

BENZESELENYNYL *p*-TOLUENESULFONATE: FORMATION AND ELECTROPHILIC ADDITION TO ACETYLENES

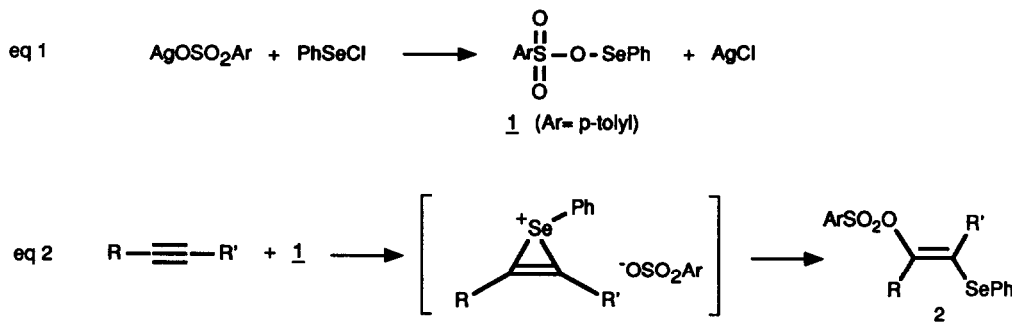
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Summary: The title compound **1** was produced in situ from PhSeCl and AgOSO₂Ar (Ar= *p*-tolyl), and underwent electrophilic addition to acetylenes to afford adducts **2**. The same products were unexpectedly formed from the reaction of ArSO₃H and AIBN, or from the pyrolysis of ArS(O)SO₂Ar, in the presence of acetylenes and PhSeSePh.

Selenenic electrophiles have numerous synthetic applications and display interesting mechanistic behaviour.¹ Examples of these compounds include selenenyl halides (RSeX), acetates (RSeOAc) and trifluoroacetates (RSeOC(O)CF₃), as well as selenoimides (N-phenylselenophthalimide and N-phenylseleno-succinimide), selenocyanates (RSeCN) and selenosulfonates (RSeSO₂R'). However, to our best knowledge, selenenyl sulfonates (RSeOSO₂R') are as yet unknown.

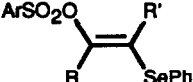
We wish to report that benzeneselenenyl *p*-toluenesulfonate (**1**) can be prepared in situ from the direct substitution of benzeneselenenyl chloride with silver *p*-toluenesulfonate in acetonitrile (Method A), as shown in eq 1. The unstable product **1** undergoes efficient electrophilic 1,2-additions to acetylenes to produce β-(phenylseleno)vinyl *p*-toluenesulfonates **2**, according to eq 2. The results are summarized in Table 1.



The addition of **1** to acetylene occurred in an *anti* stereospecific fashion, consistent with the bridged selenirenium ion intermediate² shown in eq 2. The *trans* configuration of the product **2a** was assigned on the basis of the observed coupling constant $J_{trans} = 12.3$ Hz for the vinylic signals at δ 6.31 and δ 6.79.³ The other products in Table 1 were also formed in a highly stereospecific manner and we tentatively assign the *trans* configuration to them by analogy. 1-Decyne afforded nearly equal amounts of the two possible regioisomers **2b** and **2c**, as determined by NMR integration of their respective vinylic signals at δ 6.12 and δ 6.82. On the other hand, products **2d-2f** were obtained as unique (>95%) stereo- and regioisomers. The indicated

Markovnikoff regiochemistry for **2d** was confirmed by its nearly quantitative conversion to 1-phenylethanol, instead of to 2-phenylethanol, by reduction with excess lithium aluminum hydride. These results indicate that the addition only displays high regioselectivity with acetylenes that have strongly orienting groups, such as the phenyl group.

Surprisingly, we observed the formation of the same adducts **2** when ca. equimolar amounts of p-toluenesulfonic acid, diphenyl diselenide, azobis(isobutyronitrile) (AIBN) and the acetylene were refluxed overnight in benzene (Method B). Moreover, compounds **2** were also formed when ca. equimolar amounts of sulfinyl sulfone **3**,⁴ diphenyl diselenide and the acetylene were treated under similar conditions (Method C). These results are also included in Table 1. In all cases, the products were easily isolated by preparative TLC or flash chromatography on silica-gel.

Table 1. Preparation of  (**2**)^a from R-C≡C-R'

No.	R	R'	Method ^b	Yield (%) ^c	mp
2a	H	H	A	51	49-50 ^o
2b	$\left\{ \begin{array}{cc} n\text{-C}_8\text{H}_{17} & \text{H} \\ \text{H} & n\text{-C}_8\text{H}_{17} \end{array} \right\}$	$\left\{ \begin{array}{cc} \text{H} & n\text{-C}_8\text{H}_{17} \\ n\text{-C}_8\text{H}_{17} & \text{H} \end{array} \right\}$	A	81 (2b:2c= 57:43)	oil
2c			B	85 (2b:2c= 55:45)	
			C	68 (2b:2c= 53:47)	
2d	Ph	H	A	62	80-81 ^o
			B	40	
			C	23	
2e	Ph	Me	A	75	75-76 ^o
2f	n-Bu	n-Bu	A	84	oil
			B	56	
			C	52	

a) Ar= p-tolyl

b) Method A: AgOSO₂Ar, PhSeCl, RC≡CR'; MeCN, room temp., ca. 16 h. Method B: ArSO₃H, AIBN, PhSeSePh, RC≡CR'; C₆H₆, reflux, 6-16 h. Method C: ArS(O)SO₂Ar, PhSeSePh, RC≡CR'; C₆H₆, reflux, ca. 16 h.

c) Isolated yields are reported; all products were characterized by IR, NMR and mass spectroscopy; all new compounds gave satisfactory elemental analyses or high resolution mass spectra.

A plausible mechanism for the formation of **2** under the conditions of Method B is shown in Scheme 1, where sulfonate radicals (ArSO₃•) are produced via hydrogen atom abstraction from the sulfonic acid by free radicals generated from the pyrolysis of AIBN.⁵ The sulfonate radicals then react with the diselenide⁶ to

A. Furthermore, the same Markovnikoff regioisomer **2d** was produced from phenylacetylene by all three Methods, albeit in lower yield via Methods B and C. In principle, these results could also be explained by the free-radical addition of **1** to the acetylene, followed by equilibration of initially formed *anti*Markovnikoff isomers. However, the *anti*Markovnikoff isomer **2c** did not isomerize to **2b** when refluxed in benzene alone or in the presence of diphenyl diselenide and p-toluenesulfonic acid.¹⁰ These observations all support the mechanisms in Schemes 1 and 2. Further studies of the novel electrophile **1** and the adducts **2** are in progress.

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References

1. For a review of electrophilic reactions of selenium compounds, see: a) T.G. Back in *"Organoselenium Chemistry"*, ed. D. Liotta, Wiley, New York, 1987, Chapter 1. For other recent reviews of organoselenium chemistry, see: b) *"The Chemistry of Organic Selenium and Tellurium Compounds"*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, Vol. 1, 1986, and Vol. 2, 1987. c) C. Paulmier in *"Selenium Reagents and Intermediates in Organic Synthesis"* Pergamon Press, Oxford, 1986. d) K.C. Nicolaou and N.A. Petasis in *"Selenium in Natural Products Synthesis"*, CIS, Philadelphia, 1984.
2. a) G.H. Schmid and D.G. Garratt, *Tetrahedron Lett.*, 3991 (1975). b) G.H. Schmid and D.G. Garratt, *Chem. Scr.*, 10, 76 (1976).
3. A small amount of the *cis* adduct was detected in the crude product (*trans:cis*= 9:1), but was not isolated. It had olefinic signals at δ 6.04 and δ 6.87 with J_{cis} = 5.1 Hz. These values compare favourably with the coupling constants for the *cis* and *trans* adducts of PhSeCl with acetylene, where J_{cis} = 6.3 Hz and J_{trans} = 13.6 Hz (see ref. 2b), and for the adducts of other ArSeX species; see: E.G. Kataev, T.G. Mannafov and Y.Y. Samitov, *Zh. Org. Khim.*, 11, 2324 (1975). An IR peak at 924 cm^{-1} confirms the *trans* assignment to the major isomer.
4. H. Bredereck, A. Wagner, H. Beck and R.-J. Klein, *Ber.*, 93, 2736 (1960).
5. For the free-radical decomposition of AIBN see: D.C. Nonhebel and J.C. Walton in *"Free-radical Chemistry"*, Cambridge University Press, Cambridge, 1974, pp. 25-26. The competing reaction of radicals produced from AIBN with the diselenide also occurred, as identical byproducts were formed to those from a control experiment where AIBN and the diselenide were refluxed in benzene.
6. The diselenide is a good radical trapping agent: a) M.J. Perkins and E.S. Turner, *J. Chem. Soc., Chem. Commun.*, 139, (1981). b) G.A. Russell and H. Tashtoush, *J. Am. Chem. Soc.*, 105, 1398 (1983). c) T.G. Back and M.V. Krishna, *J. Org. Chem.*, 53, 2533 (1988).
7. J.L. Kice and N.E. Pawlowski, *J. Am. Chem. Soc.*, 86, 4898 (1964).
8. a) Minor amounts of selenosulfonation^{8b} products were also observed, indicating that ArSO₂• radicals formed from **3** can add to the acetylene in a competing process. b) T.G. Back, S. Collins and R.G. Kerr, *J. Org. Chem.*, 48, 3077 (1983).
9. a) The same adducts **2b** and **2c** were also formed when **4** was produced from PhSeCl and AgOSO₂Ar,^{9b} and stirred with PhSeSePh and 1-decyne. This confirms that the disproportionation is possible. We did not observe any significant electrophilic addition of **4** to the acetylenes, suggesting that it is a less reactive electrophile than the selenium analogue **1**. b) G. Capozzi, G. Melloni and G. Modena, *J. Chem. Soc. (C)*, 2617 (1970).
10. The sample of **2** used in these control experiments had **2b:2c** = 1:9. It was obtained by the partial separation of the usual mixture of **2b** and **2c** by flash chromatography.

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