



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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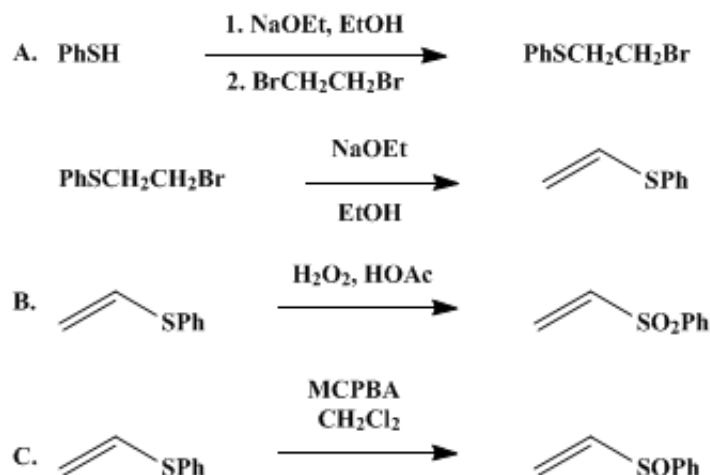
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

## PHENYL VINYL SULFONE AND SULFOXIDE

[Benzene, (ethenylsulfonyl)- and benzene, (ethenylsulfiny)-]



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### 1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

*Caution! 1-Phenylthio-2-bromoethane is a powerful alkylating agent that causes severe skin blistering. Although the present one-pot procedure eliminates the cumbersome handling of this intermediate, due care must be exercised to avoid exposure to this substance.*

A. *Phenyl vinyl sulfide*. In a 1-L, three-necked, round-bottomed flask fitted with magnetic stirrer, condenser, addition funnel, and nitrogen-inlet tube is placed 400 mL of ethanol. Sodium metal (23 g, 1 g-atom), cut into small pieces, is added with stirring. When conversion to sodium ethoxide is complete (5–15 min), the stopper of the addition funnel is removed under a positive flow of nitrogen, and benzenethiol (110 g, 1 mol) is poured into the addition funnel. The stopper is put in place, and the benzenethiol is added over 15–20 min to the cloudy, gray sodium ethoxide solution. The reaction mixture warms spontaneously and becomes clear brown. At 25°C this solution is transferred by stainless-steel cannula (Note 1) over 45 min to a stirred solution of 1,2-dibromoethane (272 g, 1.45 mol) in ethanol (28 mL) contained in a 2-L, three-necked round-bottomed flask equipped with a mechanical stirrer, addition

funnel, reflux condenser, nitrogen-inlet tube, and internal thermometer (Note 2). The reaction temperature is maintained at 25–30°C by cooling with an ice bath. The mixture is stirred under nitrogen for 30 min and treated for an additional 30 min with ethanolic sodium ethoxide prepared from 40 g (2.17 g-atom) of sodium and 800 mL of ethanol (Note 3). The resulting mixture is stirred at reflux for 8 hr (Note 4), cooled, and treated with 750 mL of benzene and 750 mL of water. The organic layer is separated, washed with water (2 × 50 mL) and brine (100 mL), and concentrated by rotary evaporation. The yellow oil that results is distilled to give 70–87 g (50–65%) of phenyl vinyl sulfide, bp 91–93°C/20 mm (Note 5) and (Note 6).

B. *Phenyl vinyl sulfone*. In a 250-mL, three-necked, round-bottomed flask fitted with a magnetic stirrer, condenser, addition funnel, and thermometer is placed 19.7 g (0.145 mol) of phenyl vinyl sulfide dissolved in 70 mL of glacial acetic acid. Hydrogen peroxide (30%, 56 mL, 0.5 mol) is added slowly at such a rate to maintain a reaction temperature of 70°C (Note 7). The reaction mixture is heated at reflux for 20 min, cooled, and treated with ether (150 mL) and water (200 mL). The organic phase is separated, washed with water (50 mL) and brine (50 mL), and concentrated at 70°C/0.3 mm for 3 hr to afford 18–19 g (74–78%) of phenyl vinyl sulfone as a colorless solid, mp 64–65°C. Although this material is sufficiently pure for most purposes, recrystallization from hexane affords colorless crystals, mp 66–67°C (Note 8).

C. *Phenyl vinyl sulfoxide*. A 500 mL, three-necked, round-bottomed flask equipped with a dropping funnel and magnetic stirrer is charged with 20 g (0.147 mol) of phenyl vinyl sulfide and 250 mL of dichloromethane. The solution is stirred and cooled to –78°C while a solution of *m*-chloroperbenzoic acid (25.4 g, 1.0 equiv) in 200 mL of dichloromethane is added dropwise during a 30-min period. The mixture is stirred and warmed to room temperature for 1 hr in a water bath at 30°C. The mixture is then poured into 300 mL of saturated sodium bicarbonate solution, and the mixture is extracted with three 250-mL portions of dichloromethane. The combined organic extracts are washed with three 250-mL portions of water and dried over anhydrous magnesium sulfate. The solvent is removed by rotary evaporation and the residual liquid is distilled to afford 15–16 g (68–70%) of phenyl vinyl sulfoxide as a colorless liquid, bp 98°C/0.6 mm (Note 9) and (Note 10).

## 2. Notes

1. The cannula is a stainless-steel tube, 16-gauge, sharpened to a needle at both ends, and 60 cm long. One end is placed through a rubber septum into the flask containing the 1,2-dibromoethane solution, while the other end is positioned under the surface of the benzenethiolate solution. Control of the nitrogen pressure allows slow transfer of the benzenethiolate solution.
2. The yield in the previously published method for the preparation of this sulfide is low, affording chiefly 1,2-bis(phenylthio)ethane.<sup>2</sup> The problem is overcome here by utilization of an inverse addition procedure.
3. Alternatively, dry powered sodium ethoxide may be substituted with a corresponding reduction of the reaction volume.
4. Thin-layer chromatographic analysis at this stage shows that 1-phenylthio-2-bromoethane is absent.
5. This product has the following spectral properties: IR (neat)  $\text{cm}^{-1}$ : 3040, 1585, 1475, 1435, 1085, 1020, 950, 735, and 680;  $^1\text{H}$  NMR (chloroform-*d*)  $\delta$ : 5.25 (superimposed doublets, 2 H,  $J = 12$  and 18, terminal vinyl), 6.50 (dd, 1 H,  $J = 12$  and 18, olefinic), 7.32 (m, 5 H, aromatic).
6. When stored at room temperature, phenyl vinyl sulfide becomes yellow-colored within 1 day and a black syrup after 1 week. This decomposition can be substantially retarded by storage under a nitrogen or argon atmosphere in a freezer.
7. The submitter observed the temperature increase to 70°C during addition of the first 10 mL of hydrogen peroxide. The checkers noted that the mixture never rose in temperature to 70°C.
8. This product has the following spectral properties: IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3020, 1445, 1380, 1315, 1145, 1080, and 965;  $^1\text{H}$  NMR (chloroform-*d*)  $\delta$ : 5.96 (d, 1 H,  $J = 10$ , olefinic), 6.33 (d, 1 H,  $J = 17$ , olefinic), 6.75 (dd, 1 H,  $J = 10$  and 17, olefinic), 7.55 (m, 3 H, aromatic), 7.85 (m, 2 H, aromatic).
9. Earlier citations<sup>3</sup> report bp 105–110°C (1.5 mm) and 93–95°C (0.2 mm).
10. This product has the following spectral properties: IR (neat)  $\text{cm}^{-1}$ : 3025, 1720, 1680, 1480, 1440,

1045, 750, and 690; <sup>1</sup>H NMR (chloroform-*d*) δ: 5.63–6.17 (m, 2 H, olefinic H), 6.44–6.87 (m, 1 H, olefinic H), 7.10–7.55 (m, 5 H, aromatic H).

### 3. Discussion

The procedure for oxidation of the sulfide to the sulfone is based on that reported earlier by Bordwell and Pitt.<sup>4</sup> The synthetic utility of [phenyl vinyl sulfone](#) and sulfoxide derives not only from their ability to serve as excellent Michael acceptors toward such reagents as enolate anions and organometallics<sup>5,6,7,8,9,10,11,12</sup> but also as moderately reactive dienophiles in Diels–Alder reactions.<sup>13,14,15,16</sup> The resulting adducts, in turn, can be chemically modified so that these electron-deficient olefins serve as useful synthons for [acetylene](#),<sup>13</sup> [ethylene](#),<sup>14</sup> terminal olefins,<sup>15</sup> vinylsilanes,<sup>17</sup> and [ketene](#)<sup>18</sup> in [4 + 2] cycloadditions. [Phenyl vinyl sulfone](#) undergoes ready cycloaddition to Danishefsky's diene in the first step of a protocol for the regiospecific  $\gamma$ -alkylation of 2-cyclohexenones.<sup>19</sup> Furthermore, the ready lithiation of phenyl vinyl sulfones<sup>20</sup> and sulfoxides<sup>21</sup> represents a convenient route to  $\alpha$ -(phenylsulfonyl) and  $\alpha$ -(phenylsulfinyl)vinylolithium reagents.

The method described here for the preparation of [phenyl vinyl sulfoxide](#) is superior to that involving reaction of [ethyl phenyl sulfinite](#) with [vinylmagnesium bromide](#).<sup>13</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 107](#)
- [Org. Syn. Coll. Vol. 9, 656](#)
- [Org. Syn. Coll. Vol. 9, 662](#)

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### References and Notes

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

brine

PHENYL VINYL SULFONE AND SULFOXIDE

benzene, (ethenylsulfiny)-

2-cyclohexenones

ethanol (64-17-5)

acetylene (74-86-2)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

sodium bicarbonate (144-55-8)

nitrogen (7727-37-9)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

ethylene (9002-88-4)

1,2-dibromoethane (106-93-4)

hydrogen peroxide (7722-84-1)

vinylmagnesium bromide (1826-67-1)

Ketene (463-51-4)

dichloromethane (75-09-2)

Benzenethiol (108-98-5)

magnesium sulfate (7487-88-9)

hexane (110-54-3)

argon (7440-37-1)

Phenyl vinyl sulfone,  
Benzene, (ethenylsulfonyl)- (5535-48-8)

1-Phenylthio-2-bromoethane (4837-01-8)

Phenyl vinyl sulfide (1822-73-7)

Phenyl vinyl sulfoxide (20451-53-0)

benzenethiolate

1,2-bis(phenylthio)ethane (622-20-8)

ethyl phenyl sulfinat

m-Chloroperbenzoic acid (937-14-4)