

**25<sup>th</sup>**



**International Chemistry Olympiad**

**5 theoretical problems  
2 practical problems**

# THE TWENTY-FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 11–22 JULY 1993, PERUGIA, ITALY

## THEORETICAL PROBLEMS

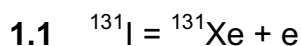
### PROBLEM 1

$^{131}\text{I}$  is a radioactive isotope of iodine ( $e^-$  emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant,  $k$ , of  $^{131}\text{I}$  is  $9.93 \times 10^{-7} \text{ s}^{-1}$ .

Questions:

- 1.1 Write the decay reaction of  $^{131}\text{I}$ .
- 1.2 Calculate the half-life of  $^{131}\text{I}$  expressed in days.
- 1.3 Calculate the time necessary (expressed in days) for a sample of  $^{131}\text{I}$  to reduce its activity to 30 % of the original value.
- 1.4 Knowing that a Geiger counter detects activities of the order of  $10^{-4} \mu\text{c}$ , calculate the minimum amount of  $^{131}\text{I}$  (in grams) which could be detected by this counter.  
1 Curie (c) is the amount of a radioisotope that produces  $3.7 \times 10^{10}$  disintegrations  $\text{s}^{-1}$ .

### SOLUTION



1.2 Decay reactions are first order reactions. Then:

$$k = \frac{\ln 2}{t_{1/2}} \quad t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{0.693}{9.93 \times 10^{-7} \times 86400 \text{ s d}^{-1}} = 8.08 \text{ d}$$

1.3 For a first order reaction:

$$\ln \frac{C_0}{c} = k t$$

where  $c_0$  and  $c$  are the concentrations at time 0 and time  $t$ , respectively. Then:

$$\ln \frac{100}{30} = 9.93 \times 10^{-7} \times t$$

$$t = \frac{1.212 \times 10^6}{8.64 \times 10^4} = 14.03 \text{ d}$$

**1.4** 1 Curie (c) is the amount of a radioisotope that produces  $3.7 \times 10^{10}$  disintegrations  $\text{s}^{-1}$

$$1 \text{ mc} = 3.7 \times 10^7 \text{ dis s}^{-1}$$

$$1 \text{ } \mu\text{c} = 3.7 \times 10^4 \text{ dis s}^{-1}$$

Then:

$$10^{-4} \text{ } \mu\text{c} \times 3.7 \times 10^4 \text{ dis s}^{-1} = 3.7 \text{ dis s}^{-1} = - \frac{dN}{dt}$$

$$t_{1/2} \text{ of } ^{131}\text{I} \text{ expressed in seconds is } = 8.08 \text{ d} \times 86400 \text{ s d}^{-1} = 6.98 \times 10^5 \text{ s}$$

$$m = - \frac{dN}{dt} \times \frac{t_{1/2} \times A_r(\text{I})}{\ln 2 \times N_A} = \frac{3.7 \times 6.98 \times 10^5 \times 131}{0.693 \times 6.02 \times 10^{23}} = 8.11 \times 10^{-16} \text{ g}$$

**PROBLEM 2**

The reflux of bile duodenal matter is suspected to be the major cause of gastritis and medical therapy is based on the treatment with antiacida that buffer the *pH* of gastric juices by binding bile acids and lysolecithin. Two bile acids, i. e. cholic acid (CA) and glycocholic acid (GCA), were chosen to study the properties of some antiacida commercial formulations. Separation and determination of the two acids in artificial and natural gastric juices were required and high performance liquid chromatography (HPLC) was used as analytical technique.

Two chromatographic columns (A and B, respectively) were selected on the base of published literature data and preliminary tests were carried out to choose the column (between A and B) which would yield the best separation of the aforementioned compounds. The retention times (*t*) of the two acids, of a substance not retained by the chromatographic columns and of a compound used as internal standard (i.s.) are shown in the first two columns of the Table. Both chromatographic columns are 25 cm long and show the efficiency of  $2.56 \times 10^4$  theoretical plates per meter ( $N\ m^{-1}$ ).

In actual analysis, an artificial gastric juice was extracted with an appropriate solvents mixture and then final solution ( $1\ cm^3$ ) contained 100 % of the two acids present in the original mixture.  $100\ \mu cm^3$  of the extract with  $2.7\ \mu moles$  of the internal standard were analysed by HPLC using the selected column. The response factors (*F*) of CA and GCA with respect to the i.s. and the chromatographic peak areas of the two compounds are reported in the Table.

	Column A <i>t</i> (s)	Column B <i>t</i> (s)	F	Area
Unretained compound	120	130	-	-
Cholic Acid (CA)	380	350	0.5	2200
Glycocholic Acid (GCA)	399	395	0.2	3520
Internal standard	442	430	-	2304

In answering to the questions remember that:

$$R = \frac{\sqrt{N}}{4} \times \frac{\alpha - 1}{\alpha} \frac{K'}{K' + 1} \quad (1)$$

$$\alpha = \frac{t_2'}{t_1'} = \frac{t_2 - t_0}{t_1 - t_0} \quad (2)$$

$$K' = K_2' = \frac{t_2'}{t_0} = \frac{t_2 - t_0}{t_0} \quad (3)$$

Questions:

- 2.1** Using  $R$ ,  $\alpha$  and  $K'$  values, demonstrate which of the two chromatographic columns would you use, considering that an accurate determination requires the best possible (baseline) separation of all compounds (do not take into account the unretained compound)?
- 2.2** Calculate the amounts of each acid in the extract solution.

## SOLUTION

Nowadays, chromatography is the most powerful technique for the separation and quantification of organic compounds from volatiles to high molecular weight substances. In conjunction with a mass-spectrometer, it can lead to the undoubted identification of compounds even in extremely complex mixtures. Liquid chromatography (HPLC) is becoming a routine analytical technique in a large variety of fields and in particular in biochemistry and in medicine where compounds are unsuitable for gas chromatographic analysis.

- 2.1** Baseline separation requires  $R \geq 1.5$  for each pair of peaks (GCA/CA, i.s./GCA).  $N$  can be calculated from  $N \text{ m}^{-1}$  value taking into account that the column length is 25 cm:

$$N = 2.56 \times 10^4 \times (25/100) = 64 \times 10^2$$

By substituting of  $\alpha$ ,  $K$  and  $N$  values in equation 1, the resolution for each pair of peaks can be found.

For column A:

$$\alpha_{GCA/CA} = \frac{399 - 120}{380 - 120} = \frac{279}{260} = 1.07$$

$$K'_{GCA} = \frac{399 - 120}{120} = 2.32$$

$$R_{GCA/CA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.07}{1.07} \times \frac{2.32}{3.32} = 0.91$$

$$\alpha_{i.s./GCA} = \frac{422 - 120}{399 - 120} = \frac{322}{279} = 1.15$$

$$K'_{i.s.} = \frac{442 - 120}{120} = 2.68$$

$$R_{i.s./GCA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.15}{1.15} \times \frac{2.68}{3.68} = 1.9$$

For column B:

$$\alpha_{GCA/CA} = \frac{395 - 130}{350 - 130} = \frac{265}{220} = 1.20$$

$$K'_{GCA} = \frac{395 - 130}{130} = 2.04$$

$$R_{GCA/CA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.20}{1.20} \times \frac{2.04}{3.04} = 2.2$$

$$\alpha_{i.s./GCA} = \frac{430 - 130}{395 - 130} = \frac{300}{265} = 1.13$$

$$K'_{i.s.} = \frac{430 - 130}{130} = 2.31$$

$$R_{i.s./GCA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.13}{1.13} \times \frac{2.31}{3.31} = 1.6$$

For column B the minimum value of  $R$  is 1.6 ( $>1.5$ ) so that complete separation is obtained. For column A,  $R = 0.91$  ( $<1.5$ ) for the pair GCA/CA which, then, is not completely separated. Therefore column B should be used.

2.2 The amount of acid in the extract solution (1 cm<sup>3</sup>) can be calculated from the relationship:

$$\frac{\mu\text{moles}_{\text{acid}}}{\mu\text{moles}_{\text{i.s.}}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F}$$

where  $F$  is the response factor.

Therefore:

$$\mu\text{moles}_{\text{acid}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F} \times \mu\text{moles}_{\text{i.s.}} \times \frac{1000}{100}$$

$$n(\text{CA}) = \frac{2200}{2304} \times \frac{1}{0.5} \times 2.7 \times 10 = 51.6 \mu\text{mol}$$

$$n(\text{GCA}) = \frac{3520}{2304} \times \frac{1}{0.2} \times 2.7 \times 10 = 206 \mu\text{mol}$$

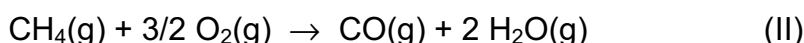
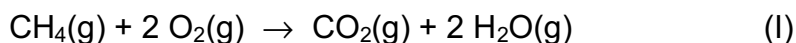
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**PROBLEM 3**

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The student may be aware that the acceptable concentration of CO in air is  $\leq 5$  ppm and the maximum tolerable level is 50 ppm.

The following reactions occur in methane burner:



Compound	CH <sub>4</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> O
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	-74.9	0	-393.5	-110.5	-241.8
$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	186.2	205.0	213.6	197.6	188.7

Questions:

- 3.1** Calculate the equilibrium constants for both reactions at  $T = 1500$  K assuming that the values  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of the temperature.
- 3.2** Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium ( $T = 1500$  K,  $p = 1$  atm) when air is admitted into the burner in such amount that the mole ratio CH<sub>4</sub> : O<sub>2</sub> is 1 : 2.

Assume the following volume composition of air: 80 % N<sub>2</sub> and 20 % O<sub>2</sub>.

Make the approximation that  $n(\text{CH}_4) \cong 0$  at equilibrium and justify it on the bases of the answers to the question 3.1.

- 3.3** Calculate the equilibrium mole fraction  $x$  of CO in the conditions given in the question 3.2. Assume that the mole fraction of CO is very small in comparison with that of CO<sub>2</sub> and consequently, the total number of moles does not appreciably vary during the combustion. Justify this assumption.



- 3.4** Repeat the calculations of items 3.2 and 3.3 assuming that twice the amount of air (compared to the conditions in question 3.2) is admitted into the burner (4 mol O<sub>2</sub> : 1 mol CH<sub>4</sub>).
- 3.5** Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of question 3.2 and 3.4, assuming that the composition does not change appreciably during the cooling from 1500 K to room temperature and neglecting the contribution of water vapour to the composition of the gas phase.

## SOLUTION

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The problem involves the calculation of equilibrium constants, consideration of simultaneous equilibria and simple stoichiometric calculations.

$$\mathbf{3.1} \quad \Delta_1 H^0 = 74.9 - 393.5 - (2 \times 241.8) = -802.2 \text{ kJ mol}^{-1}$$

$$\Delta_1 S^0 = -186.2 - (2 \times 205.0) + 213.6 + (2 \times 188.7) = -5.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_1 = \exp -\frac{\Delta_1 H^0 - T \Delta_1 S^0}{R T} = \exp \frac{802.2 - 1.5 \times 5.2}{8.314 \times 1.5} = 4.62 \times 10^{27}$$

$$\Delta_{II} H^0 = 74.9 - 110.5 - (2 \times 241.8) = -519.2 \text{ kJ mol}^{-1}$$

$$\Delta_{II} S^0 = -186.2 - (1.5 \times 205.0) + 197.6 + (2 \times 188.7) = 81.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_{II} = \exp \frac{519.2 - 1.5 \times 81.3}{8.314 \times 1.5} = 2.13 \times 10^{22}$$

- 3.2** Since  $K_1$  and  $K_{II}$  are very large, both equilibria are completely shifted to the right so that  $n_{\text{CH}_4} = 0$ .

$$\text{At equilibrium: } n_{\text{CH}_4} = 0; \quad n_{\text{H}_2\text{O}} = 2; \quad n_{\text{N}_2} = 8; \quad n_{\text{CO}_2} + n_{\text{CO}} = 1;$$

$$n_{\text{O}_2} = 2 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 0.5 n_{\text{CO}}$$

- 3.3** In reaction I the total number of moles does not vary; in reaction II it changes from 8.5 to 9 (taking into account the presence of N<sub>2</sub>), but this change affects the total number of moles only negligibly since  $K_{II} \ll K_1$ .

Before reaction:  $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 2 + 8 = 11$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{p_{\text{CO}} p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{tot}}} = \frac{1 - n_{\text{CO}}}{n_{\text{tot}}} = \frac{1}{11} \quad \text{since } n_{\text{CO}} \ll n_{\text{CO}_2} \text{ as a consequence of } K_{\text{II}} \ll K_{\text{I}}$$

$$x_{\text{CO}}^{3/2} = \frac{K_{\text{II}}}{K_{\text{I}}} \frac{(2/p)^{1/2}}{11} = \frac{2.13 \times 10^{22} \times 1.414}{4.62 \times 10^{27} \times 11} = 5.93 \times 10^{-7}$$

$$x_{\text{CO}} = 7.06 \cdot 10^{-5}$$

**3.4**  $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 4 + 16 = 21$

At equilibrium:  $n_{\text{O}_2} = 4 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 2 + 0.5 n_{\text{CO}} = 2$

$$n_{\text{CO}_2} = 1 - n_{\text{CO}}$$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}} = x_{\text{CO}} (2/21)^{1/2} \times 21 = (42)^{1/2} x_{\text{CO}}$$

$$x_{\text{CO}} = 42^{-1/2} \frac{K_{\text{II}}}{K_{\text{I}}} = 42^{-1/2} \times \frac{2.13 \times 10^{22}}{4.62 \times 10^{27}} = 7.11 \times 10^{-7}$$

**3.5** As a consequence of the condensation of water vapour, the number of moles in the gaseous phase changes from 11 to 9 in case c), and from 21 to 19 in case d).

Therefore the mole fraction of CO changes to:

$$x_{\text{CO}} = 7.06 \times 10^{-5} \times \frac{11}{9} = 8.63 \times 10^{-5} \quad \text{and to:}$$

$$x_{\text{CO}} = 7.11 \times 10^{-7} \times \frac{21}{19} = 7.86 \times 10^{-7} \quad \text{in case 3.4}$$

These values correspond to 86 and 0.8 ppm, respectively.

**PROBLEM 4**

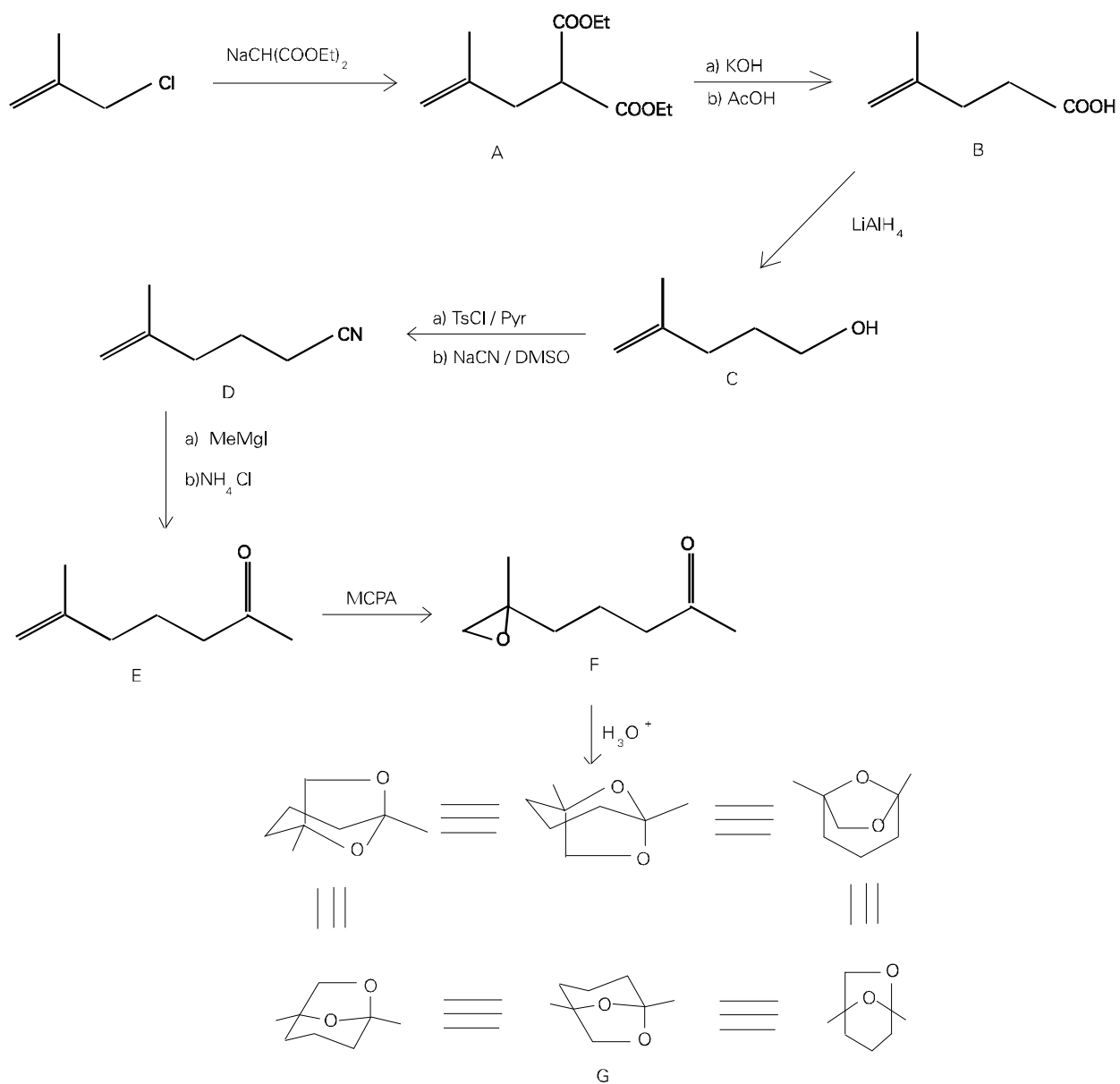
- i) Frontalin is a pheromone of the western pine beetle with composition C 67.58 %, H 9.92 %, O 22.50 %. It is an acetal that can be prepared through a rather long synthesis starting from sodium diethylmalonate (sodium salt of propanedioic acid, diethyl ester) and 3-chloro-2-methylpropene.
- ii) The product **A** resulting from this first step is subsequently hydrolyzed by conc. potassium hydroxide and then decarboxylated by treatment with hot acetic acid to give a compound **B**. The latter reacts with aq NaHCO<sub>3</sub> (gas evolution is observed) as well as with cold aq KMnO<sub>4</sub> which turns to a brown colour.
- iii) The compound **B** is then converted by LiAlH<sub>4</sub> into a new compound **C** (C<sub>6</sub>H<sub>12</sub>O).
- iv) Treatment of **C** with p-toluenesulfonyl chloride in pyridine and then sodium cyanide in dimethylsulfoxide, affords **D** (C<sub>7</sub>H<sub>11</sub>N).
- v) The subsequent reaction of **D** with methylmagnesium iodide, followed by hydrolysis, yield **E** (C<sub>8</sub>H<sub>14</sub>O). **E** shows IR absorption at ca 1700 cm<sup>-1</sup>.
- vi) The epoxidation of **E** with metachloroperbenzoic acid then affords **F** (C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>) which, by treatment with diluted acids is converted to frontalin acetal **G**.

Questions:

4.1 Draw the structures of compounds **A - G**.

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## SOLUTION



**PROBLEM 5**

By treatment with a chiral optically active hydroborating agent ( $R_2^*BH$ ) and subsequent oxidative work-up, 1-methylcyclopentene affords a mixture of alcohols that rotates the plane of the polarized light.

Questions:

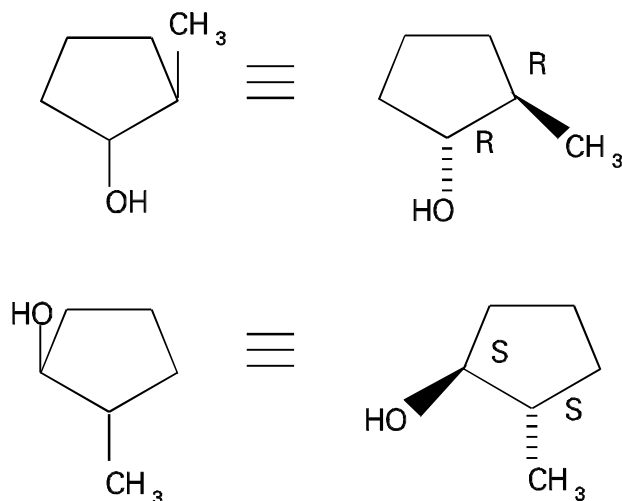
5.1 Write the structures of the alcohols.

5.2 Assign the configurations ( $R$ ,  $S$ ) to the chiral centres.

5.3 Explain in a sentence why the obtained mixture of alcohols exhibits optical activity.

**SOLUTION**

5.1, 5.2



5.3 Due to the chirality of the hydroborating agent, one enantiomer prevails against the other.

In alternative:  $R,R > S,S$  or  $S,S > R,R$

## PRACTICAL PROBLEMS

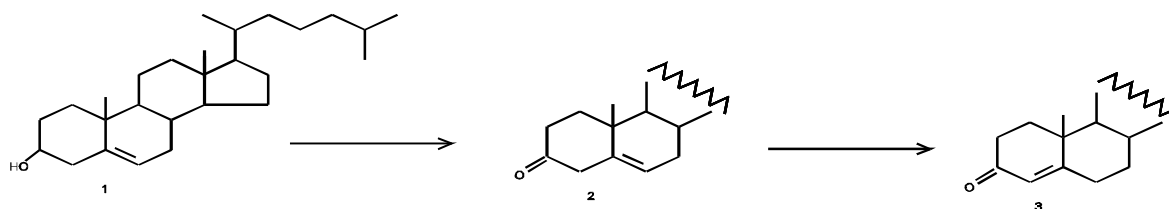
### PROBLEM 1 (Practical)

#### Synthesis

Cholesterol (1) is a natural sterol metabolite present in animal and vegetal organisms. This compound can be oxidized by Jones' reagent into its corresponding 3-ketoderivative (2). The latter, when treated with bases, undergoes isomerization of the carbon-carbon double bond leading to  $\alpha,\beta$ -unsaturated ketone (3).

The conversion of  $\Delta^5$ -3 $\beta$ -hydroxy steroids into their corresponding  $\Delta^4$ -3-ketones is an important reaction in steroid chemistry and represents the last step of the synthesis of a variety of commercial hormones.

You will be marked for the purity of the product (3).



#### Procedure:

- Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm<sup>3</sup> flask A with acetone (20 cm<sup>3</sup>) warming gently the flask in a bath tub of hot water. When the sample is completely dissolved, cool the flask containing the solution to the temperature by cold water.
- Add dropwise 0.40 cm<sup>3</sup> of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] is observed during the addition of Jones' reagent.
- Remove the green precipitate by filtration with paper filter.
- Add slowly water (10 cm<sup>3</sup>) to the clean filtrate. The ketone (2) begins to precipitate.
- Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.
- Dissolve the ketone (2) in methanol (15 cm<sup>3</sup>). Add to the solution just one drop of 5 % methanolic NaOH solution and warm the mixture in a bath of hot water for 10 min.

- g) The  $\Delta^4$ -3-ketosteroid (3) precipitates spontaneously, upon addition of water (ca. 2 cm<sup>3</sup>) to the cooled reaction mixture. Filter the crystals over the Büchner funnel under reduced pressure and recrystallize the product by methanol. If you do not get the crystals, add a few drops of water. *Remember! You are getting a mark for the purity, not the yield.*
- h) Dry carefully the crystals on a porous plate. Determine the melting point of the ketone (3) and write its value on your student's report. Taking into account the correction reported on the top of the thermometer (see example at the end).
- i) Put the crystals in the plastic vial B, write on it your personal identification number (see the left corner of your badge), and deliver it to one of the supervisors.

*The melting point of the ketone (3) will be checked by the lab supervisors.*

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## **SOLUTION**

Points were given accordingly to the amount of product.

Some additional points were given for melting point measurements.

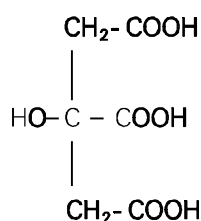
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**PROBLEM 2 (Practical)**Analysis

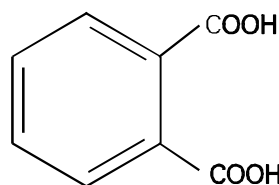
Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is widely distributed in plants and in animal tissues. Lemon juice contains from 5 to 8% of this acid. It is produced by mycological fermentation on an industrial scale using crude sugar solutions, such as molasses, and stains of *Aspergillus niger*.

It is utilized as an acidulant and antioxidant in several beverages.



MM = 192.12 g/mol

$\text{pK}_1 = 3.06$  ;  $\text{pK}_2 = 4.74$  ;  $\text{pK}_3 = 5.40$



MM = 204.23 g/mol

- a) Standardization of NaOH solution (ca 0.1 mol dm<sup>-3</sup>) by potassium hydrogen phthalate

*Procedure:*

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 cm<sup>3</sup> volumetric flask B. Dilute this sample with water to the mark. Phenolphthalein indicator (2 - 3 drops) is added to an aliquot of 25.0 cm<sup>3</sup> of the resulting solution and the solution is then titrated with the NaOH solution that has to be standardized.

Give the concentration of the NaOH solution.

- b) Titrimetric determination of citric acid

*Procedure:*

The unknown sample of citric acid is in the 100 cm<sup>3</sup> volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm<sup>3</sup> of the resulting solution into a 250 cm<sup>3</sup> Erlenmeyer flask and dilute with water. Add 2 – 3 drops of phenolphthalein indicator and titrate with the previously standardized NaOH solution.

Give the mass of citric acid.



## **SOLUTION**

Marks were given accordingly to determined mass of citric acid.

Some additional points were given for correct calculations.

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