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.

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

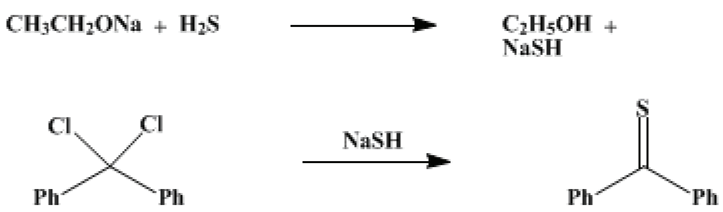
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.011.0094

Organic Syntheses, Coll. Vol. 2, p.573 (1943); Vol. 11, p.94 (1931).

THIOBENZOPHENONE

[Benzophenone, thio-]



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1. Procedure

An alcoholic solution of sodium hydrosulfide is prepared by dissolving 4.6 g. (0.2 gram atom) of sodium in 150 cc. of absolute alcohol and saturating the solution with dry hydrogen sulfide.

A 3-l. three-necked flask is equipped with a reflux condenser, a mechanical stirrer, a dropping funnel, and a tube for introducing dry carbon dioxide. Twenty-five grams (0.11 mole) of benzophenone dichloride (Note 1) is put into the flask, the air in the flask is displaced by a stream of carbon dioxide, and the sodium hydrosulfide solution is added slowly (Note 2). A vigorous reaction, which must be controlled by cooling, takes place, and the reaction mixture becomes deep blue in color.

After the reaction mixture has stood for one-half hour, water is added and the solution is extracted with ether. The ether solution is dried over calcium chloride and the ether is distilled. The residue is distilled under reduced pressure in an atmosphere of carbon dioxide (Note 3). Thiobenzophenone boils at 174°/14 mm.; it distils as a blue oil which, if pure and dry, forms beautiful blue crystals on cooling. The yield of crude product is 10–12.5 g. (50–63 per cent of the theoretical amount) (Note 4).

This product is approximately 75 per cent pure and is purified further by recrystallization from petroleum ether (b.p. 70–90°). The yield of purified product melting at 53–54° is 8.4–9.9 g. (42–50 per cent of the theoretical amount).

For preservation, the thiobenzophenone is sealed in a glass tube with dry carbon dioxide and placed in the dark.

2. Notes

1. The benzophenone dichloride was prepared by heating equivalent molecular quantities of benzophenone and phosphorus pentachloride to 145–150° for two hours and then fractionating the mixture under reduced pressure. The product used for this preparation boiled at 201–202°/35 mm.
2. It is necessary to have an excess of the chloride present at all times in order to prevent the formation of dibenzohydryldisulfide, due to reduction of the thioketone with the hydrosulfide. If the chloride is added to the sodium hydrosulfide solution, a 70 per cent yield of the pure disulfide is obtained and no thioketone is formed.
3. All the operations in the purification should be done very quickly and out of contact with the air as much as possible.
4. Larger runs using 100 g. of benzophenone dichloride gave the same percentage yields of product.

3. Discussion

Thiobenzophenone has been prepared by the action of thiophosgene on benzene in the presence of aluminum chloride;[1] by the action of phosphorus pentasulfide[2] or ethyl thioacetoacetate[3] on benzophenone; and by treating benzophenone dichloride with alcoholic potassium sulfide,[4] alcoholic sodium hydrosulfide,[5] or thioacetic acid.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 914
- Org. Syn. Coll. Vol. 4, 927

References and Notes

1. Bergreen, Ber. **21**, 341 (1888).
2. Gattermann, ibid. **28**, 2877 (1895).
3. Mitra, J. Indian Chem. Soc. **9**, 637 (1932) [C. A. **27**, 3922 (1933)].
4. Gattermann and Schulze, Ber. **29**, 2944 (1896).
5. Staudinger and Freudenberger, ibid. **61**, 1577 (1928).
6. Schönberg, Schütz, and Nickel, ibid. **61**, 1378 (1928).

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

petroleum ether

dibenzohydryldisulfide

alcohol (64-17-5)

calcium chloride (10043-52-4)

Benzene (71-43-2)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

hydrogen sulfide (7783-06-4)

carbon dioxide (124-38-9)

aluminum chloride (3495-54-3)

Benzophenone (119-61-9)

sodium (13966-32-0)

benzophenone dichloride

Thiophosgene (463-71-8)

potassium sulfide (1312-73-8)

sodium hydrosulfide

Thiobenzophenone,
Benzophenone, thio- (1450-31-3)

phosphorus pentasulfide

ethyl thioacetoacetate

thioacetic acid (507-09-5)