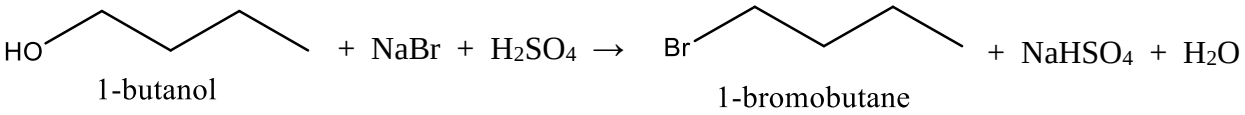
SYNTHESIS OF 1-BROMOBUTANE

Experimental procedure at microscale

(adapted from Williamson, Minard & Masters[1])

Introduction

1-bromobutane is a primary alkyl halide (primary alkyl) and therefore it is produced from bimolecular nucleophilic substitution reactions (Sn2). Figure 1 shows the reaction for the synthesis of 1-bromobutane.



1-butanol 1-bromobutane

Figure 1. Global reaction for the synthesis of 1-bromobutane.

This halide is easily prepared by reacting butan-1-ol (primary alcohol) with sodium bromide solution and excess of concentrated sulfuric acid. The reaction between sodium bromide and sulphuric acid origins hydrobromic acid (Equation 1).

$$NaBr + H_2SO_4 \rightleftarrows NaHSO_4 + HBr \quad (1)$$

The use of excess of sulphuric acid allows to increase the degree of completion of the reaction. Also, the presence of a strong acid like sulphuric acid protonates the butan-1-ol, transforming the hydroxyl group (-OH) in a better leaving group, the water (H_2O). The bromide ion from the hydrobromic acid reacts as nucleophile, occurring a substitution reaction. The mechanism of the reaction of the synthesis of 1-bromobutane is shown in Figure 2.

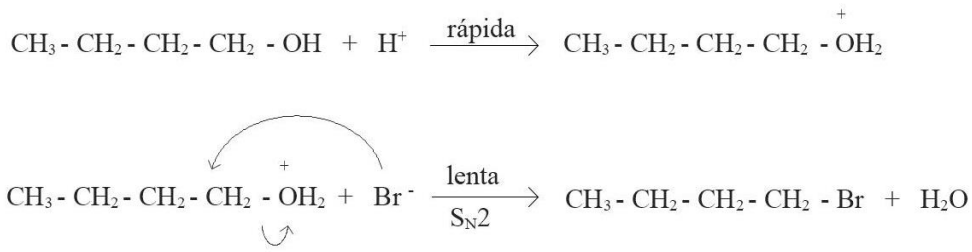


Figure 2. Mechanism of the reaction of the formation of 1-bromobutane.

The synthesis performed presents a complex experimental procedure, with several steps. After the mixture of the stoichiometric reagents, a reflux followed by a simple distillation are carried out, where some unwanted products can be separated such as, for example, sodium hydrogen sulphate and sulphuric acid. The liquid collected in the distillation is then washed with water, sulphuric acid and sodium hydroxide by liquid-liquid extraction to be isolated from other substances (but-1-ene, dibutyl ether and butan-1-ol that did not react). Finally, the product is dried with anhydrous calcium chloride and purified by simple distillation.

Experimental procedure

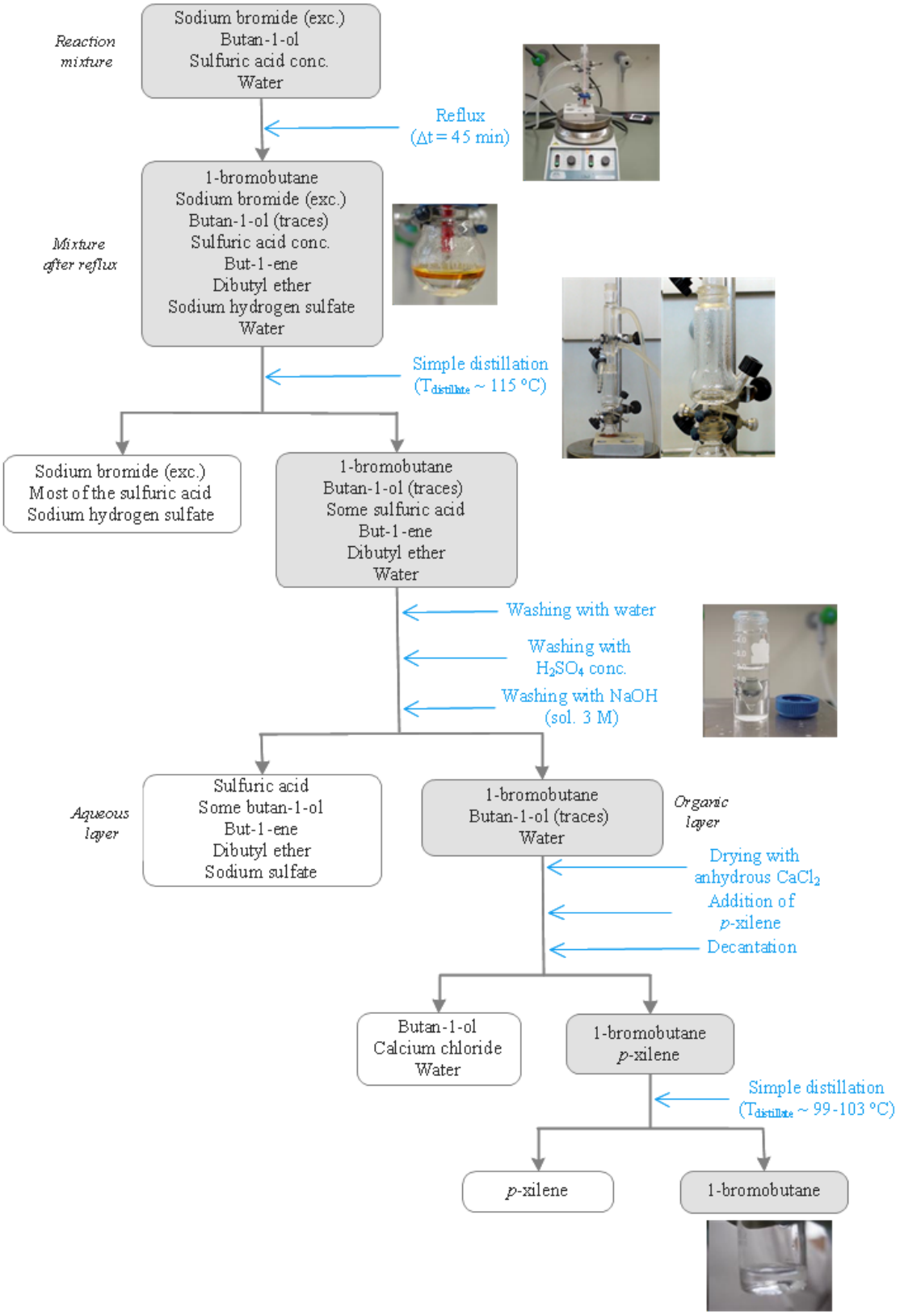


Figure 3. Experimental work for the synthesis of 1-bromobutane at microscale.

Formation of 1-bromobutane

1. In a 10 mL round bottomed flask, dissolve 1.33 g of NaBr (12.9 mmol, ~19% excess) in 1.5 mL of water and add 0.81 g of butan-1-ol (10.9 mmol).
2. Place the flask in an ice bath and, carefully and with continuous stirring, add 1.15 mL (21.6 mmol, ~98% excess) of concentrated H_2SO_4 to the solution. *An ice bath and slow stirring are used because the hot acid causes the oxidation of NaBr to Br_2, useless in the experiment. The NaBr is dissolved during heating. The acid is in a large excess to obtain a higher concentration of HBr.*

Figure 4. Addition of concentrated sulphuric acid.

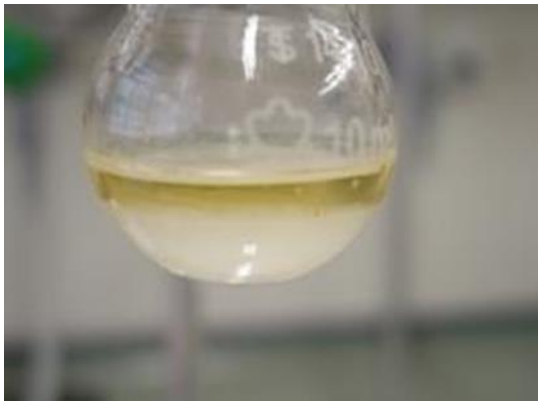


Figure 5. Mixture after addition of concentrated sulphuric acid.

3. Remove the ice, add a magnetic stirrer and reflux the reaction mixture on the aluminium plate for 45 minutes, taking care that none of the reagents distils. *The reflux is necessary because the reaction of formation of 1-bromobutane is slow at room temperature. Two distinct layers are formed and the upper layer is the 1-bromobutane.*

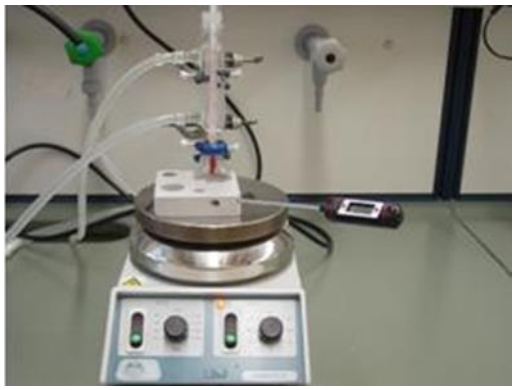


Figure 6. Reflux

Figure 7. Misture after reflux

Isolation of 1-bromobutane from byproducts and waste

4. Assemble an apparatus for simple distillation and distill the product into a collecting flask, until no more water-insoluble droplets come over ($t_{distillate} \approx 115$ ºC).

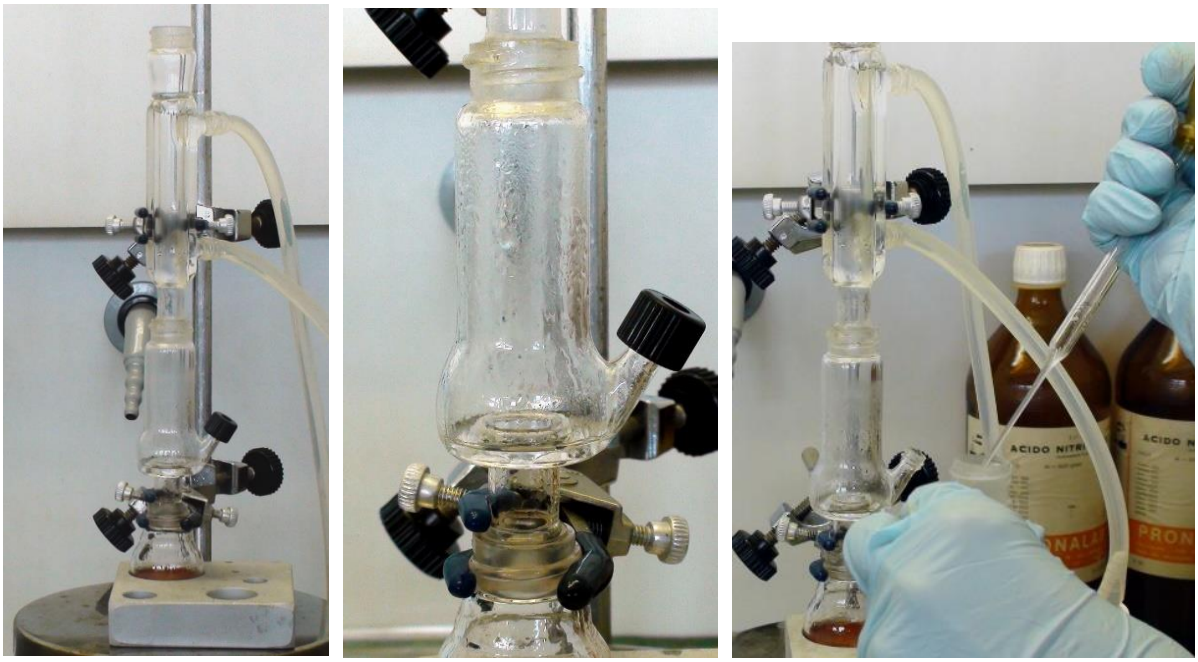


Figure 8. Initial distillation of the product.

5. To confirm that no droplets are obtained, collect 3 drops of distillate in a test tube containing about 1 mL of water and verify if they are miscible. *The collected distillate has 1-bromobutane contaminated with water, unreacted butan-1-ol, some sulphuric acid, but-1-ene and dibutyl ether. The sodium hydrogen sulphate and most of the sulphuric acid stay in the flask.*
6. Wash the Hickman's head with acetone to be used again.
7. Wash the flask with 1 mL of distilled water and add to the distillate in the vial.
8. Wash the round bottomed flask with 1 mL of ethanol and then with 1 mL of acetone and let dry in air, to be used again.
9. Remove the 1-bromobutane with a Pasteur pipet and place in a new dry vial. *1-bromobutane stays in lower layer. The washing with water allows to remove the sulphuric acid and some butan-1-ol*

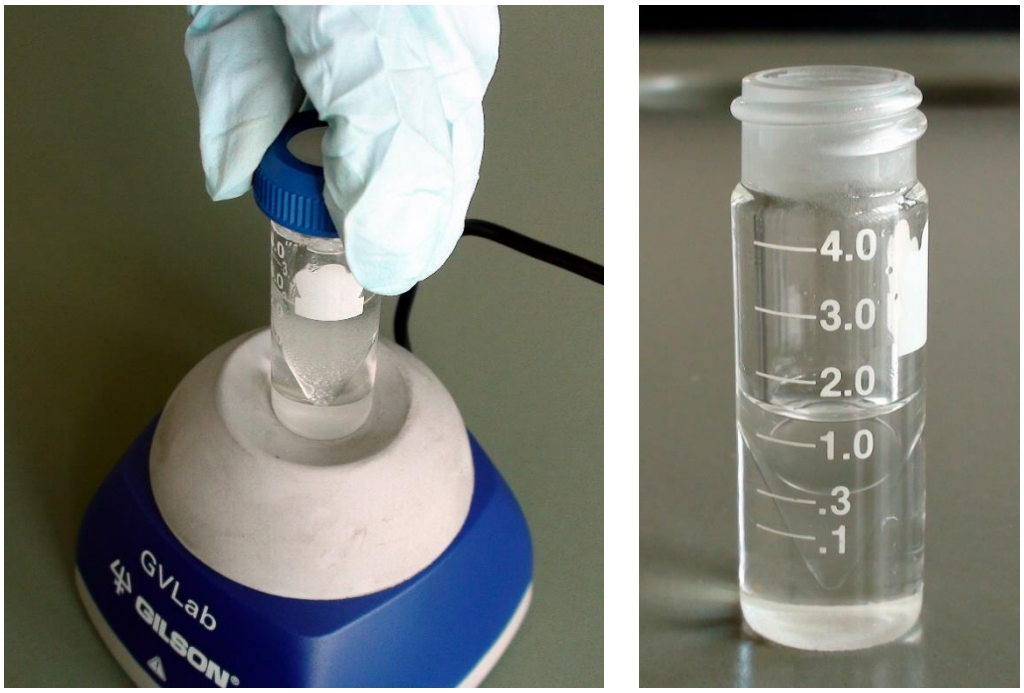


Figure 9. Washing with water.

10. Add 1 mL of concentrated H_2SO_4 and mix, stirring well.

Figure 10. Mixture after washing with sulphuric acid

11. Allow the two layers to separate completely. To distinguish both layers, collect one drop of the lower layer to a test tube and verify if the material is soluble in water (H_2SO_4) or not (1-bromobutane). *<u>1-bromobutane stays in upper layer, colourless</u>. The sulphuric acid removes any initial material which did not reacted, as well as secondary products (alcenes and ethers).*

12. Separate the layers and wash the 1-bromobutane with 1 mL of 3 mol/dm^3 sodium hydroxide solution to remove traces of the acid. *<u>1-bromobutane stays in lower layer</u>. Sodium hydroxide removes traces of sulphuric acid.*

Figure 11. Washing with sodium hydroxide solution.

13. Dry the cloudy 1-bromobutane layer by adding 0.10 g of anhydous $CaCl_2$ and stirl until the solution becomes clear. *Anhydrous calcium chloride is a drying agent; dries the compound from water and butan-1-ol.*

Figure 12. Drying with anhydrous calcium chloride.

14. After 5 minutes, decant the liquid to the round bottomed flask, previously clean and dry.

15. Wash the $CaCl_2$ left over with two 1 mL portions of *p*-xilene and decant the liquid to the flask. The *p-xylene allows to recover 1-bromobutane that remained in the vial with calcium chloride.*

Figure 13. Decantation of 1-bromobutane

Purification of 1-bromobutane

16. Add a magnetic stirrer, distill and collect the product between 99 ºC and 103 ºC, into a flask previously weighed. Stop collecting the product when the temperature reaches 103 ºC.

Figure 14. Distillation of the product.

17. Store the product in an adequate flask.

Reference

Williamson, K.L.; Minard, R.D.; Masters, K.M. *Macroscale and Microscale Organic Experiments – 5th edition*. Houghton Mifflin Company: Boston, 2007.

Synthesis of 1-bromobutane

Stoichiometric Reagents

- Butan-1-ol (CAS 71-36-3)
- Concentrated sulphuric acid (CAS 7664-93-9)
- Sodium bromide (CAS 7647-15-6)

Auxiliary Substances

- Anhydrous calcium chloride (CAS 10043-52-4)
- Concentrated sulphuric acid (CAS 7664-93-9)
- *p*-Xylene (CAS 106-42-3)
- Sodium hydroxide (aqueous 3M solution)
- Water

Waste

- But-1-ene
- Butan-1-ol (not reacted)
- Calcium chloride
- Dibutyl ether
- Hydrogen bromide
- *p*-Xylene
- Sodium bromide (excess, aqueous solution)
- Sodium hydrogen sulphate (aqueous solution)
- Sodium sulphate (aqueous solution)
- Sulphuric acid (dilute solution)
- Water

Material and Equipment

- 5 mL beaker
- 5 mL test tube
- 10 mL beaker
- 10 mL round bottomed flask
- Aluminium hotplate
- Analytical balance ± 0,1 mg
- Apparatus for simple distillation
- Condenser
- Glass bowl
- Glass rod

- Hotplate with magnetic stirring
- Liquid-liquid extraction flask: 4 mL vial
- Magnetic stirrer
- Pasteur pipet
- Power meter apparatus
- Spatula and microspatula
- Stirring apparatus
- Test tube
- Thermometer
- Universal support and claws
- Watch glass (Ø = 4,0 cm)