

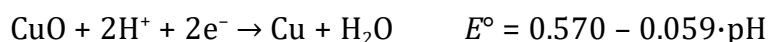
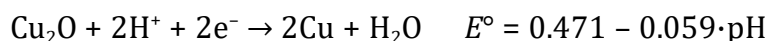
## 23rd BChO, 2015, Daugavpils, Latvia

### Problem 1 – ELECTRO – Copper Man

“Copper Man” was a Chilean copper miner who was entrapped in a copper mine in 550 AD and subsequently copperized (coated in copper). The mummy has become a subject of interest in archeology, metallurgy, and, more recently, art. Under the right conditions, charcoal dust can promote a reaction leading to Copper Man’s coating. Assume that Copper Man is coated in  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$ , originating from  $\text{Cu}^{2+}$  salts in the copper mine.

- a)** State the role of charcoal in this reaction: **i)** reducing agent; **ii)** oxidizing agent; **iii)** catalyst; **iv)** insulator; **v)** none of the above.

Consider the following reactions and reduction potentials:

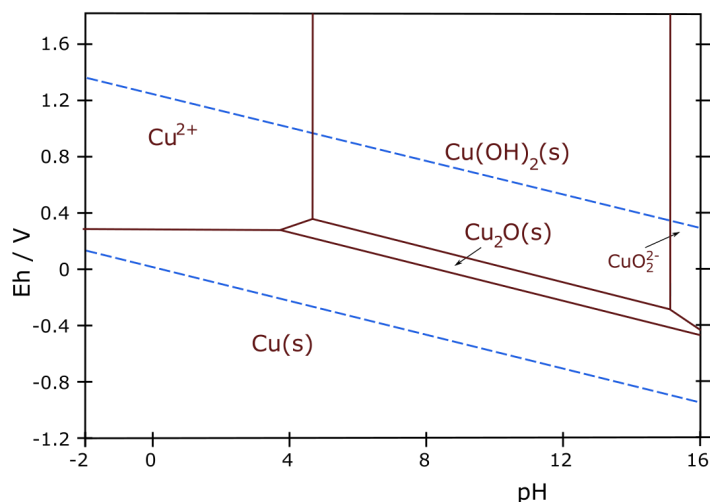


- b)** For a neutral ( $\text{pH} = 7.0$ ) environment, construct a Latimer diagram for the above couples and calculate the potential for the  $\text{CuO}/\text{Cu}_2\text{O}$ .

Chalcanthite, the pentahydrate of copper sulfate, was the mineral that Copper Man was harvesting from the mine. In order to extract copper from the chalcanthite, Copper Man heated the chalcanthite to  $>700^\circ\text{C}$  in the presence of  $\text{Na}_2\text{O}$ , at which point an explosion would occur due to the following reactions: (1)  $4\text{CuSO}_4 + 4\text{Na}_2\text{O} \rightarrow 4\text{Na}_2\text{SO}_4 + 2\text{Cu}_2\text{O} + \text{O}_2$  and (2)  $\text{Cu}_2\text{O} + \text{CO} \rightarrow 2\text{Cu}^0 + \text{CO}_2$ .

- c)** Calculate the Gibbs free change energy for these reactions using the half-reaction standard potentials. For  $\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-}$ , use  $E^\circ = 0.11\text{ V}$ , and for  $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$  use  $E^\circ = 1.23\text{ V}$ .

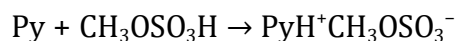
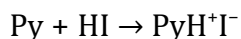
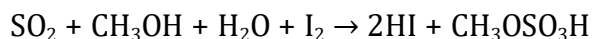
For an exhibition, you must recreate Copper Man using a galvanic cell. Consider the Pourbaix diagram of copper.



- d)** Draw a diagram of a two-compartment galvanic cell that incorporates Copper Man as an electrode in solution **X** coupled to a metal **Y** electrode in a solution of the same metal ions. Label all components, including the electrodes (cathode and anode), the electrolyte species, and the reactions occurring at the electrodes. Choose the main component of the solution **X**:  $\text{CuCl}_2$ ,  $\text{Na}_2\text{CuO}_2$ ,  $\text{Cu(OH)}_2$ ,  $\text{CuCl}$ . Choose metal **Y** suitable for copper plating in the galvanic cell: Zn, Ag, Na, Au.

## Problem 2 – CALC, SPECTRA – Determination of water content

Very small water quantities can be measured with different methods: Karl Fischer titration, nuclear magnetic resonance, infrared spectroscopy, gas chromatography, and UV-Vis spectroscopy. In Karl Fischer titration, a mixture of iodine, pyridine (Py), sulfur dioxide, and methanol is used. In the presence of water, the following reactions take place:



Usually, the limiting component of the reaction is iodine. As Karl Fischer's titrant is somewhat unstable, the practical titer (mass of analyte per volume of titrant) is often determined right before the analyses of a sample. An analyst weighed 260.3 mg of pure water and filled the 100 cm<sup>3</sup> volumetric flask with acetonitrile that did not contain any water. 10.00 cm<sup>3</sup> of the sample was taken for analyses, and 6.20 cm<sup>3</sup> of titrant was spent to reach the endpoint.

**a)** Calculate the titre (mg cm<sup>-3</sup>) of the Karl Fischer titrant.

The same titrant was used to determine the water content of commercial acetonitrile. 20.00 cm<sup>3</sup> of the commercial acetonitrile was titrated with 5.12 cm<sup>3</sup> of titrant. The density of acetonitrile is 0.786 g cm<sup>-3</sup>.

**b)** Determine the water content in commercial acetonitrile (% and ppm).

A coulometric Karl Fischer titration is used in a laboratory, where one of the reagents I<sub>2</sub> is generated electrochemically from I<sup>-</sup>. The bias of the coulometric titration was of interest. 4.113 g of acetonitrile (with an unknown amount of water) was analyzed with the coulometric Karl Fischer method, and 138.7 C was passed through a coulometer. 143.2 mg of water was weighed into a 100 cm<sup>3</sup> volumetric flask and filled with the same acetonitrile to mark. 2.714 g of the sample was taken for analysis and 145.3 C was used for complete titration of the sample.

**c)** Calculate the bias for this titration.

The same procedure was repeated with 1.356 g of water weighted into a 100 cm<sup>3</sup> volumetric flask. For titrating 1.194 g of this sample, 306.7 °C was used.

**d)** Calculate the bias for this titration.

**e)** Explain why two titrations can have a significantly different bias in this case.

Karl Fischer titration can also be used for water determination in solid samples if these can be dissolved in the appropriate solvent. However, some building materials such as cement, chalk, and ceramic materials can not be analyzed in this way due to occurring side reactions. Therefore, infrared spectroscopy was used. Two chalk-based reference materials containing 2.1 mg kg<sup>-1</sup> and 17.2 mg kg<sup>-1</sup> of H<sub>2</sub>O were measured with the attenuated total reflectance (ATR) method. At peak, maximum absorptions observed were 0.045 and 0.371 AU.

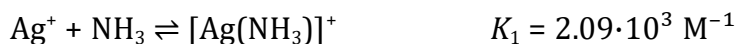
**f)** What side reaction occurs for these materials, and how does it influence the bias of Karl Fischer's method?

Lambert-Beer law states that  $A = \epsilon lc$ , where  $A$  is the absorption at wavelength  $\lambda$ ,  $\epsilon$  is the molar attenuation coefficient at wavelength  $\lambda$ ,  $l$  is the optical path length, and  $c$  is the analyte concentration. Assume that the optical path length is the same for all three measured materials.

- g) With the IR-ATR method, a chalk sample was also analyzed, and an absorbance of 0.276 AU was recorded at the peak maximum. Based on the Lambert-Beer law, calculate the water content in the chalk sample.

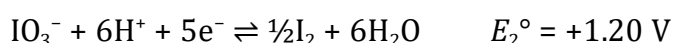
### Problem 3 – ELECTRO, EQUIL, KINETICS – Some simple physical chemistry

An equilibrium is reached in 0.10 M AgNO<sub>3</sub> and  $x$  M NH<sub>3</sub>·H<sub>2</sub>O solution:



- a) Calculate the value of  $x$  at the maximal concentration of [Ag(NH<sub>3</sub>)<sup>+</sup>].

Equal amounts of KIO<sub>3</sub> and KI (0.10 M each) react in a solution of H<sub>2</sub>SO<sub>4</sub> at an initial pH value of 3.00.



- b) Calculate the pH value of the solution at equilibrium.

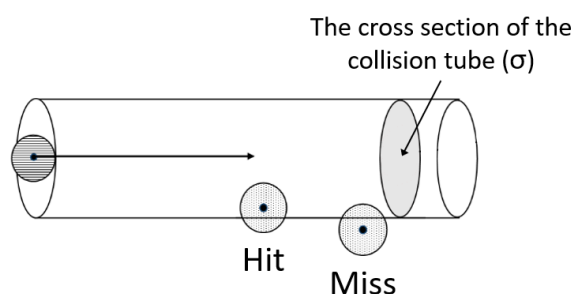
$\alpha$ -halogenation of aldehydes and ketones is an autocatalytic reaction, i.e. the byproduct H<sup>+</sup> is the catalyst for that reaction: R'COR + X<sub>2</sub> = RCORX + H<sup>+</sup> + X<sup>-</sup>. The reaction rate is expressed as:

$$r = k[\text{R}'\text{COR}][\text{X}_2][\text{H}^+].$$

- c) Calculate the concentration [X<sub>2</sub>] at which the rate is maximal if [R'COR]<sub>0</sub> = [X<sub>2</sub>]<sub>0</sub>.

### Problem 4 – CALC, KINETICS – Harpoons and collisions

When modeling the path of a single atom A, it is useful to use it as a point of reference and “freeze” all the other species in their own places. Therefore, we only have to consider any other particles when they collide with the atom whose path we are modeling. If a center of another species B is located in such a way that the atom A will hit it, it is said to be in the *collision tube* of the atom A.



- a) Given that a golf ball with a radius of 2.3 cm is touching a basketball with a radius of 12.5 cm, calculate the distance between their centers.
- b) Hence, calculate the radius ( $R$ , in meters) and area ( $\sigma$ , in square meters) of the cross-section of the collision tube created by a gaseous potassium atom moving through bromine gas. The radius of a potassium atom is 243 pm and the “radius” of a bromine molecule is 165 pm.

The collision tube as a model is used in the kinetic theory of gases. By applying this model, a useful equation for the rate constant of second-order reactions can be obtained:

$$k_2 = \sigma \bar{c} N_A \exp\left(\frac{-E_a}{RT}\right),$$

where  $\bar{c}$  is the average effective velocity of the gas molecules. The pre-exponential term describes the number of collisions occurring, while the exponential term describes the proportion of successful collisions

- c) Write the more common form of this equation.
- d) A second-order reaction has a rate constant of  $1000 \text{ M}^{-1} \text{ s}^{-1}$ , an effective cross-sectional area of the collision tube of  $1.0 \cdot 10^{-18} \text{ m}^2$ , and an average effective velocity of gas molecules of  $100 \text{ m s}^{-1}$  in standard conditions. What is the activation energy of the reaction in  $\text{kJ mol}^{-1}$ ?
- e) Consider a reaction whose activation energy is 0 J. Choose the correct statements:
- An appropriately selected catalyst would speed up this reaction;
  - Every reactant atom/molecule has sufficient energy for the reaction;
  - The reaction enthalpy change has to be zero or negative;
  - The reactants are likely to be charge free and only contain paired electrons.
- f) Referring back to the beginning of the problem, calculate the  $k$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of the reaction between gaseous potassium and bromine at  $800 \text{ }^\circ\text{C}$ . Assume that the activation energy of the reaction is 0 J.  $\bar{c} = \sqrt{8k_{\text{B}}T/\pi\mu}$ , where  $\mu$  is the reduced mass of the particles involved  $\mu = m_1 m_2 / (m_1 + m_2)$ .

However, the measured  $k$  of the reaction is larger than the calculated value at  $1.0 \cdot 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ , which seemingly suggests that *more* species react than actually collide. This is because of the so-called harpoon mechanism – the potassium atom “shoots” an electron into the bromine molecule even before the collision takes place. This occurs due to the fact that the cross-sectional area ignores the effect of the geometry of collisions on the reaction, as it assumes that all collisions, in most cases, are equal.

- g) Assess how the transfer of the electron impacts the size of the particles and, thus, the cross-sectional area of the collision tube! (Note: each incorrect answer will incur negative marks, with the total for this question not less than 0)
- i) What is the effect of ionization of the K atom on its size?
- i) It increases as the loss of the charge of one electron weakens the attraction between the nucleus and the electron cloud.
  - ii) It increases as the loss of the 4s orbital weakens the shielding experienced by other orbitals, thus diffusing them.
  - iii) It decreases as the lost electron is the only one in the 4<sup>th</sup> energy level.
  - iv) It decreases as the volume of the orbital the electron occupies is lost.
- ii) What is the effect of electron transfer to the bromine molecule on its size?
- i) It increases as the new electron occupies a bonding molecular orbital.
  - ii) It increases as the new electron occupies a non-bonding molecular orbital.
  - iii) It decreases as the new electron occupies a bonding molecular orbital.
  - iv) It decreases as the new electron occupies a non-bonding molecular orbital.
- iii) What is the net effect of the electron transfer on the cross-sectional area of the collision tube: i) It increases; ii) It decreases; iii) Insignificant effect; iv) Not enough data given.

The modified reactive cross-section area  $\sigma^*$ , which should be used for reactions proceeding by a harpoon mechanism, can be calculated from radius  $R_{\text{h}}^*$  using the equation:  $\sigma^* = \pi(R_{\text{h}}^*)^2$ .

$R_h$  describes the separation of centers of reacting species. There are three contributions to the energy of interaction between the colliding species: ionization energy of potassium (abbreviated as  $I$ ), electron affinity of bromine gas ( $E_{EA}$ ) and Coulombic interaction (CI) energy between the ions when they have been formed given by the equation:  $CI = -e^2/(4\epsilon_0 R_h)$ .  $R_h$  is a distance when all these three contributions to the energy are in balance, thus,  $0 = I - E_{EA} + CI$ .

**h)** Calculate the radius  $R_h$  and reactive cross-section area  $\sigma$ , if it is given that  $I = 420 \text{ kJ mol}^{-1}$ ,  $E_{EA} = 250 \text{ kJ mol}^{-1}$ , vacuum permittivity constant  $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ , and elementary charge  $e = 1.602 \cdot 10^{-19} \text{ C}$ .

Usually, to describe such a reaction, a steric factor  $P$  is introduced, which connects reactive cross-section area  $\sigma^*$  with collision cross-section area  $\sigma$  so that  $\sigma^* = P\sigma$ .

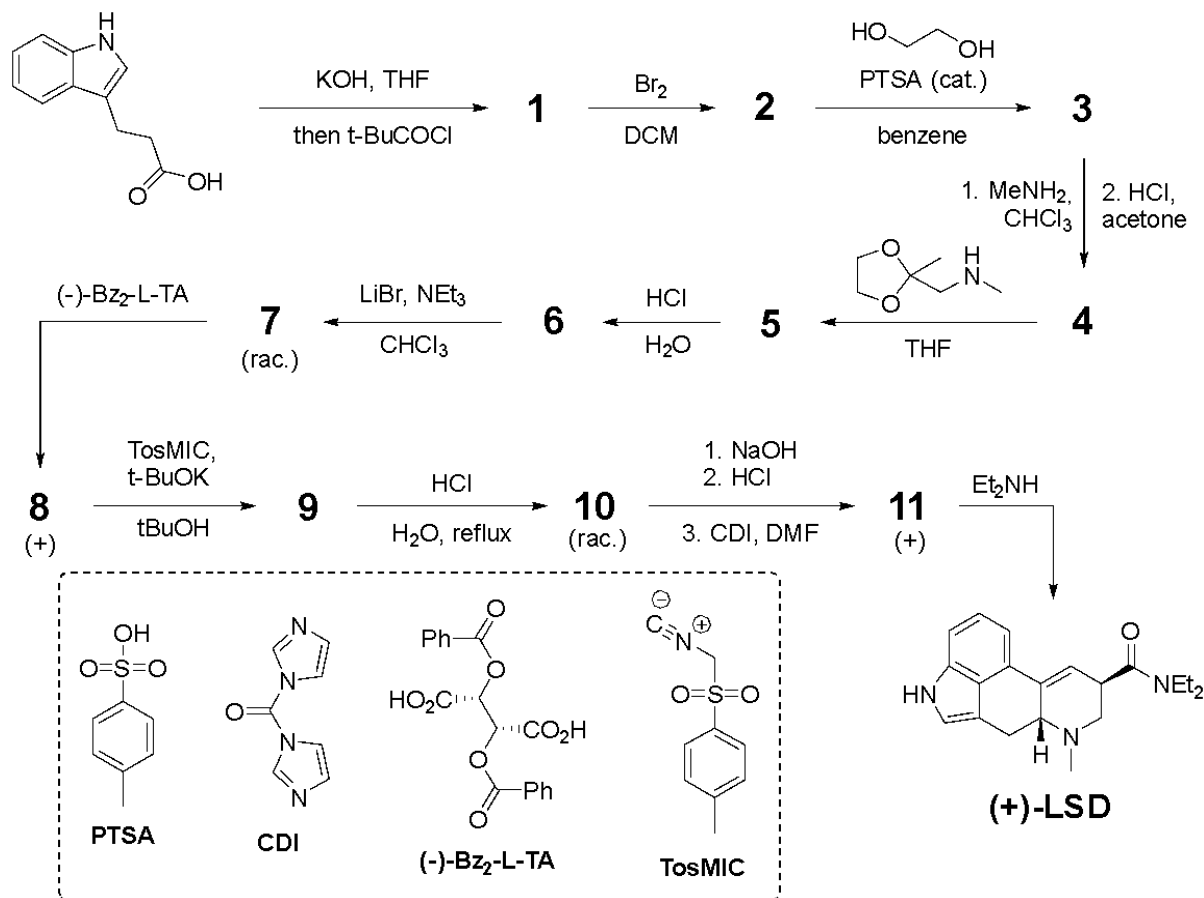
**i)** Calculate the steric factor  $P$ .

**j)** Now calculate the  $k$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of the same reaction at  $800 \text{ }^\circ\text{C}$  using  $\sigma^*$  instead of  $\sigma$ .

### Problem 5 - BIO, SYNTH - Lucy in the Sky with Diamonds

Back in the days of 1967, this famous song by the Beatles was released. It did not take long for hippies to notice that an abbreviation would be LSD. This, one of the most widely known chemical substances, was first synthesized in 1938 by Swiss chemist Albert Hofmann. Up to around 1980, it was used as a psychiatric drug or for research purposes.

Today, you will have a chance to synthesize (on paper!) this highly biologically active compound that boasts a tetracyclic carboskeleton. Such an arrangement was and still is quite problematic if one tries to devise a synthesis route from very simple starting materials. Hence, you will begin your synthesis from already bicyclic indole-3-propionic acid.

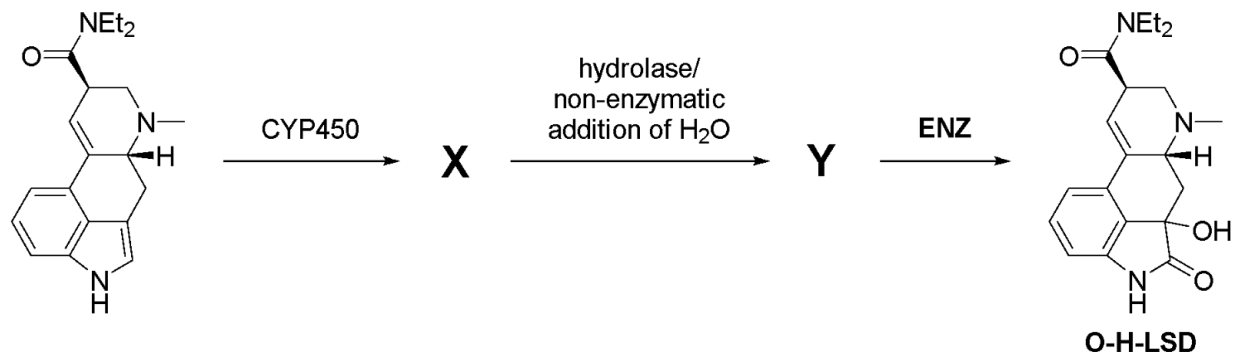


Compound **1** is known to be tricyclic; compound **7** is known to be tetracyclic; (rac.) denotes "racemate"; compound **9** has one stereocenter.

a) Draw structural formulas of compounds **1–11** with stereochemistry.

b) Draw reaction mechanism of **8** + TosCH<sub>2</sub>NC: → **9**.

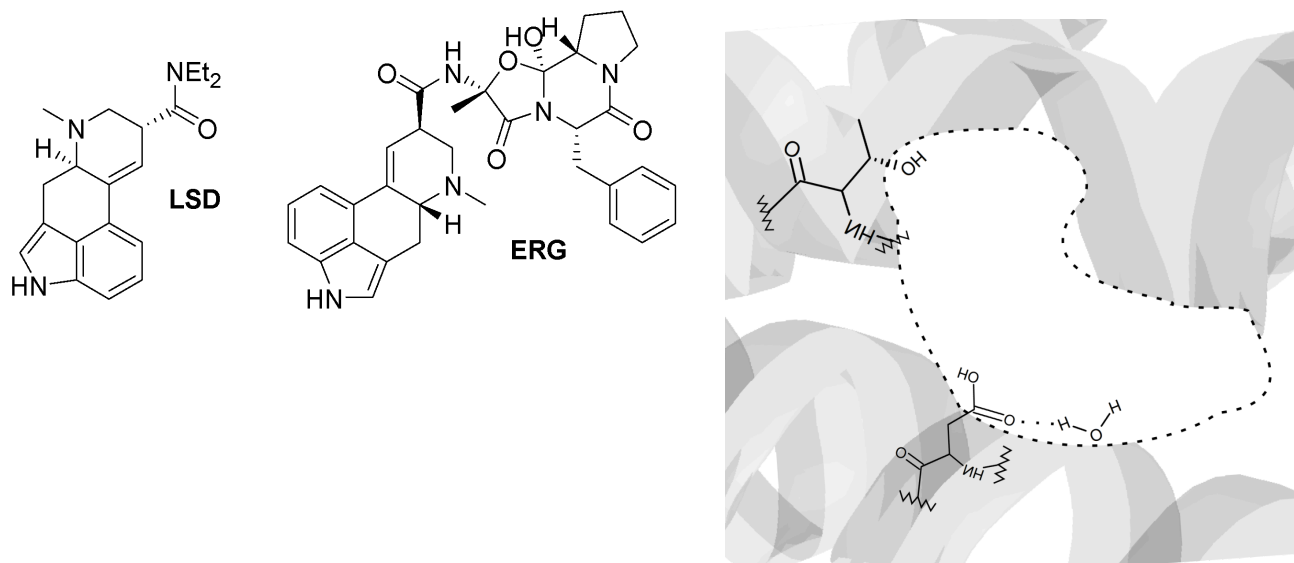
From a biochemical standpoint, lysergic acid diethylamide binds to the serotonin receptors in the body, but the hallucinogenic effect lasts for up to 6-8 hours, meaning that its metabolism is quite fast. Studies have shown that metabolism in human organisms proceeds through O-H-LSD intermediate. A mechanism of O-H-LSD formation was proposed, but it seems that some information is missing.



c) Decipher structures **X** and **Y** and suggest an enzyme (**ENZ**) for the final step. It is known that **ENZ** should belong to Oxidoreductases. Note: The substrate of the enzyme is not supposed to be specified, e.g., the answers deaminase or oxidase are specific enough.

Biochemists have shown that LSD and its precursor ergotamine ERG bind the same serotonin receptor to its active site.

d) Considering that LSD and ERG bind the same receptor site, outline the physiologically active part in each molecule.



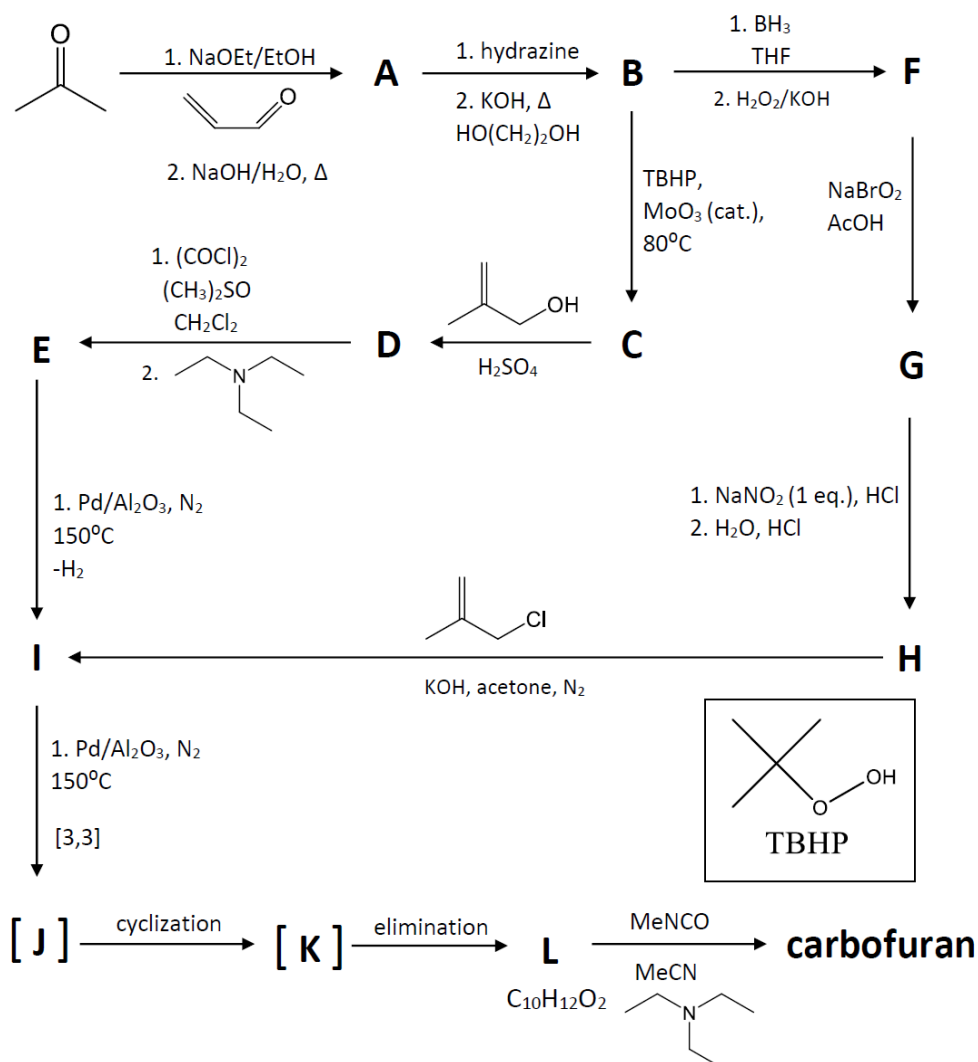
e) Fit the LSD molecule into the active site of the serotonin receptor and show molecular interactions.

### Problem 6 – SYNTH – Easy grow, easy bloom

Carbofuran is one of the most toxic insecticides and, therefore, is banned in Canada and the European Union. However, this pesticide is still widely used in other countries to control the amount of insects in potato, pumpkin, and sunflower fields.

Carbofuran can be produced quite easily from many simple chemical substances, but the main drawbacks of these processes are the expense of production and the toxicity of chemicals involved in the syntheses. However, in the 1980s, several alternative methods for carbofuran production were invented, which are relatively safe and require cheap starting materials (acetone in this case). The synthesis scheme of carbofuran, a bicyclic compound, is given below.

(*cat.*) – catalyst, (*eq.*) – equivalent



- Draw the mechanism of the reaction **A**  $\rightarrow$  **B**.
- Draw the structural formulas of **C** and **D**. Also, write all possible compound **D** stereoisomers, which can be produced in the reaction **C**  $\rightarrow$  **D**, mark all the stereocenters with "\*", and indicate their *R/S* configuration.
- Draw the structure of compound **E**. Taking into account that the reaction **D**  $\rightarrow$  **E** was carried out using only enantiomerically pure compound **D'** (one of **D** stereoisomers) with all the stereocenters having only *R*-configuration, draw the stereoisomer(s) of compound **E** which would be synthesized in the reaction **D**  $\rightarrow$  **E**.

**d)** Write the structural formulas of compounds **F**, **G**, **H** and **I**.

**e)** Show the mechanism of the reaction **G** → **H**.

Compound **E** heated with Pd/alumina catalyst in nitrogen atmosphere produces intermediate **I** which further heated under the same conditions gives more stable compound **J** and then, bicyclic compound **K**. These intermediates are not extracted in this synthesis but are further heated to produce compound **L**.

**f)** Draw the structures of compounds **J**, **K** and **L**.

**g)** In the reaction from **J** to **K**, a second ring is formed. How could the ring be named separately?

- Oxyfuran
- Dehydrofuran
- Benzofuran
- Dihydrofuran
- Ketofuran

**h)** Finally, the last step gives us the final product, carbofuran. Draw the structure of carbofuran.