

SYNTHESIS OF 1-BROMOBUTANE
Experimental procedure at macroscale
(adapted from Williamson, Minard & Masters¹)

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.

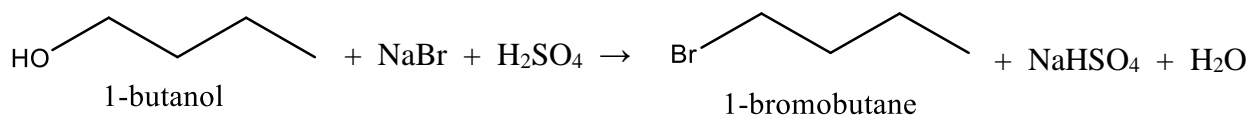


Figure 1. Global reaction for the synthesis of 1-bromobutane.

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).



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 (H₂O). 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.

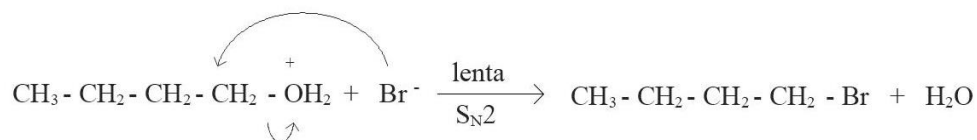
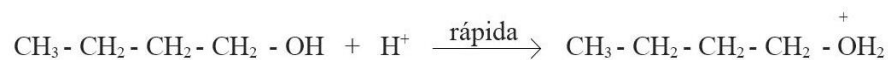


Figure 2. Mechanism of the reaction of the formation of 1-bromobutane.

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 does not reacted). Finally, the product is dried with anhydrous calcium chloride and purified by simple distillation.

Experimental procedure

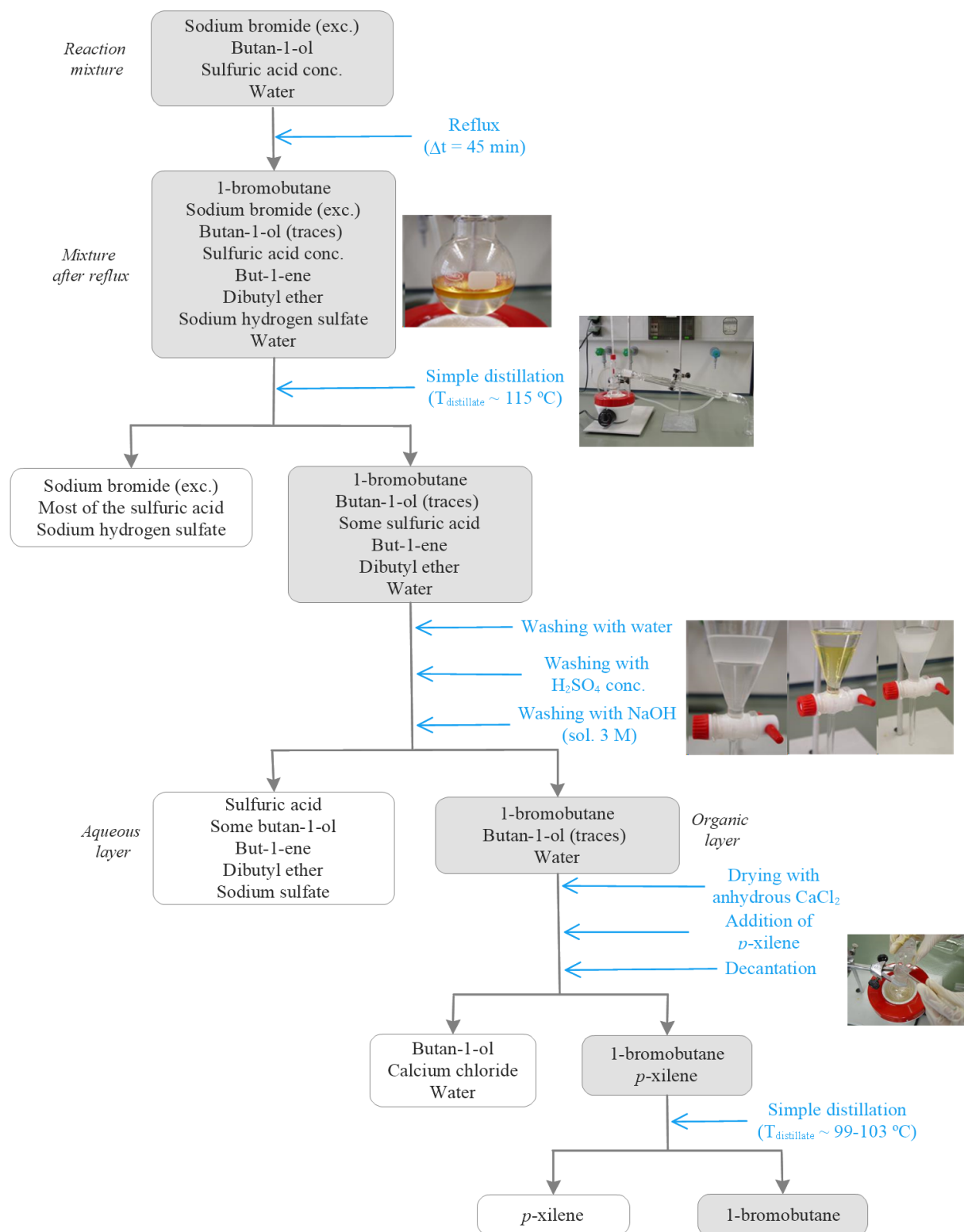
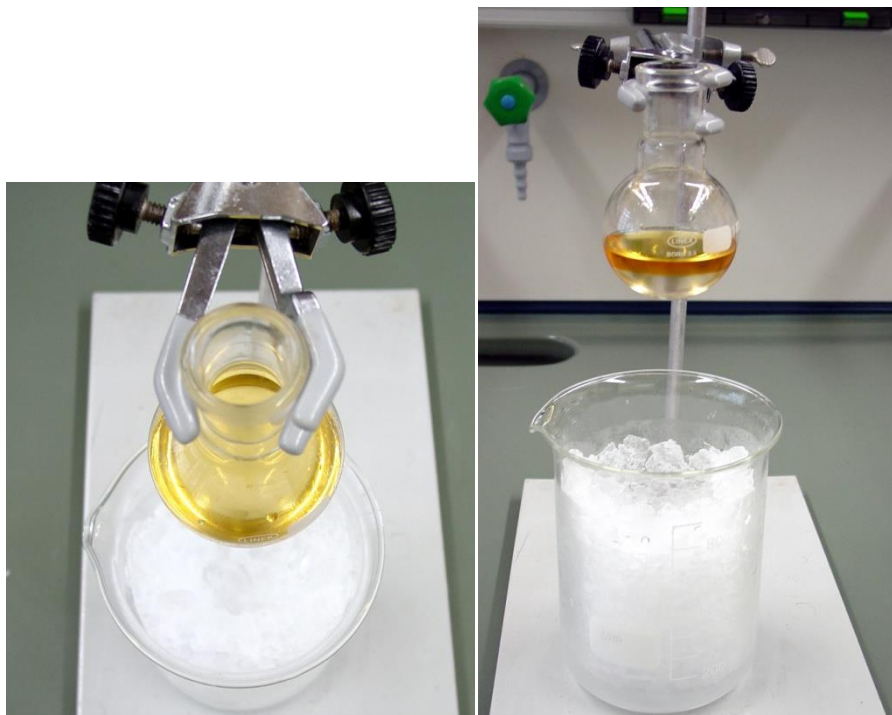


Figure 3. Experimental work for the synthesis of 1-bromobutane at macroscale.

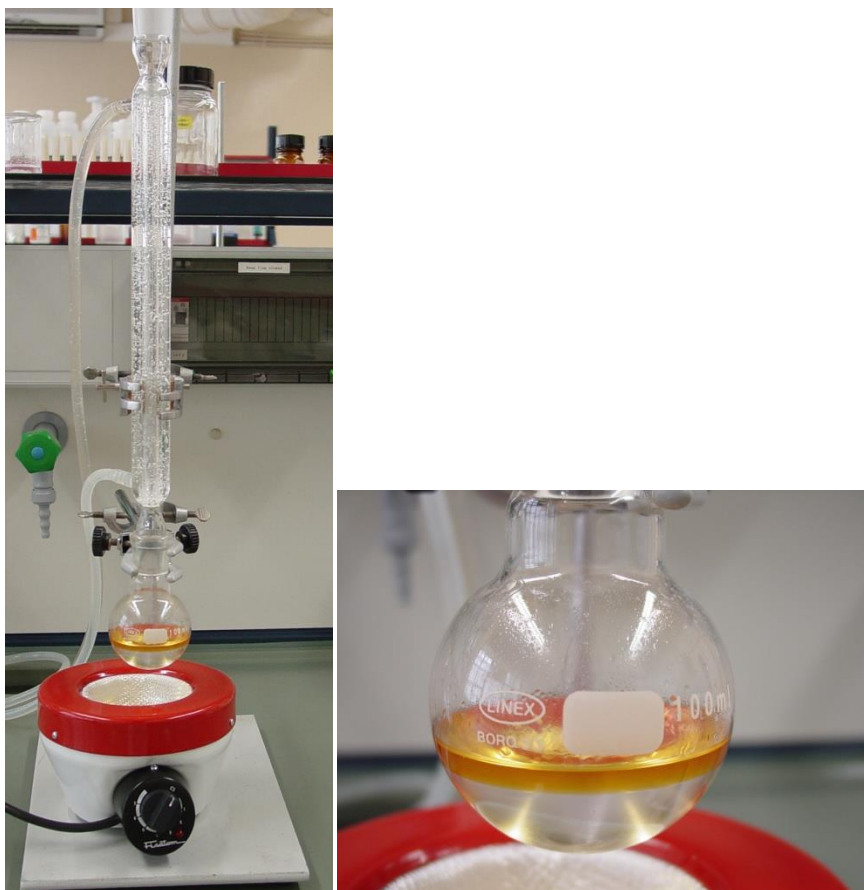
Formation of 1-bromobutane

1. In a 100 mL round bottomed flask, place 13.3 g of NaBr (129 mmol, ~19% excess), 15 mL of water and 10 mL of butan-1-ol (109 mmol).
2. Cool the mixture in an ice bath and, slowly and with continuous stirring, add 11.5 mL of concentrated H₂SO₄ (215,7 mmol, 97.4 % excess). *An ice bath and slow stirring are used because the hot acid causes the oxidation of NaBr to Br₂, useless in the experiment. The NaBr is dissolved during heating. The acid is in a large excess to obtain a higher concentration of HBr.*



Figures 4 and 5. Mixture after addition of concentrated sulphuric acid.

3. Place the flask in a heating mantle and attach a reflux condenser.
4. Heat to boiling point and adjust heating to a good reflux.
5. Reflux for 45 minutes, remove the heating and leave the condenser to operate for a few minutes. *The reflux is necessary because the reaction of formation of 1-bromobutane is slow and occurs at boiling temperature. Two layers are formed and the upper layer is the 1-bromobutane.*



Figures 6 and 7. Mixture after reflux

Isolation of 1-bromobutane from byproducts and waste

6. Remove the condenser and assemble an apparatus for simple distillation, using a 50 mL Erlenmeyer as collecting flask.
7. Distill the mixture, monitoring the temperature, until no more oily droplets come over ($t_{\text{distillate}} \approx 115\text{ }^{\circ}\text{C}$).
8. 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, excess of butan-1-ol, some drops of sulphuric acid, but-1-ene and dibutyl ether. The sodium hydrogen sulphate and most of the sulphuric acid stay in the flask.*
9. Pour the distillate into a separatory funnel, add 10 mL of water and shake it. 1-bromobutane stays in lower layer. If there is formation of a pink coloration in this layer, add a pinch of sodium hydrogen sulphite and shake again. *The washing with water allows to remove the sulphuric acid and some butan-1-ol.*



Figure 8. Mixture after washing with water.

10. Place the 1-bromobutane layer in a clean flask, wash and dry the separatory funnel and replace the compound on it.
11. Then, cool 10 mL of concentrated H_2SO_4 in an ice bath, add the acid to the funnel, shake well and let stand for 5 minutes to separate the layers.
12. Separate the layers. To find out which layer to reject, collect a few drops of the lower layer to a test tube and verify if the material is soluble in water (H_2SO_4) or not (1-bromobutane). 1-bromobutane stays in upper layer, colourless.



Figure 9. Mixture after washing with sulphuric acid.

13. Let stand another 5 minutes and separate the layers again. *The sulphuric acid removes any initial material which did not react, as well as secondary products (alkenes and ethers).*

14. Wash the 1-bromobutane with 10 mL of 3 mol/dm³ sodium hydroxide solution to remove traces of the acid, separate the layers and store the proper layer. *1-bromobutane stays in lower layer. Sodium hydroxide removes traces of sulphuric acid.*

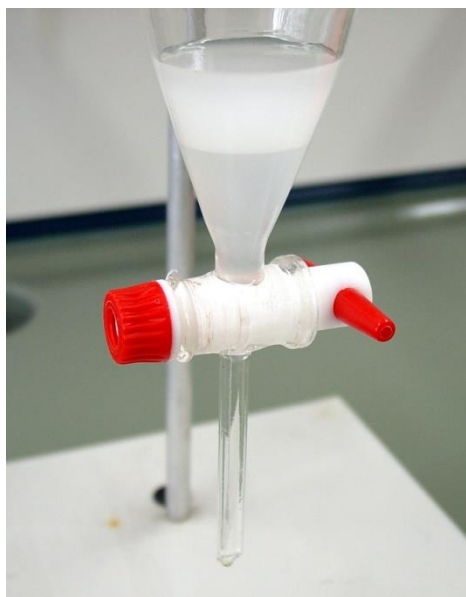


Figure 10. Mixture after washing with sodium hydroxide solution.

15. Dry the cloudy 1-bromobutane layer by adding 1 g of anhydrous CaCl₂ and stir until the solution becomes clear. *Anhydrous calcium chloride is a drying agent; dries the compound from water and butan-1-ol.*
16. After 5 minutes, decant the dried liquid to a 25 mL round bottomed flask.
17. Wash the CaCl₂ left over with two 10 mL portions of *p*-xylene and decant the liquid to the flask. *The p-Xylene allows to recover 1-bromobutane remaining in the beaker with calcium chloride.*



Figure 11. Decantation after washing with *p*-xylene.

Purification of 1-bromobutane

18. Add a boiling stone, distill and collect the material between 99 °C and 103 °C, into a flask previously weighed.
19. Store the product in an adequate flask.



Figure 12. Distillation of the product.

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

- 10 mL volumetric pipet
- 15 mL test tube
- 25 mL beaker
- 25 mL round bottomed flask
- 50 mL Erlenmeyer flask
- 100 mL heating mantle
- 100 mL round bottomed flask
- 100 mL separatory funnel

- Analytical balance $\pm 0,1$ mg
- Apparatus for simple distillation
- Boiling stones
- Condenser
- Glass bowl
- Glass rod
- Power meter apparatus
- Spatula and microspatula
- Test tube
- Thermometer
- Universal support and claws
- Watch glass ($\varnothing = 6,0$ cm)