



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.

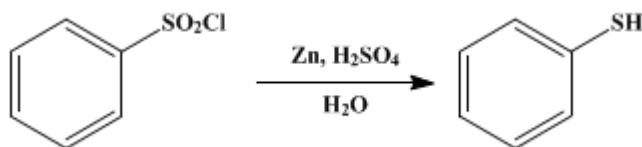
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.504 (1941); Vol. 1, p.71 (1921).

THIOPHENOL

[Benzenethiol]



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Checked by H. T. Clarke and Katharine Ogden.

1. Procedure

In a 12-l. round-bottomed flask are placed 7.2 kg. of cracked ice and 2.4 kg. (1300 cc., 23.4 moles) of concentrated [sulfuric acid](#) (sp. gr. 1.84). The mixture becomes very cold and is kept at -5° to 0° by means of an ice-salt bath. Mechanical stirring is started and 600 g. (3.4 moles) of crude [benzenesulfonyl chloride](#) (p. 84) is gradually introduced (one-half hour) ([Note 1](#)). Then 1.2 kg. (16.5 atoms) of [zinc](#) dust (90 per cent) is added ([Note 2](#)) in portions as rapidly as possible without allowing the temperature to rise above that mentioned (this requires about one-half hour) ([Note 3](#)). The contents of the flask are stirred for one to one and one-half hours longer, the temperature being kept at 0° or below during the whole period. A stopper holding an efficient reflux condenser (lower end not constricted) and stirrer is now attached; the ice bath is removed ([Note 4](#)); and the reaction mixture is allowed to warm up spontaneously or it may be warmed up with a low flame, the stirring being continued. Within a very few (two to five) minutes, in many runs, a rather vigorous reaction with the evolution of much [hydrogen](#) takes place. Under these circumstances it is advisable to cool the flask momentarily by a stream of water. The reflux condenser will, however, generally take care of the vapors satisfactorily.

After the first ebullition has subsided, no further attention is required, and the mixture is heated to boiling over a ring burner until the solution becomes clear. The stirring should be continued during the refluxing, and the stirrer should be arranged so as to suck the liquid downward from the surface. This helps distribute the [zinc](#) which holds [hydrogen](#) and floats on top of the liquid. About four to seven hours are required for the heating ([Note 5](#)). The [thiophenol](#) is then distilled with steam, this process requiring about one hour. The product is separated from the water, dried with [calcium chloride](#) (shaking with [calcium chloride](#) for three to five minutes is generally sufficient), and distilled. The crude material weighs 359 g. (96 per cent of the theoretical amount), and the pure compound boiling at $166\text{--}169^\circ$ ($71^\circ/15\text{mm.}$) weighs 340 g. (91 per cent of the theoretical amount). Ten to twelve hours are required for the whole experiment up to the final distillation.

2. Notes

1. Since [benzenesulfonyl chloride](#) solidifies at 15° , it is necessary to add it to the [sulfuric acid](#) slowly, with stirring, so that it will be as finely divided as possible when the [zinc](#) is added.
2. The directions given in the literature advise the addition of the [zinc](#) dust to the [sulfuric acid](#) and then the addition of the [benzenesulfonyl chloride](#). This procedure has been reversed in the way described above so that the minimum amount of [hydrogen](#) will be lost during the addition of the [zinc](#).
3. It is essential that the temperature during the first part of the reaction be kept at 0° or below, for otherwise poor yields are obtained. In order to hold the temperature at 0° , it is absolutely essential to add the [zinc](#) dust at least as slowly as described.
4. After the initial reaction at a low temperature had taken place, it was, in several instances, found convenient to allow the reaction mixture to stand overnight before proceeding further. The flask was thus left in the ice, which gradually melted, allowing the reaction mixture to warm up to room temperature. Under these conditions, however, a poor yield generally resulted. Upon closer study, it was discovered that the small amount of product obtained was due to the sudden vigorous reaction, with consequent loss through the condenser, which took place when a certain temperature was reached. The

reaction mixture may be safely allowed to stand only if a very efficient condenser is used. In the checking of this experiment, no sudden reaction was observed, and heating with a small flame after the initial mixing and stirring at 0° gave excellent results. The difference in the experiments may have been due to a slightly different grade of raw materials.

5. Vigorous stirring while the reaction mixture is heated reduces materially the time of the reduction (from twelve to seven hours or less), as it brings the [zinc](#), which otherwise floats, into intimate contact with the acid and sulfonyl chloride.

3. Discussion

Two general methods are available for the preparation of thiophenols. The first is by the treatment of aryldiazonium chlorides with [potassium ethyl xanthogenate](#) and then heating with alkali to give thiophenols.¹ This reaction has been used for the preparation of a large number of thiophenols, but it suffers from the disadvantage of having many side-reactions and in the danger of occasional violent explosions² when conditions are not correct. The second method involving the reduction of sulfonyl chlorides by [zinc](#) dust and [sulfuric acid](#),³ although limited to sulfonyl chlorides not having another group such as nitro which might be reduced, gives better yields of pure product than the [xanthogenate](#) process and avoids [ether](#) extraction and treatment with alcoholic [potassium hydroxide](#). [Thiophenol](#) itself has also been prepared from [diphenyl sulfide](#)⁴ and from [chlorobenzene](#)⁵ by heating with aqueous [sodium sulfide](#) under pressure.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 695](#)

References and Notes

1. Leuckart, Ger. pat. 45,120 [Winther, Pat. Org. Chem. **1**, 243 (1877–1905)]; Leuckart, J. prakt. chem. (2) **41**, 179 (1890); Lustig, Gazz. chim. ital. **21**, I, 213 (1891).
2. Bourgeois, Ber. **28**, 3240 (1895).
3. Vogt, Ann. **119**, 142 (1861); Otto, Ber. **10**, 939 (1877); Bourgeois, Ber. **28**, 2319 (1895); Rec. trav. chim. **18**, 433 (1899).
4. Vorozhtzov, Jr., and Mishchengendler, Russ. pat. 33,151 [C. A. **28**, 4073 (1934)].
5. Vorozhtzov, Jr., and Mitzengendler, Russ. pat. 34,554 [C. A. **29**, 2977 (1935)].

Appendix

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

[sulfonyl chloride](#)

[calcium chloride](#) (10043-52-4)

[sulfuric acid](#) (7664-93-9)

[ether](#) (60-29-7)

[hydrogen](#) (1333-74-0)

[Benzenesulfonyl chloride](#) (98-09-9)

chlorobenzene (108-90-7)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

sodium sulfide (1313-82-2)

Thiophenol,
Benzenethiol (108-98-5)

potassium ethyl xanthogenate (140-89-6)

xanthogenate

Diphenyl sulfide (139-66-2)