Organic Syntheses

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.

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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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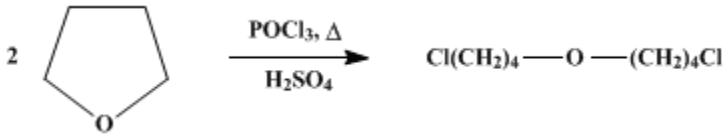
4,4'-DICHLORODIBUTYL ETHER

[Ether, *bis*(4-chlorobutyl)]



Submitted by Kliem Alexander and H. V. Towles[1].
Checked by Arthur C. Cope, Malcolm Chamberlain, and Mark R. Kinter.

1. Procedure

Caution! This preparation should be conducted in a good hood because some hydrogen chloride is evolved.

In a 2-l. three-necked flask fitted with a mercury-sealed stirrer (Note 1), a reflux condenser connected to a calcium chloride tube, and a thermometer is placed 360 g. (406 ml., 5 moles) of dry tetrahydrofuran (Note 2). The flask is surrounded by an ice bath, stirring is started, and 256 g. (153 ml., 1.67 moles) of phosphorus oxychloride is added rapidly. The mixture is cooled to 10–15°, and 50 ml. of concentrated sulfuric acid (sp. gr. 1.84) is added during the course of 3–10 minutes at a rate that does not cause the temperature to rise above 40°. The ice bath is then removed and the mixture is heated cautiously over a low luminous flame until an exothermic reaction becomes evident at about 88–90° (Note 3). By moderate cooling or warming as may be required the temperature is maintained at 90–100° until the exothermic reaction ceases, as indicated by the increased rate of heating required to maintain the reaction temperature, and thereafter for an additional 10 minutes (Note 4). Six hundred milliliters of water is added, the mixture is heated under reflux for 30 minutes and then distilled through a downward condenser until the vapor temperature reaches 99–100° (Note 5).

The dark reaction mixture is cooled to room temperature, transferred to a separatory funnel, and extracted with 225 ml. of ether. The ether extract is washed with four 100-ml. portions of water and dried over anhydrous sodium sulfate or magnesium sulfate. The mixture is filtered, the ether is removed by distillation, and the residual liquid is fractionated under reduced pressure from a modified Claisen flask. The yield of colorless 4,4'-dichlorodibutyl ether, b.p. 84–86°/0.5 mm. (116–118°/10 mm.), n_D^{25} 1.4562, d_4^{25} 1.0690, is 257–268 g. (52–54% based on tetrahydrofuran) (Note 6).

2. Notes

1. Efficient stirring is necessary to permit good control of the reaction temperature.
2. The same yield of 4,4'-dichlorodibutyl ether was obtained from redistilled tetrahydrofuran dried over sodium or a good-quality commercial grade obtained from the Electrochemicals Department of the E. I. du Pont de Nemours and Company and dried over Drierite.
3. About 30 minutes is required for the temperature to reach 88–90°. The temperature rises rapidly to 76°, at which point refluxing of tetrahydrofuran accompanied by evolution of some hydrogen chloride occurs. Thereafter refluxing gradually diminishes and the temperature increases approximately as follows: 0 minutes, 76°; 5 minutes, 77°; 10 minutes, 78°; 15 minutes, 80°; 20 minutes, 85°; 25 minutes, 94°; 27 minutes, 100°.
4. The temperature is easily kept within the range 90–100° by occasional cooling with an ice-water bath. Above 100° the reaction tends to become violent, resulting in excessive evolution of hydrogen chloride and a lower yield of the product. The exothermic phase of the reaction is usually complete in 15–20 minutes.
5. Refluxing with water serves to decompose phosphorus-containing complexes and facilitates isolation of the product. The aqueous distillate contains small amounts of 1,4-dichlorobutane and unchanged

tetrahydrofuran.
6. The product as obtained with these physical constants is analytically pure.

3. Discussion

The procedure described is based on one reported by Alexander and Schniepp.[2] 4,4'-Dichlorodibutyl ether also has been prepared by the action of thionyl chloride on tetrahydrofuran[3] or 1,4-butanediol,[4] and by heating 4-chlorobutanol and hydrogen chloride under pressure.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 529

References and Notes

1. Northern Regional Research Laboratory, U. S. Department of Agriculture, Peoria, Illinois.
2. Alexander and Schniepp, *J. Am. Chem. Soc.*, **70**, 1839 (1948).
3. Krzikalla and Maier, PB 631, Office of Technical Services, U. S. Department of Commerce; Lutkova, Kutsenko, and Itkina, *Zhur. Obshchei Khim.*, **25**, 2102 (1955) [*C. A.*, **50**, 8584 (1956)].
4. Haga et al. (to Mitsubishi Chemical Industries Co.), Jap. pats. 1268, 1271 (1953) [*C. A.*, **48**, 2086 (1954)]; Jap. pat. 5124 (1952) [*C. A.*, **48**, 8812 (1954)].
5. Trieschmann, U. S. pat. 2,245,509 [*C. A.*, **35**, 5914 (1941)].

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

Drierite

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

ether (60-29-7)

thionyl chloride (7719-09-7)

sodium sulfate (7757-82-6)

Phosphorus Oxychloride (21295-50-1)

sodium (13966-32-0)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

1,4-butanediol

4-chlorobutanol (928-51-8)

1,4-dichlorobutane (110-56-5)

Ether, bis(4-chlorobutyl),
4,4'-DICHLORODIBUTYL ETHER (6334-96-9)