



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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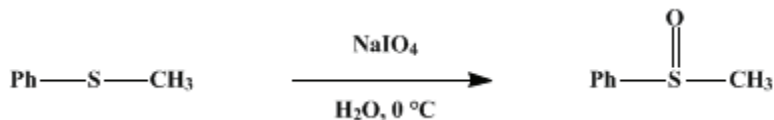
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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METHYL PHENYL SULFOXIDE



Submitted by Carl R. Johnson and Jeffrey E. Keiser¹.

Checked by Wayland E. Noland, Leonard J. Czuba, and William E. Parham.

1. Procedure

In a 500-ml. round-bottomed flask equipped with a magnetic stirrer are placed 22.5 g. (0.105 mole) of powdered sodium metaperiodate and 210 ml. of water. The mixture is stirred and cooled in an ice bath (Note 1), and 12.4 g. (0.100 mole) of thioanisole (Note 2) is added. The reaction mixture is stirred for 15 hours at ice-bath temperature and is then filtered through a Büchner funnel. The filter cake of sodium iodate is washed with three 30-ml. portions of methylene chloride. The water-methylene chloride filtrate is transferred to a separatory funnel, the lower methylene chloride layer is removed, and the water layer is extracted with three 100-ml. portions of methylene chloride. The combined methylene chloride extracts are treated with activated carbon (Note 3) and dried over anhydrous sodium sulfate (Note 4). The solvent is removed at reduced pressure to yield 13.6–13.9 g. of a slightly yellow oil (Note 5) which crystallizes on cooling. The crude sulfoxide is transferred to a 25-ml. distillation flask with the aid of a small amount of methylene chloride. After removal of the solvent, a pinch of activated carbon is added to the distillation flask (Note 6). Simple vacuum distillation (Note 7) of the crude product through a short path still affords 12.7–12.8 g. (91%) of pure methyl phenyl sulfoxide, b.p. 78–79° (0.1 mm.), m.p. 33–34° (Note 8) and (Note 9).

2. Notes

1. The periodate oxidation of aryl sulfides to sulfoxides may be carried out at room temperature; however, an ice bath is necessary to prevent overoxidation of dialkyl sulfides.
2. Thioanisole (methyl phenyl sulfide) supplied by Aldrich Chemical Company, Milwaukee, Wisconsin, was used without further purification.
3. The checkers used 1 g. of activated carbon.
4. The checkers used 3–5 g. of sodium sulfate.
5. Gas-phase chromatography shows this crude material to be sulfide-free sulfoxide containing a small amount of methylene chloride.
6. The simple technique of adding a pinch of activated carbon to the distillation pot affords a more nearly colorless distillate.
7. No fore-run is observed other than a small amount of methylene chloride which does not condense. The pot is taken nearly to dryness.
8. Methyl phenyl sulfoxide is extremely hygroscopic. The melting point is best taken by rapid transfer of the easily supercooled oil to a melting-point capillary by means of a finely drawn pipet. The sealed capillary is then cooled to effect crystallization of the sulfoxide.
9. This procedure, with slight modifications depending on the physical properties of the sulfide and sulfoxide in question, has been used to prepare a variety of sulfoxides as illustrated by examples provided in Table I. In the case of very insoluble sulfides, co-solvents such as methanol or dioxane may be employed. Very soluble sulfoxides are best isolated by continuous extraction with chloroform or methylene chloride.

TABLE I PREPARATION OF SULFOXIDES

Products	Yields, %	M.P. [B.P.], °C.
Methyl 4-ketopentyl sulfoxide	98	22.5–23.5 [99–101 (0.12 mm.)]
Thian 1-oxide	99	67–68

1,4-Oxathian 1-oxide	83	46–47
Bis(2-diethylaminoethyl)sulfoxide	85	Dipicrate 146–148
Acetoxymethyl methyl sulfoxide	72	[85–90 (0.1 mm.)]
1-Benzylsulfinyl-2-propanone	89	126.0–126.5
Phenylsulfinylacetic acid	99	118.0–119.5
Benzyl sulfoxide	96	135–136
Ethyl sulfoxide	65	[45–47 (0.15 mm.)]
Ethyl phenyl sulfoxide	93	[101–102 (1.5 mm.)]

3. Discussion

Methyl phenyl sulfoxide has also been prepared from thioanisole by the action of hydrogen peroxide,^{2,3} lead tetraacetate,⁴ and dinitrogen tetroxide,^{5,6} and from methanesulfinyl chloride and benzene with anhydrous aluminum chloride.⁷

4. Merits of the Preparation

The present procedure is a specific example of the method generalized by Leonard and Johnson.⁸ The method employs extremely mild reaction conditions and affords high yields of sulfoxides (Note 9) free of contamination by sulfides or sulfones. Sodium periodate is easily and safely handled; however, the higher cost of this reagent in comparison to certain other oxidants, e.g., hydrogen peroxide, may prohibit its use in large-scale reactions.

References and Notes

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6. D. W. Goheen, W. H. Hearon, and J. Kamlet, U.S. Patent 2,925,442 (1960) [*C.A.*, **54**, 11994a (1960)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

dinitrogen tetroxide

Benzene (71-43-2)

methanol (67-56-1)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

carbon (7782-42-5)
aluminum chloride (3495-54-3)
hydrogen peroxide (7722-84-1)
methylene chloride (75-09-2)
dioxane (123-91-1)
Methanesulfinyl chloride (676-85-7)
Methyl phenyl sulfoxide (1193-82-4)
sodium metaperiodate,
Sodium periodate (7790-28-5)
thioanisole,
methyl phenyl sulfide (100-68-5)
water-methylene chloride
Methyl 4-ketopentyl sulfoxide Thian
1-oxide
1,4-Oxathian 1-oxide
Bis(2-diethylaminoethyl)sulfoxide
Acetoxymethyl methyl sulfoxide
1-Benzylsulfinyl-2-propanone
Phenylsulfinylacetic acid
Benzyl sulfoxide (621-08-9)
Ethyl sulfoxide (70-29-1)
Ethyl phenyl sulfoxide (4170-80-3)
lead tetraacetate (546-67-8)