Russian Journal of Organic Chemistry, Vol. 39, No. 9, 2003, pp. 1292–1294. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 9, 2003, pp. 1365–1367.

Arylselenovinyl Sulfones: II.* Addition of Benzeneselenols to Aryl Ethynyl Sulfones

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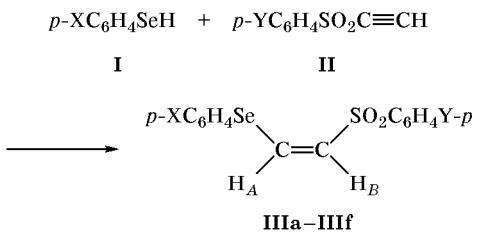
Received May 29, 2002

Abstract—Depending on the solvent nature, addition of benzeneselenols to aryl ethynyl sulfones leads to formation of a mixture of (*E*)- and (*Z*)-1-arylseleno-2-arylsulfonylethenes and 1-arylseleno-1-arylsulfonylethenes (in carbon tetrachloride and cyclohexane) or (*Z*)-1-arylseleno-2-arylsulfonylethenes as a single product (in alcohols).

Substituted vinyl selenides are promising synthons in organic chemistry [2]. A convenient procedure for the preparation of these compounds is based on the addition of benzeneselenols to acetylenic systems [2–4]. However, this reaction have been studied insufficiently. Benzeneselenols are known to react with phenylacetylene and alkylarylacetylenes in a stereoselective fashion [2, 3], while their reactions with ethynyl ketones, 2-propynoic acid, and esters derived from the latter occur exclusively as *trans*-addition to afford the corresponding adducts having *Z*-configuration [4]. Other acetylene derivatives containing electron-acceptor groups, specifically ethynyl sulfones, have not been studied in the reaction with benzeneselenols.

The present communication reports on the reaction of a series of substituted benzeneselenols **I** with phenyl and *p*-tolyl ethynyl sulfones **II** in different solvents. When the reaction was carried out in ethanol or methanol, the corresponding 1:1 adducts, (*Z*)-1-arylseleno-2-arylsulfonylethenes **III**, were obtained in high yield (Scheme 1). The structure of arylselenovinyl sulfones **III** was proved by IR and ^{1}H NMR spectroscopy. The sulfonyl group in compounds **III** gives rise to IR absorption bands in the regions of 1140 and 1306 cm^{-1}. The spin–spin coupling constants for olefinic protons in the ^{1}H NMR spectra of **III** ($^3J_{A,B}$ = 9.6–10 Hz, see table) indicate their *Z* configuration. The signals were assigned to H_A and H_B on the basis of the additivity scheme of olefinic proton shielding using ^{1}H NMR parameters of aryl vinyl selenides [5]. Moreover, the assignment was confirmed by analysis of the ^{1}H NMR spectrum of (*Z*)-1-phenylseleno-2-deutero-2-*p*-tolylsulfonylethene (**IIIg**) which was synthesized from deuterated benzeneselenol in methanol-d_4 (Scheme 2).

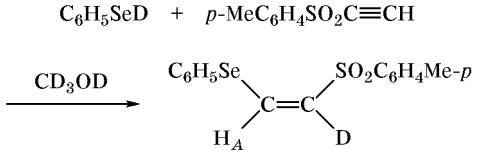
Scheme 1.



IIIa–IIIf

Y = H, X = Br (**a**), Me (**b**); Y = Me, X = H (**c**); Br (**d**), Me (**e**); MeO (**f**).

Scheme 2.



IIIg

The ^{1}H NMR spectrum of **IIIg** lacks upfield signal at δ 6.55 ppm, which is typical of compound **IIIc**, but a downfield triplet belonging to H_A is present (see table). By special experiments we showed that neither *p*-tolylethynyl sulfone nor product **IIIc** undergoes H–D exchange in deuterated methanol. The ^{1}H NMR spectra of crude adducts **III** contained no signals

* For communication I, see [1].

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Melting points, elemental analyses, and some ^{1}H NMR parameters of (*Z*)-1-arylseleno-2-arylsulfonylethenes **IIIa**–**IIIg**

Comp. no.	X	Y	mp, °C	Found, %		Formula	Calculated, %		δ, ppm	
				C	H		C	H	H_A	H_B
IIIa	Br	H	111–112	41.60	2.60	$C_{14}H_{11}BrO_2SSe$	41.81	2.75	7.56	6.64
IIIb	Me	H	105–106	53.21	4.06	$C_{15}H_{14}O_2SSe$	53.41	4.18	7.51	6.53
IIIc	H	Me	79–80	53.48	3.98	$C_{15}H_{14}O_2SSe$	53.41	4.18	7.53	6.55
IIId	Br	Me	125–126	43.16	2.94	$C_{15}H_{13}BrO_2SSe$	43.29	3.15	7.44	6.53
IIIe	Me	Me	136–137	54.69	4.35	$C_{16}H_{16}O_2SSe$	54.70	4.59	7.48	6.51
IIIf	MeO	Me	142–143	52.58	4.66	$C_{16}H_{16}O_3SSe$	52.32	4.39	7.43	6.47
IIIg	H	Me	80–81	53.40	4.30[a]	$C_{15}H_{13}DO_2SSe$	53.26	4.46[a]	7.53[b]	–

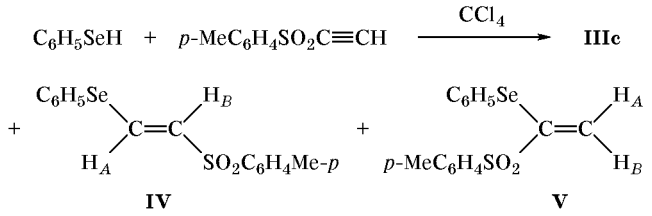
[a] H + D.

[b] Triplet, $^3J(H_A, D)$ = 1.5 Hz.

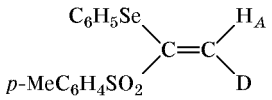
assignable to other addition products. Thus the reaction of benzeneselenols with aryl ethynyl sulfones in alcoholic solutions occurs strictly stereoselectively following the *trans*-addition pattern. Here, the electrophilic center in aryl ethynyl sulfones is the β-carbon atom of the ethynyl group.

With the goal of studying effect of the solvent on the selectivity of addition of benzeneselenols to ethynyl sulfones, we also examined the reaction of benzeneselenol with *p*-tolyl ethynyl sulfone in aprotic solvents. The reaction in carbon tetrachloride was much slower than in alcohols. According to the ^{1}H NMR data, all three possible addition products were formed: (*Z*)-1-phenylseleno-2-*p*-tolylsulfonylethene (**IIIc**), (*E*)-1-phenylseleno-2-*p*-tolylsulfonylethene (**IV**), and 1-phenylseleno-1-*p*-tolylsulfonylethene (**V**) at a ratio of 3:1:2 (Scheme 3).

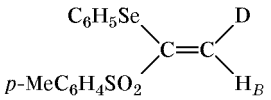
Scheme 3.



Moreover, geminally substituted product **V** is in fact a mixture of two degenerate isomers arising from *trans*- and *cis*-addition of benzeneselenol at the triple bond of ethynyl sulfone. In the product mixture obtained from deuterated benzeneselenol we detected four isomers: **IIIc**, **IV**, **Va**, and **Vb**. Isomers **Va** and **Vb** differ by mutual arrangement of the deuterium atom and phenylseleno group (*trans* and *cis*, respectively. In the ^{1}H NMR spectrum we observed two singlets at δ 5.71 (H_A) and 6.79 ppm (H_B) instead of two doublets typical of nondeuterated compound **V** (δ 5.71 and 6.79 ppm, $^2J_{AB}$ = 2.0 Hz). These data unambiguously indicate formation of two deuterated adducts **Va** and **Vb**.



Va

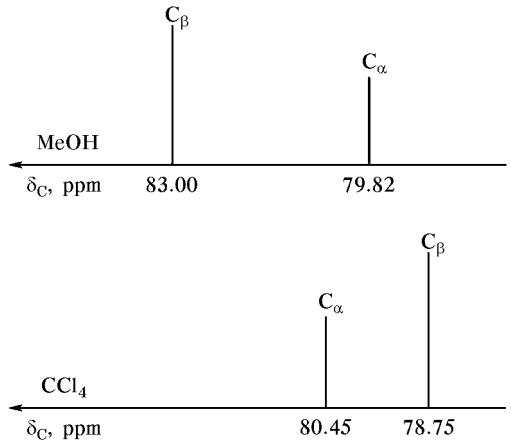


Vb

The signals from vinyl protons in isomers **IIIc**, **IV**, and **V** were assigned by comparison with the ^{1}H NMR spectra of pure isomers obtained in the present work (for **IIIc**, see table; for **IV**, see Experimental) and previously [1]. It should be noted that neither ethynyl sulfone nor compounds **IIIc**, **IV**, and **V** undergo H–D exchange in the ethynyl or vinyl group under the given conditions.

Similar results were obtained in the reaction of benzeneselenol with phenyl ethynyl sulfone in carbon tetrachloride and cyclohexane, as well as in the reaction of benzeneselenol with *p*-tolyl ethylnyl sulfone in cyclohexane. In all cases, three isomeric adducts were obtained.

Thus, the addition of benzeneselenols to ethynyl sulfones in carbon tetrachloride leads to formation of not only *cis* and *trans* isomers like **III** and **IV** but also regioisomeric adduct **V** which is in turn a mixture of degenerate *cis* and *trans* isomers **Va** and **Vb**. We believe that the observed pattern is explained in terms of comparable electrophilicities of the C_α and C_β atoms at the triple bond of ethynyl sulfone. This is confirmed indirectly by the corresponding ^{13}C chemical shifts measured in methanol and carbon tetrachloride (see figure and Experimental). In carbon



Variation of the chemical shifts of the ethynyl carbon atoms in ethynyl *p*-tolyl sulfone in going from methanol to carbon tetrachloride.

tetrachloride, the difference between δ_{C_α} and δ_{C_β} not only is smaller than in methanol but it has the opposite sign: 1.7 and –3.2 ppm, respectively.

EXPERIMENTAL

The ^{1}H NMR spectra of compounds **IIIa**–**IIIg** were recorded on a Varian-200 spectrometer from solutions in chloroform-*d* or carbon tetrachloride using HMDS as internal reference. The ^{13}C NMR spectra of ethynyl *p*-tolyl sulfone were measured in carbon tetrachloride and methanol.

Benzeneselenol-d_1. A mixture of 5 g of benzeneselenol and 15 ml of D_2O was stirred for 10 h. The organic layer was separated and treated again with D_2O. The procedure was repeated in total four times. The product was dried over magnesium sulfate and distilled. Yield 4.2 g (83%), bp 62°C (10 mm). According to the ^{1}H NMR data, the concentration of residual proton on the selenium atom was no larger than 5% (δ 1.33 ppm, s).

(*Z*)-1-Arylseleno-2-arylsulfonylethenes IIIa–IIIf. A solution of 0.01 mol of appropriate aryl ethynyl sulfone in 15 ml of methanol was added to a solution of 0.01 mol of substituted benzeneselenol in 8 ml of methanol. After 4 h, the solvent was distilled off under reduced pressure, and the residue was recrystallized from hexane, isopropyl alcohol, or their mixture. Yield 78–88%. The melting points and analytical data are given in table.

(*Z*)-2-Deutero-1-phenylseleno-2-*p*-tolylsulfonylethene (IIIg). The reaction was carried out as described above using 0.47 g (3 mmol) of deuteraded benzeneselenol and 0.54 g (3 mmol) of ethynyl *p*-tolyl sulfone in 6 ml of methanol-d_4. Yield 0.76 g (75%). ^{1}H NMR spectrum, δ, ppm: 2.37 s (3H), 7.53 t (1H, J = 1.5 Hz), 7.2–8.0 m (9H).

Reaction of benzeneselenol with ethynyl *p*-tolyl sulfone. A solution of 0.47 g (3 mmol) of benzeneselenol and an equimolar amount of ethynyl *p*-tolyl sulfone in 10 ml of carbon tetrachloride was kept for 5 days. The product composition was determined from the ^{1}H NMR data.

Reaction of benzeneselenol-d_1 with ethynyl *p*-tolyl sulfone. The reaction was carried out as described above using 3 mmol of deuterated benzeneselenol. The product composition was determined from the ^{1}H NMR data.

(*E*)-1-Phenylseleno-2-*p*-tolylsulfonylethene (IV). Triethylamine, 0.77 ml (5.5 mmol), was added to a solution of 0.79 g (5 mmol) of benzeneselenol and 1.09 g (5 mmol) of (*E*)-2-chlorovinyl *p*-tolyl sulfone in 14 ml of benzene. After 5 h, the precipitate of triethylamine hydrochloride was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was recrystallized from carbon tetrachloride. Yield 75%, mp 108–109°C. ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H), 6.13 (1H), 8.03 (1H, $^3J_{AB}$ = 14.5 Hz), 7.1–7.7 m (9H). Found, %: C 53.62; H 4.02. $C_{15}H_{14}O_2SSe$. Calculated, %: C 53.41; H 4.18.

Ethynyl *p*-tolyl sulfone was synthesized by the procedure described in [6]. ^{13}C NMR spectrum, δ_C, ppm: in CCl_4: 20.76 (CH_3); 143.87, 128.78, 126.91, 138.18 (C_{arom}); 80.45 (C^α); 78.75 (C^β); in MeOH: 20.22 (CH_3); 147.98, 129.76, 126.90, 137.82 (C_{arom}), 79.82 (C^α); 83.00 (C^β).

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