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General Information

Instructions

- You have three hours to solve the problems.
- Write all calculations and everything else legibly.
- Clearly state which assumptions you are making, if you do.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when you have been given permission to do so.
- Only legible answers written **on the question sheets** can be considered. You may use the back page if you require more space. Indicate this in the respective answer box.
- This exam has **9** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

Theoretical Final Exam 2025

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Physical Constants and Formulae

Constants

Planck constant	$h = 6.626\,070\,15 \times 10^{-34}\ \mathrm{J\,s}$
Boltzmann constant	$k_B = 1.380\,649 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
Speed of light	$c = 2.997\,924\,58 \times 10^{8}\ \mathrm{m\,s^{-1}}$
Elementary charge	$e = 1.602\,176\,634 \times 10^{-19}\ \mathrm{C}$
Avogadro constant	$N_A = 6.022\,140\,76 \times 10^{23}\ \mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\,462\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Atomic mass unit	$u = 1.660\,539\,066\,60 \times 10^{-27}\ \mathrm{kg}$
Proton mass	$m_{p^+} = 1.672\,621\,923\,69 \times 10^{-27}\ \mathrm{kg}$
Neutron mass	$m_{n^0} = 1.674\,927\,498\,04 \times 10^{-27}\ \mathrm{kg}$
Electron mass	$m_{e^-} = 9.109 \times 10^{-31}\ \mathrm{kg}$
Faraday constant	$F = 9.6485 \times 10^{4}\ \mathrm{C\,mol^{-1}}$
Standard pressure	$p_0 = 1.00 \times 10^{5}\ \mathrm{Pa}$
Electronvolt	$1\ \mathrm{eV} = 1.602\,176\,634 \times 10^{-19}\ \mathrm{J}$
Absolute zero	$0\ \mathrm{K} = -273.15\ ^{\circ}\mathrm{C}$
Ångstrom	$1\ \text{Å} = 1 \times 10^{-10}\ \mathrm{m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$

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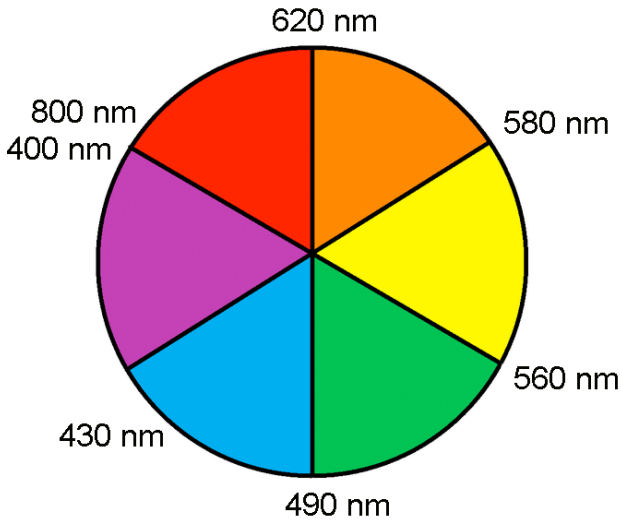
Formulae and Equations

Ideal gas law	$pV = nRT = Nk_BT$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG and K	$\Delta G = -RT \ln(K)$
Reaction quotient Q for reaction aA+bB $\rightleftharpoons$ cC+dD	$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$
Relationship between ΔG and ΔE_{cell}	$\Delta_r G^\circ = -nF\Delta E_{\text{cell}}^\circ$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^\circ + RT \ln(Q)$
Nernst equation	$E = E^\circ - \frac{RT}{zF} \ln(Q)$
Electric current	$I = \frac{q}{t}$
Arrhenius law	$k = Ae^{-\frac{E_A}{RT}}$
Lambert-Beer law	$A = \epsilon Lc = \log\left(\frac{I_0}{I}\right)$
Buffer equation	$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Half life for a first-order reaction	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$
Activity of a radioactive sample	$A = kN$
Surface area of a sphere	$A = 4\pi R^2$
Volume of a sphere	$V = \frac{4\pi}{3}R^3$

For calculations of equilibrium constants and all concentrations, refer to the standard concentration $1\,\mathrm{mol\,dm^{-3}} = 1\,\mathrm{mol\,L^{-1}}$. If not stated otherwise in the task, consider all gases ideal throughout this exam.



Periodic Table of Elements

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [212]
87 Fr [223]	88 Ra [226]	89–103	104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [270]	109 Mt [278]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]

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Score Sheet

NOT TO BE FILLED OUT BY PARTICIPANT

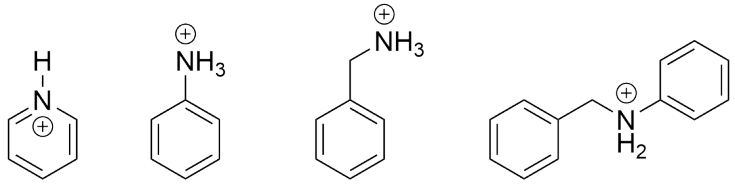
Name of participant: _____

Problem	Title	Maximum Points	Achieved Points	Tasks
Q1	On the Purification of Amines	17.5 pt		6
Q2	Perovskite Solar Cells	16.5 pt		8
Q3	Simple Complexes and Metallocenes	15.0 pt		9
Q4	Dating Fossile Bones Through Kinetics of Amino Acid Racemisation	20.0 pt		9
Q5	Boxes for Electrons	21.0 pt		10
Q6	Thermal Contraction of Rubber	16.0 pt		9
Q7	Carbocation Intermediate	20.5 pt		10
Q8	Can You See Me?	19.5 pt		14
Q9	Landiolol - a Cardioselective Beta-Blocker	16.0 pt		12
Total		163.5 pt		87

On the Purification of Amines

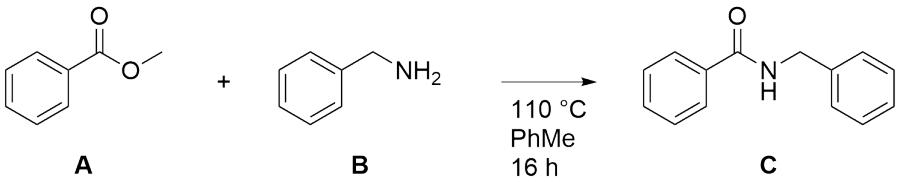
17.5 pts

Amines are ubiquitous in chemistry. Therefore, a tremendous amount of research has been done surrounding this class of compound. They are however known to be quite challenging to purify. They can act as acids and bases of various strength. This both offers opportunities and challenges to the synthetic chemist, who invariably develops a very strong and vocal opinion on amines after only a few experiments.



pK_a	5.2	4.6	9.3	3.8

Here are the pK_a values of some amines. For this problem, the effects of substituents on the rings upon the pK_a may be neglected.



A + **B** → **C**

Consider the reaction shown above, where 1 mol of **A** and 4 mol of **B** are mixed to obtain **C** . After the reaction appeared to be complete, the warm organic phase was washed *three times* with 1 L of 1 mol L^{-1} HCl solution each time. Then the aqueous phases were combined.

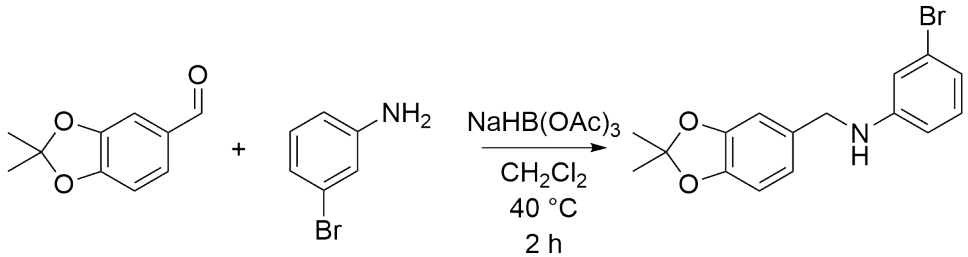
1.1 **Calculate** the pH of the combined aqueous phases. 3.0 pt
You may assume the following: The product **C** does not enter the aqueous phase, while all unreacted **B** did so. The reaction yield was 100%.

pH = _____

1.2 You find the pH in the combined aqueous phases to be 8.53. **Calculate** the yield of the reaction in %. 3.0 pt

You may assume the following: The product **C** does not enter the aqueous phase, while all unreacted **B** does.

Yield : _____%



D **E** **F**

We now turn our attention to the above reaction between 125 mmol of **D** and 200 mmol of **E** to yield **F**.

For purification of the product **F**, it was decided to extract the organic phase with a buffer solution of *formic acid* (HCOOH, pK_a = 3.80) and its sodium salt (HCOONa). A buffer was prepared so that the pH = 4.20. The aim of this is to limit the amount of **F** being washed away in its protonated form, while maximising the amount of **E** removed from the reaction mixture.

1.3 **Calculate** the maximal yield and purity of **F** that is isolated after one extraction. 3.0 pt

Yield : _____ % Purity : _____ mol%

1.4 **Calculate** the minimum amount of formate species n_{HCOOH}, n_{HCOONa} in mmol in the buffer required so that the pH does not deviate more than 0.05 units from 4.20 during workup. 5.0 pt

You may assume the following: 100% yield. All protonated species will enter the aqueous phase without affecting the protonation equilibrium. $NaHB(OAc)_3$ and its reaction products can be ignored.

$n_{HCOOH} =$ _____ mmol $n_{HCOONa} =$ _____ mmol

The solution of **F** is then concentrated so that a concentration of 0.8 mol L^{-1} is established. Then, a stream of H_2S is passed through the solution until it was saturated. The solubility of H_2S is 0.58 mol L^{-1}. After stirring for a few hours, beautiful translucent crystals start forming. The crystals are **F** · H_2S with a solubility constant K_S = 0.256 mol^2 L^{-2}.

1.5 **Calculate** the yield of this crystalization process. 2.0 pt
You may assume the following: the solubility of H_2S includes H_2S and its deprotonated forms.

Yield : _____ %

1.6 **Calculate** how many times the above procedure must be repeated to isolate at least 80% of all **F** initially contained in the solution. Each repetition consists of adjusting the concentration followed by the introduction of H_2S. 1.5 pt
Note: *If you obtained no result in the above task, you may assume a theoretical yield of 40% for the crystallisation.*

Repetitions : _____

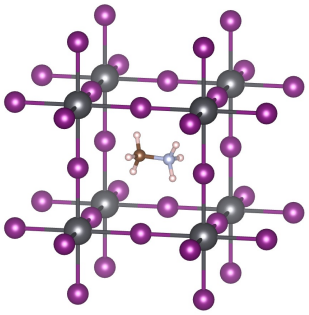
Perovskite Solar Cells

16.5 pts

Perovskite solar cells are thin-film photovoltaic devices utilizing perovskite materials for efficient sunlight-to-electricity conversion. Methylammonium Lead Iodide ($MAPbI_3$, MA = $CH_3NH_3^+$) is a key material in this context, valued for its high efficiency and cost-effectiveness. Its ideal band gap for photovoltaic applications, strong light absorption, and efficient charge transport make it widely used in achieving high-performance solar cells.

Unit Cell

2.1 Below, you find a structural representation of $MaPbI_3$. **Assign** the Lead (Pb) and the Iodine (I) atoms as either the gray or purple atom. 2.0 pt



Structural representation of $MAPbI_3$.

Colour	Lead	Iodine
Purple	☐	☐
Grey	☐	☐

Explain your reasoning.

2.2 **Select** the correct coordination number for the Pb ion. 1.0 pt

☐ 2 ☐ 3 ☐ 6 ☐ 12

2.3 The cell constants and angles for the full $MAPbI_3$ unit cell are listed in the table below. Based on the given data, **choose** the appropriate crystal system. 1.0 pt

a = 8.8392 Å
b = 8.8392 Å
c = 12.6948 Å
α = 90°
β = 90°
γ = 90°

☐ Cubic
☐ Tetragonal
☐ Orthorhombic
☐ Hexagonal
☐ Trigonal (Rhombohedral)
☐ Monoclinic
☐ Triclinic

2.4 **Calculate** the density ρ in kg cm^{-3} of the structure using $Z = 4$ for the calculation, where Z represents the number of formula units in the unit cell. 3.0 pt

$\rho =$ _____ kg cm^{-3}

Synthesis and Degradation

Methylammonium iodide (MAI) is synthesized using 24 mL of methylamine (MA) solution and 10 mL of hydroiodic acid (HI) solution. The two solutions are mixed in a round-bottom flask and stirred at 0 °C for 120 minutes to obtain a white solution. The solution is then evaporated at 80 °C for 120 minutes, producing a white precipitate. The precipitate is washed several times with diethyl ether until it becomes colorless, forming a white crystalline powder. The solution is then filtered and desiccated in a vacuum oven at 60 °C for 24 hours.

2.5 **Write** the balanced equation of the synthesis of MAI under the conditions given in the introductory text. 1.0 pt

To make the perovskite thin film, a two-step process is applied. First, a solution of PbI_2 (0.4 g in 2 mL of DMF) is coated onto a thin polymer layer. Using the spin coating technique, it is spun at 100 °C for 10 minutes. Next, a solution of MAI (0.01 g in 2 mL of DMF) is added to the PbI_2 layer. After that, the film is heated and spun again at 100 °C for another 10 minutes. During this process, the color of the film changes from light yellow to dark brown.

2.6 a) **Write** the balanced equation of the synthesis of $MAPbI_3$ from MAI and PbI_2 under the conditions given in the introductory text. 1.5 pt

b) **Assign** the oxidation states of lead (Pb) and iodine (I) in the product and starting materials.

2.7 $MAPbI_3$ degrades when it comes into contact with water. **Write** the balanced chemical reaction for the reaction of $MAPbI_3$ with water. 2.0 pt

Band gaps

The band gap of a compound is defined as the difference in energy between the valence band and the conduction band of a solid material. The range of the band gap describes of the range electron energies that cannot be adopted.

2.8 The band gap of $MAPbI_3$ is between 1.55 eV and 1.64 eV. 5.0 pt

a) **Calculate** the corresponding wavelengths λ in nm of light absorbed at 1.55 eV and 1.64 eV.

$\lambda_{(1.55\,\text{eV})} =$ _____ nm

$\lambda_{(1.64\,\text{eV})} =$ _____ nm

b) **Reason** how this affects the utilization of this compound in solar cells.

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Simple Complexes and Metallocenes — 15.0 pts

Simple Complexes

In 1913, Alfred Werner, a former ETH student and at this point Professor at University of Zurich, received the first Nobel Prize in the field of inorganic chemistry. He developed entirely new theories on how inorganic complex compounds are spatially arranged, which created the basis for modern complex chemistry. Ammine cobalt complexes played a central role in his discoveries.

Let's consider the complex $[Co(NH_3)_4Cl_2]Cl$.

3.1 **Determine** the oxidation state of the central metal ion in $[Co(NH_3)_4Cl_2]Cl$. 1.0 pt

Oxidation state = _____

3.2 **Draw** all stereoisomers and **describe** the relationship between the stereoisomers of $[Co(NH_3)_4Cl_2]Cl$. 2.5 pt

3.3 **Determine** the d^n electron configuration of $[Co(NH_3)_4Cl_2]Cl$. 1.0 pt

n = _____

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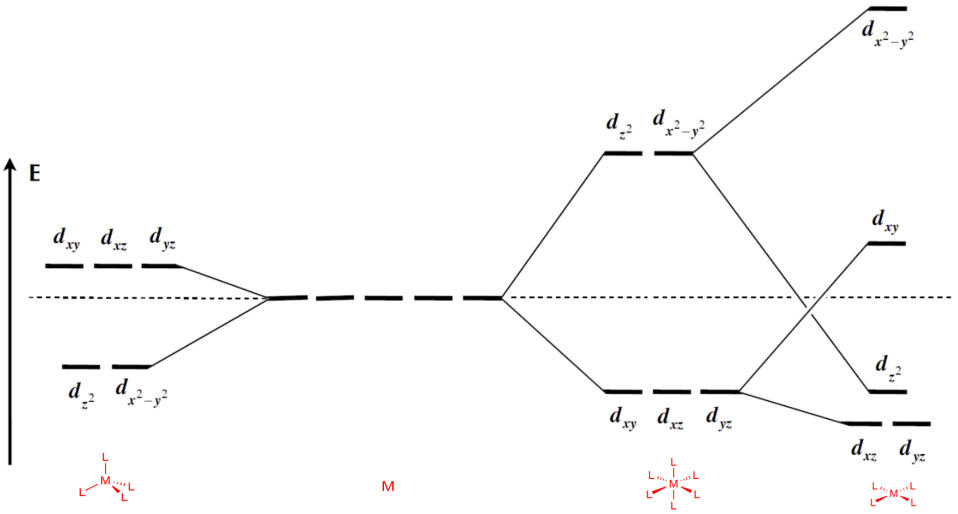
Many properties of transition metal complexes, such as visible light absorption and magnetism, are determined by the way the degeneracy of the d-orbitals is lifted when the ligands are added to the central metal. The new energy levels can be predicted through the ligand field splitting model, where the complex geometry and the nature of the ligands is considered.



Overview of different common crystal field splittings for different geometries.

The spectrochemical series shows which ligands and metal ions generate a weaker or stronger splitting.

Ligand:

$$O_2^{2-} < I^- < Br^- < S^{2-} < \mathbf{S}CN^- < Cl^- < N_3^- < F^- < NCO^- < OH^- < ONO^- < C_2O_4^{2-} \approx H_2O < \mathbf{N}CS^- < CH_3CN < NH_3 < NO_2^- < PPh_3 < CN^- < CO$$

Metal ion:

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Cu^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Rh^{3+} < Ir^{3+} < Pt^{4+}$$

3.4 a) **Draw** the energy diagram for $[Co(NH_3)_4Cl_2]Cl$ and **fill** in the d-electrons. 3.0 pt

b) **Select** whether the complex is high-spin or low-spin and **explain** your choice.

☐ low-spin
☐ high-spin

Explanation:

c) **Select** the correct magnetic properties for the complex.

☐ diamagnetic
☐ paramagnetic
☐ not clearly any of the above

Now consider two other ammine cobalt complexes, $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$. You have isolated both, one sample is orange and absorbs light at 475 nm, while the other is purple.

3.5 **Assign** the correct color to each complex and **explain** your answer. 2.0 pt

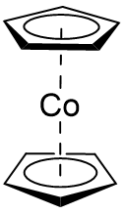
Complex	Color	Explanation
$[Co(NH_3)_6]Cl_3$		
$[Co(NH_3)_5Cl]Cl_2$		

3.6 **Calculate** the crystal field splitting Δ of the orange complex in $kJ\,mol^{-1}$ under the assumption that the crystal field splitting is responsible for the color. 0.5 pt

$\Delta =$ _____ $kJ\,mol^{-1}$

Metallocenes

Cobaltocene ($CoCp_2$), another cobalt complex, is composed of a cobalt-ion packed between two planar cyclopentadienyl anions, just like a sandwich. The complex is neutral and stable, but should be kept under an inert atmosphere.



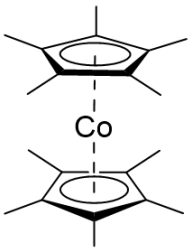
Structure of cobaltocene, $CoCp_2$.

3.7 **State** the oxidation state of the central atom and **determine** the total valence electron count of cobaltocene. 2.0 pt

Oxidation state = _____

Total electron count = _____

3.8 **Predict** the reactivity of cobaltocene. 1.0 pt



Structure of decamethylcobaltocene, $CoCp^*_2$.

When using two pentamethylcyclopentadienyl anions as ligands the resulting metallocene is called cobaltocene star ($CoCp^*_2$, shown above).

3.9 **Predict** the change in reactivity compared to cobaltocene. **Explain** your answer. 2.0 pt

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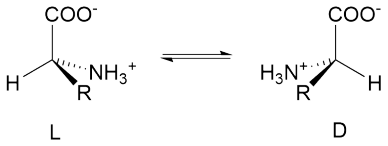
Dating Fossile Bones Through Kinetics of Amino Acid Racemisation — 20.0 pts

Only L-stereoisomers of amino acids (L-amino acids, see figure below) usually occur in the proteins of living organisms - although some D-amino acids are present in certain bacteria. The full isomerisation reaction of an L-amino acid into an D-amino acid includes a step with the creation of an enolate intermediate, however overall it can be simplified to:

$$\text{L—amino acid} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{D—amino acid}$$

with rate constants k_1 and k_2 . The figure below shows the respective 3-dimensional structures of the L- and D-stereoisomers of an amino acid.



For amino acids which have only one stereogenic centre, L- and D-amino acids are present in equal amounts under conditions of chemical equilibrium, so a system containing exclusively L-amino acids is thermodynamically unstable: the amino acid racemisation reaction will, after a period of time which is characteristic of each amino acid, eventually convert pure L-amino acids into a racemic mixture (i.e. one in which the D- and L-enantiomers are present in equal amounts).

4.1 For the forward racemisation reaction 3.0 pt

$$\text{L}-\text{amino acid} \longrightarrow \text{D}-\text{amino acid}$$

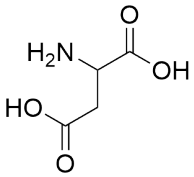
of an amino acid with only one stereogenic centre, **indicate** if the changes of enthalpy $\Delta_r H$, of Gibbs free energy $\Delta_r G$, and of entropy $\Delta_r S$ are respectively greater than zero ($>$), equal to zero ($=$), or smaller than zero ($<$) when going from an initial state with 100% L-amino acid (0% D-amino acid) to a final state with 50% L-amino acid and 50% D-amino acid. **Explain** each of your answers.

$\Delta_r H$ _____ 0, $\Delta_r S$ _____ 0, $\Delta_r G$ _____ 0

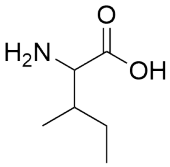
Explanations:

4.2 Based on the chemical formulas given below for the amino acids **Asp**, **Ile** and **Ala**, clearly **mark** the carbon atoms which are stereogenic centers with a $*$. For each of these three amino acids, **indicate** if the rate constant k_1 of the forward isomerisation reaction from the L- to the D- stereoisomer of the amino acid is expected to be equal to the rate constant k_2 of the reverse reaction, or if it is not possible to predict the relationship between k_1 and k_2. In each case, **explain** why. 3.0 pt

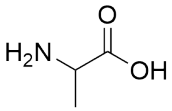
Asp



Ile



Ala



Explanations:

For relatively low extent of racemisation (small D/L ratios), the racemisation process can be considered as an irreversible first-order reaction, and k_1 may be written as

$$\ln(1 + [\mathrm{D}]/[\mathrm{L}]) - \ln(1 + [\mathrm{D}]_0/[\mathrm{L}]_0) = k_1 t$$

where $[\mathrm{D}]$ and $[\mathrm{L}]$ denote the respective concentrations of the D- and L-amino acids at time t and $[\mathrm{D}]_0$ and $[\mathrm{L}]_0$ denote the respective initial concentration. This equation can be used to obtain an order of magnitude for the time scale of the racemisation process.

For the historical conditions of Egypt, k_1 could be established as $9.9 \cdot 10^{-5}$ year^{-1} for the amino acid **Asp**.

4.3 Using the equation above and assuming that the initial concentration of D-**Asp** is zero, **calculate** the time $t_{1/2}$ in years required for the racemisation reaction to proceed halfway towards the equilibrium state. 2.0 pt

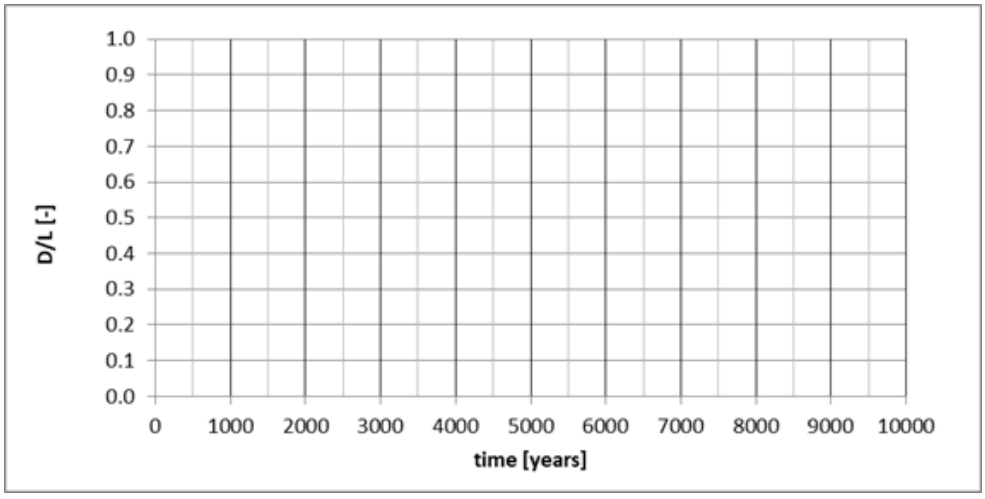
$t_{1/2} =$ _____ years

The full kinetic equation for the racemisation of the amino acid **Asp**, which takes into account the reverse reaction, has been established as:

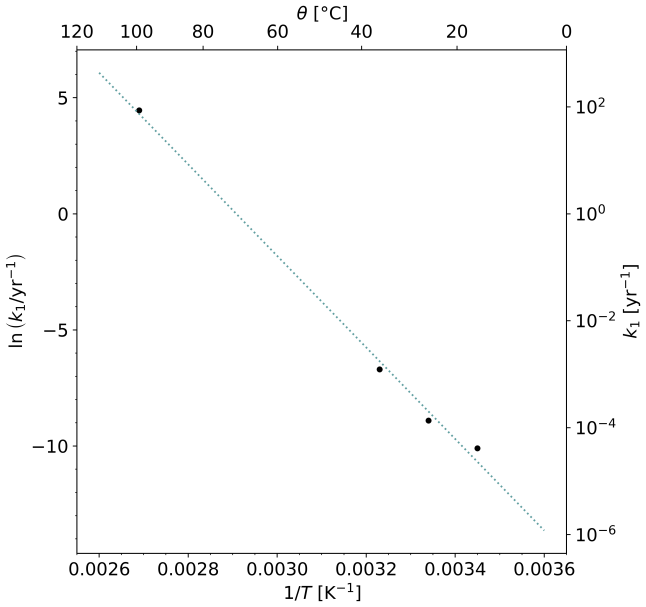
$$2k_1 t = \ln\left[\frac{1+[\mathrm{D}]/[\mathrm{L}]}{1-[\mathrm{D}]/[\mathrm{L}]}\right] - \ln\left[\frac{1+([\mathrm{D}]_0/[\mathrm{L}]_0)}{1-([\mathrm{D}]_0/[\mathrm{L}]_0)}\right]$$

4.4 For the cases where $[D]_0/[L]_0 = 0$, **determine** an equation to provide the ratio ($[D]/[L]$) as a function of time. Using the value of k_1 provided in task **4.3** and the template below, **represent** on a chart the results at the times $t = 0, 2500, 5000, 7500$ and 10000 years. 2.0 pt

Note: *If you couldn't find an equation for* $[D]/[L]$ *as a function of* t*, you may use the equation* $[D]/[L] = kt - (k^3t^3)/3 + (2k^5t^5)/15$ *to prepare the chart.*



4.5 Assuming that the average annual temperature for the region of Egypt is 26.3 °C, **calculate** the ratios $\frac{k_{T=27.3\,°C}}{k_{T=26.3\,°C}}$ and $\frac{k_{T=25.3\,°C}}{k_{T=26.3\,°C}}$ to find the sensitivity (% variation) of k_1 for **Asp** to an imprecision of 1 °C in the measurements, using the chart below and the Arrhenius law. 5.0 pt



$\frac{k_{T=27.3\,°C}}{k_{T=26.3\,°C}} =$ _____ % $\frac{k_{T=25.3\,°C}}{k_{T=26.3\,°C}} =$ _____ %

4.6 Using the relation provided in task **4.4** for t as a function of [D]/[L] (with $k_1 = 9.9 \cdot 10^{-5}$ year^{-1}) and assuming $[\mathrm{D}]_0$ of **Asp** is zero, **<u>determine</u>** the age range in years considering an average temperature $T = 26.3\,^{\circ}\mathrm{C}$, for a bone sample found in the region of Egypt with a [D]/[L] ratio of 0.6. The bounds are determined by an imprecision of $1.0\,^{\circ}\mathrm{C}$ from the average temperature. 2.0 pt

Note: *If you couldn't solve task **4.5**, assume* $\frac{k_{T=27.3\,^{\circ}\mathrm{C}}}{k_{T=26.3\,^{\circ}\mathrm{C}}} = 120\%$ *and* $\frac{k_{T=25.3\,^{\circ}\mathrm{C}}}{k_{T=26.3\,^{\circ}\mathrm{C}}} = 80\%$

Mean value for $t_{0.6} =$ _____ years

Lower bound for $t_{0.6} =$ _____ years

Upper bound for $t_{0.6} =$ _____ years

4.7 **Compare** the usefulness of the method of amino acid racemisation dating with that of radiocarbon dating, given the following data: 2.0 pt

- Radiocarbon dating has a 0.3% precision with samples aged up to $10'000$ years and a 10% precision up to $50'000$ years. After that, the method is no longer useful.
- The method of amino acid racemisation has a hypothetical boundary of [D]/[L] < 0.95, as the precision decreases as the ratio approaches 1.0.

4.8 **Assess** a method based on **Ala** against the radiocarbon dating method. 0.5 pt
The **Ala** racemisation rate is much slower than **Asp**, approximated to $k_{\textbf{Ala}} = 3.466 \times 10^{-5}$ year^{-1} for the same conditions as before.

4.9	**Justify** why the effect of temperature on the ages obtained with the **Ala** racemisation may or may not be expected to be the same as for the **Asp** racemisation.	0.5 pt

Boxes for Electrons

21.0 pts

The dynamics of π-electrons in a chain of conjugated double bonds can be modeled with the simple "particle in a box" model. The model assumes a one-dimensional box in which the electrons are confined and subjected to a constant potential. This leads to distinct energy levels for the electrons, given by

$$E(n) = \frac{n^2 h^2}{8 m_e L^2}$$

where $n = \{1, 2, 3, \dots\}$ is the principal quantum number of the electron, h is Planck's constant, m_e is the mass of the electron and L is the length of the one-dimensional box.

In the ground state, the π-electrons occupy the lowest possible energy states (orbitals). Remember that according to Pauli's principle maximum two electrons are permitted in an orbital. The highest occupied orbital is called HOMO and the lowest unoccupied orbital is called LUMO. Interactions between electrons will be neglected in the entire problem.

1D-Boxes

In the following, we will consider linear conjugated alkenes such as 1,3,5-hexatriene:

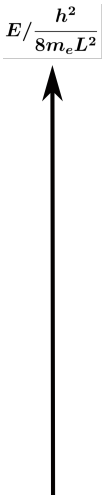
$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

The system can be approximated as a one-dimensional box with length $L = \left(k - \frac{1}{2}\right) \cdot 2.4\,\text{Å}$, where k corresponds to the number of double bonds, so in this case $k = 3$.

5.1 **Determine** the number n_π of π-electrons in 1,3,5-hexatriene. 1.0 pt

$n_\pi =$ _____

5.2 **Add** the energy levels for $n = 1, 2, 3, 4$ to the molecular orbital diagram template provided below and **fill in** the π-electrons for 1,3,5-hexatriene. **Indicate** the principal quantum number n of the orbitals with labels. 2.0 pt



5.3 **Determine** the wavelength λ in nm that is required to excite an electron from the HOMO to the LUMO in 1,3,5-hexatriene, assuming they behave as particles in a box. 2.0 pt

$\lambda =$ _____ nm

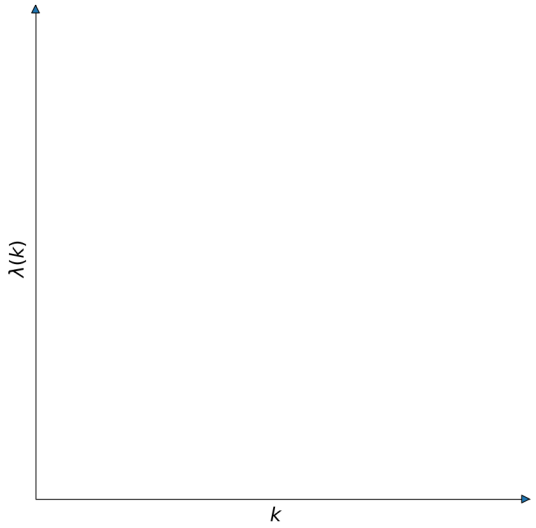
5.4 1,3,5-hexatriene also absorbs light at $\lambda = 74$ nm. **Explain** why and **support** your explanation with a calculation. 2.0 pt

5.5 Using the model developed, **develop** a formula for the dependence of the wavelength $\lambda(k)$ required to excite the HOMO-LUMO transition on the number of double bonds k. 2.0 pt

$\lambda(k) =$ _____

5.6 For molecules with many double bonds, qualitatively **sketch** the relationship of the HOMO-LUMO transition wavelength $\lambda(k)$ against the number of double bonds k in the template below. 1.0 pt

Note: *If you could not determine the formula for $\lambda(k)$ in the previous task, assume* $\lambda(k) = \frac{k^2-k+0.25}{2k+1} \cdot 190\,\text{nm}$.



5.7 **Determine** the number of conjugated double bonds k required for a linear molecule to absorb light at $\lambda = 2140\,\text{nm}$ through the HOMO-LUMO transition within the model developed. **Support** your answer with a calculation. 2.0 pt

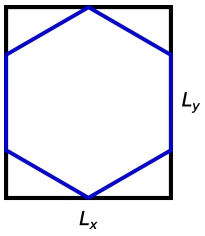
Note: *If you could not determine the formula for $\lambda(k)$ you may use the alternative provided in the previous task.*

$k =$ _____

2D-Boxes

So far we have been limited to linear molecules that can be approximated with a one-dimensional box. In the following we will try to extend the model to two dimensions so we can derive the molecular orbital diagram of benzene (C_6H_6).

5.8 Given the C–C bond length $L_B = 1.4\,\text{Å}$ in benzene and the template below, **determine** the minimal required side lengths L_x (horizontal) and L_y (vertical) in Å for the rectangular box to accommodate the benzene molecule as it's shown. 2.0 pt



$L_x =$ _____ Å, $L_y =$ _____ Å

The energy levels for an electron in a two-dimensional box with side-lengths L_x, L_y are given by

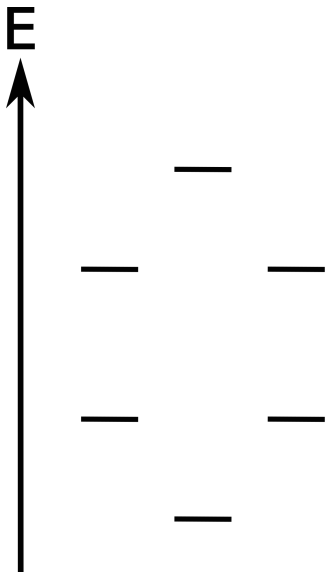
$$E(n_x, n_y) = \frac{h^2}{8m_e}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

where n_x, n_y denote the principal quantum numbers.

5.9 **Draw** the energy diagram of benzene (up to the LUMO) within the discussed model into the template provided below. **Indicate** the principal quantum numbers n_x, n_y on the energy axis. **Fill** the orbitals with the π-electrons. 3.0 pt

Note: *If you cold not determine L_x, L_y in the previous task, assume $L_x = 2.0\,Å$ and $L_y = 2.5\,Å$.*

The molecular orbital diagram of benzene without the crude approximations employed looks a bit different:

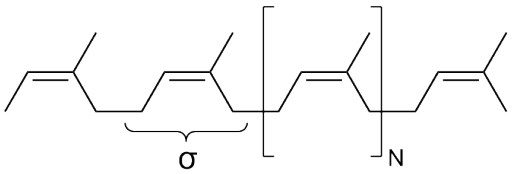


5.10 **Highlight** and **explain** the differences between the actual molecular orbital diagram of benzene and the one derived from our simplified model. 4.0 pt

Thermal Contraction of Rubber

16.0 pts

Most materials expand in volume upon heating. This is commonly explained as molecules begin to vibrate and move faster, resulting in an increased distance between the individual molecules. Rubber, however exhibits the special property that it contracts when heated. This question aims to explain this observation with fundamental statistical thermodynamics.

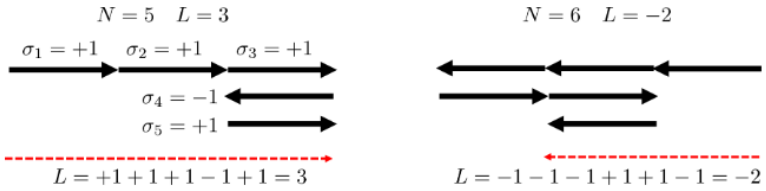


Structure of polyisoprene, the material of which rubber is made. The length of the repeating unit (indicated segment) is treated as $\sigma = 1$ if it is aligned towards to the right direction and $\sigma = -1$ if it is aligned to the left direction.

Rubber consists of polymeric materials (for example polyisoprene, shown above), consisting of $N \gg 1$ repeating units. For simplification, we model a rubber band in one dimension, where the N segments σ_i of length 1 can point only in $\pm x$ direction. The end-to-end length of the rubber band is then given by

$$L = \sum_{i=1}^{N} \sigma_i = \sigma_1 + \sigma_2 + \cdots + \sigma_N,$$

so we distinguish between positive and negative length. Two examples to illustrate the model are provided below.



Examples for $(N, L) = (5, 3)$ and $(6, -2)$.

6.1 **State** the set of all possible values for the end-to-end length L of a rubber band consisting of $N = 5$ segments. 1.0 pt

$L \in \{$ $\}$

The entropy of a system can be quantified using the Boltzmann equation:

$$S(L, N) = k_B \ln(\Omega(L, N)),$$

where $\Omega(L, N)$ corresponds to the number of distinct configurations, given a fixed value for the length L and number of particles N.

For example in the figure above, for $(N, L) = (5, 3)$ there exist $\Omega_{5,3}(N = 5, L = 3) = 5$ possible configurations, of which one is shown.

6.2 **State** the number of possible configurations $\Omega_{7,-7}(N = 7, L = -7)$. 1.0 pt

$\Omega_{7,-7}(N = 7, L = -7) =$ _____

6.3 **Determine** the number of possible configurations $\Omega_{6,4}(N = 6, L = 4)$. 1.0 pt

$\Omega_{6,4}(N = 6, L = 4) =$ _____

6.4 Using the Stirling approximation: $\ln(N!) \approx N \ln(N)$, **show** that 3.0 pt

$$S(N, L) = k_B \left[N \ln(N) - \frac{N+L}{2} \ln\left(\frac{N+L}{2}\right) - \frac{N-L}{2} \ln\left(\frac{N-L}{2}\right) \right]$$

Hint: *If the order is not of concern,*

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

different possibilities exist to drawing n samples from N objects.

6.5 For a fixed value of N, **determine** all values L_{min} and L_{max} for which the entropy $S(N, L)$ is minimal/maximal. 2.0 pt

$L_{\text{min}} =$ _____ $L_{\text{max}} =$ _____

6.6 Because the segments in polyisoprene interact only very weakly, we may assume that the enthalpy for different arrangements (values of the length L) remains constant: $\Delta H = 0$. Using the free energy $G = H - TS$, qualitatively **describe** the relationship between the force F required on the rubber band in order to stretch/contract it to a given length L and the number of segments N. 2.0 pt

A mathematical derivation of the formula for F from the previous task and inversion to $L(T, f, N)$ should yield the length L depending on the applied force:

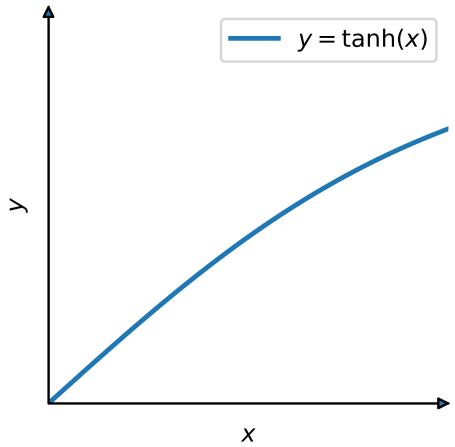
$$L = N \tanh\left(\frac{F}{k_B T}\right) = N \frac{e^{\frac{F}{k_B T}} - e^{-\frac{F}{k_B T}}}{e^{\frac{F}{k_B T}} + e^{-\frac{F}{k_B T}}}$$

6.7 **Determine** and **interpret** the limit where the force applied to the rubber band approaches $+\infty$. 2.0 pt

$\lim_{F \to +\infty} L(T, F, N) =$ _____

Interpretation:

The temperature dependence of the length L of the rubber band when a fixed force F is applied can be described through analysis of the graph of the $\tanh(x)$ function:



6.8 **Reason** mathematically why for a fixed force $F > 0$ we have a negative thermal expansion ($|L|$ becomes smaller as the temperature rises). 3.0 pt

6.9 **Explain** the negative thermal expansion (that smaller $|L|$ values are more favorable at higher temperature) in thermodynamic (phenomenological) terms. 1.0 pt

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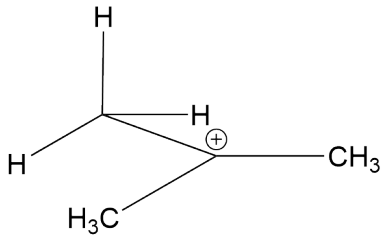
Q7-1

English (Official)

Carbocation Intermediate — 20.5 pts

Introduction

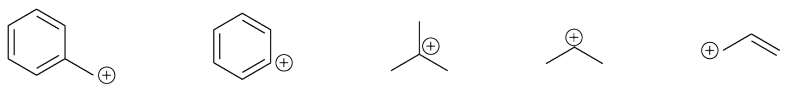
In this problem we're going to deal with reactions involving a common unstable intermediate, which is the carbocation. Although elusive for long, the study of carbocations earned George Olah the Nobel Prize in 1994.



7.1 For the molecule in the figure above, **predict** the hybridization of the carbon that bears the positive charge. 0.5 pt

Carbocations are unstable because they do not obey the octet rule. However, they can be stabilized either by resonance or an effect called hyperconjugation, in which the σ-bond of the neighbouring C–H and C–C bonds donate their electron density to the carbocation.

7.2 **Compare** the stability of the following carbocations, with either (>) or (<) sign to indicate the more stable carbocation. 2.5 pt



1 2 3 4 5

3 1

4 5

4 2

5 1

1 2

Carbocations can be produced by elimination of water from alcohols under acidic conditions. Usually H_2SO_4 is employed because it also has dehydrating properties, which promote the formation of carbocations.

7.3 From the chemical formula $C_5H_{12}O$, **determine** how many isomers n_{isom} (including stereo- and regioisomers) are alcohols and **draw** their structures. 2.5 pt

$n_{\text{isom}} =$ _____

Interestingly, 2-methylbutan-2-ol and 3-methylbutan-2-ol yield the same cationic intermediate and thus also the same product when treated with HBr.

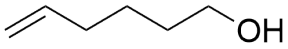
7.4 **Draw** the structures of the intermediate and the product of the reaction with HBr mentioned above. 1.0 pt

Intermediate	Product

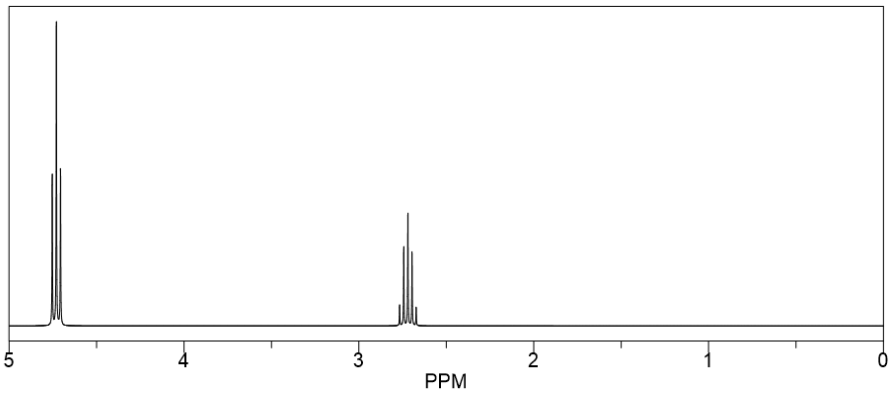
Reactions

Carbocations may react with nucleophilic moieties that exist in the same molecule, giving rise to a cyclic product through an intramolecular reaction.

7.5 **Draw** the structure of the major product when the compound shown below is treated with H_3PO_4. The OH group is observed to be present in the carbocation intermediate and the product has been determined to be a heterocyclic compound. 1.0 pt

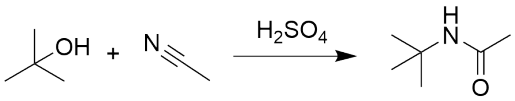


Cyclic building blocks are very common in organic reactions, both as intermediates and precursors. Here is an ^{1}H-NMR spectrum of a simple cyclic ether **A** with $\%w(\mathrm{C}) = 62.0\%$ and $\%w(\mathrm{H}) = 10.3\%$.



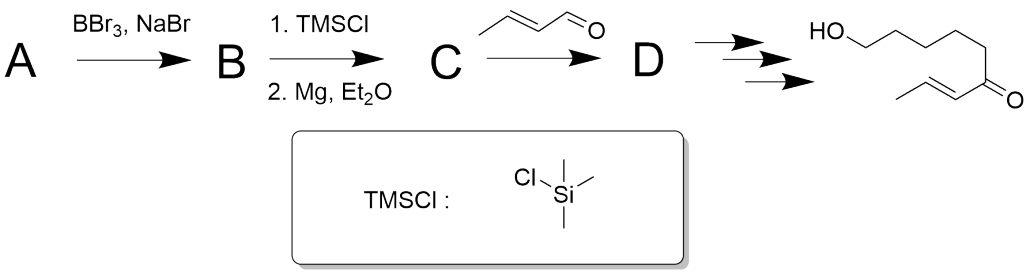
7.6 **Draw** the structure of the organic compound **A** based on the NMR spectrum and data given. 2.0 pt

Another reaction that utilizes a carbocation intermediate was discovered by John J. Ritter in 1948. In the Ritter reaction, an amide is generated through nitrile attack on a carbocation, followed by hydrolysis and keto-enol tautomerization.

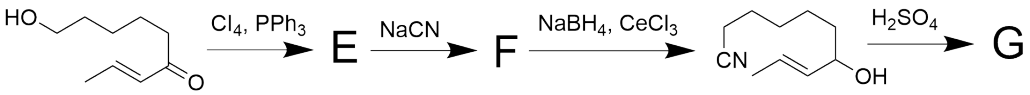


With this reaction in mind, let's synthesize a fascinating cyclic amide from the cyclic ether **A** encountered previously.

Compound **A** is treated with BBr_3 to generate a haloalcohol **B**, which is protected by a silyl derivate and converted into a very famous reagent in organic synthesis **C**. The scientist who first discovered this reagent was awarded with Nobel Prize in Chemistry in 1912. After that, **C** is reacted with an aldehyde to generate product **D**, which will be transformed further more.



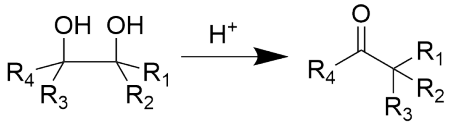
After deprotection and homologation, the compound is subjected to the Appel reaction using carbon tetraiodide (CI_4) to yield **E**, which then undergoes an S_N2 reaction, providing **F**. The alcohol obtained through Luche reduction of **F** then produces a heterocyclic compound **G** through the Ritter reaction, which was catalyzed by H_2SO_4.



7.7 **Draw** the structures of compounds **B-G**. 6.0 pt

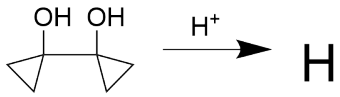
B	C
D	E
F	G

Another reaction that involves a carbocation is the pinacol rearrangement and it goes as follows:

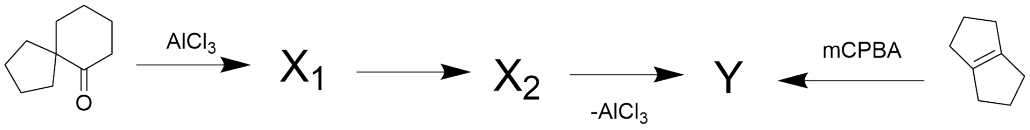


In a first step, the alcohol is protonated, yielding a carbocation through the elimination of water. The adjacent hydroxyl group then donates its lone pair, forming a C=O bond and causing an alkyl shift to form a quarternary center.

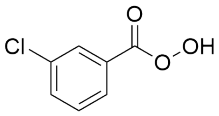
7.8 **Draw** the structure of the product **H** in the following transformation. 1.0 pt



Lastly, a product of a similar transformation was subjected to a Lewis acid, which leads to a rearrangement to generate a tricyclic structure **Y**. Additionally, **Y** can be produced by the reaction of mCPBA (*meta*-chloroperoxybenzoic acid) with a bicyclic alkene as follows.



mCPBA :



7.9 **Draw** the structures of intermediates $\mathbf{X_1}$, $\mathbf{X_2}$, and product **Y**. 3.0 pt

X_1

X_2

Y

7.10 **Draw** the precursor of the ketone, assuming it was formed through a pinacol rearrangement. 1.0 pt

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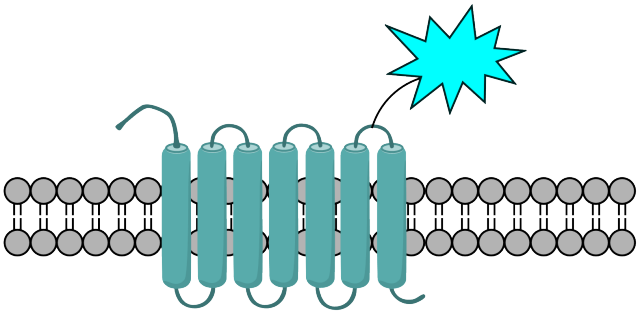
Q8-1

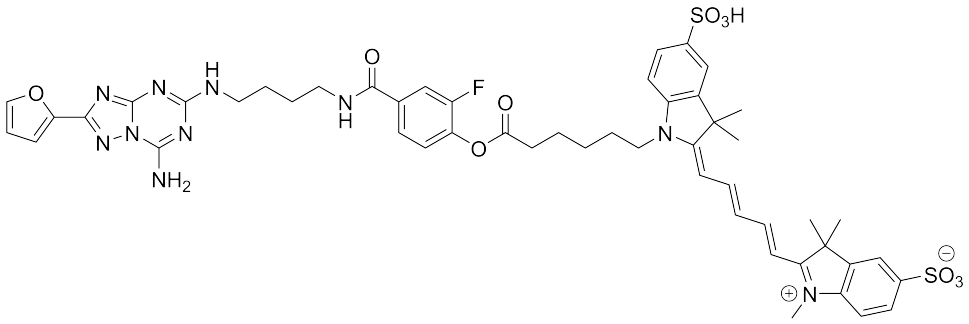
English (Official)

Can You See Me? 19.5 pts

Introduction



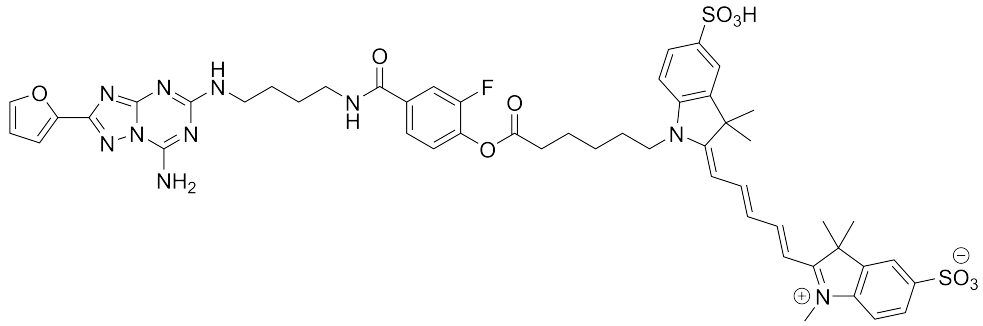
Seeing is believing. The fluorescent labeling of biomolecules allows scientists, among other things, to track the localisation and the dynamics of production and degradation of these molecules. Labeling methods have become better and more specific over time. In this task, you will learn about ligand-directed covalent labeling of a cell-surface receptor and the requirements of such a probe to fulfill the desired function. In this approach, a small molecule, the ligand, binds reversibly to the receptor. Upon binding, the probe can then react with nucleophilic residues of the protein, which leads to the formation of a covalent bond and thus irrversible labeling. The probe you will be analysing is shown below.



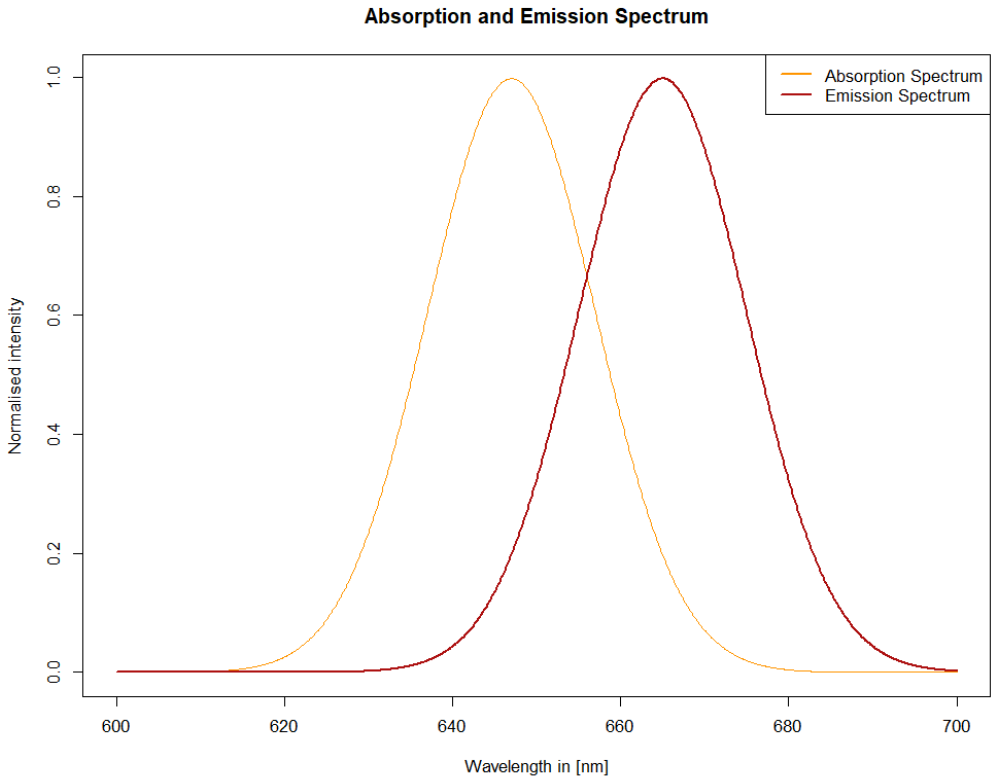
Probe Properties

The probe is composed of three parts: A ligand, a fluorophore and a linker with a reactive moiety. The ligand will bind to the receptor in a reversible fashion. The fluorophore will ultimately be the observable entity and the linker connects the two parts and contains the reactive handle, which will lead to covalent labeling.

8.1 Below, the probe is shown again. **Identify** and **clearly mark** ligand (I), fluorophore (II) and linker (III) in the molecule below. 1.5 pt



A special characteristic property of a fluorophore is the so-called Stokes shift. The Stokes shift is the difference in the maximum of the emission vs. absorption wavelength of the fluorophore. Below, the absorption and emission spectrum of our probe is shown.



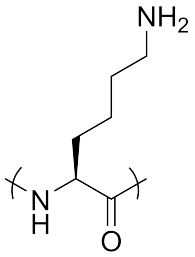
Absorption and emission spectrum of our probe.

8.2 From the provided spectrum, **estimate** the Stokes shift $\Delta\lambda$ of your probe in nm. 1.0 pt

$\Delta\lambda =$ _____ nm

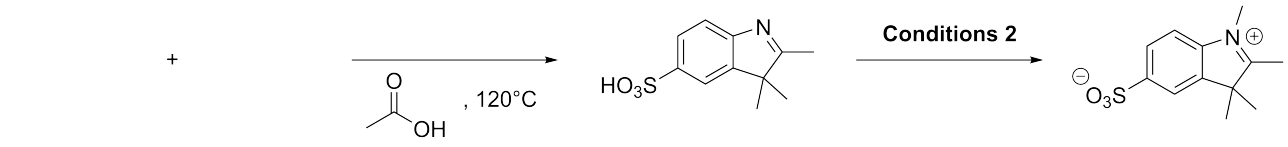
Upon binding of the ligand to the receptor, a lysine residue in the vicinity of the binding pocket can react with the probe. The lysine residue reacts with the reactive handle in the linker of the probe to form a stable covalent bond, labeling the receptor.

8.3 Below, a lysine residue is shown. **Draw** the product of the reaction between the lysine side-chain and the probe. You may use the structure below as a template to complete your drawing. Further, you may use the abbreviations -L for ligand and -Fl for fluorophore. 2.0 pt



Probe Synthesis

Let's take a closer look at the synthesis of the probe. Different parts of the probe are synthesised separately and connected in the end. In the scheme below, the synthesis of one part of the probe is shown.



$C_6H_8N_2O_3S$ $C_5H_{10}O$

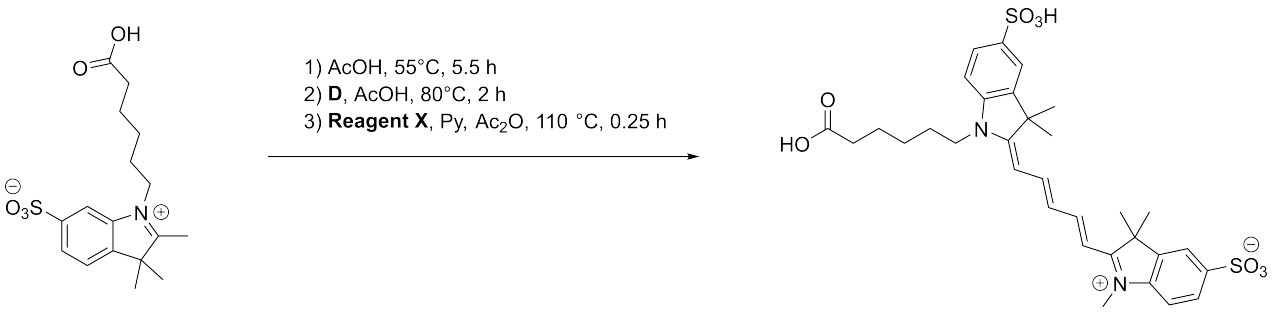
A **B** **C** **D**

8.4 According to the scheme above, please **provide** the structures of compounds **A** and **B**. **Hint:** *In the transformation to compound* **C**, *a gas is released.* 2.0 pt

A	**B**

8.5 From the list below, **choose** the most suitable conditions for the transformation of compound **C** to compound **D**. 1.0 pt

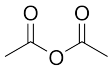
☐ cat. H_2SO_4, MeOH, 50 °C
☐ Formaldehyde, MeOH, 50 °C
☐ MeI, CH_3CN, 80 °C
☐ Acetylchloride, $AlCl_3$, $CHCl_3$, 50 °C



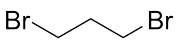
E **F**

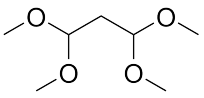
AcOH = 

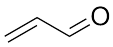
Py = 

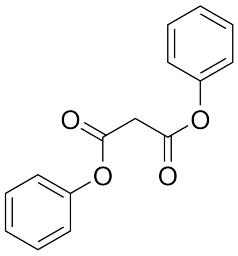
Ac_2O = 

8.6 From the options below, **choose** a suitable **Reagent X** for the transformation of compound **E** to compound **F**. 1.0 pt









☐ ☐ ☐ ☐

Let's take now a look at the synthesis of another part of the molecule. In the scheme below, a synthetic outline for that part is shown.

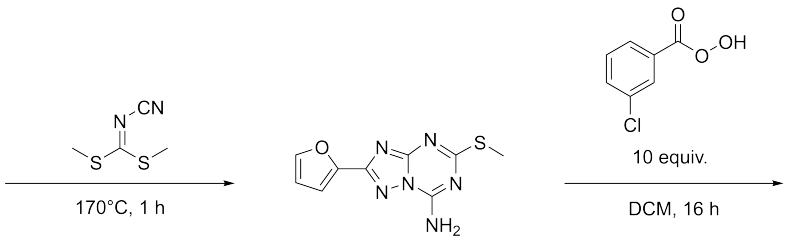
G | **H** $C_6H_8N_4O_2$ | **I**

8.7 **Draw** the structures of compounds **H** and **I**. **Hint:** *In the transformation of compound* **H** *to* **I**, *one equivalent of water is lost from the molecule.* 2.0 pt

H	**I**

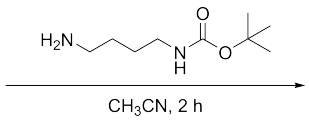
8.8 What is the driving force for the transformation of compound **H** to **I**? **Select** the appropriate answer from the list below. 1.0 pt

☐ Formation of a C-N bond
☐ Release of ring-strain
☐ Generation of aromaticity
☐ Extrusion of water



I **J** **$C_9H_8N_6O_3S$ K**

8.9 **Draw** the structure of compound **K.** 1.0 pt

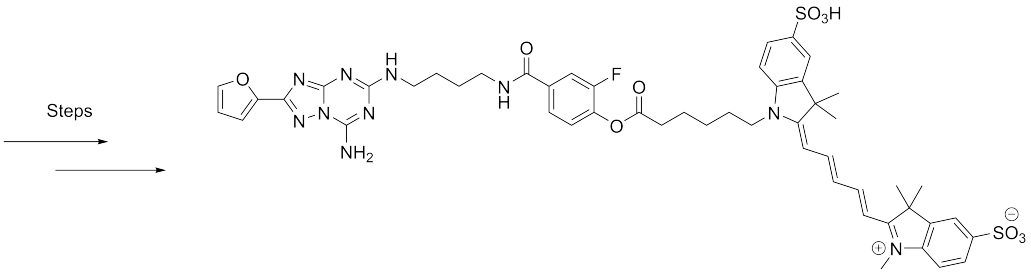


$C_9H_8N_6O_3S$

K

$C_{17}H_{24}N_8O_3$

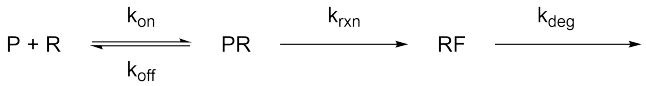
L



8.10 **Draw** the structure of compound **L**. 1.0 pt

The Labeling Reaction

Now, we'll take a closer look at the labeling reaction and what is needed in order for us to actually see the receptor. Below, a schematic representation of the labelling process is shown. In a first step, the probe, P, binds to the receptor, R, in a reversible equilibrium forming the probe-receptor complex, PR. If the probe is bound, it can also react with a close-by lysine residue in an irreversible fashion, leading to the fluorescent labeling of the receptor, RF. The cell constantly produces and degrades this receptor. The receptor, independent of whether it is labelled or not, is degraded in a zeroth-order reaction with a rate constant k_{deg}.



For the following tasks, you may use the following assumption and values:

- The receptor and probe are in a rapid equilibrium of binding, while the formation of RF from PR is much slower.
- The total receptor concentration is kept constant by the cellular regulatory processes and can be assumed to be 3 µmol L^{-1}, $[R]_{tot} = 3\ \mu mol\ L^{-1}$.
- The dissociation constant of the probe-receptor complex is 50 µmol L^{-1}: K_D = 50 µmol L^{-1}.
- The maximum concentration of the probe you can use is 6 µmol L^{-1}, $[P]_{max}$ = 6 µmol L^{-1}.

8.11 **Derive** an equation for the change in concentration of the labeled receptor, $\frac{d[RF]}{dt}$, using the equilibrium concentrations of [P], [R] and the given rate and equilibrium constants. 2.0 pt

From a different experiment, you have established that the half-life time of your receptor on the cell surface is 240 min. The formula for the half-life time of a zero-order process is given below.

$$t_{1/2} = \frac{[\mathrm{R}]_0}{2 \cdot k_{\mathrm{deg}}}$$

8.12 Considering all the information given above, **<u>calculate</u>** the value of k_{deg} in $\mathrm{mol\,L^{-1}\,s^{-1}}$. 1.0 pt

$k_{\mathrm{deg}} =$ _____ $\mathrm{mol\,L^{-1}\,s^{-1}}$

8.13 Consider the very start of the labeling reaction, just after addition of the probe. **Calculate**, in s^{-1}, the value k_{rxn} needs to have at least, so we can observe any labeling at all. 2.0 pt

In case you couldn't solve the previous questions, assume:

- $\frac{d[RF]}{dt} = \frac{k_{rxn} \cdot K_D \cdot [P]}{[R]} - k_{deg}$
- $k_{deg} = 2.00 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$

$k_{rxn} \geq$ _____ s^{-1}

You have performed your labeling experiment and it seems to work. However, you're not quite satisfied with the labeling you can achieve and you would thus like to increase the initial rate of labeling.

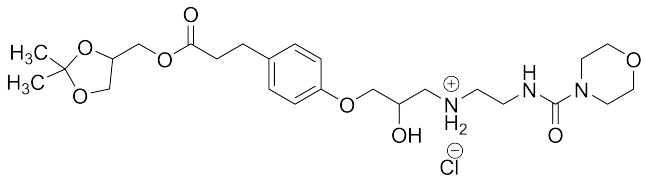
8.14 From the options below, **choose** which strategies could be worth investigating to achieve this. 1.0 pt

☐ Find/develop a ligand with a higher binding affinity for our receptor
☐ Use a larger fluorophore
☐ Increase the reactivity of the reactive handle
☐ Change the solvent to a more apolar one

Landiolol - a Cardioselective Beta-Blocker 16.0 pts

Introduction

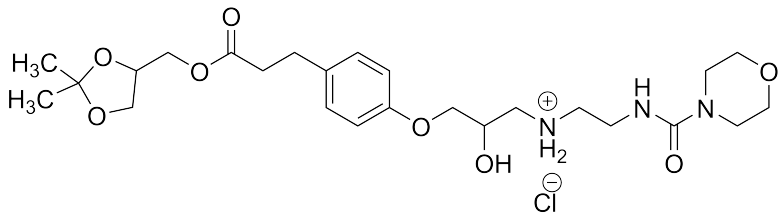
Every year, the food and drug administration (FDA) in the USA approves new therapeutics. In 2024, Landiolol, a beta-blocker, was approved for the treatment of supraventricular tachycardia. Landiolol was developed in Japan and already approved in Germany as a drug in 2017. As of 2024, Landiolol is the most cardioselective beta-blocker known. The structure of Landiolol is shown below.



Stereochemistry

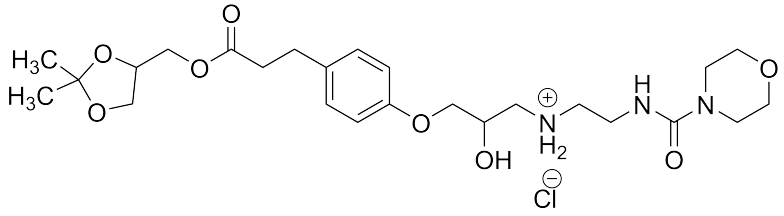
Landiolol is a chiral molecule, containing more than one stereocenter. As it is the case with almost any approved drug, Landiolol is administered as a single stereoisomer. Due to the inherent chiral nature of biological systems, different stereoisomers, even entantiomers, can have very different activity, which is why the different stereoisomers will have to be evaluated independently for their activity and possible off-target effects.

9.1 In the structure of Landiolol, **mark** all stereogenic centers with an asterisk (*). 1.0 pt



9.2 **Calculate** how many stereoisomers Landiolol can have. 0.5 pt

9.3 In the FDA-approved structure of Landiolol, all stereocenters are *S*-configured. **Draw** the structure of Landiolol with the correct stereochemistry at all stereogenic centers. **Note:** *You may abbreviate parts of the molecule, which are not relevant for stereochemistry with -R or use the template of Landiolol provided below.* 2.0 pt



Theoretical Final Exam 2025

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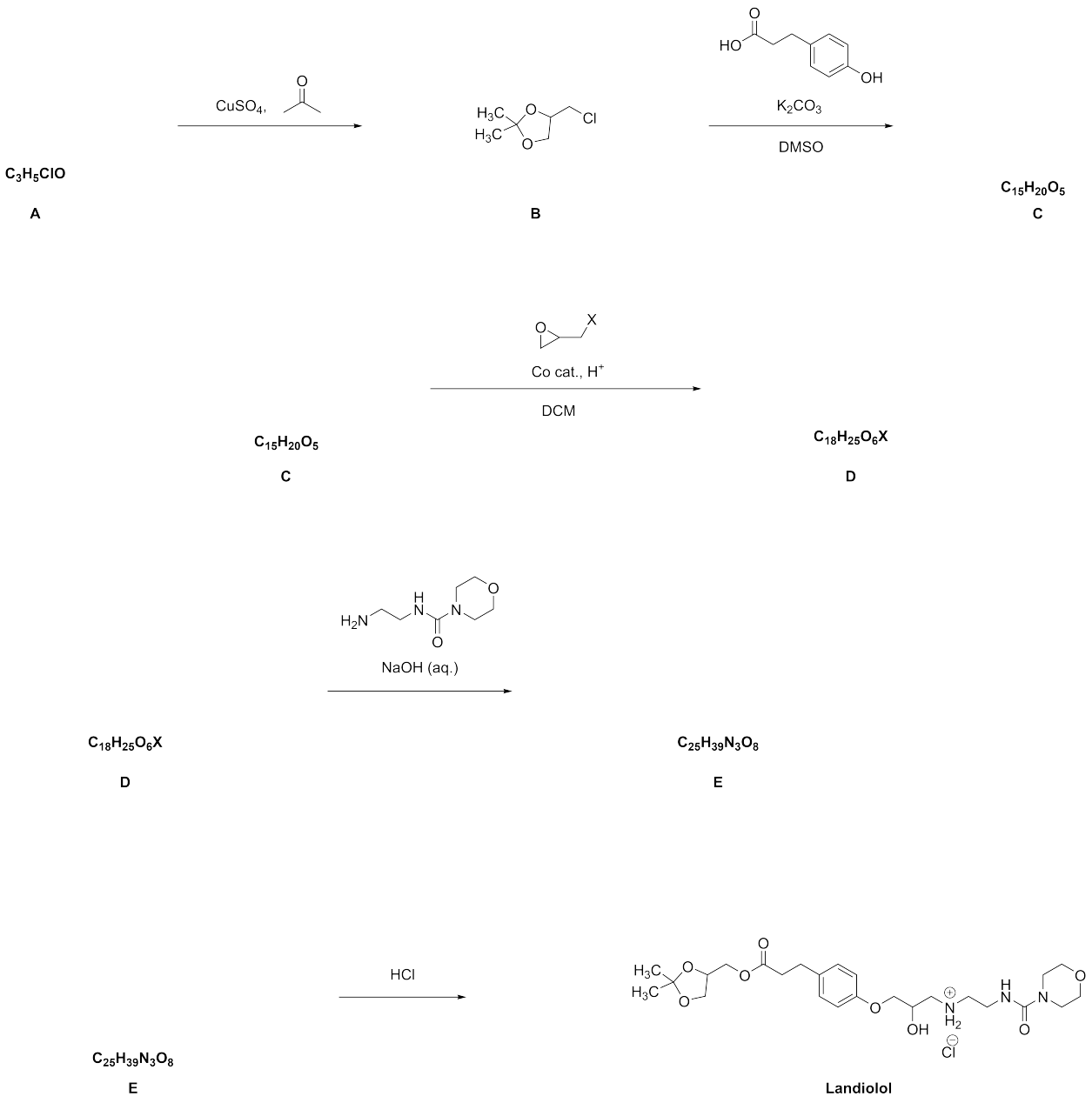
English (Official)

Synthesis of Landiolol

In the figure below, a synthetic strategy for Landiolol is depicted. The synthetic sequence starts from enantiomerically pure epichlorohydrin. In the following tasks, you will be asked to complete this synthetic scheme step by step.



9.4 **Draw** the structure of epichlorohydrin, compound **A**. 1.0 pt

9.5 **Give** the structures of compounds **C**, **D** and **E**. 3.0 pt

C

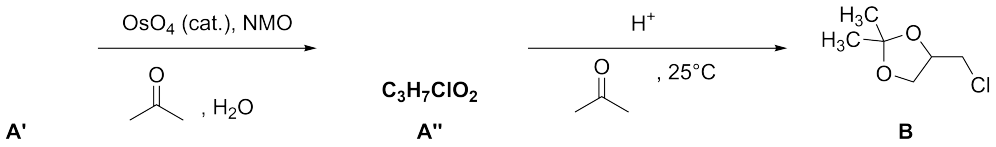
D

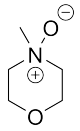
E

9.6 For the transformation of compound **C** to **D**, **suggest** a suitable substituent **X** to enable this transformation. 1.0 pt

Synthesis of Individual Building Blocks

Unfortunately, your supplier of epichlorohydrin, compound **A**, has run out of stock of this chemical building block. Thus, you have to come up with a different route for compound **B**. Lucky you, one of your interns in your company has seen this coming and already come up with a possible solution. However, his notes are hard to read and you have to fill the gaps now. The synthetic scheme is shown below:

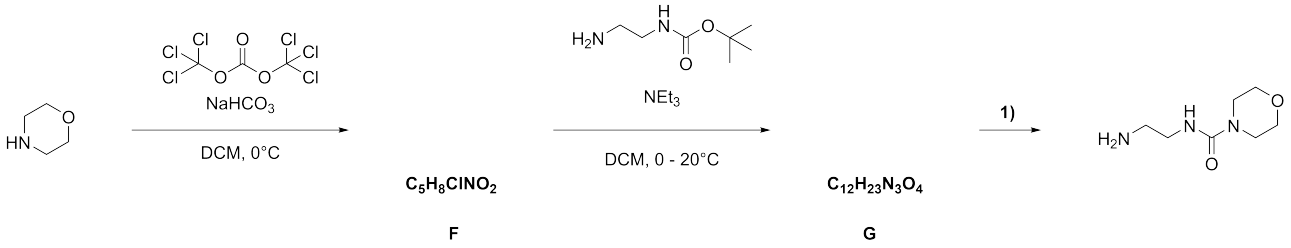


NMO = 

9.7 **Draw** the structures of the compounds **A'** and **A''**. **Hint:** ***A'*** *contains only one heteroatom.* 2.0 pt

A'	**A''**

Some of the reagents used in the synthetic scheme above are not available from commercial sources at reasonable prices. Thus, let's take a closer look at the synthesis of the amine used in the transformation from compound **D** to **E**. A synthetic scheme is provided below. The synthesis starts form morpholine, which is commercially available.



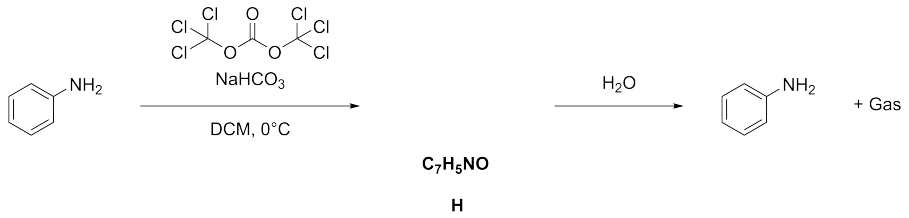
9.8 **Draw** the structures of the missing intermediates **F** and **G**. 2.0 pt

F	**G**

9.9 For the transformation **1) select** the most suitable reaction conditions from the options below: 1.0 pt

- ☐ $LiAlH_4$, THF, -78°C
- ☐ $KMnO_4$, H_2SO_4 (aq.), 25°C
- ☐ trifluoroacetic acid, DCM, 0°C
- ☐ K_2CO_3, DMF, 80°C
- ☐ $Pd(PPh_3)_4$, benzene, 35°C

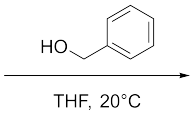
If instead of a secondary amine, a primary amine is subjected to the conditions for the formation of compound **F**, a slightly different product is obtained. This is illustrated in the example with aniline below. Both compound **F** and compound **H** are not stable towards moisture and will react with water under the release of a gas back to the initial amine starting material.



9.10 **Draw** the structure of compound **H**. 1.0 pt

9.11 **Provide** the name or chemical formula of the gas released upon hydrolysis of compound **H**. 0.5 pt

Both compound **F** and compound **H** react with a variety of nucleophiles. In case of the nucleophile being an alcohol, a stable linkage between the two moieties is formed. This type of linkage is often encountered in peptide chemistry.



C_7H_5NO (H) → $C_{14}H_{13}NO_2$ (I)

9.12 **Draw** the structure of compound **I**. 1.0 pt