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.

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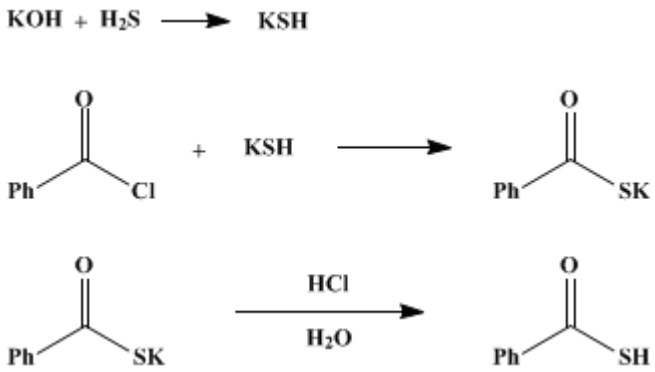
THIOBENZOIC ACID

[Benzoic acid, thio]



Submitted by Paul Noble, Jr. and D. S. Tarbell[1].
Checked by William S. Johnson and Robert A. Kloss.

1. Procedure

A solution of 200 g. (3 moles) of potassium hydroxide (85%) pellets in 800 ml. of 90% ethanol (Note 1) is prepared with mechanical stirring in a 2-l. three-necked round-bottomed flask. The flask is fitted with a 500-ml. dropping funnel and a gas inlet tube extending to the bottom of the flask, and hydrogen sulfide is passed in through the inlet tube with stirring and cooling until the solution is saturated and does not give an alkaline reaction with phenolphthalein (Note 2) and (Note 3). The mixture is further cooled to 10–15° by means of an ice bath, and 200 g. (1.41 moles) of freshly distilled benzoyl chloride (Note 4) is introduced drop-wise over a period of about 1.5 hours with stirring while the temperature is kept below 15°. After the addition of the benzoyl chloride has been completed, the reaction mixture is stirred for an additional hour. The potassium chloride which precipitates during the addition is separated quickly by filtration through a Büchner funnel and is washed with about 200 ml. of 95% ethanol. The filtrate is placed in a 2-l. round-bottomed flask fitted with a condenser arranged for distillation and evaporated to dryness under reduced pressure on a steam bath (Note 5). The solid residue, consisting mainly of potassium thiobenzoate, is dissolved in about 700 ml. of cold water (Note 6), and the solution is filtered if considerable insoluble material is present (Note 4). The alkaline solution is extracted with 500 ml. of benzene in order to remove any neutral material. The aqueous layer is then acidified with cold 6*N* hydrochloric acid (Note 6) and extracted with two 500-ml. portions of peroxide-free ether (Note 7). The ether layer is washed with several portions of cold water and dried over anhydrous sodium sulfate. The ether is evaporated under reduced pressure on a steam bath (Note 5), and the residue is fractionated immediately through a short (15–20 cm.) Vigreux column at reduced pressure, dry nitrogen being admitted through the capillary (Note 8). After a very small fore-run, the yellow-orange thiobenzoic acid distils at 85–87°/10 mm. (95–97°/15 mm.); yield 120–150 g. (61–76%); n_D^{20} 1.6027. Upon refractionation, the light-yellow thiobenzoic acid, as determined by titration with standard base or alcoholic iodine, is about 99.5% pure; n_D^{20} 1.6030.

2. Notes

1. No improvement in yield was observed by substitution of absolute ethanol. The 90% is preferable to 95% ethanol, because a much smaller volume is required to dissolve the potassium hydroxide.
2. The preparation should be conducted in a well-ventilated hood or provision should be made for an exhaust tube and attachment to a gas-absorption trap.
3. The gas inlet tube should be of moderately large diameter to prevent becoming plugged with crystals during the saturation with hydrogen sulfide.
4. The use of benzoyl chloride which has not been redistilled lowers the yield by 20–30%. The use of a

molar equivalent of benzoyl chloride leads to the formation of considerable benzal *bis*-thiobenzoate, $C_6H_5CH(SCOC_6H_5)_2$, which has been isolated previously as a product from the action of benzoyl chloride on potassium sulfide in ethanol.[2]

5. In order to prevent oxidation, it is inadvisable to allow the solution to stand for any appreciable time up to this point. The evaporation should be carried out without the use of a capillary. The checkers found it convenient to employ mechanical stirring (rubber-sealed stirrer) during the reduced-pressure distillation in order to prevent bumping.

6. If the temperature is allowed to rise, considerable oxidation may occur.

7. Suitable peroxide-free ether is prepared by washing ether with an equal volume of a dilute, weakly acidic solution of ferrous sulfate.

8. It is necessary to fractionate as rapidly as possible in order to prevent oxidation to the disulfide, which occurs almost completely even in the presence of nitrogen if the column is too long or if the distillation is carried out too slowly. Oil-pumped nitrogen is dried through an absorption tower containing soda lime and calcium chloride before passing to the distillation apparatus. The column should be vacuum jacketed or provided with a heated jacket.

3. Discussion

The method described is adapted from the procedures of Kym[3] and Engelhardt, Latschinoff, and Malyscheff.[4] Thiobenzoic acid has been prepared by the reaction of benzoyl chloride with potassium sulfide,[4] hydrogen sulfide in pyridine,[5,6] and magnesium bromide hydrosulfide.[7] It is formed from dibenzoyl disulfide with potassium hydrosulfide,[4] potassium hydroxide,[4,8] and ammonia.[9] It is also formed from dibenzoyl sulfide, from phenyl benzoate, and from benzoic anhydride with alcoholic potassium hydrosulfide.[4] It has been obtained from dibenzoyl sulfide and hydrogen sulfide,[10] carbon oxysulfide and phenylmagnesium bromide,[11,12] dibenzyl disulfide and sodium ethoxide,[13] benzyl chloride and sulfur in the presence of potassium hydroxide,[14] and benzylthiosulfuric acid and alkali.[15,16]

References and Notes

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

carbon oxysulfide

peroxide-free ether

dibenzoyl sulfide

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

hydrogen sulfide (7783-06-4)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

sulfur (7704-34-9)

ferrous sulfate (13463-43-9)

iodine (7553-56-2)

benzoyl chloride (98-88-4)

Benzoic anhydride (93-97-0)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

sodium ethoxide (141-52-6)

benzyl chloride (100-44-7)

potassium hydrosulfide (1310-61-8)

Phenylmagnesium bromide (100-58-3)

potassium sulfide (1312-73-8)

phenolphthalein (77-09-8)

potassium chloride (7447-40-7)

phenyl benzoate (93-99-2)

dibenzoyl disulfide (644-32-6)

Thiobenzoic acid,
Benzoic acid, thio (98-91-9)

potassium thiobenzoate

magnesium bromide hydrosulfide

dibenzyl disulfide (150-60-7)

benzylthiosulfuric acid

benzal bis-thiobenzoate