PRACTICAL PROBLEMS

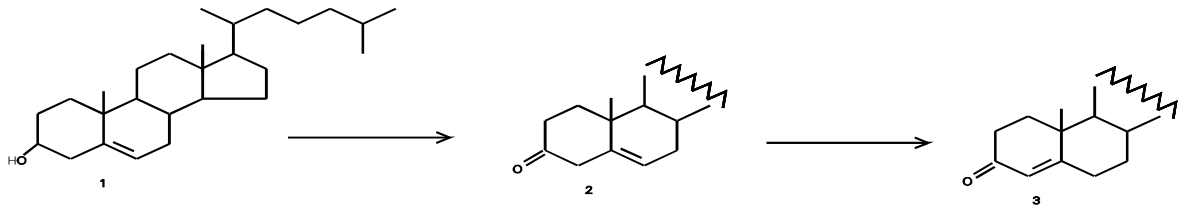
PROBLEM 1 (Practical)

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 α,β-unsaturated ketone (3).

The conversion of Δ^5-3β-hydroxy steroids into their corresponding Δ^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:

a) Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm^3 flask A with acetone (20 cm^3) 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.

b) Add dropwise 0.40 cm^3 of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [$Cr_2(SO_4)_3$] is observed during the addition of Jones' reagent.

c) Remove the green precipitate by filtration with paper filter.

d) Add slowly water (10 cm^3) to the clean filtrate. The ketone (2) begins to precipitate.

e) Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.

f) Dissolve the ketone (2) in methanol (15 cm^3). 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 Δ^4-3-ketosteroid (3) precipitates spontaneously, upon addition of water (ca. 2 cm^3) 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.

SOLUTION

Points were given accordingly to the amount of product.

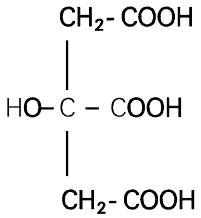
Some additional points were given for melting point measurements.

PROBLEM 2 (Practical)

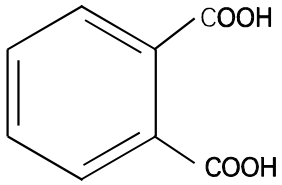
Analysis

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



MM = 204.23 g/mol

$pK_1 = 3.06$; $pK_2 = 4.74$; $pK_3 = 5.40$

a) Standardization of NaOH solution (ca 0.1 mol dm^{-3}) by potassium hydrogen phthalate

Procedure:

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 cm^3 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^3 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^3 volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm^3 of the resulting solution into a 250 cm^3 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.