



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.

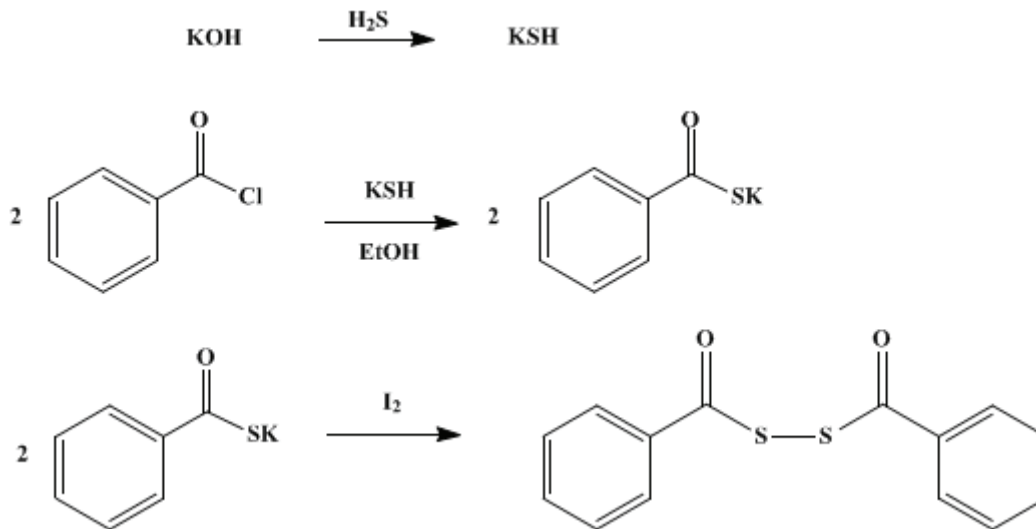
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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BENZOYL DISULFIDE



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1. Procedure

A solution of 315 g. (4.76 moles) of **potassium hydroxide** in 3150 ml. of commercial absolute **ethanol** is prepared with mechanical stirring in a 5-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 until the solution is saturated and no longer gives an alkaline reaction with **phenolphthalein** (Note 1), (Note 2). The mixture is cooled to 10–15° by means of an ice bath, and 346.5 g. (2.46 moles) of redistilled **benzoyl chloride** is introduced dropwise with stirring while the temperature is kept below 15°. The **potassium chloride** which precipitates during the addition (Note 3) is separated by filtration with suction through a Büchner funnel and is washed with about 200 ml. of **ethanol** (Note 4). The filtrate and washings are cooled to 10–15°, and solid **iodine** is added slowly, with constant agitation, until a slight excess is present, as shown by a faint permanent coloration of the solution. The amount of **iodine** required varies from 336 g. to 407 g. (1.32–1.61 moles) (Note 5). **Benzoyl disulfide** precipitates during the addition. It is collected on a filter and washed with 750 ml. of 95% **ethanol** followed by 3 l. of water. The crude product, after drying at room temperature, or in an oven at a temperature which does not exceed 60° (Note 6), weighs 325–333 g.

The crude material is dissolved with stirring in 910 ml. of **ethylene chloride** heated to 60° in a water bath (Note 6). The solution is allowed to cool to room temperature, 122 ml. of a saturated aqueous solution of **sodium bicarbonate** is added to the resulting slurry, and the mixture is stirred for 1 hour (Note 7). The layers are then separated in a separatory funnel, and the **ethylene chloride** slurry is heated to 60° in a water bath. The resulting solution is filtered through a small cotton plug in a preheated funnel. Absolute **ethanol** (313 ml.) is added to the filtrate, and the mixture is stored in an icebox overnight while the product crystallizes. The crystals are collected on a filter and washed with 40 ml. of **ether**. The product is recrystallized by dissolving it in **ethylene chloride** (3.0 ml. per g. of product) heated to 60° in a water bath (Note 6) and cooling. The yield of white to light pink plates, m.p. 129–130°, is 230–246 g. (68–73%).

2. Notes

1. It is convenient during this step to use the dropping funnel as an exhaust tube by attaching its upper

end to a gas-absorption trap. If this is not done, the preparation should be conducted in a well-ventilated hood.

2. The gas inlet tube should be of moderately large diameter or it may become plugged with crystals during the later stages of the saturation with [hydrogen sulfide](#).

3. Stirring is discontinued after the [benzoyl chloride](#) has been added. The precipitate of [potassium chloride](#) can be separated more easily if the mixture is allowed to stand overnight before filtration.

4. After the filtration and washing, the application of suction is continued until bubbles of [hydrogen sulfide](#) no longer form in the filtrate. Much of the excess [hydrogen sulfide](#) is removed during the filtration.

5. The amount of [iodine](#) required is presumed to vary according to the presence of variable amounts of [hydrogen sulfide](#) and to the extent of oxidation by atmospheric [oxygen](#). In one unsatisfactory preparation in which a relatively large amount of [hydrogen sulfide](#) must have remained in the solution a total of 493 g. (1.94 moles) of [iodine](#) was required and the final product contained free [sulfur](#).

6. If the temperature exceeds 60°, discoloration occurs and the product cannot be decolorized by recrystallization or treatment with activated charcoal.

7. This operation is carried out at room temperature because heating in the presence of alkalis decomposes [benzoyl disulfide](#).

3. Discussion

[Benzoyl disulfide](#) has been obtained by the reaction of [benzoyl chloride](#) with [hydrogen sulfide](#),² [hydrogen disulfide](#),³ [hydrogen trisulfide](#),^{3,4} [potassium sulfide](#),⁵ [sodium disulfide](#),⁶ [lead sulfide](#),⁷ ⁸ [sodium hydrosulfite](#),⁹ [sodium thiosulfate](#),¹⁰ [sulfhydrylmagnesium bromide](#),¹¹ and [thiobenzamide](#).¹² It is also formed by reaction of [benzoic anhydride](#) with [hydrogen sulfide](#).¹³ The better preparative methods involve the oxidation of [thiobenzoic acid](#) by means of air,^{7,8,14,15} [hydrogen peroxide](#),^{16,17} or [sulfur monochloride](#),¹⁸ or of the sodium or potassium salt by means of air,^{17,19} [chlorine](#),²⁰ [iodine](#),^{7,15,16,21,22} [copper sulfate](#),^{7,8,17} [potassium ferricyanide](#),^{7,8,17,23} or [ferric chloride](#).^{7,8,17}

References and Notes

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

sulphydrylmagnesium bromide

ethanol (64-17-5)

ether (60-29-7)

sodium bicarbonate (144-55-8)

hydrogen sulfide (7783-06-4)

lead sulfide

oxygen (7782-44-7)

sodium thiosulfate (7772-98-7)

ethylene chloride (107-06-2)

copper sulfate (7758-98-7)

sodium hydrosulfite (7775-14-6)

sulfur (7704-34-9)

iodine (7553-56-2)

benzoyl chloride (98-88-4)

Benzoic anhydride (93-97-0)

chlorine (7782-50-5)

potassium hydroxide (1310-58-3)

hydrogen peroxide (7722-84-1)

ferric chloride (7705-08-0)

sulfur monochloride

sodium disulfide

potassium sulfide (1312-73-8)

phenolphthalein (77-09-8)

potassium ferricyanide (13746-66-2)

potassium chloride (7447-40-7)

Benzoyl disulfide (644-32-6)

hydrogen disulfide

hydrogen trisulfide

thiobenzamide (2227-79-4)

Thiobenzoic acid (98-91-9)