



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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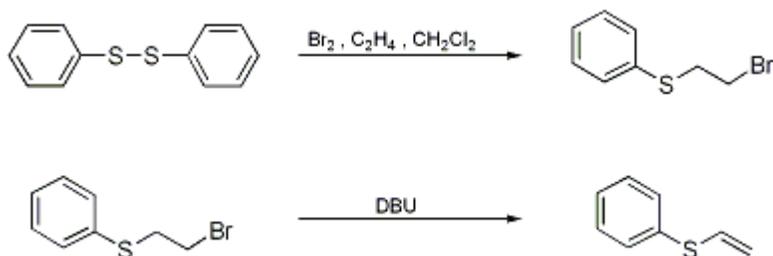
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 9, p.662 (1998); Vol. 74, p.124 (1997).

PHENYL VINYL SULFIDE

[Benzene, (ethenylthio)-]



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Checked by David A. Barda and William R. Roush.

1. Procedure

CAUTION! The intermediate, 1-phenylthio-2-bromoethane, produced in the first step of this one pot reaction sequence is a strong alkylating agent, and some bromine escapes from the reaction vessel. Therefore the reaction should be run in a properly operating ventilation hood, and care must be exercised to avoid exposure to these substances.

A 2-L, three-necked, round-bottomed flask fitted with a reflux condenser, an addition funnel, a magnetic stirring bar, thermometer, and nitrogen inlet is charged with diphenyl disulfide (200 g, 917 mmol) and dichloromethane (320 mL) (Note 1). The addition funnel is charged with bromine (161 g, 52 mL, 1.01 mol). After the diphenyl disulfide dissolves, the nitrogen inlet is replaced with a calcium sulfate-packed drying tube, and the flask is fitted with a gas-dispersion tube. Ethylene (73.1 g, 2.61 mol) (Note 2), (Note 3) is slowly bubbled into the solution through a gas dispersion tube, and the bromine is added in 2–3-mL portions over 5 hr (Note 4), (Note 5). After addition of the bromine and ethylene is complete, the drying tube is replaced with the nitrogen inlet, and the flask is fitted with a clean addition funnel. The addition funnel is charged with 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU, (306 g, 300 mL, 2.01 mol) (Note 6). DBU is added at a rate such that the temperature of the reaction mixture does not exceed 55°C. After the DBU is added the reaction mixture is maintained at about 50°C for 15–18 hr. A 1.0 M ammonium hydroxide solution (600 mL) is added to the reaction mixture, and the mixture is transferred to a separatory funnel. The layers are separated, and the aqueous layer is extracted with 300 mL of dichloromethane. The organic fractions are combined, washed with water (600 mL), and dried with 10 g of magnesium sulfate. The mixture is filtered, and the solvent is evaporated under reduced pressure. Distillation of the residue affords 162–184 g (65–74%) of phenyl vinyl sulfide, bp 80–84°C/11–12 mm (Note 7), (Note 8), (Note 9) and (Note 10). The purity is greater than 98% by GC analysis (Note 11), (Note 12).

2. Notes

- All the materials used in this process were obtained from the Aldrich Chemical Company, Inc., and were used as received.
- Initiation of the ethylene addition should precede the introduction of the first portion of bromine by 2–4 min. Ethylene is then added continuously at a slow rate until all the bromine is consumed (see (Note 4)).
- The submitters reported that use of less than 1.41 equiv (2.62 mol) of ethylene reduces the yield of product. The checkers used a 145–174- μm fritted gas dispersion tube, and up to 1.84 equiv of ethylene (3.38 mol) was required to consume all the bromine (see (Note 4)). However, on one occasion the checkers obtained excellent results (83% yield) using only 1.26 equiv of ethylene (2.30 mol). In this

instance, a 25–50- μm fritted gas dispersion tube was used, which permitted a slower and more efficient rate of [ethylene](#) introduction.

4. The first 2–3-mL portion of [bromine](#) is added until the reaction mixture is intensely violet. Subsequent portions of [bromine](#) are added when the reaction mixture fades to an amber color. After all the [bromine](#) has been added, [ethylene](#) addition is continued until the color fades to amber.

5. A competing process involving halogenation of the phenyl substituent occurs when the [bromine](#) concentration becomes too high. The slow addition of [bromine](#) specified here minimizes the competing aromatic bromination.

6. The submitters report that use of less than this amount of DBU reduces the yield of [phenyl vinyl sulfide](#).

7. The checkers obtained 204–207 g (82–84%) of [phenyl vinyl sulfide](#), bp 83–84°C/11–12 mm.

8. [Phenyl vinyl sulfide](#) has the following spectral properties: EI MS 136; ^1H NMR (400 MHz, CDCl_3) δ : 5.35 (d, 1 H, $J = 16.9$), 5.36 (d, 1 H, $J = 9.8$), 6.55 (dd, 1 H, $J = 9.8, 16.9$), 7.22–7.40 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ : 115.4, 127.1, 129.1, 130.4, 131.8, 134.2.

9. [Phenyl vinyl sulfide](#) prepared using this procedure is stable at room temperature under a [nitrogen](#) atmosphere for months. The submitters have kept samples for over nine months at ambient temperature without any visible degradation.

10. This procedure was used by the submitters to prepare 97 kg of [phenyl vinyl sulfide](#) from 100 kg of [diphenyl disulfide](#) (78% yield).

11. The GC analysis was performed with a Hewlett-Packard, HP-1 column (10 m \times 0.53 mm \times 2.65 μm). The temperature program was as follows: initial temperature, 50°C; initial time, 2.0 min; rate, 20° C/min; final temperature, 250°C; final time, 8 min.

12. The checkers identified the two major impurities as [p-bromophenyl vinyl sulfide](#) (see (Note 5)) and [2-chloroethyl phenyl sulfide](#) by GCMS analysis.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

[Phenyl vinyl sulfide](#) possesses a number of synthetically useful attributes. It participates as an electron-rich alkene in 1+2,³ 2+2,⁴ 3+2,⁵ and 4+2⁶ cycloaddition reactions. Deprotonation of [phenyl vinyl sulfide](#) with strong base affords an α -metallated sulfide that reacts with electrophiles.⁷ The metallation-electrophile sequence and the cycloaddition reactions afford products amenable to further synthetic manipulation via the sulfide functionality. Furthermore, [phenyl vinyl sulfide](#) is a convenient precursor to the synthetically useful [phenyl vinyl sulfoxide](#) and [phenyl vinyl sulfone](#).⁸

The procedure described here affords [phenyl vinyl sulfide](#) in a high yield using common reagents and mild conditions. The material obtained via this procedure is stable at room temperature under a [nitrogen](#) atmosphere for months. As indicated in (Note 10), this process is readily scaled up. Other methods either afford lower yields,^{8,9,10} less stable product,⁸ or require more extreme conditions.^{11,12}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 107](#)
- [Org. Syn. Coll. Vol. 9, 656](#)

References and Notes

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

DBU

[bromine](#) (7726-95-6)

[nitrogen](#) (7727-37-9)

[ethylene](#) (9002-88-4)

[ammonium hydroxide](#) (1336-21-6)

[dichloromethane](#) (75-09-2)

[magnesium sulfate](#) (7487-88-9)

[diphenyl disulfide](#) (882-33-7)

[Phenyl vinyl sulfone](#) (5535-48-8)

[1-Phenylthio-2-bromoethane](#) (4837-01-8)

[Phenyl vinyl sulfide,](#)
[Benzene, \(ethenylthio\)-](#) (1822-73-7)

[Phenyl vinyl sulfoxide](#) (20451-53-0)

[1,8-diazabicyclo\[5.4.0\]undec-7-ene](#) (6674-22-2)

p-bromophenyl vinyl sulfide

2-chloroethyl phenyl sulfide (5535-49-9)

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