44th National Chemistry Olympiad

University of Leiden

Leiden

PRACTICAL TEST

Marking scheme

Tuesday June 13, 2023

SCHEIKUNDE OLYMPIADE

55TH INTERNATIONAL CHEMISTRY OLYMPIAD SWITZERLAND 2023

Universiteit Leiden

Experiment 1 Synthesis of Hantzsch ester and oxidation to the pyridine form (46 points)

Maximum score 10

The following practical skills are assessed:

- safety, working clean and independence 5
- handling of the glassware 5

□1 Maximum score 4

per correctly noted mass, with unit, and absorbance 0.5

If the unit is not stated, penalize a maximum of twice.

□2 Maximum score 9

A correct calculation could be shown as follows:
The yield of Hantzsch pyridine after recrystallization is:
mass of filled sample vial - mass of empty sample vial
The maximum yield of Hantzsch pyridine is:

$$\text{max. yield of Hantzsch pyridine} = \frac{1.14}{253.29} \times 251.28$$

The percentage yield of Hantzsch pyridine after recrystallization is:

$$\frac{\text{amount of g of Hantzsch pyridine after recrystallisation}}{\text{max. yield of Hantzsch pyridine}} \times 100\%$$

- calculation of the yield of Hantzsch pyridine 1
- calculation of the amount of moles of Hantzsch ester 1
- calculation of the maximum amount of g of Hantzsch pyridine that can be formed 1
- calculation of the percentage yield 1

result maximum 5

▫3 Maximum score 5

A correct answer could be stated as follows:

Chemical shift (ppm)	Integral	Signal	Justification
1.5	6	1 and 7	Triplet by 2 H's on the neighboring atom.
3.2	6	3 and 5	Singlet of six H's because there is no H on the neighboring atoms.
4.6	4	2 and 6	Quadruplet/quartet of four H's by 3 H's on the neighboring atoms. or Four identical H's. or The chemical shift belongs to that of H's next to an O.
8.7	1	4	Singlet of one H and no H on neighboring atoms.

· chemical shifts and integrals correct 1

per correctly assigned signal with corresponding correct justification 1

Note
If a justification is given such as: „This remains after allocating three signals.", do not award a score point.

▫4 Maximum score 2

$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$ (2x)

$C_{13}H_{19}NO_4 \rightarrow C_{13}H_{17}NO_4 + 2\ H^+ + 2\ e^-$ (1x)

$C_{13}H_{19}NO_4 + 2\ HNO_2 \rightarrow C_{13}H_{17}NO_4 + 2\ NO + 2\ H_2O$

· half-reaction of the reducing species correct 1

· half-reactions with the correct multiplication factors added together and H^+ before and after the arrow crossed out 1

▫5 Maximum score 13

A correct calculation could be shown as follows:
The yield of Hantzsch ester is:
mass of the filter paper with product - mass of the clean filter paper

A maximum of $0.0150 \times 253.29 = 3.80$ g of Hantzsch ester can be formed.

The percentage yield is: $\frac{\text{amount of g of Hantzsch ester}}{3.80} \times 100\%$

- calculation of the yield of Hantzsch ester 1
- notion that a maximum of 15.0 mmol Hantzsch ester can be formed 1
- calculation of the maximum mass of Hantzsch ester that can be formed 1
- calculation of the percentage yield 1

result maximum 9

▫6 Maximum score 3

- calculation of the concentration of the solution of Hantzsch ester from the measured absorbance: divide the measured absorbance by the molar absorptivity from experiment 2 (and by 1.00 cm) 1
- calculation of the concentration of Hantzsch ester if the weighed mass were pure Hantzsch ester: divide the weighed amount of mg Hantzsch ester by 253.29 ($mg\,mmol^{-1}$) and by 100 (mL) 1
- calculation of the percentage purity: divide the concentration of the solution of Hantzsch ester from the measured absorbance by the concentration of Hantzsch ester if the weighed mass were pure Hantzsch ester and multiply the quotient by 100% 1

Experiment 2 Determination of the molar absorptivity (extinction coefficient) of Hantzsch ester at 400 nm (34 points)

Maximum score 10

The following practical skills are assessed:

· safety, working clean and independent 5
· handling glassware and other materials 5

□7 Maximum score 2

· mass of Hantzsch ester used noted correctly 1
· absorbances noted correctly 1

□8 Maximum score 6

A correct calculation could be shown as follows:

$$\text{concentration of the stock solution} = \frac{\dfrac{\text{weighed mg of Hantzsch ester}}{253.29}}{100} \text{ mol L}^{-1}.$$

Concentrations of dilutions 1 – 4: multiply the concentration of the stock solution respectively by $\frac{1.00}{25.00}$, $\frac{4.00}{25.00}$, $\frac{7.00}{25.00}$ and $\frac{10.0}{25.00}$.

· calculation of the amount of mmoles of Hantzsch ester 1
· calculation of the concentration in mol L^{-1} of the stock solution 1

per correct calculation of the concentrations in dilutions 1 - 4 1

□9 Maximum score 4

· concentration (mol L^{-1}) is correctly displayed as label on the *x*-axis and at least one numerical value is displayed 1
· *A* or absorbance (or *E* or extinction) shown as label on the *y*-axis and at least one number value shown 1
· optimal use of the graph paper/chart provided 1
· the four measuring points are shown correctly 1

□10 Maximum score 12

a justified straight line drawn based on the measuring points maximum 5

If the drawn straight line does not pass through the origin of the diagram maximum 4

· determination of the slope of the straight line drawn 1
· correct unit for the slope: L mol^{-1} cm^{-1} 1

result of the determination of ε maximum 5