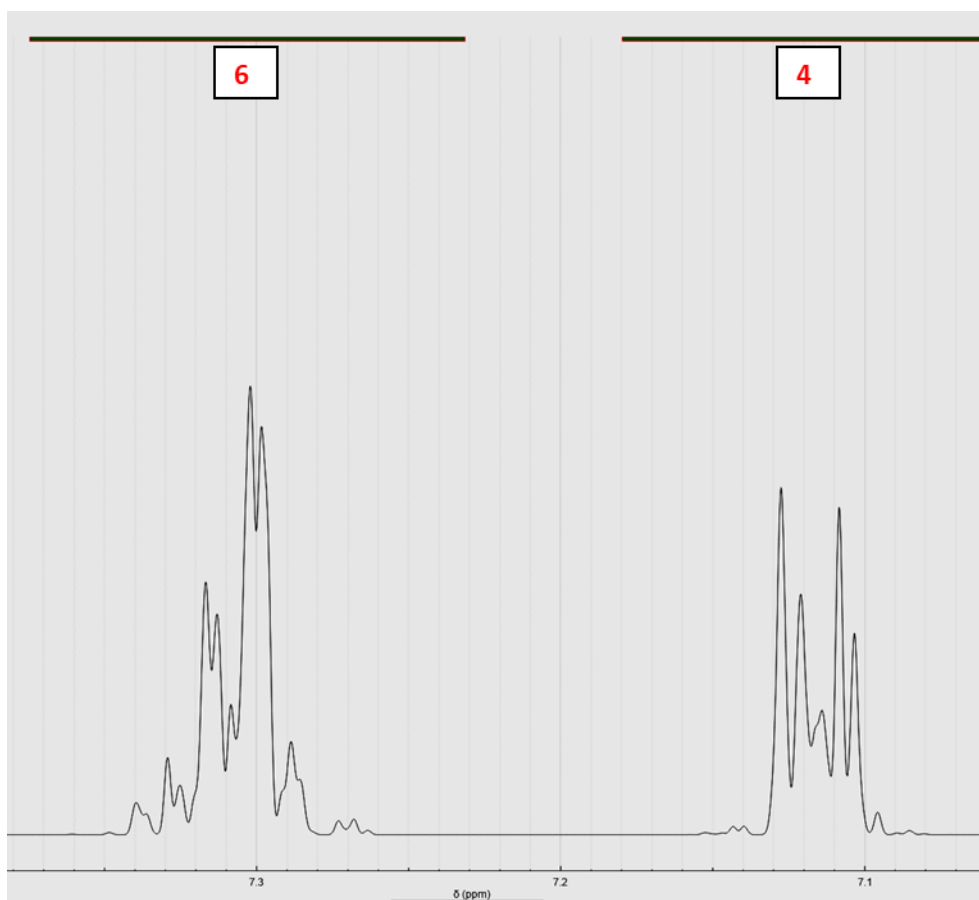
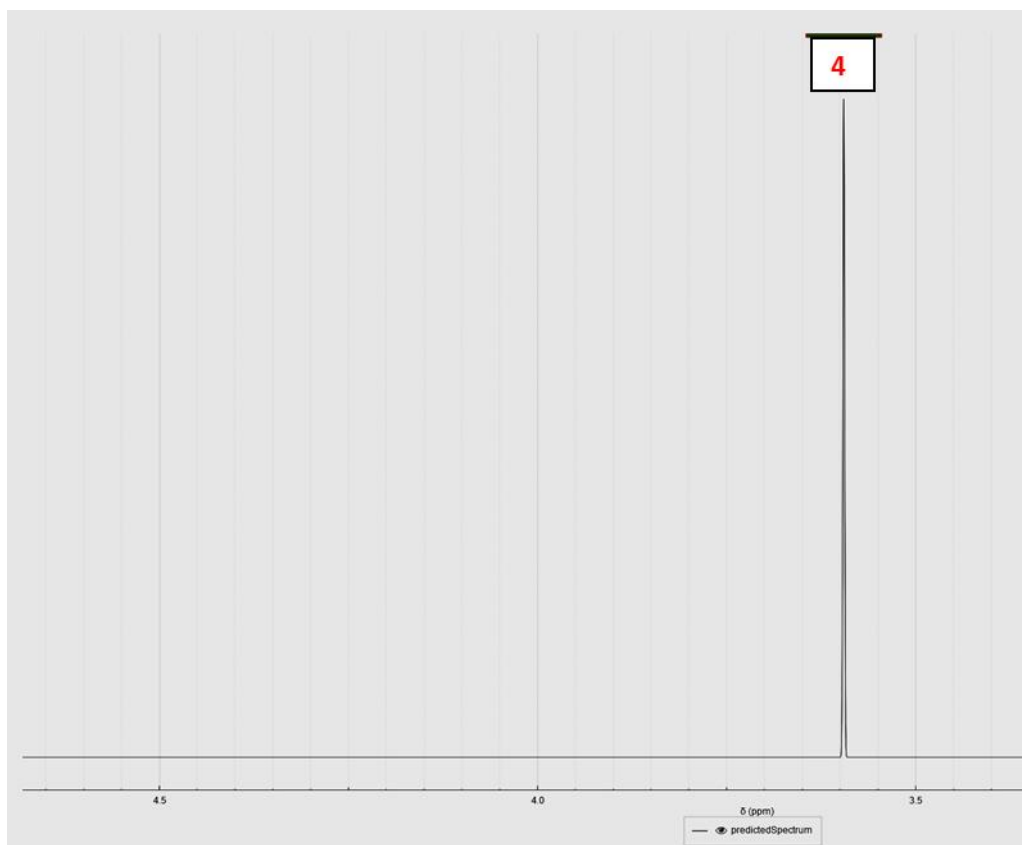
f) Detail in what way the ^1H -NMR spectrum will be different from $\text{C}_{15}\text{H}_{14}\text{O}$ in terms of chemical shift and multiplicity.

The singlet at 4 ppm will disappear (1pt) and will be replaced by a doublet of doublets (1pt) around 3 ppm (1pt) with an integral of 2 (1pt), a doublet of triplets (1pt) around 6.5 ppm (1pt) with an integral of 1 (1pt) and another doublet of triplets (1pt) around 6.5 ppm (1pt) with an integral of 1 (1pt)



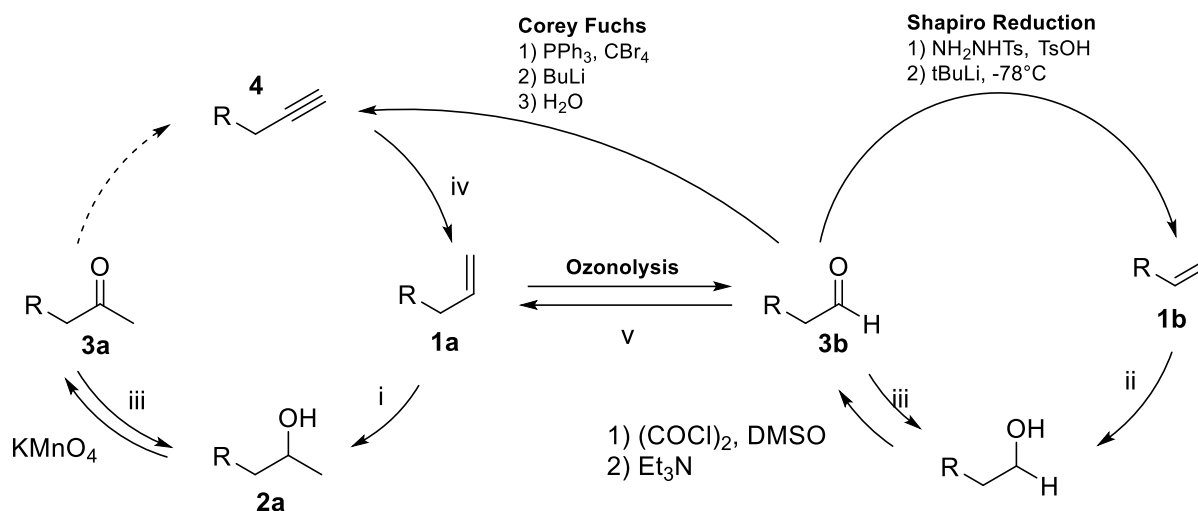
Compound **C₁₅H₁₄O**





Problem 9 – Functional Group Interconversion

Functional Group Interconversions are reactions which interchange different functional groups into each other. This is important in the total synthesis of many natural products, as changing functional groups gives rise to new ways of thinking about the synthesis of a natural product. Below you will find two seemingly similar circles, with ways to interchange functional groups into one another.

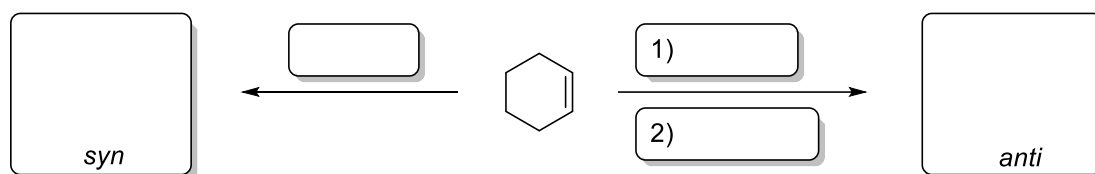


a) Firstly, let's have a look at the two alkenes in the circle. The goal is to install a hydroxy group at the double bond of 1a and 1b. Please provide conditions i and ii which to achieve the conversion to 2a and 2b.

i

ii

b) Instead of one hydroxy group, we want to install two in a vicinal relationship. Give the conditions and the product for two ways which produce different diastereoselectivities.



c) 2a and 2b are oxidized to yield 3a and 3b. Please provide conditions iii for the backreaction.

iii

d) What would be the product, when using $KMnO_4$ on 2b?

Product with $KMnO_4$

e) 3a is converted to 4 via a series of reactions. 4 is then reacted to the 1a under conditions iv. Please give reaction conditions iv.

iv

f) 1a can be converted to 3b by ozonolysis (cond. vi). The reverse reaction is achieved using conditions v. Please state the reaction conditions v and vi as well as the name corresponding to conditions v.

Conditions v

Name:

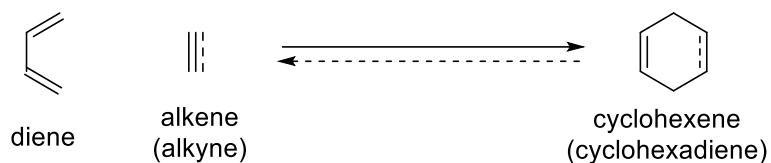
Conditions vi

Name: Ozonolysis

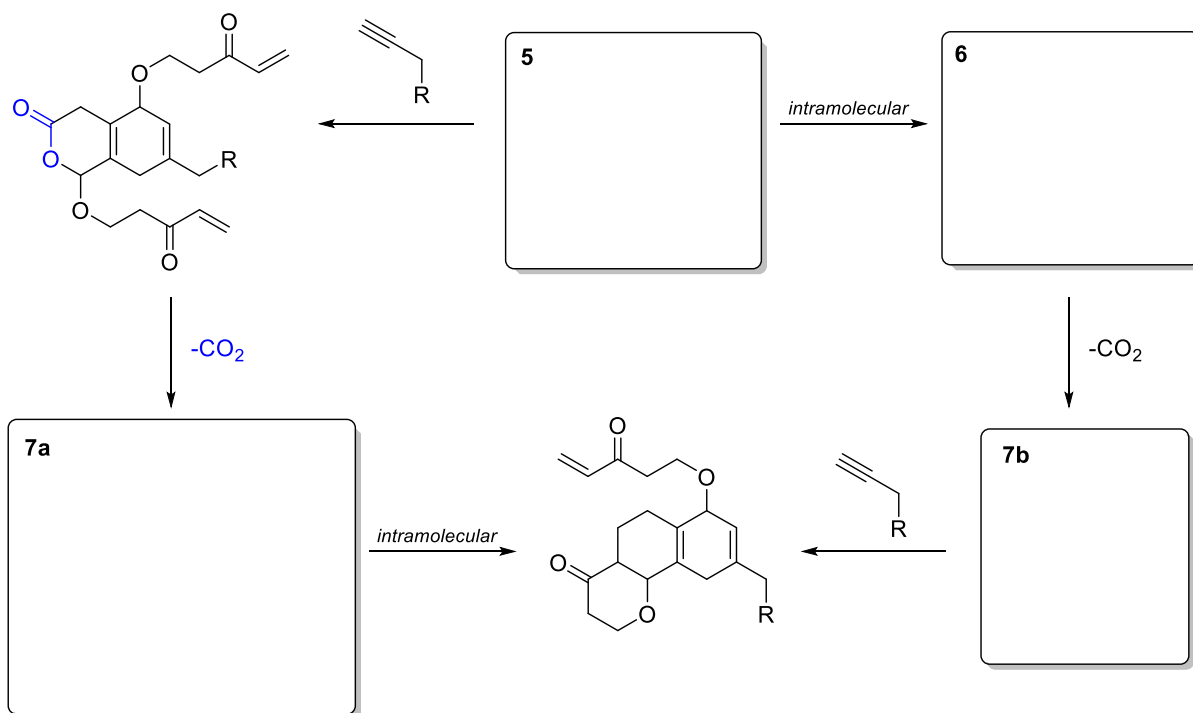
g) As discussed before, can the ketone 3a be converted to the alkyne 4 via a series of reactions. Please state the a feasible way of how to do so. (Hint: This can be achieved by using only the reactions stated in the scheme above)



h) Now, that we discussed some functional group interconversions, we want to do some chemical transformations with one of these products. The reaction we are going to look at is called Diels Alder Cycloaddition and is depicted below. The reaction converts a diene and an alkene or an alkyne into a cyclohexene or a cyclohexadiene. This reaction can also run in the opposite direction under the given conditions.

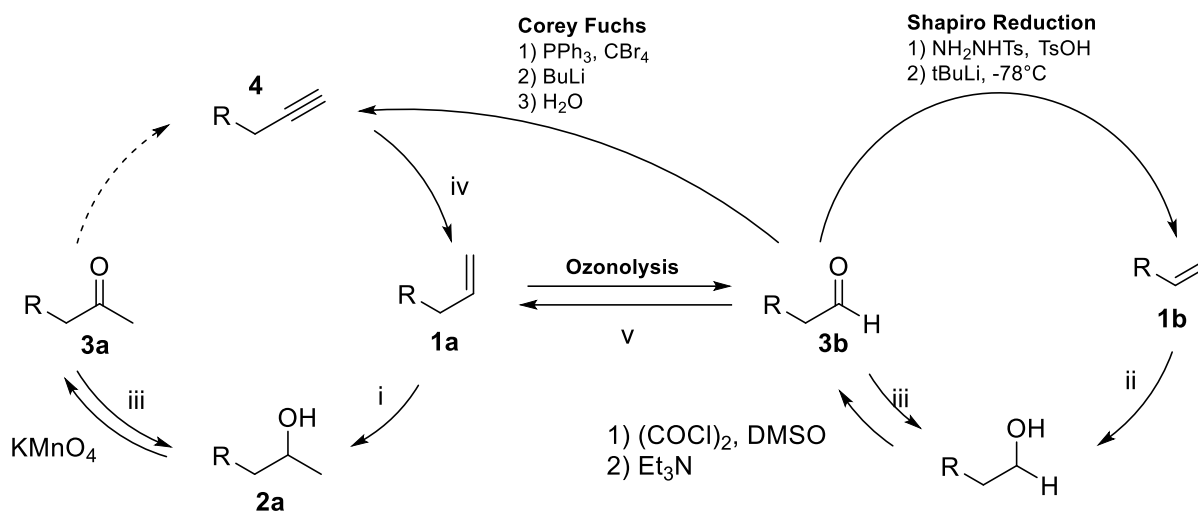


The alkyne 4 could also react with substrate 5 in the following reactions to yield in the product shown below. However, 5 could also react with itself to yield in product 6. Both products can then react further to products 7a and 7b. Which react further to the final product of this Reaction. Please provide substrates 5 to 7.



Problem 9 – Functional Group Interconversion

Functional Group Interconversions are reactions which interchange different functional groups into each other. This is important in the total synthesis of many natural products, as changing functional groups gives rise to new ways of thinking about the synthesis of a natural product. Below you will find two seemingly similar circles, with ways to interchange functional groups into one another.

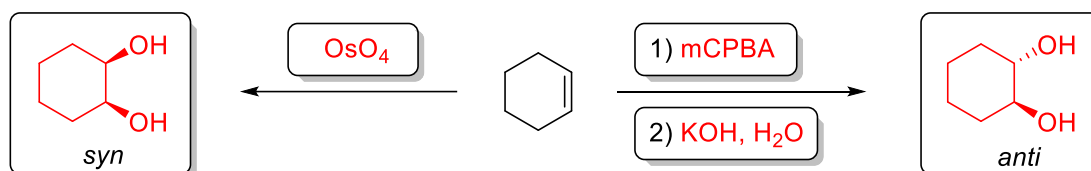


a) Firstly, let's have a look at the two alkenes in the circle. The goal is to install a hydroxy group at the double bond of 1a and 1b. Please provide conditions i and ii which to achieve the conversion to 2a and 2b.

i H_2O , H^+

ii BH_3 , then $\text{NaOH}/\text{H}_2\text{O}_2$

b) Instead of one hydroxy group, we want to install two in a vicinal relationship. Give the conditions and the product for two ways which produce different diastereoselectivities.

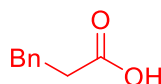


c) 2a and 2b are oxidized to yield 3a and 3b. Please provide conditions iii for the backreaction.

iii e.g. LiAlH_4

d) What would be the product, when using KMnO_4 on 2b?

Product with KMnO_4



e) 3a is converted to 4 via a series of reactions. 4 is then reacted to the 1a under conditions iv. Please give reaction conditions iv.

iv H_2 , lindlars cat.

f) 1a can be converted to 3b by ozonolysis (cond. vi). The reverse reaction is achieved using conditions v. Please state the reaction conditions v and vi as well as the name corresponding to conditions v.

Conditions v
[MePPh₃]⁺, NaH

Name: Wittig

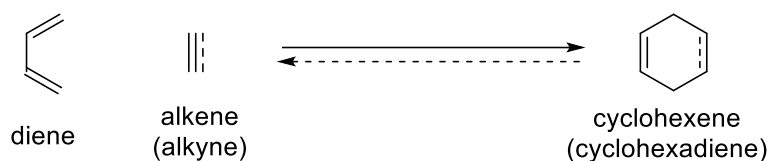
Conditions vi
O₃, -78°C, then SMe₂

Name: Ozonolysis

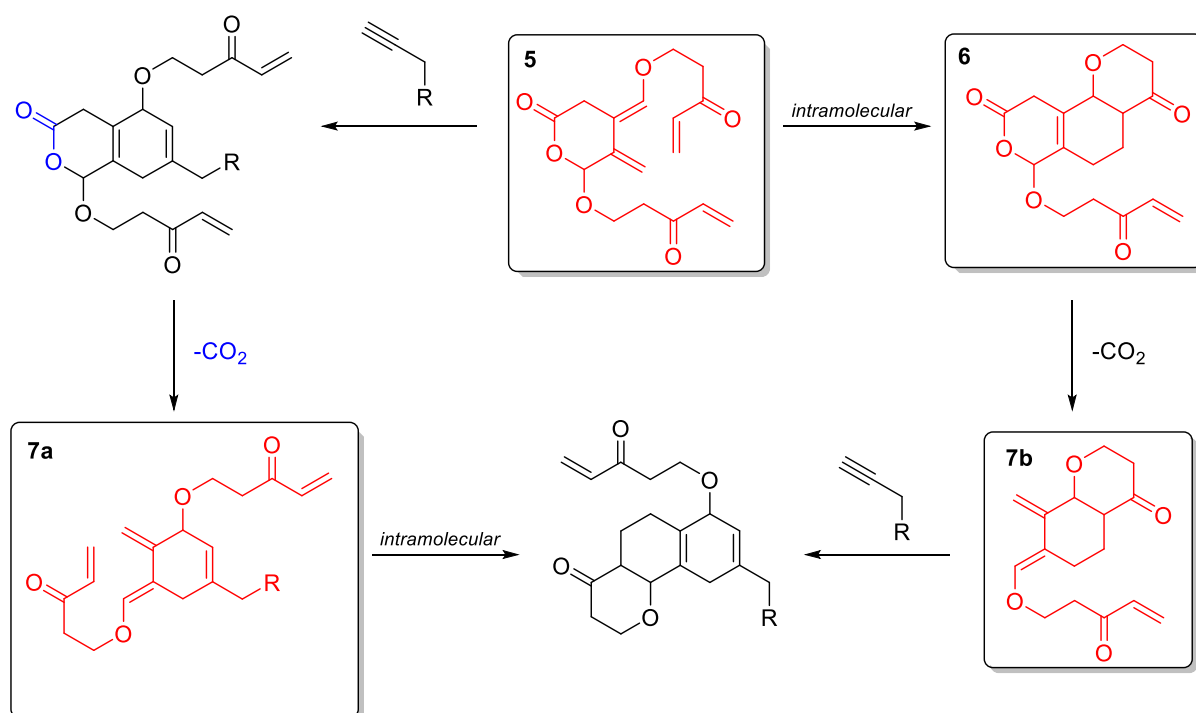
g) As discussed before, can the ketone 3a be converted to the alkyne 4 via a series of reactions. Please state the a feasible way of how to do so. (Hint: This can be achieved by using only the reactions stated in the scheme above)

Shapiro
Ozonolysis
Corey Fuchs

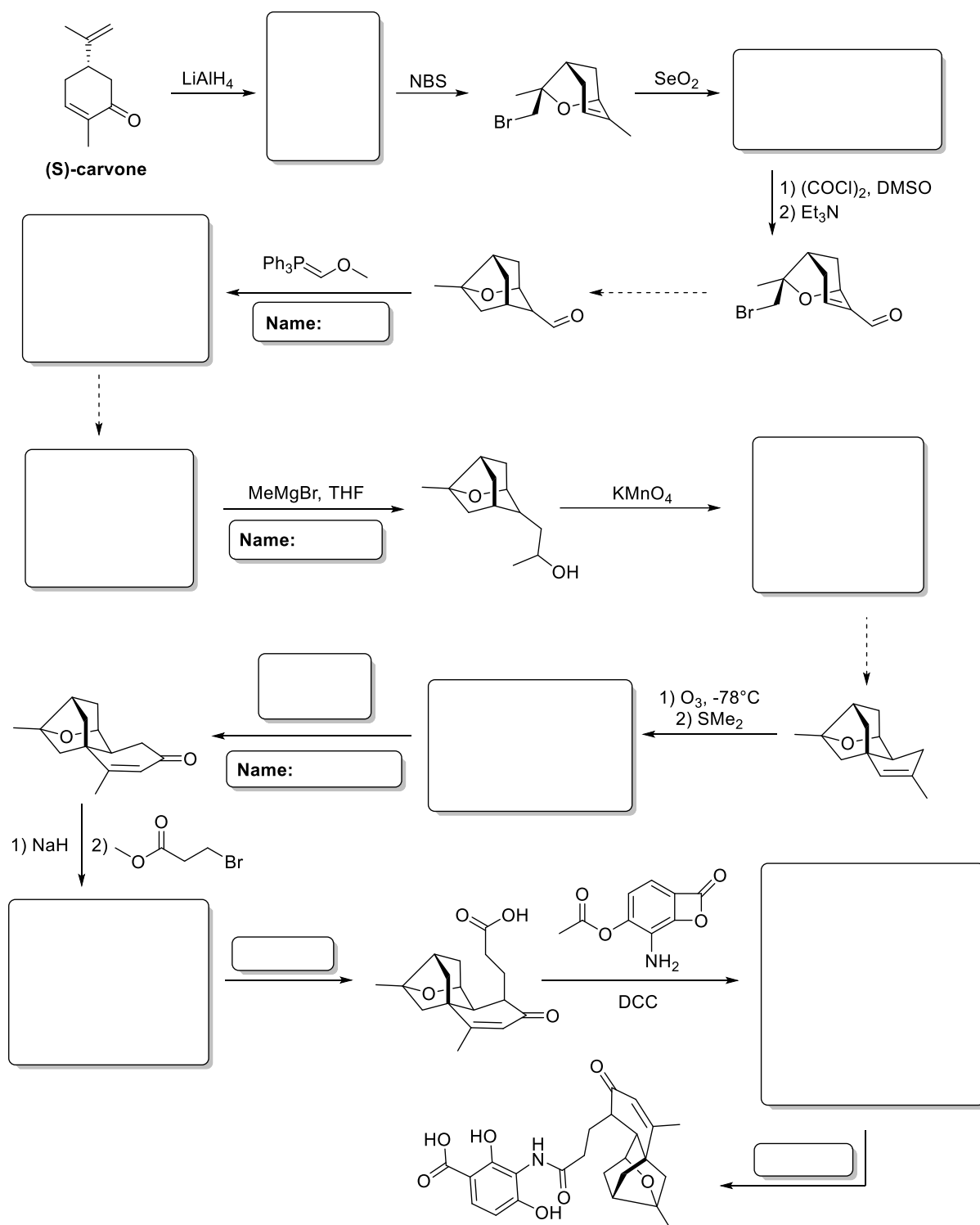
h) Now, that we discussed some functional group interconversions, we want to do some chemical transformations with one of these products. The reaction we are going to look at is called Diels Alder Cycloaddition and is depicted below. The reaction converts a diene and an alkene or an alkyne into a cyclohexene or a cyclohexadiene. This reaction can also run in the opposite direction under the given conditions.



The alkyne 4 could also react with substrate 5 in the following reactions to yield in the product shown below. However, 5 could also react with itself to yield in product 6. Both products can then react further to products 7a and 7b. Which react further to the final product of this Reaction. Please provide substrates 5 to 7.

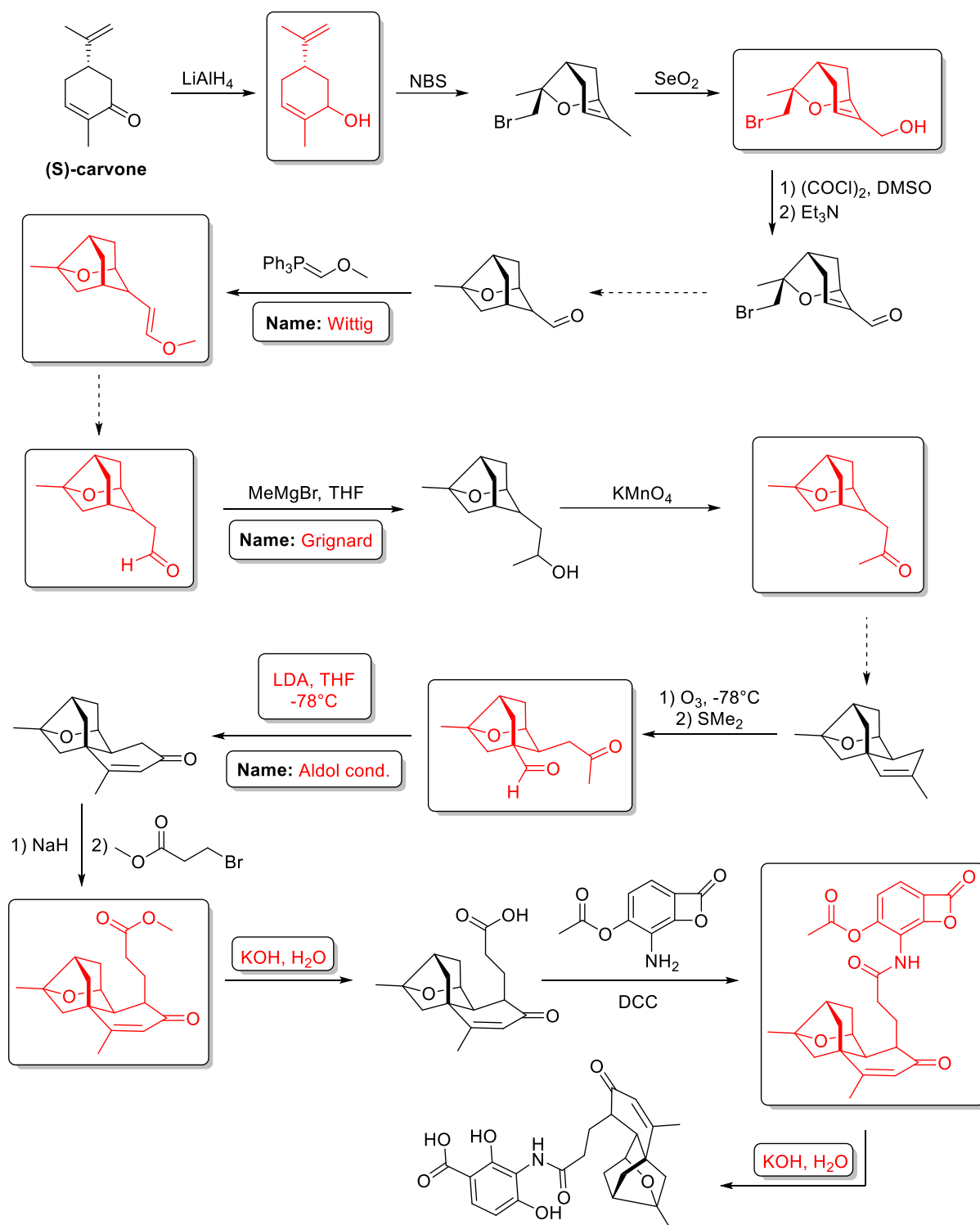


Problem 10 – Total Synthesis of Platensimycin from (S)-carvone



a) Fill in the missing reagents, reaction intermediates/products and names of the reactions where indicated.

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