

SELENOSULFONATION OF ACETYLENES.  
PREPARATION OF NOVEL  $\beta$ -(PHENYLSELENO)VINYL SULFONES<sup>1a</sup>

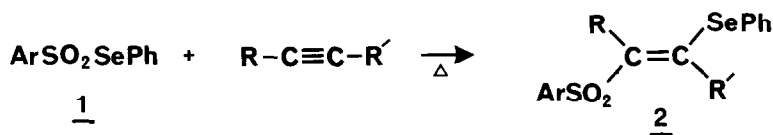
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T2N 1N4

**Abstract:** Se-Phenyl p-tolueneselenosulfonate (1) undergoes thermal addition to acetylenes to afford  $\beta$ -(phenylseleno)vinyl sulfone adducts 2 in a stereo- and regioselective fashion.

We recently reported that Se-phenyl areneselenosulfonates (e.g. 1) add to olefins on heating or at room temperature in the presence of boron trifluoride etherate to give  $\beta$ -(phenylseleno) sulfones<sup>2</sup>. Lewis acid-catalyzed additions of 1 to olefins proceed with predominantly Markovnikoff orientation and are stereospecifically anti. An electrophilic addition mechanism involving bridged seleniranium ions has been proposed<sup>2b</sup>. In contrast, thermally initiated additions of 1 afford adducts of opposite regiochemistry and are nonstereospecific. A free radical addition mechanism has been implicated in this case<sup>2b,3</sup>.

We now report that 1 adds to acetylenes under thermal conditions to afford  $\beta$ -(phenylseleno)vinyl sulfones 2<sup>4</sup> (eqn. 1).

eqn. 1

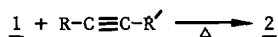


Ar = p-tolyl



This result confirms that the addition of 1 to phenylacetylene proceeds with anti orientation<sup>7</sup>. Since the elimination of selenoxides occurs stereospecifically syn<sup>8</sup>, the phenylseleno moiety in 2b must be cis to the vinylic hydrogen atom. Furthermore, this experiment suggests that the selenosulfonation of acetylenes, followed by oxidation - elimination, may offer a simple, efficient route to acetylenic sulfones<sup>9</sup>.

The synthetic utility of adducts 2 and the selenosulfonation of other unsaturated systems is under continued investigation in this laboratory.

Table<sup>a</sup>

Product	R	R'	Method (Time, h) <sup>b</sup>	Yield (%)	Mp (°C)
<u>2a</u>	H <sub>A</sub>	H <sub>B</sub>	A (72)	45 <sup>c</sup>	107-109
<u>2b</u>	Ph	H	B (72) C (4)	86 93	152
<u>2c</u>	-CO <sub>2</sub> Me	H	D (96)	70	90-92
<u>2d</u>	-(CH <sub>2</sub> ) <sub>7</sub> Me	H	B (84)	82	oil
<u>2e</u>	Ph	Ph	B (72)	52	176-178

a) All products were characterized by their IR, <sup>1</sup>H-NMR and mass spectra; all products gave satisfactory combustion analyses and were homogeneous (tlc, gc).

b) A- the reactants were heated in dichloromethane solution at 70° in a pressure vessel. B- performed at reflux in benzene solution. C- performed at reflux in benzene solution in the presence of 5 mole % of AIBN. D- performed at reflux in chloroform solution.

c) Since an excess of acetylene was used, the yield of 2 is based on 1.

References and Notes

1. a) Financial support from the Natural Sciences and Engineering Research Council of Canada and the Research Corporation is gratefully acknowledged. b) Recipient of an NSERC Postgraduate Scholarship.
2. a) T.G. Back and S. Collins, Tetrahedron Lett., 1980, 2215. b) T.G. Back and S. Collins, J. Org. Chem., 1981, 46, 3249.
3. The photochemical addition of 1 to olefins has also been reported: R.A. Gancarz and J.L. Kice, Tetrahedron Lett., 1980, 4155.
4. Thermal additions of selenosulfonates to acetylenes and olefins have been independently observed by M. Kobayashi and T. Miura, Abstr. of the 9th Internat. Symp. on Org. Sulfur Chem., Riga, U.S.S.R., June, 1980, p. 165.
5. Related additions of sulfonyl iodides and bromides to acetylenes under thermal conditions are known. See inter alia: a) W.E. Truce and G.C. Wolf, J. Org. Chem., 1971, 36, 1727. b) Y. Amiel, Ibid., 1974, 39, 3867.
6. Mp 83-84 °C, (lit.<sup>5a</sup> mp 83-84 °C).
7. Although the stereochemistry of the addition was shown to be anti for 2a and 2b; such a conclusion is tentative for the other adducts in the Table.
8. The syn eliminations of other vinyl selenoxides have been reported: H.J. Reich and W.W. Willis Jr., J. Amer. Chem. Soc., 1980, 102, 5968.
9. Acetylenic sulfones are of considerable synthetic interest. For a review see: a) P.D. Magnus, Tetrahedron, 1977, 33, 2019. For more recent examples see: b) A.P. Davis and G.H. Whitham, J. Chem. Soc., Chem. Commun., 1980, 639. c) B.B. Snider, T.C. Kirk, D.M. Roush and D. Gonzalez, J. Org. Chem., 1980, 45, 5015, and references cited therein.

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