



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.

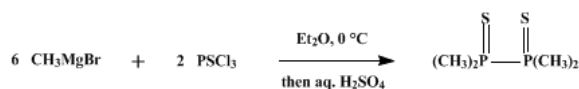
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

TETRAMETHYLBIPHOSPHINE DISULFIDE

[Diphosphine, tetramethyl-, disulfide]



Submitted by G. W. Parshall¹
Checked by W. S. Wadsworth and William D. Emmons.

1. Procedure

Caution! See the discussion in Org. Synth. 1990, Coll. Vol. 7, 533 with regard to potential hazards associated with the title compound.

A 3-l. round-bottomed flask equipped with mechanical stirrer, condenser (surmounted by a drying tube), thermometer, and addition funnel is charged with 800 ml. of 3*M* methylmagnesium bromide solution (2.4 moles) (Note 1) and 600 ml. of anhydrous ether. The solution is stirred and cooled to 0–5° while a solution of 135 g. (83 ml., 0.80 mole) of thiophosphoryl chloride (Note 2) in 85 ml. of ether is added over a period of 3 hours. A thick white precipitate forms during the course of the addition. After completion of the addition, the reaction mixture is poured onto 500 g. of ice in a 4-l. beaker. Sulfuric acid (900 ml. of 10% solution) is added over a period of 20 minutes with gentle stirring. The mixture is filtered, and the white solid product is washed with 4 l. of water and recrystallized from 2 l. of ethanol. The product is dried over phosphorus pentoxide in a vacuum desiccator to give 50–55 g. (67–74%) of white crystalline tetramethylbiphosphine disulfide, m.p. 223–227° (Note 3). Evaporation of the mother liquor to a volume of 900 ml. gives an additional 3 g. of tetramethylbiphosphine disulfide, m.p. 222–225°.

2. Notes

1. A suitable 3*M* solution of methylmagnesium bromide in diethyl ether can be purchased from Arapahoe Chemical Co., Boulder, Colorado.
2. Although practical grade thiophosphoryl chloride obtained from Eastman Organic Chemicals will serve in this reaction, a much cleaner product is obtained if the thiophosphoryl chloride is redistilled (b.p. 122–123°).
3. Tetramethylbiphosphine disulfide melts sharply at 227° when pure, but the material obtained as described above is satisfactory for most reactions.

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3. Discussion

Tetramethylbiphosphine disulfide has been prepared by reaction of methylmagnesium halides with thiophosphoryl chloride.^{2,3,4}

4. Merits of the Preparation

Tetramethylbiphosphine disulfide is an extremely versatile intermediate for the preparation of compounds containing two methyl groups on phosphorus, for example, dimethylphosphine.⁵ Most other methods for the preparation of such compounds give large amounts of mono- and trimethylated by-products. Tetramethylbiphosphine disulfide has been converted in high yields to dimethylphosphinic acid,^{3,4} dimethylphosphinyl chloride,^{4,6} dimethylchlorophosphine,⁷ and dimethylthiophosphinic bromide.⁸ Other tetraalkylbiphosphine disulfides have been converted to tetraalkylbiphosphines, dialkylthiophosphoryl bromides, and dialkylphosphinic anhydrides.⁹ Addition of tetramethylbiphosphine disulfide to ethylene followed by desulfurization gives tetramethylethylenediphosphine, a powerful chelating agent.¹⁰ Other alkyl Grignard reagents also react with thiophosphoryl chloride under the conditions of the present procedure to give the corresponding tetraalkylbiphosphine disulfides in high yield.^{5,11}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 7, 533

References and Notes

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Appendix

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

Tetramethylbiphosphine disulfide

Diphosphine, tetramethyl-, disulfide

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ether,

diethyl ether (60-29-7)

PHOSPHORUS (7723-14-0)

ethylene (9002-88-4)

methylmagnesium bromide (75-16-1)

thiophosphoryl chloride (3982-91-0)

dimethylphosphine (676-59-5)

dimethylphosphinic acid (3283-12-3)

dimethylphosphinyl chloride (1111-92-8)

dimethylchlorophosphine (811-62-1)

dimethylthiophosphinic bromide (6839-93-6)

tetramethylethylenediphosphine

phosphorus pentoxide (1314-56-3)

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