



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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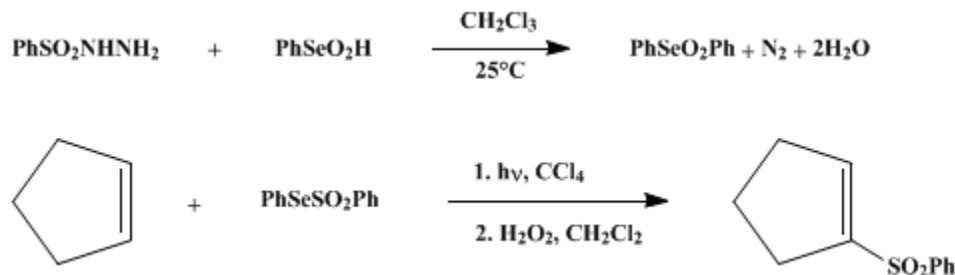
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## DIENOPHILE ACTIVATION VIA SELENOSULFONATION: 1-(PHENYLSULFONYL)CYCLOPENTENE

[Benzene, (1-cyclopenten-1-ylsulfonyl)-]



Submitted by Ho-Shen Lin, Michael J. Coghlan, and Leo A. Paquette<sup>1</sup>.  
Checked by Tony Haight and Edwin Vedejs.

### 1. Procedure

A. *Phenyl benzeneselenosulfonate*. A 1-L, three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a 250-mL addition funnel containing 17.2 g (100 mmol) of benzenesulfonyl hydrazide (Note 1) and 125 mL of dichloromethane is charged with 18.9 g (100 mmol) of phenylseleninic acid (Note 1) and 125 mL of dichloromethane. The seleninic acid is stirred at 25°C as the hydrazide slurry is added over 1 hr (Note 2). After an additional hour at 25°C, the reaction mixture is dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue is dissolved in 250 mL of hot methanol and the solution of selenosulfonate is cooled overnight at ca. 5°C in a refrigerator to induce crystallization. The yellow product that precipitates is filtered and recrystallized from methanol to afford 24.3–25.2 g (83–85%) of phenyl benzeneselenosulfonate, mp 56°C (Note 3).

B. *1-(Phenylsulfonyl)cyclopentene*. A one-necked, flat-bottomed, cylindrical flask (5 cm in diameter and 23 cm in height) equipped with a Teflon-coated magnetic stirring bar is charged in turn with phenyl benzeneselenosulfonate (15.0 g, 50.5 mmol), carbon tetrachloride (160 mL), and cyclopentene (11.1 mL, 126 mmol) (Note 4). The flask is equipped with a Friedrichs condenser and the stirred reaction mixture is blanketed with nitrogen. Following irradiation with 150-W sunlamp at room temperature for 45 min, the solution is transferred to a 500-mL, one-necked, round-bottomed flask and concentrated on a rotary evaporator.

A Teflon-coated magnetic stirring bar is placed atop the residue, which is dissolved in 140 mL of dichloromethane. The stirred solution is cooled in an ice–water bath to 0°C as 60 mL of 15% hydrogen peroxide is added dropwise via an addition funnel over 30 min (Note 5). Vigorous stirring is maintained at this temperature for 1.5 hr. The mixture is transferred to a 1-L separatory funnel, diluted with 400 mL of ethyl acetate and washed twice with 150-mL portions of water. The organic layer is dried over anhydrous magnesium sulfate, filtered, and freed of solvent under reduced pressure. The residual yellowish solid is dissolved in a small amount of dichloromethane and eluted with 5% ethyl acetate in dichloromethane through a column of 80 g of neutral alumina (activity III) to afford 8.28–9.19 g (79–87%) of colorless crystals, mp 65–66°C. <sup>1</sup>H NMR analysis shows this material to be of very high purity (Note 6).

### 2. Notes

1. Benzenesulfonyl hydrazide is available from the Fluka Chemical Company, 255 Oser Avenue, Hauppauge, NY 11788.
2. This addition time ensures a slow, steady evolution of nitrogen during admixture of both slurried

reactants.

3. Although this selenosulfonate is temperature- and light-sensitive, it can be stored indefinitely at refrigerator temperatures in an opaque glass container.<sup>2</sup>

4. Cyclopentene was purchased from the Aldrich Chemical Company, Inc. and used without further purification.


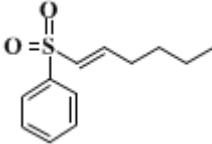

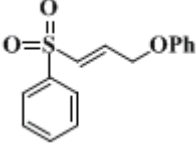

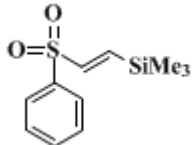
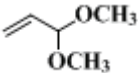
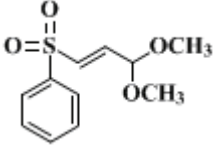
5. The peroxide is added at such a rate that the mildly exothermic oxidation–elimination reaction is well controlled. Faster addition of hydrogen peroxide can result in uncontrollable foaming.

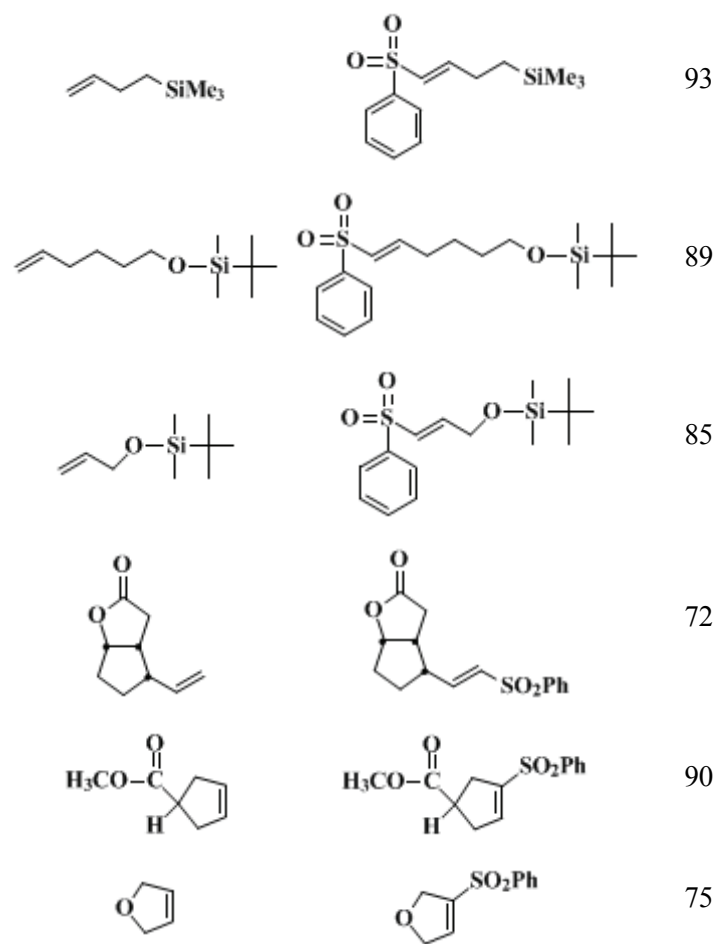
6. The product has the following spectral properties: IR (KBr)  $\text{cm}^{-1}$ : 3060, 2960, 2920, 2840, 1610, 1580, 1440, 1300, 1150, 1085, 935, 825, 745, 710, 680, 600;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.8–2.2 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{-CH}_2$ ), 2.2–2.6 (m, 4 H,  $\text{CH}_2\text{C=}$ ), 6.6 (br s, 1 H, =CH), 7.3–8.0 (m, 5 H);  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$ : 208.0558. Found 208.0553. Anal. calcd. for  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$ : C, 63.43, H, 5.81. Found: C, 63.49; H, 5.83.

### 3. Discussion

Recent investigations into the chemistry of vinyl sulfones have revealed that they are versatile synthetic intermediates, serving either as dienophiles<sup>3</sup> or Michael acceptors.<sup>4</sup> Methods for the preparation of vinyl sulfones from unactivated olefins have customarily involved the catalyzed (boron trifluoride or benzoyl peroxide) addition of  $\text{PhSO}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or SePh}$ ), followed by elimination of  $\text{HX}$ .<sup>5</sup> However, when phenylsulfonyl halides are employed, yields are variable, reactions are frequently incomplete, and the Lewis acid or free-radical catalyst employed can potentially interfere with any other functionality present. On the other hand, the selenosulfonation method, particularly when photochemically induced,<sup>3,6</sup> proceeds smoothly to completion in high yield and is compatible with several functional groups (Table I).<sup>3</sup> A further consequence of the *trans* disposition of the phenylselenenyl and phenylsulfonyl groups is invariant elimination to give the  $\alpha,\beta$ -unsaturated sulfone.

TABLE I  
PHOTOINDUCED SELENOSULFONATION–ELIMINATION OF  
OLEFINS

Olefin	Product	Yield(%)
		62
		89
		84
		73



This preparation is referenced from:

- [Org. Syn. Coll. Vol. 8, 38](#)

## References and Notes

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

ethyl acetate (141-78-6)

methanol (67-56-1)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

hydrogen peroxide,  
peroxide (7722-84-1)

dichloromethane (75-09-2)

benzoyl peroxide (94-36-0)

magnesium sulfate (7487-88-9)

Cyclopentene (142-29-0)

boron trifluoride (7637-07-2)

vinyl (2669-89-8)

benzenesulfonyl hydrazide (80-17-1)

phenylsulfonyl

phenylselenenyl

phenylseleninic acid (6996-92-5)

1-(Phenylsulfonyl)cyclopentene,  
Benzene, (1-cyclopenten-1-ylsulfonyl)- (64740-90-5)

Phenyl benzeneselenosulfonate (60805-71-2)