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](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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red “Caution Notes” within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.*
DIENOPHILE ACTIVATION VIA SELENOSULFONATION: 1-(PHENYLSULFONYL)CYCLOPENTENE

[Benzen(e, (1-cyclopenten-1-ylsulfonyl)-]

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. 1H 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
3. Although this selenosulfonate is temperature- and light-sensitive, it can be stored indefinitely at refrigerator temperatures in an opaque glass container.2
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) cm⁻¹: 3060, 2960, 2920, 2840, 1610, 1580, 1440, 1300, 1150, 1085, 935, 825, 745, 710, 680, 600; ¹H NMR (CDCl₃) δ: 1.8–2.2 (m, 2 H, CH₂CH₂-CH₂), 2.2–2.6 (m, 4 H, CH₂C=), 6.6 (br s, 1 H, =CH), 7.3–8.0 (m, 5 H); m/z calcd. for C₁₁H₁₂O₂S: 208.0558. Found 208.0553. Anal. calcd. for C₁₁H₁₂O₂S: 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 dienophiles³ or Michael acceptors.⁴ Methods for the preparation of vinyl sulfones from unactivated olefins have customarily involved the catalyzed (boron trifluoride or benzoyl peroxide) addition of PhSO₂X (X = Cl, Br, I, or SePh), followed by elimination of HX.⁵ 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,³,⁶ proceeds smoothly to completion in high yield and is compatible with several functional groups (Table I).³ A further consequence of the trans disposition of the phenylselenenyl and phenylsulfonyl groups is invariant elimination to give the α,β-unsaturated sulfone.

| TABLE I |
| PHOTINDUCED SELENOSULFONATION–ELIMINATION OF OLEFINS |
| Olefin | Product | Yield(%) |
| O═S | O═S | 62 |
| OPh | O═S | 89 |
| SiMe₃ | O═S | 84 |
| OCH₃ | O═S | 73 |
This preparation is referenced from:


**References and Notes**

1. Department of Chemistry, The Ohio State University, Columbus, OH 43210.
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)
v 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)