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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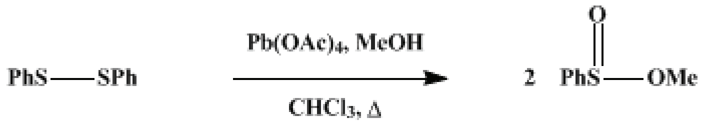
METHYL BENZENESULFINATE

[Benzenesulfinic acid, methyl ester]



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Checked by John J. Miller and William D. Emmons.

1. Procedure

Caution! Care should be taken to keep methyl benzenesulfinate off the skin (Note 1).

In a 5-l., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer and a reflux condenser carrying a drying tube are placed 54.6 g. (0.25 mole) of diphenyl disulfide (Note 2), 450 ml. of chloroform (Note 3), and 450 ml. of methanol. To the stirred solution at the reflux temperature is added 443.4 g. (1.00 mole) of lead tetraacetate (Note 4) in 2 l. of chloroform during 8 hours. Owing to formation of lead dioxide, the initially yellow solution becomes dark brown during the addition. The mixture is kept at the reflux temperature overnight (about 12 hours), after which 2 l. of chloroform is removed by distillation at atmospheric pressure (Note 5). The mixture then is cooled to room temperature, and 330 ml. of distilled water is added with stirring to decompose any excess lead tetraacetate. Lead dioxide is removed by filtration of the entire mixture using a Celite®-coated filter paper. The chloroform layer is washed with distilled water until the washings are free of lead ions (Note 6). The chloroform solution is dried over anhydrous magnesium sulfate and, after separation of the drying agent, is concentrated by means of a rotating-flask evaporator. The oily yellow residue is left overnight under vacuum (about 0.1 mm.) to remove any traces of hexachloroethane (Note 7). Distillation is effected through a 15-cm. Vigreux column under reduced pressure (Note 8). The yield of methyl benzenesulfinate is 48.6–53 g. (62–68%), b.p. 59–60° (0.04 mm.), 76–78° (0.45 mm.); n^{25}D 1.5410–1.5428, reported n^{20}D 1.5400,[3] 1.5440.[4]

2. Notes

1. The checkers experienced an extreme and prolonged burning sensation on contact.
2. Diphenyl disulfide, supplied by Distillation Products Industries, Rochester 3, New York, was used as received.
3. Reagent grade chloroform is satisfactory.
4. Used as received from Arapahoe Chemicals, Inc., Boulder, Colorado. This product, usually about 85–96% lead tetraacetate moist with acetic acid, is stored at about 5°. The molar amount specified is based on occasional iodometric titration (Arapahoe brochure) as follows:[5] An accurately weighed sample of about 0.5 g. is dissolved in 5 ml. of glacial acetic acid with gentle warming, and 100 ml. of an aqueous solution of 12 g. of anhydrous sodium acetate and 1 g. of potassium iodide is added. After several minutes, with occasional swirling, the flask wall is rinsed with water. Liberated iodine is titrated with 0.1*N* sodium thiosulfate to a starch end point. The percent of lead tetraacetate is calculated from the formula 22.17 (milliliters of thiosulfate) (normality of thiosulfate)/(weight of sample).
The submitters recommend that the lead tetraacetate be added in eight separate portions of 0.125 mole of lead tetraacetate, each in 250 ml. of chloroform, because the solution of lead tetraacetate decomposes on standing.
5. This can be done conveniently by removing the reflux condenser and replacing it with apparatus for downward distillation.
6. A solution of sodium sulfide can be used to test for the presence of lead ions in the wash liquors. The checkers found that the yield can be improved somewhat by extraction of the initial water layer with

chloroform.

7. The small amount of hexachloroethane produced during the reaction presumably is formed from chloroform by a free radical process.

8. The residue after distillation is diphenyl disulfide. It may be recovered by recrystallization from ethanol. The methyl benzenesulfinate may be pale yellow when first distilled, but if so it becomes colorless on standing. If possible, a spinning-band column should be used for distillation, and distillation should be as rapid as possible; use of a 47-cm. spinning-band column gave analytically pure ester, n^{25}D 1.5436 (cf. Field and co-workers).[6]

3. Discussion

Methyl benzenesulfinate has been prepared by the three-stage process of reduction of benzenesulfonyl chloride to benzenesulfinic acid, conversion of the acid to benzenesulfinyl chloride, and esterification of the chloride with methanol.[3,7] It has been prepared also by ozonolysis of methyl benzenesulfenate.[4] Alkane- and arenesulfinate esters have been prepared from thiols or disulfides by the following sequence: conversion to a sulfinyl chloride by treatment with chlorine, reaction with the appropriate alcohol, treatment with an amine to remove any sulfonyl chloride, and distillation of the sulfinate.[8] The present procedure is based on one reported by Field, Hoelzel, and Locke.[6]

4. Merits of the Preparation

This procedure affords a one-step synthesis of aromatic sulfinic esters from readily available starting materials. It is successful with a variety of types of aromatic sulfinic esters.[6] The method is rather unattractive for aliphatic disulfides, however, because the nature of by-products formed makes rigorous purification of the sulfinic esters impracticable.[9]

References and Notes

1. Department of Chemistry, Vanderbilt University, Nashville, Tennessee. This work was partly supported by the U.S. Army Research Office, Durham, North Carolina.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

acetic acid (64-19-7)

methanol (67-56-1)

sodium acetate (127-09-3)

chloroform (67-66-3)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

iodine (7553-56-2)

Benzenesulfonyl chloride (98-09-9)

chlorine (7782-50-5)

sodium sulfide (1313-82-2)

magnesium sulfate (7487-88-9)

benzenesulfinic acid (618-41-7)

Methyl benzenesulfinate,
Benzenesulfinic acid, methyl ester (670-98-4)

diphenyl disulfide (882-33-7)

hexachloroethane (67-72-1)

benzenesulfinyl chloride (4972-29-6)

methyl benzenesulfenate

lead dioxide

lead tetraacetate (546-67-8)