



Dobeles novads

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NACIONĀLAIS
ATTĪSTĪBAS
PLĀNS 2020



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NACIONĀLA UN STARPTAUTISKA MĒROGA PASĀKUMU ĪSTENOŠANA
IZGLĪTOJAMO TALANTU ATTĪSTĪBAI



29th Baltic Chemistry Olympiad
Dobeles, Latvia, April 19-21, 2023

THEORETICAL EXAM SOLUTIONS

April 20th, 2023
Dobeles, Latvia

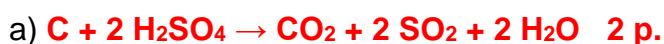
Problem No.1 – Determination of protein content by Kjeldahl method (10% of total)

The Kjeldahl method was developed in 1883 by the Danish chemist Johan Kjeldahl. It was designed to determine the nitrogen content in organic compounds. Although 140 years have passed, this method is still used to determine protein content in food. The method consists of three stages: digestion, distillation, titration and calculations.

I. Digestion stage

At the digestion stage, nitrogen in sample is converted into ammonium ions. Digestion is achieved by adding excess of concentrated sulfuric acid to sample and boiling mixture for a few hours.

1.1. **Write** the balanced equation for the reaction between heated concentrated sulfuric acid and: a) C, b) S.



1.2. Will boiling concentrated sulfuric acid convert nitrate ions into ammonium ions? **Circle** the correct answer.

Yes / **No** 2 p.

Concentrated sulfuric acid is 98 % H_2SO_4 solution. Interestingly, pure, anhydrous sulfuric acid contains not only H_2SO_4 molecules. As the equilibrium is reached, HSO_4^- ; $HS_2O_7^-$; $H_2S_2O_7$; H_3O^+ ; $H_3SO_4^+$ are also found.

1.3. **Fill in** the table by entering formulas.

Compound	Quantity (mmol) in 1 kg pure H_2SO_4
HSO_4^-	14.9
$H_3SO_4^+$	11.3
H_3O^+	8.0
$HS_2O_7^-$	4.4
$H_2S_2O_7$	3.6

Explanation: since total charge of solution should be equal 0, c(cations) = c(anions).

4 p for all 3 correct. 0 p for any mistake.

1.4. **Tick** the correct answer.

The addition of NaCl and/or Na_2SO_4 will increase the boiling point of H_2SO_4 . There is little to no difference, if NaCl or Na_2SO_4 is used.

The addition of NaCl will increase the boiling point of H₂SO₄. For faster digestion it is significantly better to add NaCl than Na₂SO₄.

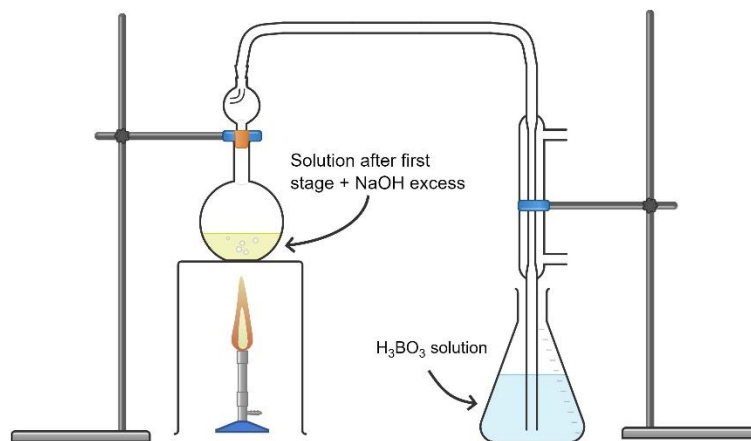
The addition of Na₂SO₄ will increase the boiling point of H₂SO₄. For faster digestion it is significantly better to add Na₂SO₄ than NaCl.

The addition of NaCl and/or Na₂SO₄ will reduce the boiling point of H₂SO₄.

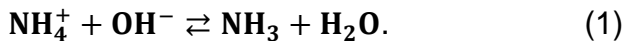
The addition of NaCl and/or Na₂SO₄ will reduce the boiling point of H₂SO₄, however, salt will act as a catalyst.

2 p.

II. Distillation stage



At the distillation stage, solution from digestion stage with formed (NH₄)₂SO₄, is exposed to an excess of NaOH solution. Ammonium ions react with hydroxide ions:



1.5. Is solution after first stage mixed with NaOH excess is buffer solution? **Circle** the correct answer.

Yes / **No** 2 p.

1.6. **Calculate** the equilibrium constant for (1) reaction, knowing that the pH of the 0.50 mol/l (NH₄)₂SO₄ solution is 4.63.

$$c(\text{NH}_4^+) = 1,0 \text{ mol/l. pH}=4.63, \text{ so } c(\text{H}_3\text{O}^+) = 10^{-4.63} = 2.344 \times 10^{-5} \text{ mol/l}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{NH}_4^+]} = \frac{(2.344 \times 10^{-5})^2}{1} = 5.5 \times 10^{-10} \quad \mathbf{3 \text{ p}}$$

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-, K_b = \frac{1 \times 10^{-14}}{K_a} = 1.8 \times 10^{-5}$$

$$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}, K = \frac{1}{K_b} = \frac{1}{1.8 \times 10^{-5}} = 5.5 \times 10^4 \quad \mathbf{3 \text{ p}}$$

Answer: 5.5×10^4

Generated ammonia reacts with boric acid excess. Boric acid is very convenient to use, since there is no need to know its exact concentration. After reaction, solution can be titrated with a strong acid. In solution boric acid is ionized by water:

$H_3BO_3 + H_2O \rightleftharpoons [H_2BO_3]^- + H_3O^+$ $pK_{a1} = 9.24$ ($pK_{a1} \gg pK_{a2}; pK_{a3}$). However, studies have shown that boric acid solution contains $[H_4BO_4]^-$ ions due to the reaction below:

$H_3BO_3 + 2H_2O \rightleftharpoons [H_4BO_4]^- + H_3O^+$, reaction $pK = 9.14$.

1.7. Assume that both reactions occur in the boric acid solution. **Calculate** 0.10 mol/l H_3BO_3 pH.

$$H_3BO_3 + H_2O \rightarrow [H_2BO_3]^- + H_3O^+, K_1 = \frac{[[H_2BO_3]^-][H_3O^+]}{[H_3BO_3]} \approx \frac{[[H_2BO_3]^-][H_3O^+]}{0.1}$$

$$H_3BO_3 + 2H_2O \rightarrow [H_4BO_4]^- + H_3O^+, K_2 = \frac{[[H_4BO_4]^-][H_3O^+]}{[H_3BO_3]} \approx \frac{[[H_4BO_4]^-][H_3O^+]}{0.1}$$

$$\{0.1K_1 = [[H_2BO_3]^-][H_3O^+] \quad 0.1K_2 = [[H_4BO_4]^-][H_3O^+] \quad [H_3O^+] = [[H_2BO_3]^-] + [[H_4BO_4]^-] \quad \mathbf{4 p.}$$

$$[H_2BO_3]^- = [H_3O^+] - [[H_4BO_4]^-]$$

$$0.1K_1 = ([H_3O^+] - [[H_4BO_4]^-])[H_3O^+] = [H_3O^+]^2 - [[H_4BO_4]^-][H_3O^+] = [H_3O^+]^2 - 0.1K_2$$

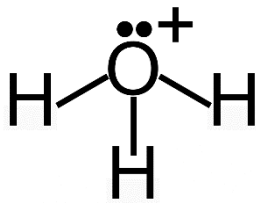
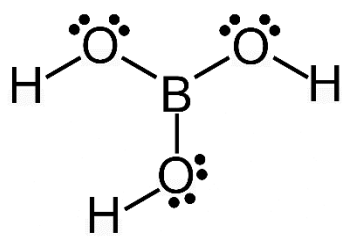
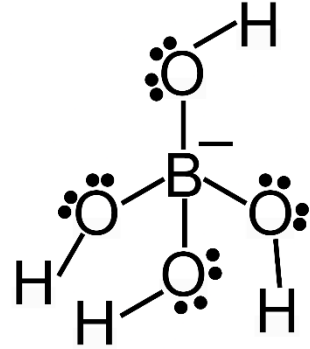
$$\mathbf{4 p.}$$

$$[H_3O^+]^2 = 0.1K_1 + 0.1K_2$$

$$pH = -\log \log \sqrt{0.1K_1 + 0.1K_2} = -\log \sqrt{0.1 \times 10^{-9.24} + 0.1 \times 10^{-9.14}} = 4.94 \quad \mathbf{2 p.}$$

Answer: 4.94

1.8. **Draw** H_3O^+ , H_3BO_3 and $[H_4BO_4]^-$ Lewis structures, including formal charges. Determine central atom geometry (by VSEPR) and **write** it in the table.

	H_3O^+	H_3BO_3	$[H_4BO_4]^-$
Lewis structure			
Geometry (IN CAPITAL LETTERS)	Trigonal pyramid	Trigonal planar	Tetrahedral

1 p. for each correct Lewis structure and geometry, 1 p. for all correct formal charges. Total 7 p.

III. Titration and calculations stage

After titration is performed, amount of nitrogen in sample is calculated. To calculate amount of protein, amount of nitrogen is multiplied by specific factor. This factor for milk, rice and meat is 6.38, 5.95 and 6.25, respectively.

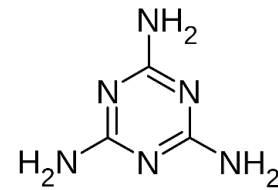
1.9. After testing 10.0 g of rice, 19.50 ml of the 1.00 mol/l HCl solution was used to titrate the final solution. **Calculate** how much grams of protein is in the rice sample.

$$n(\text{HCl}) = 0.0195 \times 1.00 = 0.0195 \text{ mol} = n(\text{N})$$

$$m(\text{N}) = 0.0195 \times 14 = 0.273 \text{ g}$$

$$m(\text{protein}) = 0.273 \times 5.95 = 1.624 \text{ g} \quad \mathbf{3 \text{ p.}}$$

Knowing that the protein content is determined by the Kjeldahl method, the Chinese company "Sanlu Group" added melamine to their production for babies. The aim was to increase the amount of protein to be determined. This led to the deaths of 6 children. After investigation, imprisonments and death penalties were assigned for responsible people.



Structure of melamine

1.10. Consider that all nitrogen atoms in melamine are converted to ammonium ions. **Calculate** how much grams of protein 1.00 grams of melamine imitates in milk, analyzed by Kjeldahl method.

$$M(\text{melamine}) = 126.1 \text{ g/mol}$$

$$n(\text{melamine}) = \frac{1.0 \text{ g}}{126.1 \frac{\text{g}}{\text{mol}}} = 0.00793 \text{ mol}$$

$$n(\text{N}) = 0.00793 \times 6 = 0.04758 \text{ mol}$$

$$m(\text{N}) = 0.04758 \times 14 = 0.666 \text{ g}$$

$$m(\text{protein}) = 0.666 \times 6.38 = 4.25 \text{ g} \quad \mathbf{4 \text{ p.}}$$

Answer: 4.25 g

Problem No.2 – Current and future applications of the 7th group elements (10% of total)

Part I. Manganese –coryphaeus among battery materials

Manganese is predominantly used in making alloys and batteries. Interestingly, manganese compounds were used in one of the first rechargeable batteries (Leclanché cell) and are still considered promising materials for future batteries.

Fill in the table to show that novel aqueous Mn-ion battery to compare it to metal-ion and lead-acid batteries from the following considerations. In the case of metal-ion batteries, neglect the electrolytes, respectively; in the case of Pb-acid, account for 35wt% H₂SO₄ aqueous electrolyte.

2.1. **Calculate** the theoretical energy density of the batteries (electrodes and, in the case of Pb-acid battery, also the electrolyte). **Assign** letters (A–F) denoting advantages and disadvantages (pros & cons) to the corresponding batteries.

A: Electrolyte instability and high cost, low abundance of elements used.

B: Good overall safety, low electrode and electrolyte cost, high abundance of elements used.

C: Robustness, low electrode and electrolyte cost, and wide temperature range.

D: High energy density and good overall performance.

E: Low energy density and environmental issues.

F: Low voltage and moderate energy density.

X: Good safety, high abundance of Mg.

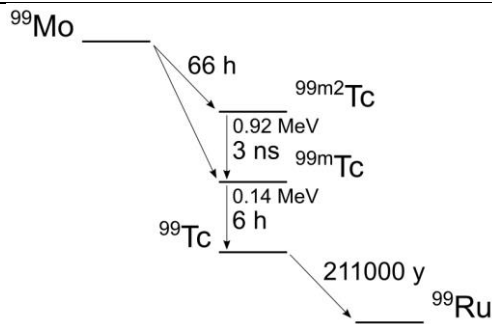
Y: Electrolyte instability and high cost, low energy density and voltage.

Battery	Reaction	EMF (V)	Theoretical energy density (Wh kg ⁻¹)	Pros & cons
Li-ion battery	$\text{LiC}_6 + \text{FePO}_4 \rightleftharpoons \text{LiFePO}_4 + 6\text{C}$	3.3	$M(\text{LiC}_6 + \text{FePO}_4) = 229.8 \text{ g}\cdot\text{mol}^{-1}$ $\text{TED} = 3.3 \text{ V} \cdot 1 \cdot 96485 \text{ A}\cdot\text{s}\cdot\text{mol}^{-1} / 3.6 / 230 \text{ g}\cdot\text{mol}^{-1} = 385 \text{ Wh}\cdot\text{kg}^{-1}$	A & D (2)
Pb-acid battery	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	2.1	$M(\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_{4(\text{aq})}) = (207.2 + 239.2 + 2 \cdot 98.1 / 35.65) \text{ g/mol}$ (1) $\text{TED} = 2.1 \text{ V} \cdot 2 \cdot 96485 \text{ A}\cdot\text{s}\cdot\text{mol}^{-1} / 3.6 / 1007 \text{ g}\cdot\text{mol}^{-1} = 112 \text{ Wh}\cdot\text{kg}^{-1}$	C & E (2)
Mn-ion	$\text{Mn}_{0.2}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O} + 0.8\text{Mn} \rightleftharpoons \text{MnV}_2\text{O}_5 \cdot \text{H}_2\text{O}$	1.3	$M(\text{MnV}_2\text{O}_5 \cdot \text{H}_2\text{O}) = 254.8 \text{ g}\cdot\text{mol}^{-1}$ $\text{TED} = 1.3 \text{ V} \cdot 2 \cdot 0.8 \cdot 96485 \text{ A}\cdot\text{s}\cdot\text{mol}^{-1} / 3.6 / 255 \text{ g}\cdot\text{mol}^{-1} = 219 \text{ Wh}\cdot\text{kg}^{-1}$	B & F (2)
Mg-ion	$2\text{Mg} + \text{Mo}_6\text{S}_8 \rightleftharpoons \text{Mg}_2\text{Mo}_6\text{S}_8$	1.1	134	X, Y

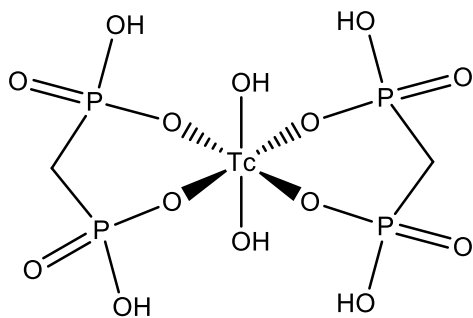
Part II. Technetium – the lightest of unstable elements

2.2. **Fill in** the blanks in the text and **add** missing groups (O, OH, H₂O) to the structures below.

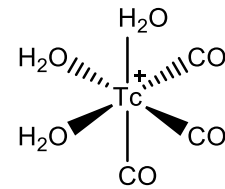
^{99m}Tc is one of the most frequently used isotopes in medicinal nuclear imaging. It is prepared in technetium-99m generators as a decay product of ⁹⁹Mo, obtained in a nuclear reactor in the fission of uranium-235: $^{235}\text{U} + ^1_0\text{n} \rightarrow ^{134}\text{Sn} (1) + ^{99}\text{Mo} + 3^1_0\text{n}$. Obtained ⁹⁹Mo undergoes **beta (1)** decay into meta-stable isomers ^{99m}Tc and ^{99m2}Tc according to the generic decay diagram (with half-lives and energy levels).



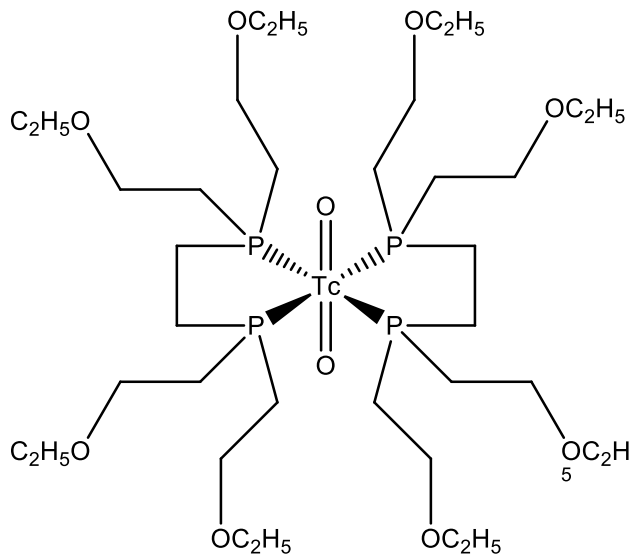
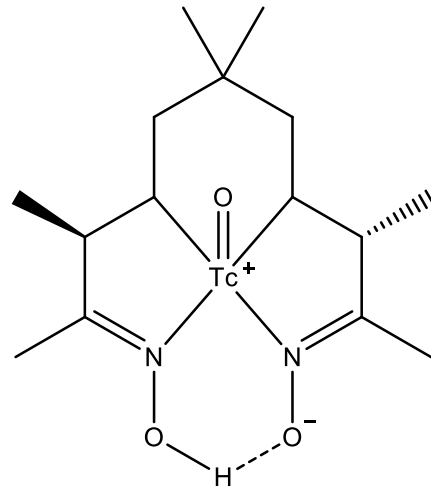
$^{99\text{m}}\text{Tc}$ undergoes **gamma (1)** decay of **140 (1)** keV comparable to 20–150 keV X-ray range used in conventional radiography. Differently from the latter, detecting the $^{99\text{m}}\text{Tc}$ radiation from within the patient's body in a gamma camera gives **three (1)**-dimensional images of tissues and organs. The imaging is taken before half of $^{99\text{m}}\text{Tc}$ decayed, i.e., within **6 (1)** hours after administrating the radiopharmaceutical. $^{99\text{m}}\text{Tc}$ radioactivity reduces to 1% of the initial activity in **40 (2)** hours. The radioactivity of ^{99}Tc is **$3 \cdot 10^{-7}$ (1)**% of the initial activity of $^{99\text{m}}\text{Tc}$. In most $^{99\text{m}}\text{Tc}$ radiopharmaceuticals, $^{99\text{m}}\text{Tc}$ (eluted from a technetium-99m generator) is turned into a coordination compound with specific biochemical properties: **diphosphonate (1)** attaches to hydroxyapatite and is used to scan bones, **tetrofosmin (1)** penetrates lipid membranes and is used to scan the heart, **exametazime (1)** crosses the blood–brain barrier and is used to scan the brain.



diphosphonate (1)



carbonyl (1)

tetrofosmin (R = CH₃CH₂O) (1)

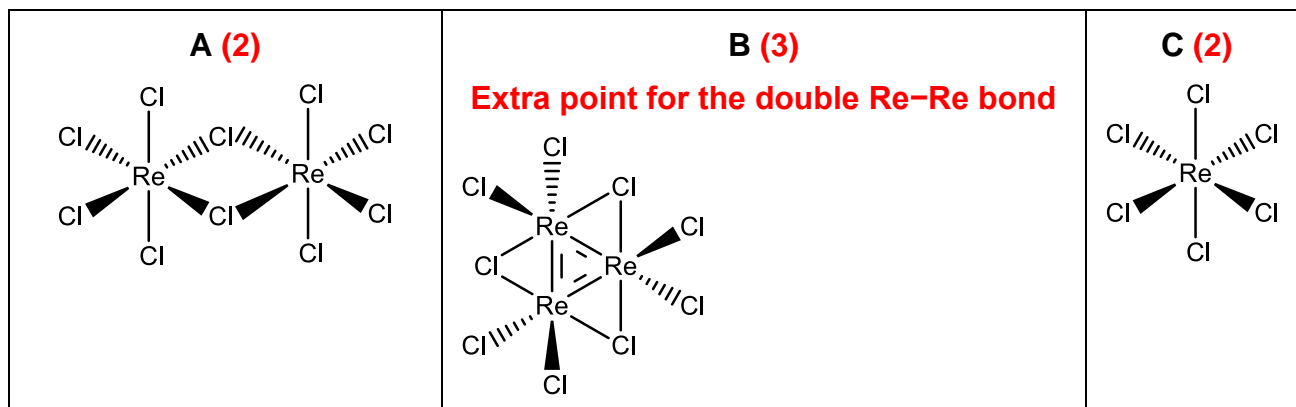
exametazime (1)

With more targeted imaging and therapy, the future applications of ^{99m}Tc for labeling biomolecules will likely be diverse and far-reaching. Technetium **carbonyl (1)** is an essential precursor to specific coordination compounds; it contains two types of ligands – one is a good leaving group, and the other one is strongly bound to technetium.

Part III. Rhenium – an element of supermaterials

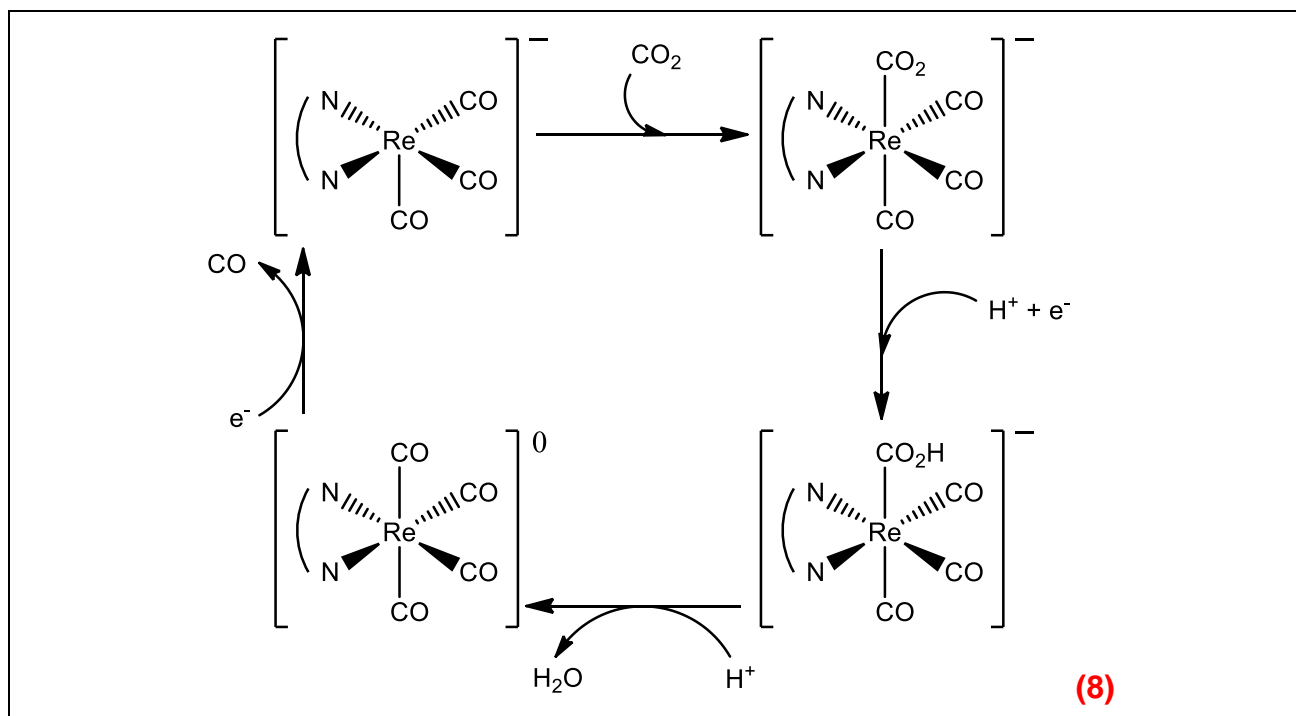
Rhenium is used in superalloys and catalysts. Rhenium chlorides are precursors for making catalytic coordination compounds. In reaction with chlorine, rhenium forms solid compound **A** ($w_{\text{Cl}} = 48.77\%$), which thermally decomposes into molecular chloride **B** ($w_{\text{Cl}} = 36.35\%$) and chlorine. Chloride **A** is also formed in the decomposition of molecular chloride **C**, which is unstable at room temperature. The coordination number of Re (including Re–Re bonds) is the same in molecules of **A** [Cl_aRe(μ-Cl)]₂, **B** [Cl_bRe(μ-Cl)]₃, and **C**, where μ denotes that chloride is bridging two rhenium atoms (Re–Cl–Re).

2.3. **Draw** structures of the **A–C** molecules.



Rhenium possible applications in catalysis include reduction of CO₂ to CO.

2.4. **Fill in** in the blanks (charges, reagents, and products) in the catalytic cycle illustrating the electrochemical reduction mechanism (with H⁺ and e⁻).



Part IV. Bohrium – probably the most boring element in the Universe

Bohrium belongs to the family of superheavy elements, which could act as powerful nuclear fuel, for example, for future fission-propelled space missions. Isotopes with the magical number of protons (114) or neutrons (184) could theoretically have half-lives large enough to be used in nuclear reactors. The half-life of synthesized isotopes (2.9 s for ²⁷¹Bh, 8.8 s for ²⁷²Bh, and 54 s for ²⁷⁴Bh) shows a trend for stabilization ($\log T_{1/2} = aA^{1/6} + b$) towards the “island of stability” near the double-magic ²⁹⁸Fl.

1.5. **Estimate** the half-life (in years) of the most stable isotope of Bh. **Make** a prediction on whether bohrium would find any application in the future.

Half-life:

The most stable isotope ²⁹¹Bh has the magical number of neutrons. (1)

$$T_{1/2}({}^{291}\text{Bh}) = 10^{[a(291)^{1/6} + b]} / 3600 \text{ s} \cdot \text{h}^{-1} / 24 \text{ h} \cdot \text{d}^{-1} / 365.25 \text{ d} \cdot \text{y}^{-1} = \mathbf{5\text{--}215 \text{ years}} \quad (1)$$

Where a and b can be obtained from the $\log T_{1/2} \sim ZA^{1/6}$ dependence. (2)

The lowest estimate is obtained with:

$$a = \log(54/8.8) / (274^{1/6} - 272^{1/6}) = 253.36 \text{ and } b = \log(54) - a274^{1/6} = -643.96$$

$$\log T_{1/2}({}^{291}\text{Bh}) = 253.36 \cdot (291)^{1/6} - 643.96 = 8.25 \Rightarrow T_{1/2}({}^{291}\text{Bh}) = 5.6 \text{ y}$$

The highest estimate is obtained with:

$$a = \log(8.8/2.9) / (272^{1/6} - 271^{1/6}) = 308.61 \text{ and } b = \log(8.8) - a272^{1/6} = -784.61$$

$$\log T_{1/2}({}^{291}\text{Bh}) = 308.61 \cdot (291)^{1/6} - 784.61 = 9.83 \Rightarrow T_{1/2}({}^{291}\text{Bh}) = 215 \text{ y}$$

Prediction:

Any meaningful answer is graded with 1 points.

The author's prediction is that the estimated half-life might even be suitable for applying ^{291}Bh as nuclear fuel. However, synthesis of such a heavy isotope would be complicated because the reacting isotopes have a lower neutron-to-proton ratio. That is the main present obstacle to the "island of stability". Suppose (somehow synthesized) ^{297}Nh (in the middle of the island) undergoes a series of 3 α decays – the resulting ^{285}Bh is by 6 neutrons lighter than the targeted ^{291}Bh and would have a much shorter half-life. Thus, applications of bohrium seem illusive.

Problem No.3 – Simple Surface Chemistry (10% of total)

The surface coverage ($\theta = \frac{N_{occ}}{N_{max}}$, where N_{occ} is number of occupied sites and N_{max} is maximal number of adsorption sites) dependence on pressure is described by adsorption isotherms. The most used adsorption isotherm is Langmuir adsorption isotherm. To derive the Langmuir isotherm, we consider the following rates for adsorption and desorption:

$$r_{ad} = k_{ad}p(1 - \theta)^n$$

$$r_{des} = k_{des}\theta^n$$

3.1. Assuming steady state **show** that the surface coverage θ dependence on pressure p and adsorption/desorption rate constant ratio ($\alpha = \frac{k_{ad}}{k_{des}}$) takes form $\theta = \frac{(\alpha p)^{1/n}}{1 + (\alpha p)^{1/n}}$.

In steady state $r_{ad} = r_{des}$, and so we can write $k_{ad}p(1 - \theta)^n = k_{des}\theta^n$. (1pt)

Divide both sides by k_{des} to yield $\alpha p(1 - \theta)^n = \theta^n$. (1pt)

Take n'th root of both sides to yield $(\alpha p)^{1/n}(1 - \theta) = \theta$. (1pt)

Bring terms with θ to one side to yield $\theta(1 + (\alpha p)^{1/n}) = (\alpha p)^{1/n}$ (1pt)

Express θ to yield required expression. (1pt)

5 pts total

Additional information: Commonly the equation is written in form $\theta = \frac{(Kp)^{1/n}}{1 + (Kp)^{1/n}}$, where K is the equilibrium constant; however, strictly speaking it is not correct as that would mean that K has units of kPa^{-1} . Therefore, we instead introduce the parameter α which has the correct dimensions.

Further we will consider a special case – the non-dissociative adsorption – in which first order rate law is observed for adsorption and desorption ($n = 1$).

In this case adsorption isotherm is

$$\theta = \frac{\alpha p}{1 + \alpha p}.$$

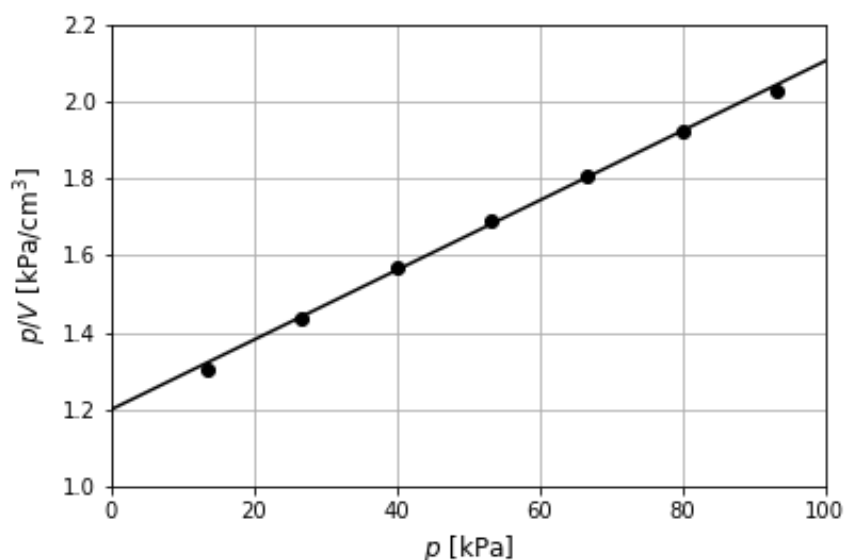
However, in experiments we cannot measure occupied sites directly. Instead, we consider the volume of gas adsorbed V versus volume of gas adsorbed at full coverage V_{max} and therefore the resulting isotherm in terms of volumes is

$$\theta = \frac{V}{V_{max}} = \frac{\alpha p}{1 + \alpha p}.$$

With simple algebra we can linearise the equation to yield that

$$\frac{p}{V} = \frac{1}{\alpha V_{max}} + \frac{1}{V_{max}} p.$$

In an experiment of CO adsorption on charcoal at 273 K the following plot was obtained. Solid dots show experimental datapoints, and the solid line shows best fit line.



3.2. Using the plot **determine** α and V_{max} .

Slope should yield $\frac{1}{V_{max}}$ and using the plot we estimate the slope to be $\frac{1.38-1.2}{20} = 9 \cdot 10^{-3}$

(1pt)

Therefore, $V_{max} = 1/9 \cdot 10^{-3} = 111 \text{ cm}^3$ (1pt)

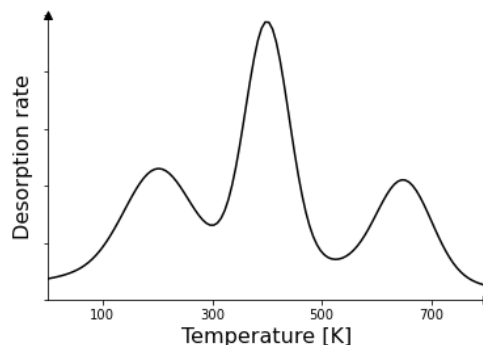
Now from intercept we can obtain $\frac{1}{\alpha V_{max}} = 1.2$ (1pt)

Solving for α yields $\alpha = \frac{1}{111 \cdot 1.2} = 7.5 \text{ kPa}^{-1}$ (1pt)

4 pts total

Additional information: For the derivation of linearised form of equation refer to Atkins – Physical Chemistry 9ed p833.

An useful method to study kinetics of desorption and determine the desorption activation energy is *thermal desorption spectroscopy* (TDS). In this method sample is heated with linear change in temperature and the rate of desorption is observed. At the temperature where rapid desorption starts to occur, a peak in rate is observed, but after the sample is heated further the rate decreases due to lack of adsorbed species. Schematic representation of spectra observed in the studies is shown in figure – multiple peaks represent multiple adsorption sites with their respective desorption activation energies.



To extract desorption activation energy E_d , we start from the desorption rate equation and consider that desorption rate constant follows Arrhenius law, where ν is the preexponential factor,

$$-\frac{d\theta}{dt} = k_{des}\theta = \nu e^{-\frac{E_d}{k_B T}} \theta.$$

By considering that the temperature change during the experiment is $T = T_0 + \beta t$, where β is the heating rate, and integrating the rate law, one obtains the relation, where T_{max} is the temperature at the top of the peak.

$$\frac{E_d}{k_B T_{max}^2} = \frac{\nu}{\beta} e^{-\frac{E_d}{k_B T_{max}}}.$$

3.3. **Show** that the expression can be rewritten as $E_d = k_B T_{max} (\ln(\nu T_{max}/\beta) - 3.64)$.
Hint: the quantity $\ln(E_d/k_B T_{max}) \approx 3.64$.

$$\frac{E_d}{k_B T_{max}^2} = \nu/\beta e^{-\frac{E_d}{k_B T_{max}}}$$

$$\frac{\beta E_d}{\nu k_B T_{max}^2} = e^{-\frac{E_d}{k_B T_{max}}}$$

$$\ln\left(\frac{\beta E_d}{\nu k_B T_{max}^2}\right) = -\frac{E_d}{k_B T_{max}} \quad (1\text{pt})$$

$$E_d = -k_B T_{max} \ln\left(\frac{\beta E_d}{\nu k_B T_{max}^2}\right)$$

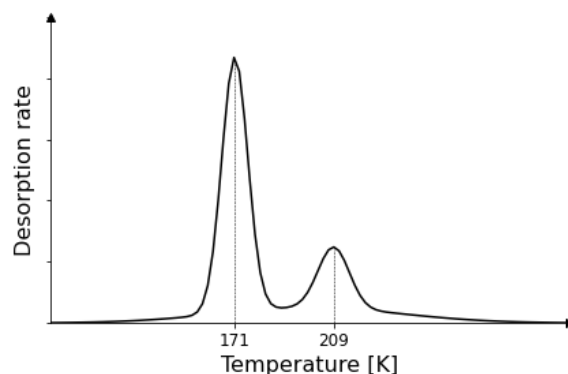
$$E_d = k_B T_{max} \ln\left(\frac{\nu k_B T_{max}^2}{\beta E_d}\right) \quad (1\text{ pt})$$

$$E_d = k_B T_{max} \left(\ln\left(\frac{\nu T_{max}}{\beta}\right) + \ln\left(\frac{k_B T_{max}}{E_d}\right) \right) \quad (1\text{ pt})$$

$$E_d = k_B T_{max} \left(\ln\left(\frac{\nu T_{max}}{\beta}\right) - 3.64 \right) \quad (1\text{pt})$$

4 pts total

TDS experiment was performed to investigate desorption of ethylbenzene on pyrolytic graphite. Two peaks in the spectra were observed, one at **171 K**, and one at **209 K**. Peak at **209 K** corresponds to desorption from adsorption layer directly on the surface, while the peak at **171 K** corresponds to desorption from further layers.



3.4. **Calculate** the desorption activation energies (expressed in kJ mol^{-1}) for ethylbenzene desorption from pyrolytic graphite. Assume heating rate $\beta = 1 \text{ K s}^{-1}$, preexponential factor $\nu = 10^{12} \text{ s}^{-1}$.

Hint: the formula from 3.3 provided results in desorption activation energy per atom.

$$E_d = k_B T_{max} \left(\ln \left(\frac{\nu T_{max}}{\beta} \right) - 3.64 \right)$$

$$E_{d,\text{molar}} = RT_{max} \left(\ln \left(\frac{\nu T_{max}}{\beta} \right) - 3.64 \right) \text{ (1pt)}$$

$$= 8.314 * 209 \left(\ln \left(\frac{10^{12} * 209}{1} \right) - 3.64 \right) = 51 \text{ kJ mol}^{-1} \text{ (1pt)}$$

and

$$= 8.314 * 171 \left(\ln \left(\frac{10^{12} * 171}{1} \right) - 3.64 \right) = 41 \text{ kJ mol}^{-1} \text{ (1pt)}$$

3 pts total

One of the method's shortcomings is that it relies on a good guess of the preexponential factor.

3.5. **Calculate** error in the predicted desorption activation energy for desorption at 209 K if the actual preexponential factor is 1000 times larger.

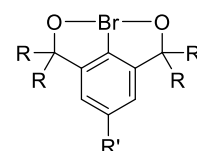
$$\Delta E_d = RT_{max} \ln \left(\frac{\nu_{new}}{\nu_{old}} \right) \text{ (1 pt)}$$

$$= 8.314 * 209 * \ln(1000) = 12 \text{ kJ mol}^{-1} \text{ (1 pt)}$$

2 pts total

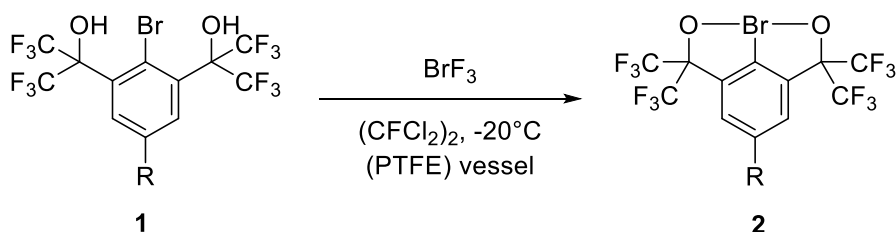
Problem No.4 – Bromine goes hyper mode (10% of total)

Bromine (III) reagents are fascinating compounds in the realm of organic chemistry due to their unique attributes. While their stability and high oxidizing power can make them difficult to handle, they have also served as tools for innovative synthetic conversions. In this problem, you will explore



synthesis of some hypervalent bromine (III) reagents (such as the one on the right), some of which have been investigated at the Latvian Institute of Organic Synthesis (LIOS).

Traditionally compounds like **2** have been synthesised from BrF_3 and an aryl bromide **1** according to the following scheme:



4.1. Preparation of BrF_3 through a chemical process is difficult since it involves using two dangerous compounds, Br_2 and F_2 , which require special safety measures. Additionally, the reaction produces two other substances that need to be separated using fractional distillation, which adds to the complexity of the process. **Write** the formulas for the two side products.

BrF , BrF_5

(2 pt. = 1 pt. each)

Another complication arises from the fact that BrF_3 is highly reactive and can react not only with water (forming two acids and oxygen), but also other common solvents like acetonitrile CH_3CN (yielding a fluoroalkane and 2 elementary substances) and even glass (yielding two gases and a brown liquid) at room temperature.

4.2. **Write** balanced equations of the reactions of BrF_3 with a) water; b) acetonitrile; c) silicon dioxide.



(4 pt. = 2 pt. for equation, 2 pt. for balancing)



(4 pt. = 2 pt. for equation, 2 pt. for balancing)



(4 pt. = 2 pt. for equation, 2 pt. for balancing)

4.3. Another complication arises from BrF_3 's ability to homolyse into radicals and promoting unwanted side reactions. **Provide** a radical mechanism (should consist of three separate radical reactions) of a potential fluorination of a generic alkane RCH_3 . Note – any other trivalent bromine compounds are highly unlikely to form!



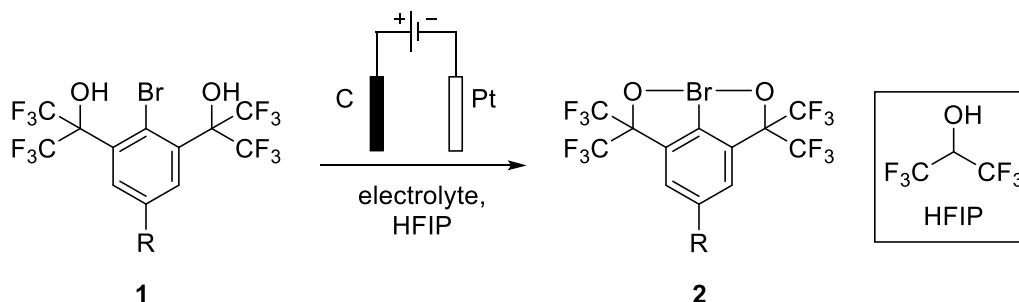
(6 pt. = 2 pt. each)

4.4. **Provide** two more side products that might form from different termination steps.

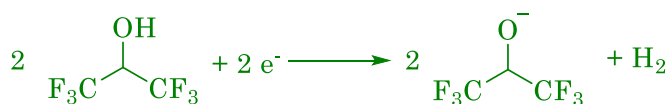
F₂; RCH₂CH₂R

(2 pt. = 1 pt. each, give points if RCH₂F here and other termination above)

A novel method of synthesizing compound **2** has been developed at LIOS, which involves oxidation of **1** in an undivided electrochemical cell:



4.5. Since the reaction is happening in an undivided cell, there should be a counter reaction occurring on the opposite electrode. **Give** a balanced half-reaction equation. **Circle** the correct answers in the text. Hint: Balancing the oxidation half-reaction equation might help.



(6 pt. = 3 pt. for equation, 3 pt. for balancing)

The reaction is occurring on the (a) electrode and it is the (b).

a) carbon / platinum

b) anode / cathode

In the reaction **1** → **2**, the bromine's hybridisation changes from (c) to (d), while its geometry (according to VSEPR) changes from (e) to (f) with the angle O-Br-C in compound **2** being close to (g).

c) sp / sp² / sp³ / sp³d / sp³d² / sp³d³

d) sp / sp² / sp³ / sp³d / sp³d² / sp³d³

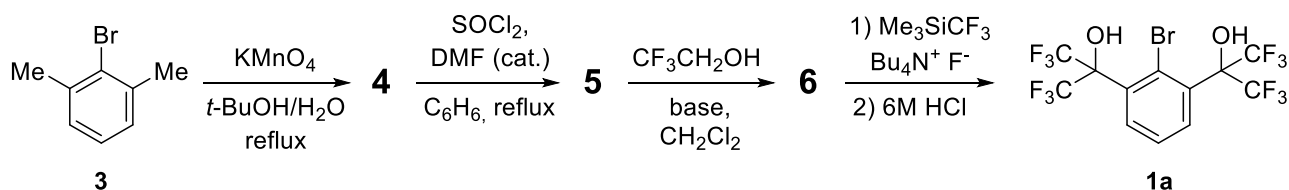
e) linear / bent / T-shaped / tetrahedral / octahedral / trigonal bipyramidal

f) linear / bent / T-shaped / tetrahedral / octahedral / trigonal bipyramidal

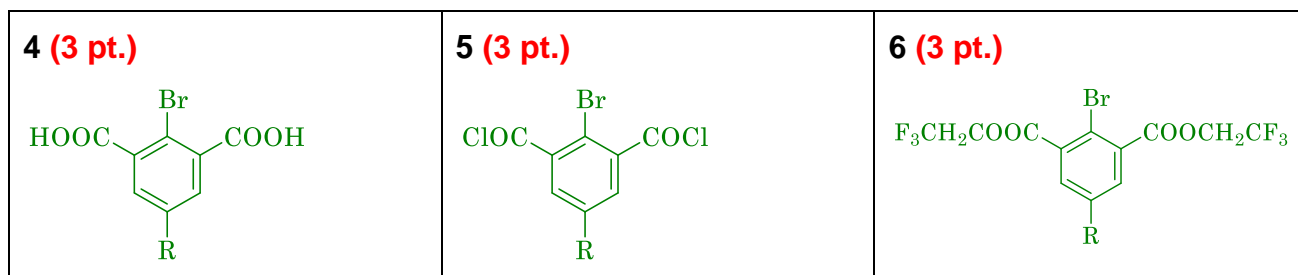
g) 45° / 60° / 75° / 90° / 105° / 120°

c) **(7 pt. = 1 pt each)**

The synthesis of compound **1a** can be implemented starting from compound **3** according to the following scheme:



4.6. **Draw** the structures of the intermediate compounds **4** – **6**! Note: Brutto formula of compound **6** is **C₁₂H₇BrF₆O₄**!



The electrochemical modification is also appealing due to its non-intrusive nature to monitor the reaction's progress without external interference.

By interrupting the chemical reaction and conducting a cyclic voltammetry experiment, we can obtain a cyclic voltammogram that shows the relationship between current and the electric potential. Since the same redox event is being observed, the potential will be the same, enabling the comparison of the peak current i_p at various timepoints. The peak current i_p is proportional to the surface area A and the potential sweep rate v . This relationship is represented by the Randles-Sevcik equation:

$$i_p = 2.69 \cdot 10^5 \cdot z^{\frac{3}{2}} \cdot A \cdot c \cdot D^{\frac{1}{2}} \cdot v^{\frac{1}{2}}$$

, where z = number of electrons transferred; A = reactive surface area; c = concentration; D = diffusion coefficient; v = potential sweep rate

4.7. Assume that you have acquired peak currents of the oxidation of **1** before starting the experiment ($i_{p,0}$) and at a certain timepoint t ($i_{p,t}$). **Derive** an equation for calculating the yield of the reaction at a timepoint t .

(7 pt. total)

$$\text{yield} = \frac{n_0 - n_t}{n_0} = 1 - \frac{n_t}{n_0} \quad \text{(2 pt.)}$$

$$\frac{i_{p,t}}{i_{p,0}} = \frac{2.69 \cdot 10^5 \cdot z^{\frac{3}{2}} \cdot A \cdot c_t \cdot D^{\frac{1}{2}} \cdot v^{\frac{1}{2}}}{2.69 \cdot 10^5 \cdot z^{\frac{3}{2}} \cdot A \cdot c_0 \cdot D^{\frac{1}{2}} \cdot v^{\frac{1}{2}}} = \frac{c_t}{c_0} \quad \text{(3 pt.)}$$

$$\frac{n_t}{n_0} = \frac{c_t V}{c_0 V} = \frac{c_t}{c_0} = \frac{i_{p,t}}{i_{p,0}} \quad \text{(1 pt.)}$$

$$\text{yield} = 1 - \frac{i_{p,t}}{i_{p,0}} \quad \text{(1 pt.)}$$

However, the Randles-Sevcik equation only applies to reversible systems and experimental evidence suggests that the functional group R could alter whether a particular compound for this reaction will undergo reversible oxidation, therefore, rendering this method unsuitable for monitoring reaction progress.

An alternative technique involves utilizing quantitative IR spectroscopy to monitor the formation of the Br-O bond through measurement of its absorption (at a constant λ) using the Beer-Lambert equation. However, there are a few issues, namely: 1) ambiguity regarding the

molar extinction coefficient and pathlength, 2) background absorption, 3) a synthetic chemist's laziness to calculate intermediate values.

These challenges may be overcome by 1) obtaining absorption values of the product at a known concentration, 2) acquiring background absorption, 3) deriving the equation for them.

4.8. **Derive** the equation for calculating the yield of the reaction $1 \rightarrow 2$ and **calculate** it for a reaction with a starting concentration of 1 , $c_0 = 1 \text{ mM}$, where the measured absorption at a timepoint t is $A_t = 0.986 \text{ AU}$, if the background absorption $A_0 = 0.054 \text{ AU}$ and the measured absorption of a 0.5 mM sample of 2 is $A_x = 0.729 \text{ AU}$.

(11 pt. total)

The Beer-Lambert equation for the following system would be: $A = 2\epsilon c l + A_0$ the coefficient is because we form 2 Br-O bonds for a single molecule of 2 (Since later on the $2\epsilon l$ will be subtracted, $A = \epsilon c l + A_0$ is also acceptable; 2 points)

Thus, $A_t = 2\epsilon c_t l + A_0$ and $A_x = 2\epsilon c_x l + A_0$

Transforming : $\frac{A_t - A_0}{c_t} = 2\epsilon l$ & $\frac{A_x - A_0}{c_x} = 2\epsilon l$; Combining $\frac{A_t - A_0}{c_t} = \frac{A_x - A_0}{c_x}$ (2 pt.)

Expressing c_t we get: $c_t = \frac{c_x(A_t - A_0)}{A_x - A_0}$ (2 pt.)

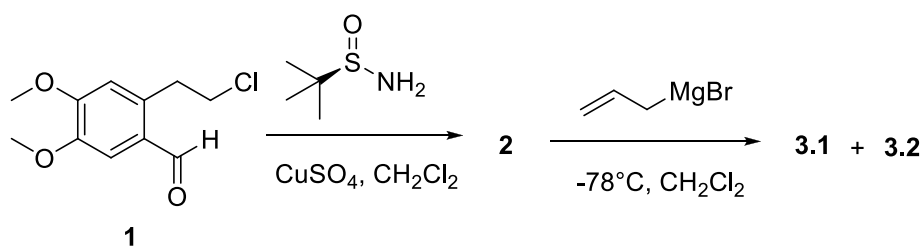
yield = $\frac{n_t}{n_{t, \text{theor.}}} = \frac{c_t V}{c_0 V} = \frac{c_t}{c_0}$ (2 pt.)

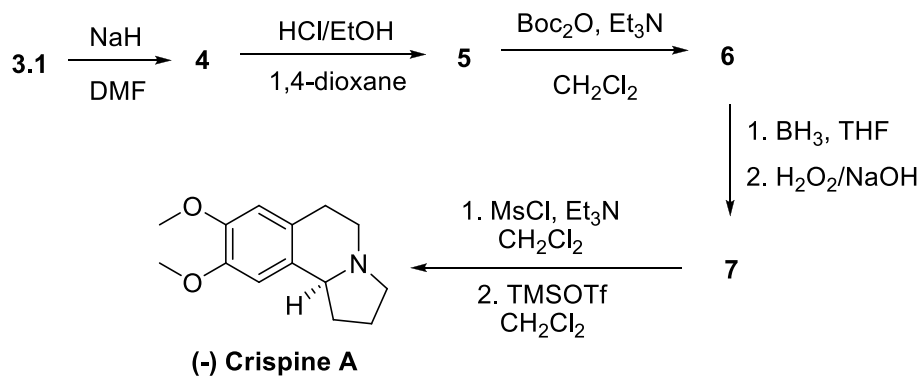
$\frac{c_t}{c_0} = \frac{c_x(A_t - A_0)}{c_0(A_x - A_0)}$ (1 pt.) = $\frac{0.5 \cdot 10^{-3}(0.986 - 0.054)}{1 \cdot 10^{-3}(0.729 - 0.054)} = 0.69$ (2 pt.)

Problem No.5 – Synthetic alkaloids (10% of total)

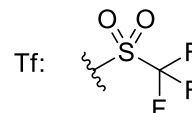
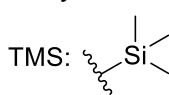
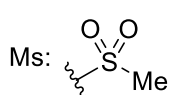
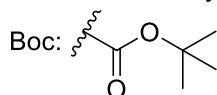
Alkaloids crispine A and crispine B have been isolated as bioactive constituents from a plant *Carduus crispus* L. which has been used for the treatment of cold, stomachache and rheumatism. Significant cytotoxic activities of these compounds on some human-cancer cells have also been reported. Crispine A and crispine B both are very similar in structure, both belong to a family of pyrroloisoquinoline alkaloids.

Synthesis of enantiopure (-) crispine A started from aldehyde **1**. Treatment of this aldehyde **1** with (R)-*tert*-butanesulfinamide in the presence of anhydrous CuSO_4 afforded compound **2**. Addition of allylmagnesium bromide to compound **2** at -78°C in CH_2Cl_2 gave the mixture of two diastereomers **3.1** (major) and **3.2** (minor). The diastereomeric mixture was easily separated by column chromatography and only compound **3.1** was used in further synthesis steps. Over next several steps compound **3.1** was finally converted to (-) crispine A as shown in the scheme below.

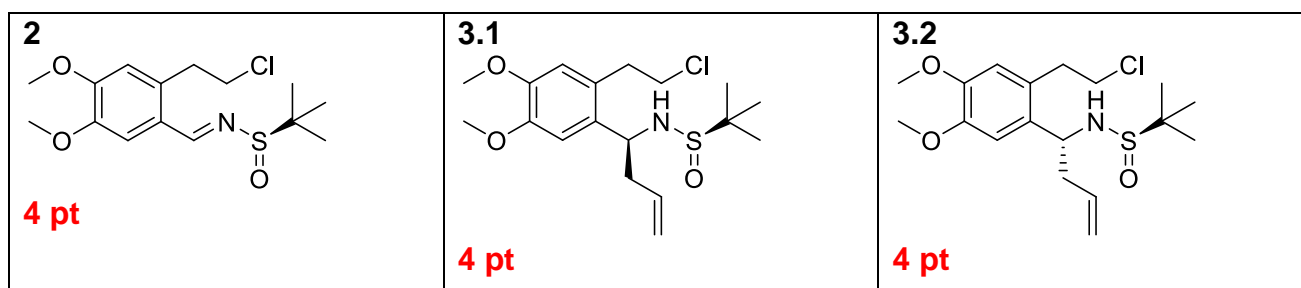




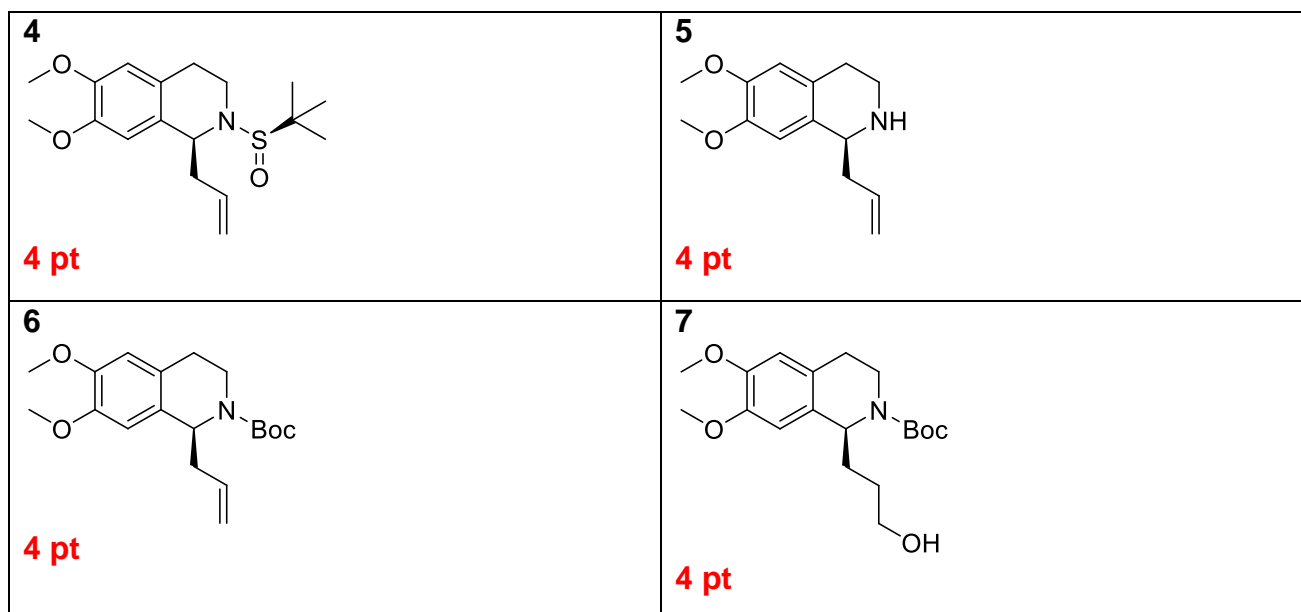
DMF – dimethylformamide; THF – tetrahydrofuran



5.1. **Provide** structures of compounds **2**, **3.1** and **3.2** with stereochemical information.



5.2. **Provide** structures of compounds **4**, **5**, **6** and **7** with stereochemical information.



5.3. **Give** absolute configuration of (-) crispine A stereocenter using *R/S* nomenclature.

S **2 pt**

If the mixture of compounds **3.1** and **3.2** was used in the synthesis without separation, the liquid mixture of two enantiomers (-) crispine A and (+) crispine A would be finally obtained.

This mixture had specific rotation of -72.8° . Enantiopure (-) crispine A has specific rotation of -91.0° .

Formula for enantiomeric excess calculation: $ee = (\omega_1 - \omega_2)/(\omega_1 + \omega_2)$

ω_1 – fraction of one enantiomer in the mixture

ω_2 – fraction of other enantiomer in the mixture

5.4. **Calculate** enantiomeric excess of this mixture of (-) crispine A and (+) crispine A. **Calculate** ratio of enantiomers in the mixture and clearly indicate which enantiomer is major and which is minor.

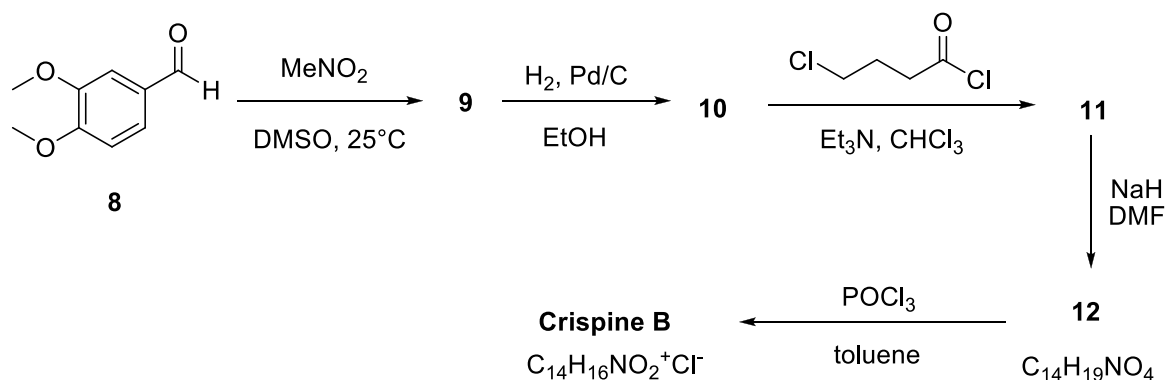
$ee = -72.8/(-91) = 0.8 \rightarrow 80\%$ 3 pt
 $(\omega_1 - \omega_2)/(\omega_1 + \omega_2) = 0.8 \rightarrow \omega_1/\omega_2 = 9$ 3 pt
 (-) crispine is major enantiomer; (+) crispine is minor enantiomer 2 pt

5.5. **Choose** correct statement(-s).

- (-) enantiomer is always (R) isomer
 (-) enantiomer is always (S) isomer
 (-) enantiomer always has positive specific rotation value
 (-) enantiomer always has negative specific rotation value (4 p.)
 There are no correct statements

(4 pt.)

Synthesis of crispine B started from aldehyde **8**. After several chemical transformations crispine B was obtained. It is known that crispine B is a salt whose cation has molecular formula $C_{14}H_{16}NO_2^+$.



DMSO – dimethyl sulfoxide

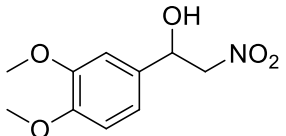
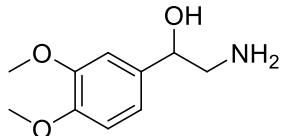
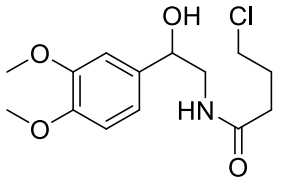
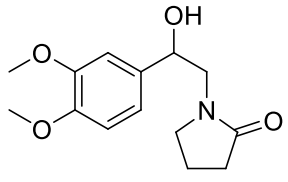
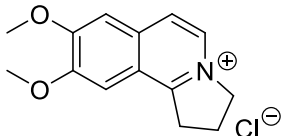
^1H NMR spectral data of compounds **9** and crispine B:

Compound **9** ^1H NMR (CDCl_3) δ : 2.74 (br. s., 1H), 3.88 (s, 3H), 3.90 (s, 3H), 4.50 (dd, $J = 3.2, 13.2$ Hz, 1H), 4.62 (dd, $J = 9.6, 13.2$ Hz, 1H), 5.42 (dd, $J = 3.2, 9.6$ Hz, 1H), 6.86-6.94 (m, 3H).

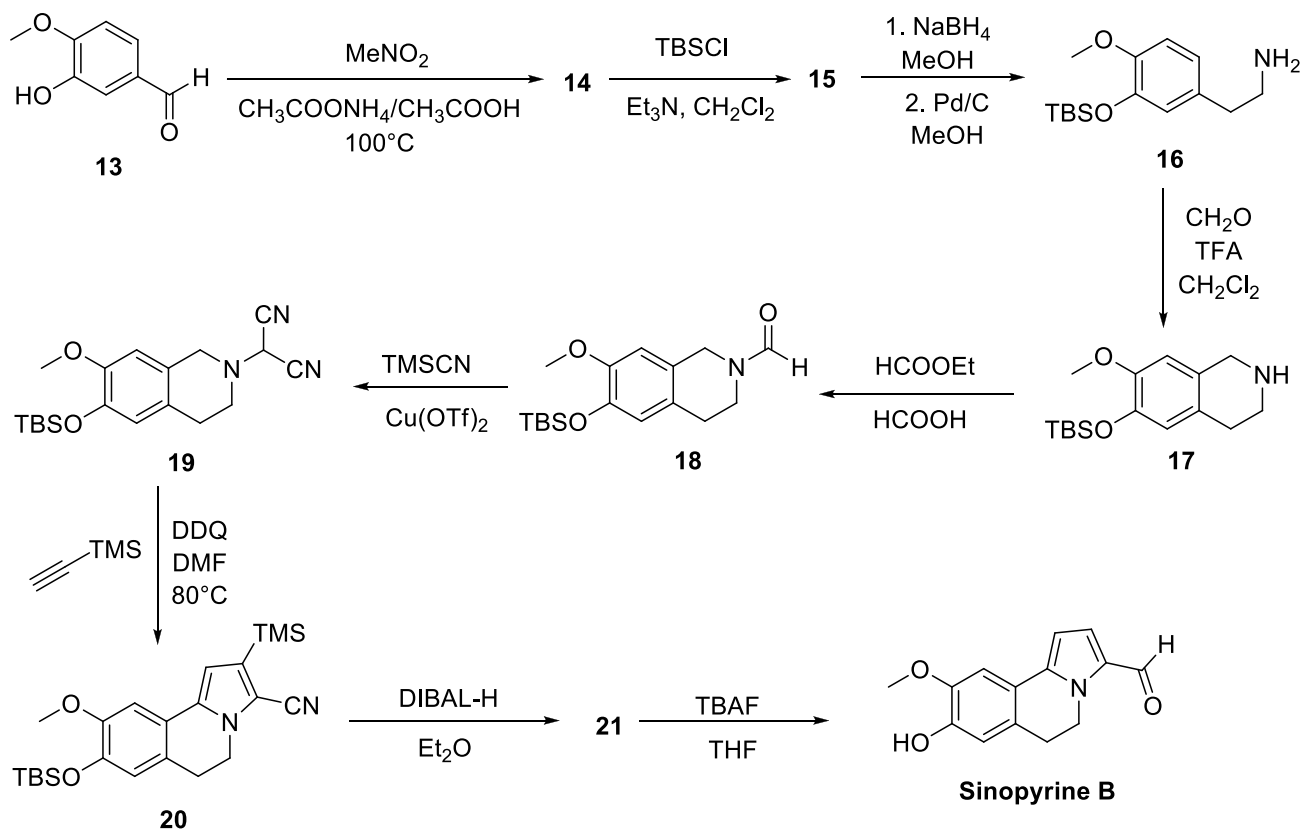
Crispine B ^1H NMR (deuterated MeOH) δ : 2.63 (q, 2H), 3.89 (t, 2H), 4.08 (s, 3H), 4.10 (s, 3H), 4.91 (t, 2H), 7.57 (s, 1H), 7.65 (s, 1H), 8.07 (d, $J = 6.8$ Hz, 1H), 8.36 (d, $J = 6.8$ Hz, 1H).

Meanings of abbreviations: s – singlet, br. s. – broad singlet, d – doublet, dd – doublet of doublets, t – triplet, q – quartet, m – multiplet.

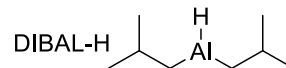
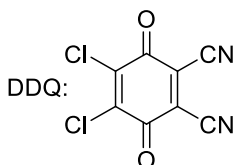
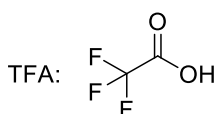
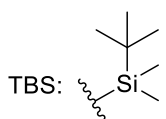
5.6. **Provide** structures of compounds **9**, **10**, **11**, **12** and **crispine B**. Stereochemical information is not required.

<p>9</p>  <p>4 pt</p>	<p>10</p>  <p>4 pt</p>
<p>11</p>  <p>4 pt</p>	<p>12</p>  <p>4 pt</p>
<p>Crispine B</p>  <p>4 pt</p>	

Another alkaloid structurally very similar to crispine A and crispine B is sinopyrine B which is found in plant *Sinomenium acutum*. It can be synthesized from aldehyde **13**.



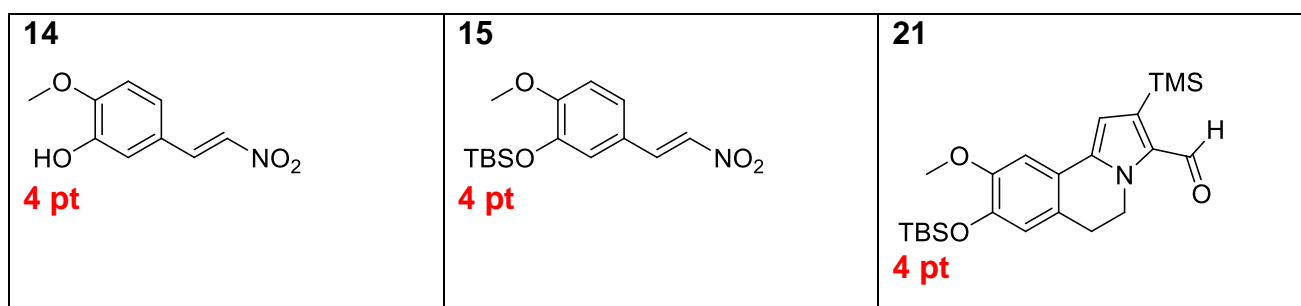
TBAF – tetrabutylammonium fluoride



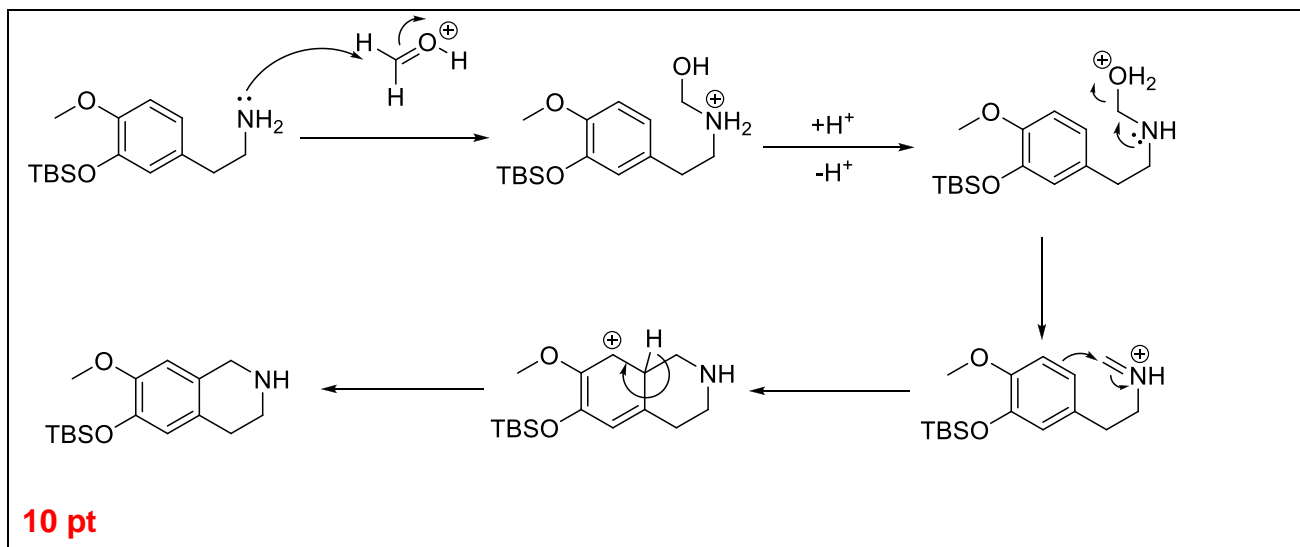
^1H NMR spectral data of compound **14**:

Compound **14** ^1H NMR (deuterated DMSO) δ : 3.81 (s, 3H), 6.84 (d, $J = 8.2$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 1H), 7.46 (s, 1H), 8.01 (d, $J = 13.4$ Hz, 1H), 8.13 (d, $J = 13.4$ Hz, 1H), 10.00 (br. s., 1H).

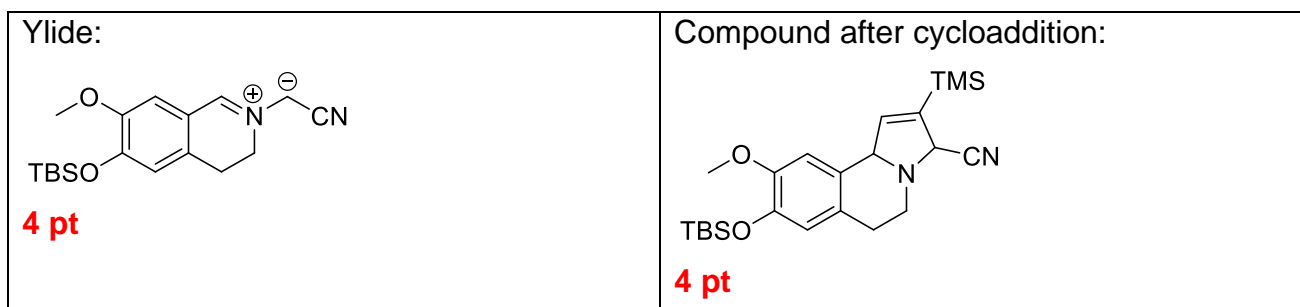
5.7. **Give** structures of compounds **14**, **15** and **21**.



5.8. The reaction **16** \rightarrow **17** is so called Pictet-Spengler Isoquinoline Synthesis reaction. **Draw** the mechanism of **16** \rightarrow **17**.



5.9. One of the key steps in this synthesis is three-stage reaction **19** \rightarrow **20** when pyrrole ring is formed. Everything starts with ylide formation after HCN removal. Then, cycloaddition reaction occurs. And finally, pyrrole ring is formed in presence of DDQ. **Give** correct resonance structure of most stable intermediate ylide which is formed after HCN removal and which actually participates in further reaction steps. Also **give** structure of compound which forms just after cycloaddition reaction (before DDQ starts acting).



5.10. **Give** name for cycloaddition reaction using two different systems by writing appropriate numbers instead of letters α , β , γ and δ . When written in parentheses (), numbers indicate amount of **atoms** in each reactant which participated in cycloaddition reaction. When written in brackets [], numbers indicate amount of **electrons** in each reactant which participated in cycloaddition reaction.

$(\alpha+\beta)$

$[\gamma+\delta]$

$\alpha= 3$

$\gamma= 4$

$\beta= 2$

$\delta= 2$

(8p.)

5.11. What is the role of DDQ in this reaction? **Choose** correct answer.

Oxidizing agent (4p.)

Reducing agent

Catalyst

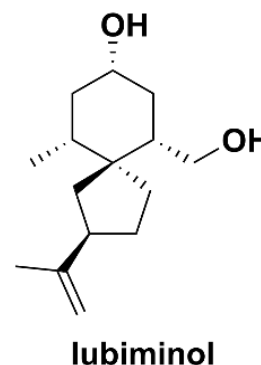
Inhibitor

Problem No.6 – Toxic fungus among us (12% of total)

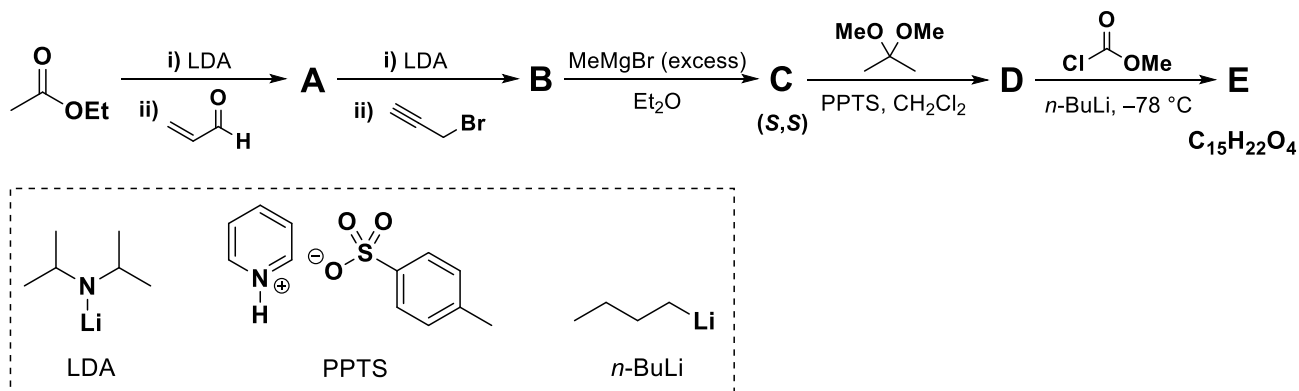
Synthesis adapted from: M. T. Crimmins, Z. Wang, L. A. McKerlie. *Tetrahedron Lett.*, 37(48): 8703-8706, 1996.

Phytoalexins are naturally occurring antimicrobial compounds, which are produced by plants in response to pathogens at the site of infection. In this way, they serve an important role in the general defence mechanism against plant diseases. Phytoalexins can counter the invading organism in a variety of different ways, including by delaying the maturation, disrupting metabolism, breaking down cell walls or inhibiting its reproduction.

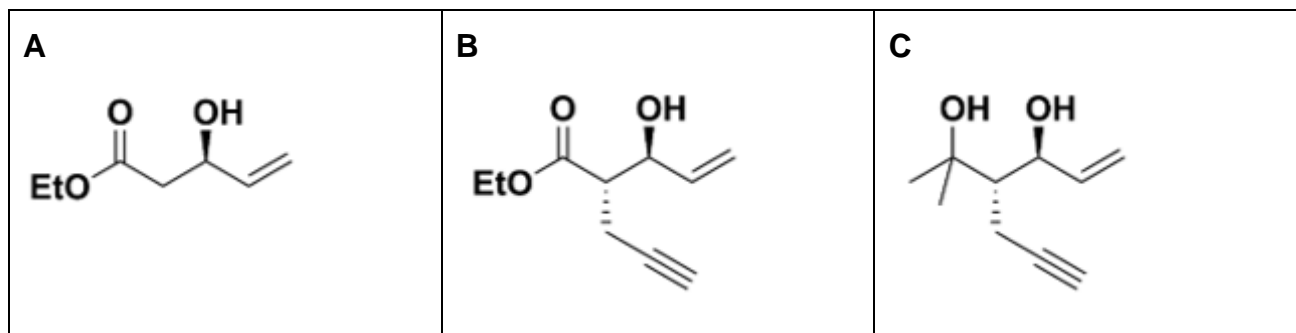
Lubiminol is a spirocyclic phytoalexin first isolated from potato plants infected with a particular species of fungus (*Phytophthora infestans* or *Glomeralla cingulata*). Although lubiminol has bioactive properties itself, it is an intermediate in the biosynthetic pathway of more substantial and potent antifungal agents.

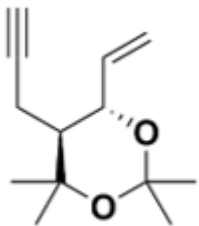
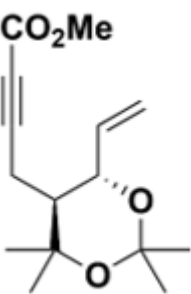


In this task, you will look into the highly stereoselective total synthesis of lubiminol utilising a radical cascade as the key step in constructing its spirocyclic core. The sequence began with a stereoselective aldol addition of ethyl acetate lithium enolate to acrolein, which gave the beta-hydroxyester **A** predominantly as its *R*-isomer. Propargylation with propargyl bromide in the presence of LDA then yielded **B**, which in turn was converted into **C** with an excess of methyl Grignard. Protection of **C** as an acetone acetal and subsequent treatment with methyl chloroformate gave compound **E**.



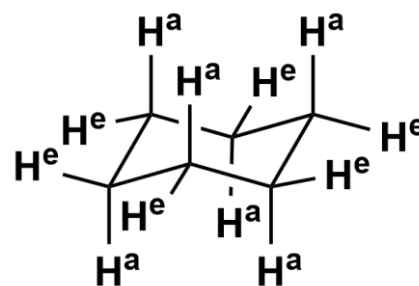
6.1. **Draw** the structures of **A-E**, taking stereochemistry into account.



D	E	Corrections (if needed)
		

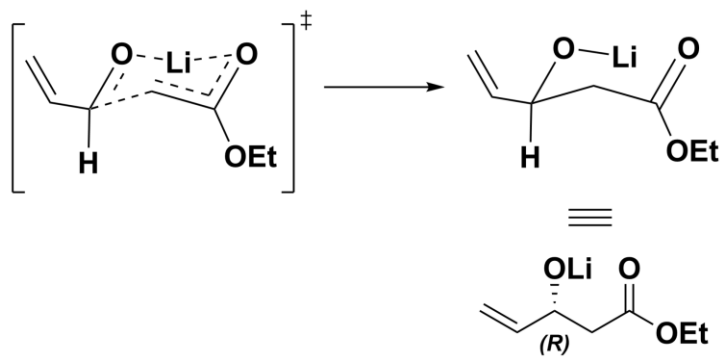
2 points for every structure. One-time penalty of -1 point if structure is correct, but stereochemistry is incorrect and the mistake carries forward. -1 point for every new mistake.

The stereoselectivity of the formation of **A** derives from the energetic differences in the two possible transition states and the outcome can be rationalised by the Zimmerman-Traxler model. By this rationale, addition of the lithium enolate proceeds via a cyclic six-membered chair-like transition state, resembling of the chair-conformation of cyclohexane (see figure). Stereochemical outcome is ultimately determined by the spatial arrangement of the electrophile in the transition state. The lowest energy transition state is such where the electrophile's bulkiest substituent is positioned equatorially and the smallest substituent is positioned axially. In the figure, axial protons of C₆H₁₂ are denoted as H^a and equatorial protons as H^e.



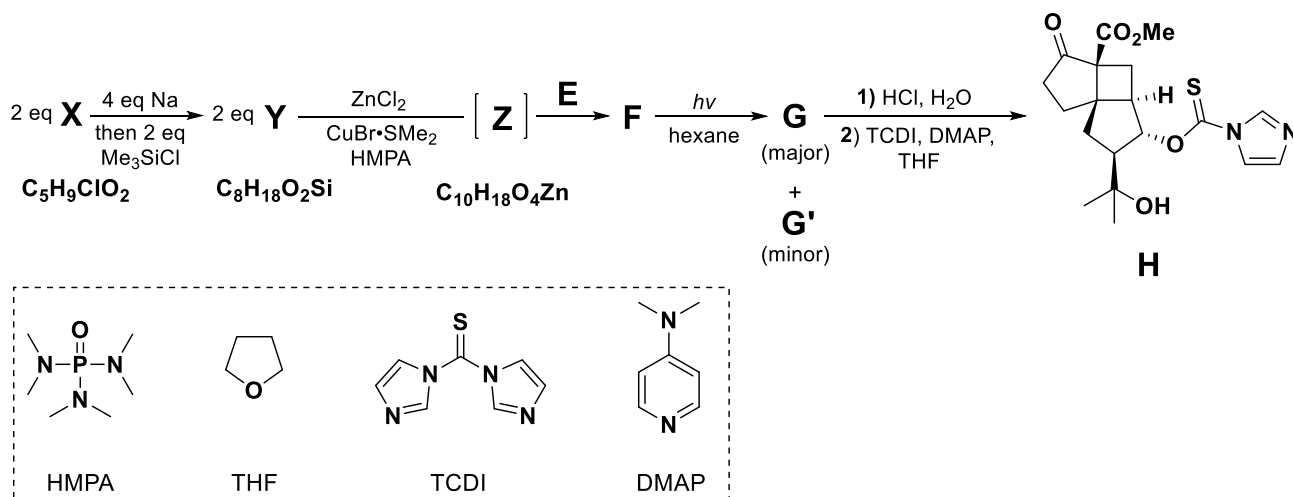
6.2. **Account for** the stereochemistry of **A** by applying the Zimmerman-Traxler model. Denote bonds which are being formed or broken with a dashed line (- -).

Lower energy TS: vinyl group is equatorial, H is axial

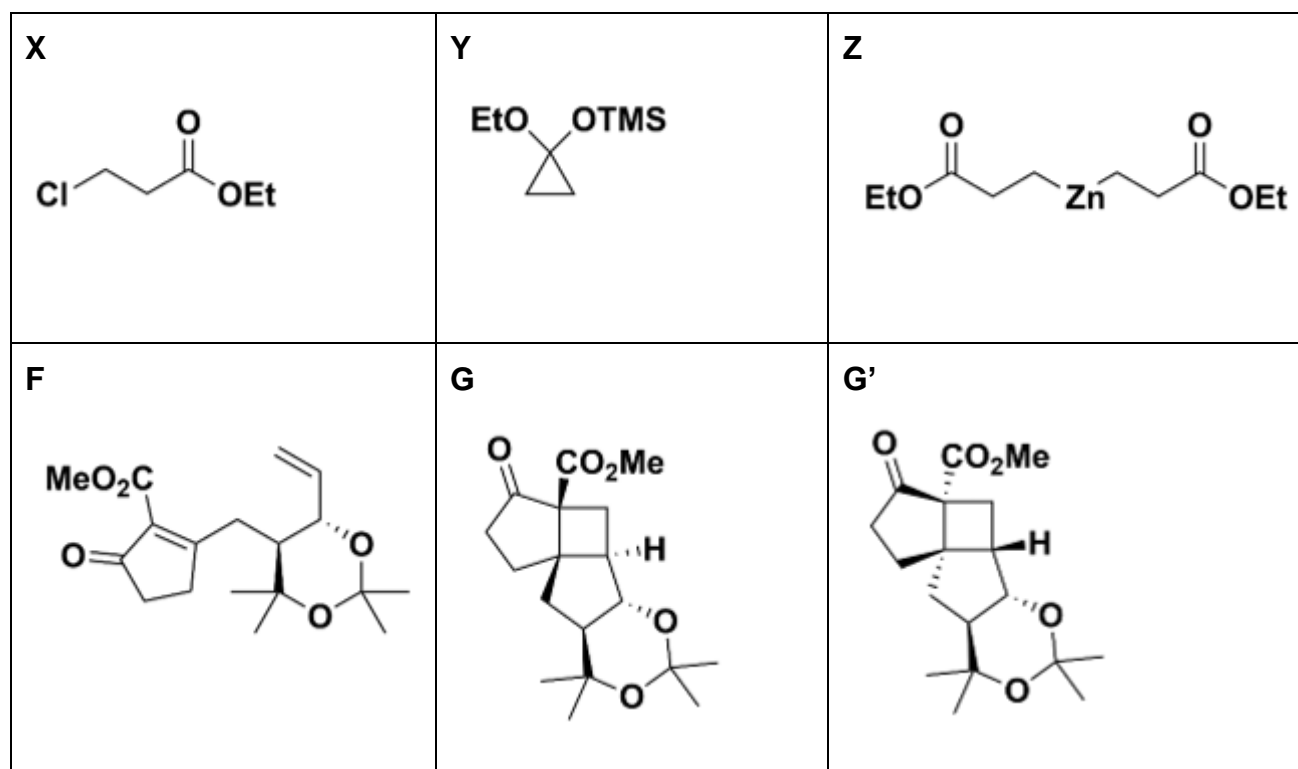


Correct arrangement of the electrophile and nucleophile (in chair conformation) - 3 points. Alternative correct depictions of the TS are equally valid and yield full points. Stating or showing that the vinyl group is equatorial in the TS and thus it is lower in energy than the other possible TS - 2 points.

Next, compound **E** was converted into enone **F** via a formal (3+2) cycloaddition. For this purpose, a zinc homoenolate **Z** was generated *in situ* from 2 equivalents of **Y** and 1 equivalent of ZnCl_2 . Note that 1 equivalent of **Z** can react with up to 2 equivalents of **E**. Compound **Y** can be formed by treating **X** with sodium and trapping the resulting alkoxide with trimethylsilyl chloride. It is known that **Y** is cyclic, whereas **X** and **Z** are not. Irradiation of **F** with UV light yielded **G** and **G'** as the major and minor products, respectively. Upon deprotection and carbamothioate formation, compound **H** was obtained.



6.3. **Draw** the structures of **X**, **Y**, **Z**, **F**, **G** and **G'**, taking stereochemistry into account.



2 points for X, 3 points for Y, Z, F, G and G'. One-time penalty of -1 point if structure is correct, but stereochemistry is incorrect and the mistake carries forward. -1 point for every new mistake.

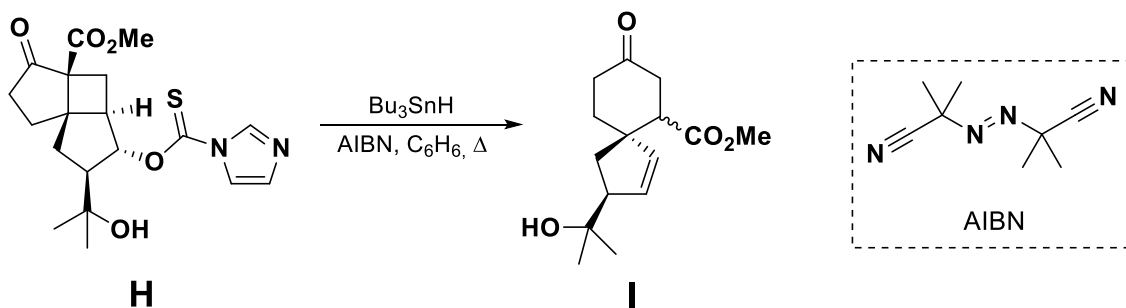
6.4. **Circle** the correct classification for the pericyclic reaction $\mathbf{F} \rightarrow \mathbf{G}$.

electrocyclisation / **cycloaddition (2p.)** / sigmatropic rearrangement /
cycloreversion / cheletropic reaction / ene reaction / the correct answer is not listed

6.5. **Circle** the correct answer. Based on Woodward-Hoffman rules, reaction **F**→**G** is:

Conrotatory (2p.) / disrotatory / neither conrotatory nor disrotatory

Compound **H** paved the way to the key step: a radical cascade which gave access to spirocycle **I**. First step of the cascade is a well-known name reaction.

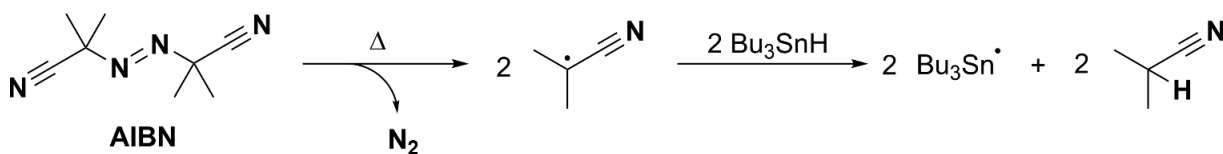


6.6. **Tick** the correct answer. First step of the radical cascade is called a:

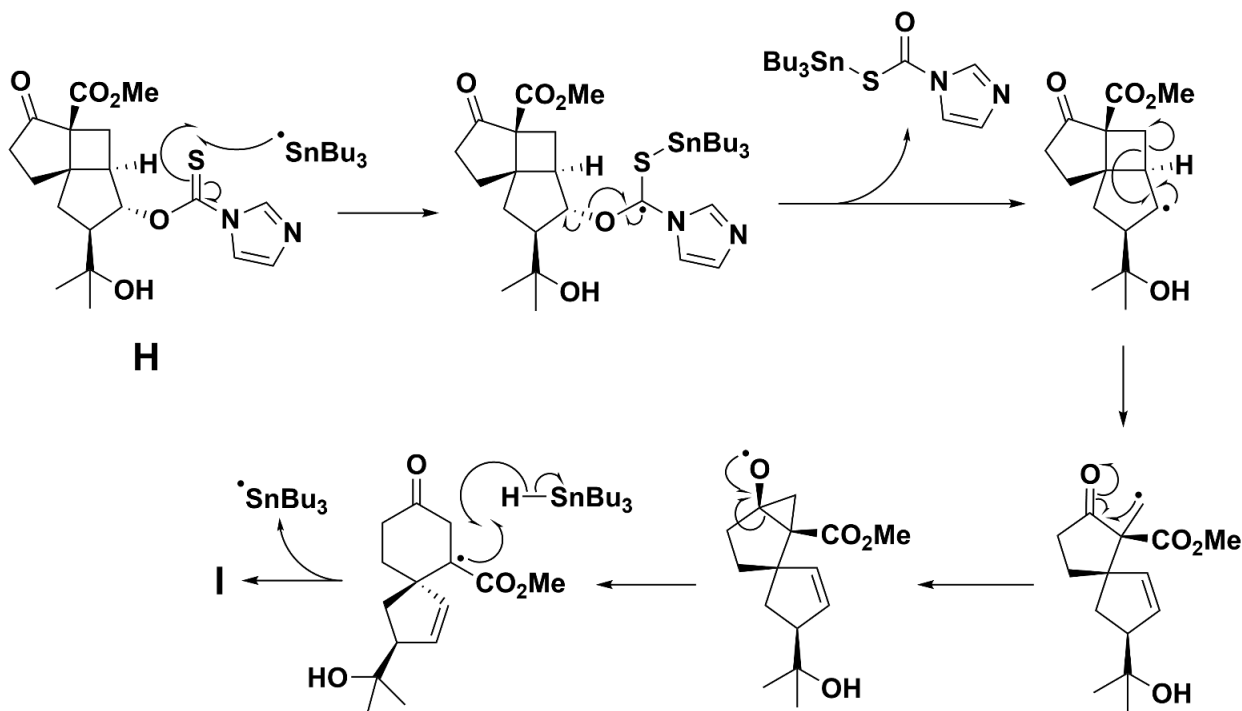
- Barton-McCombie reaction (2p.)**
- Mitsunobu reaction
- Wolff-Kishner reduction
- Julia olefination
- Corey-Fuchs reaction

6.7. **Sketch** the mechanism of the reaction **H**→**I** using curly fish-hook arrows to indicate the flow of electrons. Clearly **indicate** any by-products that are formed in the process.

1. Decomposition of AIBN and formation of tributyltin radicals



2. Radical cascade



Decomposition of AIBN - 1 point.

H-abstraction from Bu_3SnH by radicals formed from AIBN - 1 point.

Addition of tributyltin radical to carbamothioate - 1 point.

Deoxygenation - 1 point.

Cyclobutane fragmentation and methyl radical formation - 1 point total.

Cyclopropane formation - 1 point.

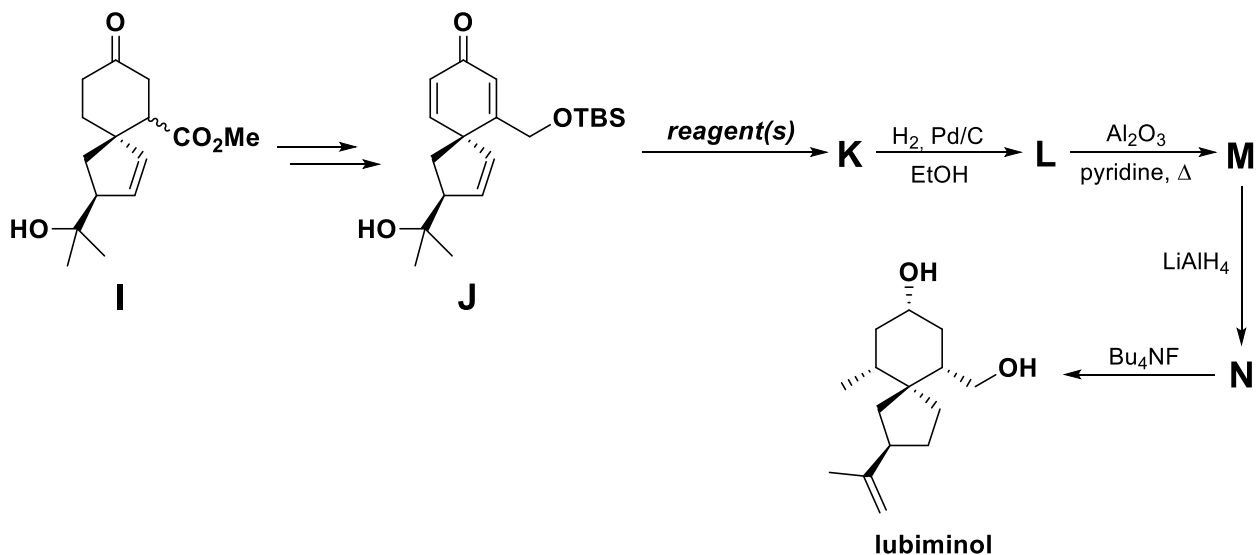
Ring expansion to cyclohexanone - 1 point.

Regeneration of tributyltin radical at the final step - 1 point.

By-products (N_2 , Me_2CHCN , carbamothioate) - 1 point each, 3 points total.

Correct stereochemistry throughout the mechanism, including epimerisation at the beta-position of cyclohexanone - 1 point.

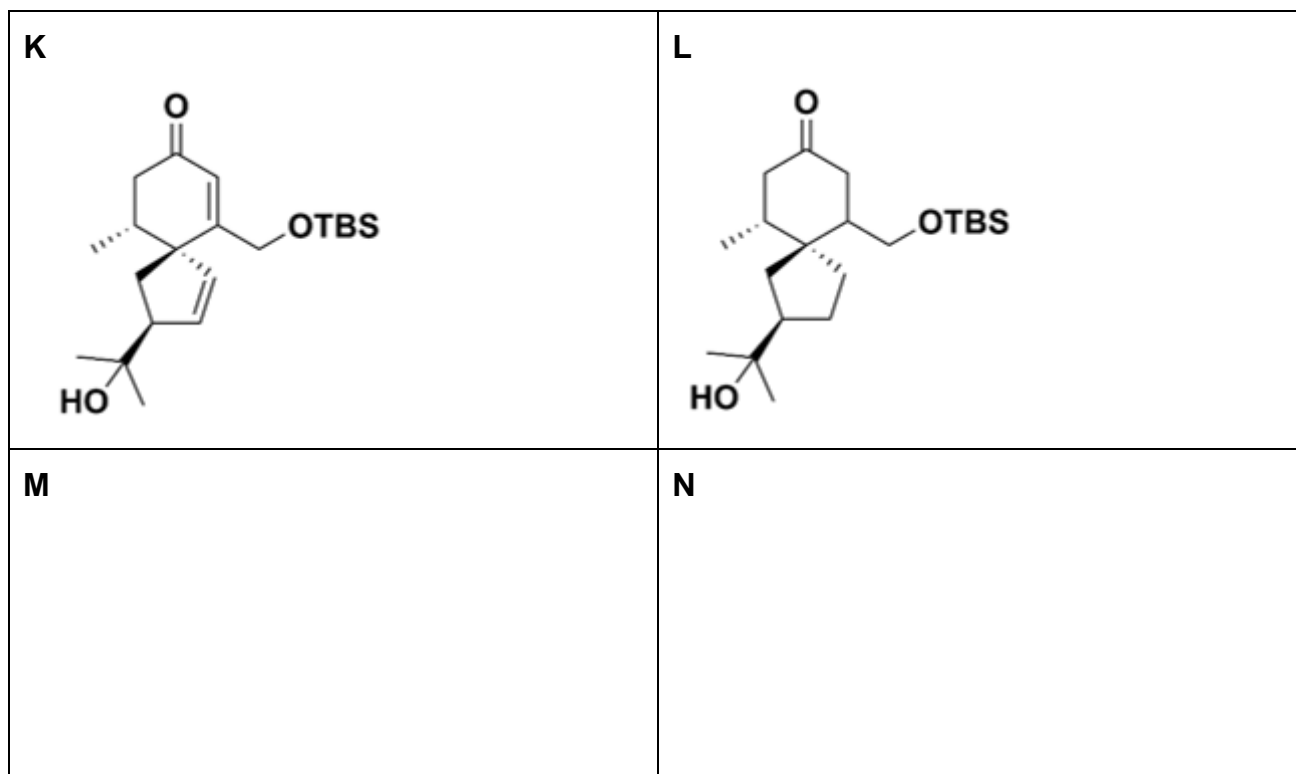
From compound **I**, precursor **J** was prepared over 7 steps. Subjecting **J** to **conditions** gave compound **K** stereoselectively. This in turn was hydrogenated to give compound **L**, in which all carbon-carbon bonds are saturated. From there, only two trivial steps remained to complete the synthesis.

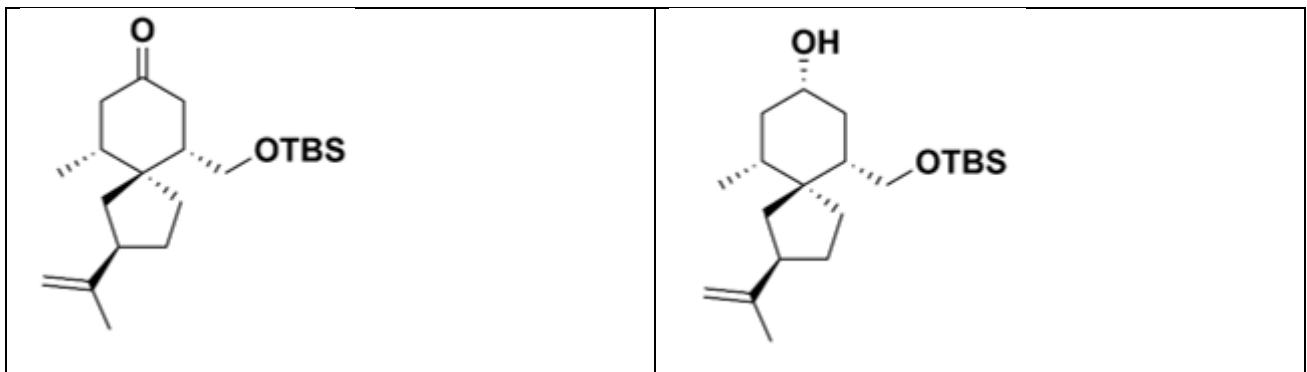


6.8. **Select** the appropriate **reagent(s)** for converting **J** into **K**. There is only one correct answer.

- $i\text{-Pr}_2\text{NLi}$, MeI
 MeMgBr
 $(\text{Me}_3\text{O})\text{BF}_4$
 Me_2CuLi (2p.)
 Me_3Si , NaH

6.9. **Draw** the structures of **K-N**, taking stereochemistry into account.





2 points for every structure. One-time penalty of -1 point if structure is correct, but stereochemistry is incorrect and the mistake carries forward. -1 point for every new mistake.