



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.

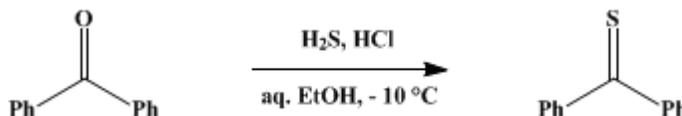
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.927 (1963); Vol. 35, p.97 (1955).

THIOBENZOPHENONE

[Benzophenone, thio-]



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Checked by Charles C. Price and J. Frank Gillespie.

1. Procedure

Caution! This preparation should be conducted in a good hood.

A 250-ml. three-necked flask is equipped with a rubber-sealed mechanical stirrer, two gas-inlet tubes, and a mercury-sealed escape valve consisting of an outlet tube dipping into a test tube of mercury. A solution of 25 g. (0.14 mole) of benzophenone in 125 ml. of 95% ethanol is placed in the flask, which is cooled in an ice-salt freezing mixture. Hydrogen sulfide and hydrogen chloride are passed simultaneously into the stirred solution for 3 hours (Note 1). Within 1 hour the solution becomes blue. After 3 hours, the flow of hydrogen chloride is stopped and hydrogen sulfide alone is passed for a further 20 hours, with continued ice cooling. Toward the end of the reaction, the contents of the flask assume an intense violet color. The solid thiobenzophenone (23–25 g.) is filtered from the ice-cold solution in an atmosphere of carbon dioxide (Note 2), immediately dried under high vacuum (Note 3), and recrystallized twice from about 20 ml. of petroleum ether (b.p. 60–80°), giving long needles, m.p. 53–54°. The yield of purified product, is 18–21 g. (66–77%).

2. Notes

1. Hydrogen chloride was generated by dropping concentrated sulfuric acid on ammonium chloride. Hydrogen sulfide was generated in a Kipp's apparatus from iron sulfide and hydrochloric acid. (The checkers used tank hydrogen sulfide.)
2. A convenient filtration apparatus for this purpose may be constructed by cutting the bottom off a bottle and then inserting a Büchner funnel through a stopper in the mouth of the bottle. The space between the bottle and the funnel is then packed with Dry Ice.
3. It has been found essential to dry the crude material immediately after filtration; otherwise it changes into a blue oil after standing for a few hours.

3. Discussion

The method described here is adapted from the procedure of Staudinger and Freudenberg.² It has been found to be more convenient and to give more reproducible results than the two-stage procedure given in *Organic Syntheses*,³ where references to other methods of preparation are also cited. Thiobenzophenone has been prepared also from benzophenone anil and thiolacetic acid.⁴

References and Notes

1. Imperial College of Science and Technology, London, England.
2. Staudinger and Freudenberg, *Ber.*, **61**, 1577 (1928).
3. *Org. Syntheses Coll. Vol. 2*, 573 (1943).
4. Mihailov and Savel'eva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **1959**, 1304 [*C. A.*, **54**, 1372 (1960)].

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

petroleum ether

benzophenone anil

ethanol (64-17-5)

sulfuric acid (7664-93-9)

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

ammonium chloride (12125-02-9)

hydrogen sulfide (7783-06-4)

mercury (7439-97-6)

carbon dioxide (124-38-9)

Benzophenone (119-61-9)

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

iron sulfide

Thiolacetic acid