

43rd Austrian Chemistry Olympiad

National Competition

Theoretical Tasks

2017-05-25

Solutions

Task 1 60 bp ≙16 rp

Bicyclic Nitrogen Compounds and their Syntheses

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| 1.1 Draw the configuration formulae of the compounds **A**, **B** and **H** and the constitutional formulaeof the compounds **C, D, F, G, I** and chemical formula of **X.** |
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| 1.2 Write the mechanism of the reaction **F→G.** Name the corresponding reaction type. |
| **Type of reaction:** nucleophilic addition **1 bp** |
| 1.3 Name the type of stereoisomerism that occurs in **A** and **B.** |
| Diastereomers (exo-endo isomers) **1 bp** |

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| 1.4 Draw arrows in the structural formula in the starting material leading to compound **C**, which clarify the formation of **C**. Name the occurring reaction type. |
| **type of reaction:** pericyclic [4+2] cycloaddition (dipolarophile and dipolar (=diene)) **2 bp** | |

**B. Synthesis of ferruginine**

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| 1.5 Draw the configurational formulae of **A**, **B** und **H** and the constitutional formulae of the compounds **C**, **D, E, F, G, I, J, K, L** and **X.** |
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Task 2 27.5 bp ≙ 8 rp

Pharmaceuticals, Stereochemistry and Spectroscopy

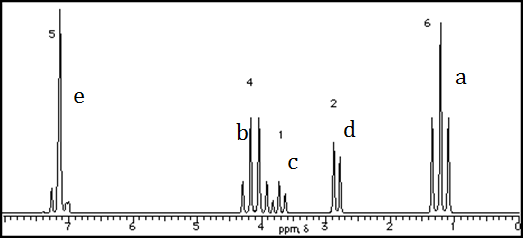
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| 2.1. Draw the configuration formulae into the boxes as appropriate. | |
| S – enantiomer:  **1 bp** | R – enantiomer:  **1 bp** |
| 2.2 Assign all signals of the 13C-NMR spectrum to the corresponding C atoms of Adrafinil. For that purpose, assign each carbon atom of the configuration formula below the corresponding number (1 to 7). | |
| 0.25 bp each 🡪 **1.75 bp** | |
| 2.3 Write the number of the 1H-NMR spectrum of Adrafinil into the box below. Assign chemical shifts in ppm to at least two different protons in the constitutional formula below to clearly justify your selection of spectrum. | |
| Spectrum No.: 1 | |
| Assignment:  **3 bp** | |
| 2.4 Assume that the solvent is replaced by CD3OD. Does the spectrum still contain all signals in this case? If „no“: Draw the resulting – changed – constitutional formula. | |
| O yes X no (tick the correct answer) **0,5 bp** | |
| **2 bp** | |
| 2.5 Mark the chiral center(s) with an asterisk. Furthermore, state the absolute configuration(s) of Vedaclidine by assigning the correct stereo descriptor tot he respective center(s). | |
| *S - configuration* **2 bp** | |

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| 2.6 State the reason, why afloqualone is chiral. |
| chiral axis **1 bp** |

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| 2.7 Draw the configuration formula of afloqualone and state the corresponding stereo descriptor(s). |
| **3 bp** |

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| 2.8 Explicitly mark those C atoms in the formula of linezolid that lead to the same signal in 13C-NMR and state how many signals in the spectrum are caused by more than one C atom. |
| Number of signals from more than one C atom: **2** **0.5 bp** |
| *Linezolide:*  **2 bp** |

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| 2.9 Calculate the molecular formula of the unknown compound: |
| *m(C)=0.3360g p(C)=67.20%*  *assumed mass 100g:*  *⟶ C3.5H4.5O1 ⟶ C7H9O2*  ***sum formula****: C14H18O4* **4 bp** |



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| 2.10 Draw the constitutional formula of the unknown compound. Clearly assign each signal of the 1H NMR spectrum to a proton in the molecule by assigning lower-case letters a, b, c, etc. both to the peaks in the spectrum and the corresponding protons of the constitutional formula. |
| structure: **4.5 bp**  correct assignments 0.25 bp each 🡪 **1.25 bp** assignment |

Task 3 23.5 bp ≙ 7 rp

Aluminum and Complexes

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| 3.1 Draw spheres representing Al atoms into the unit cell below so that they reach cubic closest packing. |
| **1 bp** |
| 3.2 Calculate the lattice parameter a in pm. |
| **3 bp** |

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| 3.3 Assign the correct systematic names to the ions formed during both processes: | |
| [Al(H2O)6]3+ | name: hexaaquaaluminium(III) - cation **1 bp** |
| [Al(OH)4]- | name: tetrahydroxido aluminate(III) **1 bp** |
| 3.4 Give the reaction equations of both dissolution processes mentioned above: | |
| 2 Al + 6 H+ + 12 H2O 🡪 2 [Al(H2O)6]3+ + 3 H2 **1 bp** | |
| 2 Al + 2 OH- + 6 H2O 🡪2 [Al(OH)4]- + 3 H2 **1 bp** | |
| 3.5 Complete the following reaction equations of the Bayer process by inserting correct stoichiometric coefficients and missing species, if necessary. | |
| Al2O3 + 2 OH- + 7 H2O ⟶ 2 [Al(OH)4(H2O)2]- **1 bp** | |
| SiO2 + 2 OH- ⟶ **1 bp** | |
| + Ca2+ ⟶ + H2O**1 bp** | |
| [Al(OH)4(H2O)2]-  ⟶ Al(OH)3 + OH- + 2 H2O**1 bp** | |
| 2 Al(OH)3 ⟶ Al2O3 + 3 H2O**1 bp** | |

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| 3.6 Calculate the number of Cr3+ ions in this rod of ruby. |
| **2 bp** |

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| 3.7 Write into each of the predefined box, whether the orbital in question belongs to the t2g‑ or the eg- orbitals. |
| 0.5 each 🡪 **2.5 bp** |

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| 3.8 Fill up the d-orbital scheme of Cr3+ by using arrows for each electron in the usual way. |
| **3 bp** |

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| 3.9 Give equations for both nuclear reactions of 24Al decay. |
| **2 bp** |

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| 3.10 Write the nuclear reaction scheme for this electron capture process. |
| **1 bp** |

Task 4 29.5 bp ≙ 8 rp

Aluminium, Chemical Bonds and Thermochemistry

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| 4.1 Calculate the minimum temperature needed for the equilibrium to lie on the side of the product. |
| **1 bp**  **1 bp**    (1136°C) **1 bp** |

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| 4.2 Write down a balanced equation for this reaction: |
| AlCl3 + 3 LiAlH4 → 4 AlH3 + 3 LiCl **1.5 bp** |
| 4.3 Tick the right configuration of AlH3 according to VSEPR  X trigonal planar **1 bp** |
| 4.4 The figure shows an empty MO-scheme for AlH3. Fill in all (!) electrons of AlH3 using arrows.  Indicate HOMO and LUMO und tick the appropriate magnetic behavior.    X diamagnetic O paramagnetic  correct number of e- **1 bp**, correct occupation **1 bp**, HOMO/LUMO **1 bp**, magnetic **1 bp** |
| 4.5 Complete the Natta projection for the adduct. Indicate formal charges if necessary. |
| **2.5 bp** |

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| 4.6 Write AlH3 and NMe3 respectively into the boxes  4.7 Draw arrows for the electron pair of the Lewis base on the correct HOMO. |
| box correct **2.5 bp**, e-pair **0.5 bp** |
| 4.8 Calculate the enthalpy of reaction for the formation of the adduct in kJ/mol |
| per electron **1 bp**  **1.5 bp** |
| 4.9 Calculate the wavelength corresponding to the transition between the bonding  (-11.9 eV) and the antibonding (3.7 eV) MO. |
| **1.5 bp** |
| 4.10 Calculate the mass of aluminium that had to be used for such a flash. |
| **2 bp** |
| 4.11 Calculate the lattice energy for Al2O3 in kJ/mol. |
| **1 bp**  from 4 Al (s) + 3 O2 (g) → 2 Al2O3 (s) we have    **4 bp** |
| 4.12 Calculate the time required for the electrolytic production of the aluminium apex in days. |
| height of the Al-pyramid: 169.26-169.04m = 22 cm **0.5 bp**  **1 bp**  **2 bp** |

Task 5 27.5 bp ≙ 7 rp

Sulfur Compounds, Kinetics and Electrochemistry

A. . Peroxodisulfate as oxidising agent

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| 5.1 Draw a valence bond formula of the peroxodisulfate ion including formal charges. |
| structure **2 bp**  formal charges **0.5 bp** |
| 5.2 Assign the correct oxidation number to all atoms in the structure. **1 bp** |
| 5.3 Specify the smallest integer values of the coefficients a, b, c, and d. |
| a = 1, b = 2, c = 2, d = 1; **1 bp** |
| 5.4 Write down the rate law for the reaction (R1) and specify the overall reaction order. |
| *v* = *k*·*c*(S2O82-)x·*c*(I-)y  measurements (1) and (2): *c0*(S2O82-)(2)/*c0*(S2O82-)(1)=1.4   *c0*(I-)(2)=*c0*(I-)(1) *v0*(2)/*v0*(1)=1.4 => *x* = 1 **1 bp**  measurements (1) and (3): c0(S2O82-)(3)/c0(S2O82-)(1)=1.8  c0(I-)(3)/c0(I-)(1)=1.5*v0*(3)/*v0*(1)=2.7=1.8⋅1.5 => *y*= 1 **1 bp**  *v* = *k*·*c*(S2O82-)·*c*(I-) **0.5 bp**  overall reaction order: 2 **0.5 bp** |
| 5.5 Calculate the reaction rate constant k from the values given above. |
| *k = v/c(*S2O82-*)·c*(I-) *= 1.1·10-8/(0.1·10-3. 1.10-2) = 0.011 L·mol-1·s-1* **1.5 bp** |
| 5.6 Calculate the temperature (in °C), which must be chosen, in order to increase the reaction rate tenfold under otherwise identical conditions. |
| Use Arrhenius law:  *with k1/k2 = 1/10*  ⇒ ⇒ ⇒ T2 = 345 K ~ 72oC **2.5 bp** |
| 5.7 Write down a balanced equation for the reduction of iodine with thiosulfate. |
| 2 S2O32- + I2 ⇄ 2 I- + S4O62- **0.5 bp** |
| 5.8 Write down the rate law for this variant of the reaction (R1). |
| The iodide concentration remains constant, because the iodine being formed is quickly reduced to iodide by thiosulfate, the latter being in excess  → reaction pseudo-first order: *v* = *k‘*·*c*(S2O82-) **2 bp** |

B. Peroxodisulfate in the iodine clock reaction

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| 5.9 Derive an equation for the rate of formation of I3- Use the steady state approximation for all reaction intermediates. |
| **4 bp** |

C. Electrochemistry of sulfur compounds

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| 5.10 Calculate the missing potentials x and y. |
| V **1 bp**  V **1 bp** |
| 5.11 Prove by calculation that S(0) is stable against disproportionation. |
| S(0) is stable, because < **1 bp** |
| 5.12 Provide a balanced equation for the disproportionation of S(II) with the species indicated in the Latimer diagram. |
| S2O32- ⇄ SO32- + S **1.5 bp** |

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| 5.13 Calculate the equilibrium constant for this disproportionation at 25 °C. |
| V **1 bp**  ⇒ ⇒   **1.5 bp** |

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| 5.14 Does hydrogen peroxide react with Na2S2O8 under standard conditions as a reducing or as an oxidising agent? Tick the correct answer. |
| x reducing agent O oxidizing agent **0.5 bp** |
| 5.15 Write down the correct redox equation and calculate ΔE0. |
| Red: S2O82- + 2 e- ⇌ 2 SO42- Ox: H2O2 ⇌ O2 + 2 H+ + 2e-  S2O82- + H2O2 ⇌ 2 SO42- + O2 + 2 H+ **1.5 bp**  ΔE0 = 1.96 V – 0.69 V = 1.27 V **0.5 bp** |

Task 6 34 bp ≙ 7 rp

Lead, Calcium and Equilibrium

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| 6.1 Calculate the concentrations of Pb2+ and Ca2+ in the aqueous solution. |
| **1.5 bp**  **1.5 bp** |

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| 6.2 Calculate the concentration of free lead ions in the solution at the end of the first titration. Assume that in this calculation only the ions Pb2+, EDTA4- and [PbEDTA2-] have to be considered. It is possibly necessary to make another assumption and to check if it is reasonable. |
| **2 bp**  assumption: **1 bp**  **1 bp**  ⇒ **2 bp**  ⇒ assumption is correct **2 bp** |

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| 6.3 Show by calculation that no precipitation occurs. For [Pb2+], use the result of 6.2. If you were not able to get a result in 6.2, use [Pb2+] = 3.0 · 10-11 mol/L. Use [Ca2+] at the beginning of the 2nd titration. |
| **2 bp**  no precipitation **1 bp**  **1 bp**  **1 bp**  no precipitation **1 bp** |

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| 6.4 Calculate the concentrations of all EDTA species at pH = 6.00 without simplification. The autoprotolysis of water does not have to be considered, the activity coefficients of all ions are equal to 1. |
| *CTotal* = 0.0100 mol/L; *pH* =6.00 ⇒ *[H+]* = 10-6 mol/L  Simplified variable names:  *[H4EDTA] = e0; [H3EDTA-] = e1; [H2EDTA2-] = e2; [HEDTA3-] = e3; [EDTA4-] = e4*  Equations: (1) *e0* + *e1* + *e2* + *e3* + *e4* = 0.01 **1 bp**  (2) **1 bp**  (3) **1 bp**  (4) **1 bp**  (5) **1 bp**  Calculations:  **1 bp**  **1 bp**  **1 bp**  **1 bp**  0.01 = *e4* + *e3* + *e2* + *e1* + *e0*  **2 bp**  **2 bp**  **1 bp**  **1 bp**  **1 bp**  **1 bp** |

Task 7 28.5 bp ≙ 7 rp

Fuel and Otto engine

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| 7.1 Indicate the molar masses: |
| Hep: Oct: **0.5 bp** |
| 7.2 Calculate the standard enthalpy of combustion ΔcH° for heptane in the units given below. |
| C7H16 + 11 O2 → 7 CO2(g) + 8 H2O (g)        **3 bp** |
| 7.3 Calculate the standard enthalpy of formation ΔfH° of iso-octane in kJ/mol. |
| C8H18 + 12.5 O2 → 8 CO2(g) + 9 H2O (g)      **1.5 bp** |
| 7.4 Calculate the density of this test mixture in g/L. |
| **1 bp** |

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| 7.5 Calculate the standard enthalpy of combustion for the test mixture in kJ/mol. |
| Mass in 1000mL: 47.6 g Hep and 643.6 g Oct  Amount of substance in 1000mL: Hep and Oct  Total amount of substance in 1000mL : 6.108 mol  Mole fractions: and **1.5 bp**  **1.5 bp** |
| 7.6 Calculate the standard entropy and the standard Gibbs energy of mixing for 100 mL of the test mixture at 298 K. |
| 100 mL are 0.6108 mol  **1.5 bp**  1.39 JK-1 **1.5 bp** |

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| 7.7 In which of the four steps (A-B-C-D) no work is done?  Indicate the correct letter(s):  B, D **1 bp** |
| 7.8 In one of the four steps (A-B-C-D) the combustion of the fuel takes place – so fast, that the Volume can be considered constant.  Indicate the correct letter:  B **0.5 bp** |
| 7.9 In one of the four steps (A-B-C-D) the entropy of the working gas is lowered.  Indicate the correct letter:  D **0.5 bp** |

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| 7.10 Indicate V1 and V2 . |
| and therefore = 1.176 L **1 bp**  **0.5 bp** |
| 7.11 Calculate T2 and T4. |
| *T*3 = 2073 K    **3 bp** |
| 7.12 Calculate the molar amount of air in the cylinder. |
| **1 bp** |

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| 7.13 Calculate the changes in internal energy... |
| ... for step A (ΔAU)  air gives **1 bp**  **1 bp** |
| ... for step B (ΔBU)  **1 bp** |
| ... for step C (ΔCU)  **1 bp** |
| ... for step D (ΔDU)  **1 bp** |

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| 7.14 Calculate the efficiency of the idealized Otto engine. |
| **2 bp**  Only in step B energy is being added. Therefore  **2 bp** |