Addition of Phenyl Areneselenosulphonates to Acetylenes: a Route to Acetylenic Sulphones

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Treatment of phenyl areneselenosulphonates (**1**) with terminal acetylenes resulted in the formation of β-(phenylseleno)vinyl sulphones (**2**), which on treatment with excess of hydrogen peroxide in tetrahydrofuran at room temperature gave acetylenic sulphones (**3**) in good yields.

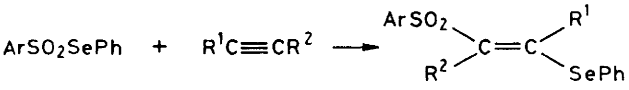
We[1] and others[2,3] have recently reported the addition reactions of phenyl areneselenosulphonates (**1**) to olefins. We now report that selenosulphonates (**1**) also react with numerous acetylenes to give β-(phenylseleno)vinyl sulphones (**2**), which afford acetylenic sulphones (**3**) by *syn*-elimination of the selenoxide under very mild conditions. This addition of selenosulphonates (**1**) to acetylenes appears to be new, and is a useful reaction.

Reich and Willis[4] recently reported the formation of acetylenes and allenes by *syn*-elimination of vinyl selenoxides. In

Table 1. Addition reactions of (**1**) to acetylenes.

Seleno-sulphonate	Acetylene	Reaction Time/h	Temp.[a]	Product[b]	Yield, %[c]
(**1a**)	$PhC{\equiv}CH$	16	A	(**2a**)	86
(**1a**)	p-$BrC_6H_4C{\equiv}CH$	18	A	(**2b**)	83
(**1b**)	p-$MeC_6H_4C{\equiv}CH$	16	A	(**2c**)	79
(**1a**)	$Me[CH_2]_4C{\equiv}CH$	18	B	(**2d**)	52
(**1a**)	$MeOCH_2C{\equiv}CH$	48	B	(**2e**)	59
(**1a**)	$EtC{\equiv}CEt$	16	B	(**2f**)	75

[a] A: C_6H_6, reflux. B: sealed glass tube, 80 °C. [b] All products were identified by their ^1H n.m.r., i.r., and elemental analysis. [c] The yields refer to pure isolated products.



(1) **(2)**

	Ar
a;	Tol
b;	Ph

	R^1	R^2	Ar
a;	Ph	H	Tol
b;	p-BrC_6H_4	H	Tol
c;	Tol	H	Ph
d;	$Me[CH_2]_4$	H	Tol
e;	$MeOCH_2$	H	Tol
f;	Et	Et	Tol

Tol = p-MeC_6H_4

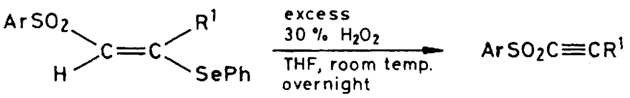
Scheme 1

their work, high temperatures and the presence of special amines such as 1,4-diazabicyclo[2.2.2]octane were required. We found that elimination from the selenoxyvinyl sulphones **(2)**, by oxidation with hydrogen peroxide, occurred very readily at room temperature with high yield.

The addition of selenosulphonates **(1)** to acetylenes was carried out as follows: a solution of **(1a)** (2.0 mmol) and phenylacetylene (2.5 mmol) in 10 ml of benzene was refluxed for 16 h. After evaporation to remove the solvent, the residual solid was purified by column chromatography on silica gel using hexane–ether as eluant. Recrystallization from ethanol afforded the *trans*-β-(phenylseleno)vinyl sulphone **(2a)** in 86% yield. Results for a series of acetylenes are shown in Table 1. The addition occurred in a highly stereoselective fashion (Scheme 1).

Mechanistically, it seems that the product **(2)** was formed either partially or entirely *via* a free radical intermediate, since thermolysis of **(1a)** in benzene in the presence of 2-methyl-2-nitrosopropane led to the detection of e.s.r. signals from the adducts formed by trapping the p-tolyl sulphonyl radical:[5] $g = 2.0063$; $a_N = 12.4$ G. In addition, the formation of **(2a)** was suppressed by the addition of 2-methyl-2-nitrosopropane to a solution of **(1a)** and phenylacetylene in benzene. Treatment of **(1a)** with 1.2 equiv. of phenylacetylene in benzene in the presence of 1.0 equiv. of 2-methyl-2-nitrosopropane at 80 °C for 16 h gave only 6% of **(2a)**.

β-(Phenylseleno)vinyl sulphones **(2)** derived from **(1)** and terminal acetylenes are converted smoothly with excess of hydrogen peroxide into acetylenic sulphones **(3)** (Scheme 2). For example, the oxidation of **(2a)** with 4 equiv. of 30% hydrogen peroxide in tetrahydrofuran (THF) at room temperature gave 1-phenyl-2-p-tolylsulphonylethyne[6] **(3a)** in 93% yield. The results are summarized in Table 2.



(2) **(3)**

Scheme 2

Table 2. Oxidation of **(2)** with hydrogen peroxide.[a]

Vinyl sulphone	Product[b]	Yield, %[c,d]
(2a)	PhC≡CTos	**(3a)** 93
(2b)	p-$BrC_6H_4C{\equiv}CTos$	**(3b)** 83
(2c)	p-$MeC_6H_4C{\equiv}CSO_2Ph$	**(3c)** 84
(2d)	$Me[CH_2]_4C{\equiv}CTos$	**(3d)** 75
(2e)	$MeOCH_2C{\equiv}CTos$	**(3e)** 64

[a] All reactions were carried out using a 0.1 M solution of **(2)** in tetrahydrofuran and 4 equiv. of 30% hydrogen peroxide. [b] Tos = $C_6H_4SO_2Me$-p. [c] Isolated yield. [d] All new compounds exhibited satisfactory ^1H n.m.r., i.r., and elemental analysis.

In some cases, the oxidation of **(2)** under our conditions gave the corresponding selenoxides as isolatable colourless solids. For instance, the selenoxide derived from **(2a)** could be isolated in 59% yield when a solution of **(2a)** and hydrogen peroxide in tetrahydrofuran was stirred for 2 h at room temperature.

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