



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

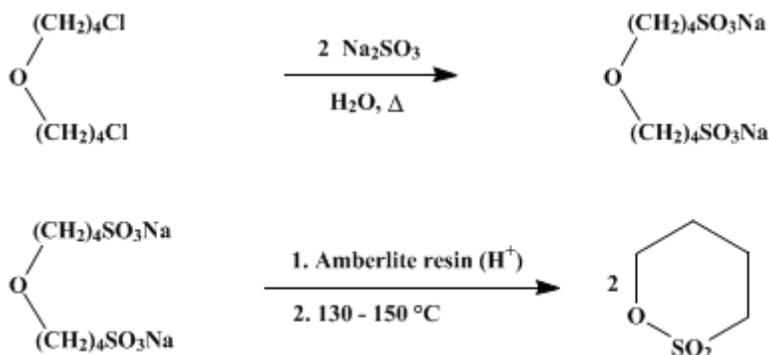
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4-HYDROXY-1-BUTANESULFONIC ACID SULTONE

[1-Butanesulfonic acid, 4-hydroxy-, δ -sultone]



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1. Procedure

A mixture of 132.5 g. (1.05 moles) of sodium sulfite, 99.5 g. (0.5 mole) of bis-4-chlorobutyl ether (Note 1), and 450 ml. of water is placed in a creased 1-l. three-necked flask fitted with an efficient sealed stirrer and a reflux condenser. The third neck of the flask is closed with a stopper, and the mixture is heated and stirred vigorously under reflux until the ether has dissolved (Note 2). At the end of this time, heating is discontinued, and 60 ml. of concentrated C.P. hydrochloric acid is cautiously added to the solution. The mixture is then boiled with stirring until sulfur dioxide is no longer evolved. Solid barium chloride dihydrate (or a 10% aqueous solution of this salt) is added to the hot solution (Note 3) until all sulfate has been precipitated; then the barium sulfate is removed by suction filtration through a layer of filter aid.

The filtered solution is diluted to 2l. with water and passed through a column of ion-exchange resin (Note 4) and (Note 5). A test portion of the effluent should yield no ash on evaporation and ignition of the residue. The column is washed with water until the effluent is no longer acid to litmus, and the washings are added to the original eluent. The total eluent is evaporated (Note 6) at reduced pressure (water aspirator) until the volume is about 250 ml.; then it is transferred to a 500-ml. pot which is equipped for vacuum distillation and attached to a short Vigreux column. After most of the remaining water and hydrochloric acid have been removed at the pressure obtainable with an aspirator, an oil pump is attached (Note 7), and the heating bath is cautiously raised to a temperature in the range 130–150°. The distillate is allowed to stand in a separatory funnel until the layers have separated (several hours may be required), then the crude sultone is withdrawn and distilled (Note 8) at reduced pressure. The yield of sultone, b.p. 134–136°/4 mm., is 99–109 g. (72–80%), n_D^{25} 1.4619–1.4625, d_4^{25} 1.3347, m.p. 12.5–14.5°.

2. Notes

1. Material supplied by Matheson, Coleman and Bell was used without purification.
2. This reaction may be carried out under pressure in a rocking autoclave at 180° in about 8 hours. When it is carried out under reflux with vigorous stirring in a creased flask it is complete in about 20 hours, whereas 50–60 hours is required if an ordinary flask is used.
3. Any sulfate ions resulting from oxidation of sulfite should be removed; otherwise they will be converted to sulfuric acid in the subsequent procedure and destroy sultone. Ordinarily, 12–13 g. of barium chloride dihydrate is required. The end point of the addition is conveniently determined with tetrahydroquinone indicator used in spot tests on filter paper [cf. *Ind. Eng. Chem., Anal. Ed.*, **9**, 331 (1937)].

4. Rohm & Haas Amberlite IR-120, which has been developed with 3*N* hydrochloric acid and then washed free from chlorides with water, is used in the form of a column 6 cm. in diameter and 55 cm. in length. Such a column contains approximately 1.1 kg. of resin (50% moisture) and is equivalent to about 2.2 moles of hydrogen chloride.

5. The checkers found that the procedure of Helberger and Lantermann,² which avoids the use of an ion-exchange resin, is also satisfactory in case it is regarded as inconvenient to set up the resin column. According to this procedure, after completion of the reaction with sodium sulfite, anhydrous hydrogen chloride is passed into the hot solution to liberate sulfur dioxide. After removal of sulfate as in the described procedure, the undiluted aqueous solution is saturated with hydrogen chloride gas at a temperature below 25°. The precipitated sodium chloride is removed by suction filtration, the filter cake is washed with two 50-ml. portions of 12*N* hydrochloric acid, and then the combined filtrate and washings are worked up as described for the eluent from the resin column.

6. The checkers found that satisfactory results may also be obtained if the water is evaporated by heating the solution on a steam bath as air is aspirated through it.

7. At the bath temperature specified, and low pressure, dehydration and distillation occur; if a pressure of about 4 mm. is maintained, the vapor temperature is in the range 132–138°. The temperature of the bath should be raised slowly and with caution, or else the contents of the pot may froth through the column into the distillate. The receiver should be cooled in a Dry Ice-acetone bath to prevent vapors from reaching the oil pump.

8. Water is nearly insoluble in the sultone. The small amount of water and a very volatile impurity which are present in the crude sultone distil rapidly before the sultone is collected. An efficient cold trap should be used to protect the pump from the volatile materials.

3. Discussion

4-Hydroxy-1-butanefulfonic acid sultone has been made through the chlorosulfonation of 1-chlorobutane,³ from 4-chlorobutyl acetate^{2,4} which is prepared through the reaction of tetrahydrofuran and acetyl chloride,² from 4-chlorobutanol,⁴ and from bis-4-chlorobutyl ether.² 4-Hydroxy-1-butanefulfonic acid sultone also has been obtained by treating sodium 4-hydroxybutane-1-sulfonate with cation-exchange resins,⁵ by heating methoxybutanesulfonic acid under reduced pressure at 150–180°,⁶ by concentrating an alcohol solution of 4-hydroxy-butanefulfonic acid under reduced pressure,⁷ and by heating 4-chloro-butanefulfonic acid with copper oxide and steam.⁸

Both 4-chlorobutanol and bis-4-chlorobutyl ether can be prepared from tetrahydrofuran (p. 266). The procedure described is based on the method of Helberger and Lantermann.²

References and Notes

1. The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati 31, Ohio.
2. Helberger and Lantermann, *Ann.*, **586**, 158 (1954).
3. Helberger, Manecke, and Fischer, *Ann.*, **562**, 23 (1949); Helberger, Manecke, and Heyden, *Ann.*, **565**, 22 (1949).
4. Truce and Hoerger, *J. Am. Chem. Soc.*, **76**, 5357 (1954).
5. Böhme Fettchemie G.m.b.H., Brit. pat. 774,563 [*C. A.*, **51**, 16519 (1957)].
6. Böhme Fettchemie G.m.b.H., Ger. pat. 902,615 [*C. A.*, **50**, 9443 (1956)].
7. Willems, *Bull. soc. chim. Belges*, **64**, 747 (1955).
8. Henkel & Cie. G.m.b.H., Ger. pat. 860,637 [*C. A.*, **48**, 1412 (1954)].

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

1-Butanesulfonic acid, 4-hydroxy-, δ -sultone

tetrahydroquinone

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium sulfite (7757-83-7)

acetyl chloride (75-36-5)

sodium chloride (7647-14-5)

sulfur dioxide (7446-09-5)

barium sulfate (7727-43-7)

1-chlorobutane (109-69-3)

copper oxide (1317-38-0)

barium chloride dihydrate (10326-27-9)

Tetrahydrofuran (109-99-9)

4-chlorobutanol (928-51-8)

4-Hydroxy-1-buthanesulfonic acid sultone (1633-83-6)

4-hydroxy-buthanesulfonic acid

bis-4-chlorobutyl ether (6334-96-9)

4-chlorobutyl acetate (6962-92-1)

sodium 4-hydroxybutane-1-sulfonate

methoxybutanesulfonic acid

4-chloro-butanesulfonic acid