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Reactions of Alkynylselenonium Salts with Sodium Benzenesulfinate

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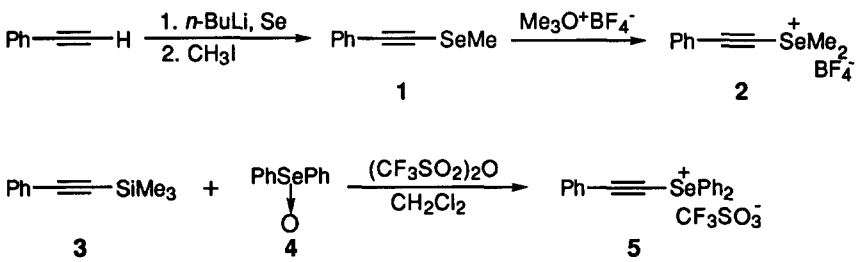
Abstract: Alkynylselenonium salts **2** and **5** were synthesized and treated with benzenesulfinic acid or its sodium salt in an alcohol. The reactions with sodium benzenesulfinate gave (Z)-β-alkoxyvinylsulfones **6** as main products, while the reactions with benzenesulfinic acid afforded the β-sulfonylvinylselenonium salts **11** and **12** in good yields.

Among the alkynyl onium salts, a variety of alkynyliodonium salts has been synthesized and their reactions have been intensively studied.[1] In striking contrast, only one alkynylselenonium salt, ethyl(methyl) phenylethynyl selenonium picrate, has been prepared, but no reaction of the selenonium salt has been reported because of its hygroscopicity.[2] We recently synthesized some alkynylselenonium salts and investigated their reactions with mild nucleophiles. This paper describes synthesis and reactions of the alkynylselenonium salts with benzenesulfinic acid and its sodium salt.

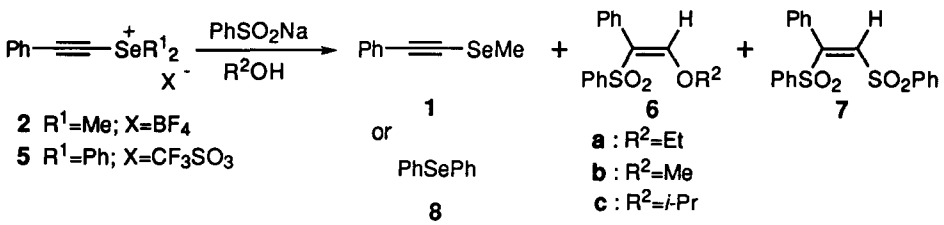
Dimethyl(phenylethynyl)selenonium tetrafluoroborate[3] **2** was prepared by methylation of methyl phenylethynyl selenide[4] **1** with the Meerwein reagent in 62% yield. Diphenyl derivative[3] **5** was synthesized by the reaction of trimethyl(phenylethynyl)silane[5] **3** and diphenyl selenoxide **4** with trifluoromethanesulfonic anhydride in dichloromethane in 87% yield (Scheme 1).



Scheme 1

If a nucleophile acts as a base in a reaction of the selenonium salt **2** with the nucleophile, **2** would be demethylated. Sodium benzenesulfinate was selected as a nucleophile because it has weak basisity. Reactions of the selenonium salts **2** and **5** with sodium benzenesulfinate were conducted in an alcohol (Scheme 2). In a typical procedure, to the alkynylselenonium salt in R^2OH one equivalent of sodium benzenesulfinate was added in one portion and the mixture was stirred at the temperature indicated in Table 1 for 3 hours under N_2. The

solvent was then evaporated under reduced pressure and the residue was separated by preparative TLC on silica gel. The results are summarized in Table 1.

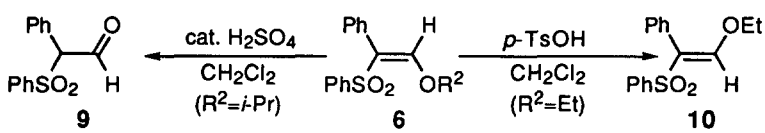


Scheme 2

Table 1. Reactions of Selenonium Salts **2** and **5** with Sodium Benzenesulfinate

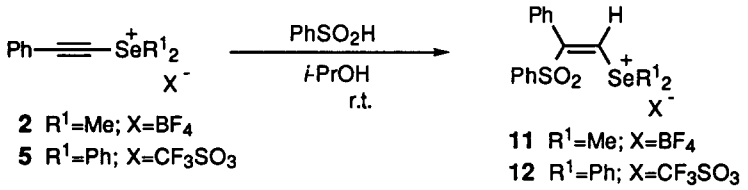
Entry	Selenonium Salt	Solvent	Temp.	Products (%Yield)		
1	**2**	EtOH	r.t.	**1** (21)	**6a** (74)	
2	**2**	EtOH	-78°C	**1** (4)	**6a** (92)	
3	**2**	EtOH	60°C	**1** (33)	**6a** (25)	**7** (20)
4	**2**	MeOH	r.t.	**1** (25)	**6b** (60)	
5	**2**	*i*-PrOH	r.t.	**1** (12)	**6c** (68)	
6	**5**	EtOH	r.t.	**8** (73)	**6a** (69)	**7** (7)
7	**5**	EtOH	-78°C	**8** (67)	**6a** (64)	
8	**5**	EtOH	60°C	**8** (73)	**6a** (64)	**7** (5)
9	**5**	MeOH	r.t.	**8** (80)	**6b** (64)	**7** (7)
10	**5**	*i*-PrOH	r.t.	**8** (80)	**6c** (71)	**7** (12)

The reaction of the dimethyl salt **2** with sodium benzenesulfinate yielded a (*Z*)-alkoxyvinylsulfone **6** as the main product although the reaction gave rise to demethylation to some extent to give methyl phenylethynyl selenide **1**. On the reaction of the diphenyl salt **5**, the sulfone **6** and diphenyl selenide **8** were isolated in good yields. The reactions at room temperature or 60°C afforded the (*Z*)-bis(phenylsulfonyl)styrene **7** as a by-product. The structure of the alkoxyvinylsulfone **6** was determined by spectral data[6] and an acid-catalyzed hydrolysis giving a sulfonyl aldehyde[7] **9** (Scheme 3). The (*Z*)-configuration of **6a** was elucidated in comparison with the spectral data of **6a** and the (*E*)-isomer[8] **10** prepared by treatment of **6a** with *p*-toluenesulfonic acid. The NOE experiment of **6a** showed the enhancement of the *ortho*-protons of the *cis*-phenyl group (11.4%) and the methylene protons of the geminal ethoxy group (7.5%) on irradiation of the vinyl proton.



Scheme 3

In contrast, the reactions of alkynylselenonium salts **2** and **5** with benzenesulfinic acid in isopropanol afforded (*Z*)-(β-phenylsulfonyl)vinylselenonium salts[9] **11** and **12** in yields of 76% and 72%, respectively (Scheme 4). Neither β-alkoxyvinylsulfone **6c** nor the vinyldisulfone **7** was obtained from these reactions. The (*Z*) stereochemistry of **11** and **12** was determined by observation of the NOE enhancement (8.4%, 8.0%) between the vinylic proton and *ortho*-protons of the cis-phenyl group. Since nucleophilic additions to alkynes generally proceed with anti stereochemistry[10], the (*Z*)-alkenylselenonium salts **11** and **12** would be formed by the trans-Michael addition of benzenesulfinic acid to alkynylselenonium salts **2** and **5**, respectively.

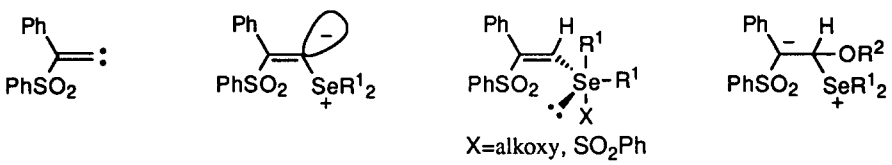


2 R^1=Me; X=BF_4
5 R^1=Ph; X=CF_3SO_3

11 R^1=Me; X=BF_4
12 R^1=Ph; X=CF_3SO_3

Scheme 4

Three reaction pathways can be considered for the formation of the products **6** and **7**. If the reactions proceed via an alkylidene carbene intermediate **13**, the products would be phenyl phenylethynyl sulfone (rearrangement product)[11] and a mixture of (*E*)- and (*Z*)-alkoxyvinylsulfones (RO-H insertion products).[12] Actually, the (*E*)-alkoxyvinylsulfones were not obtained from the reactions of **2** and **5** with sodium benzenesulfinate, and, therefore, the pathway via the alkylidene carbene **13** is excluded. Our results indicate that the Michael adduct **14** did not undergo the α-elimination, namely, **14** did not transform to the carbene **13** different from the iodonium compound.[11, 13] The second route to **6** and **7** involves the formation of the selenurane intermediate **15** followed by the ligand coupling between the X group and the alkenylcarbon. However, the ligand coupling reaction usually occurs in an aprotic solvent[14] and reactions in a protic solvent are not feasible by this mechanism. The third route is a pathway going through the vinylselenonium ion intermediate **11** or **12** which is formed by protonation of **14** with an alcohol. The alkoxide ion thus formed or the sulfinate ion adds to **11** or **12** to form the betaine **16** and the subsequent elimination of a selenide leads to the vinylsulfone **6** or **7** with retention of configuration.[15] Reaction of **12** with sodium isopropoxide gave **6c** in 89% yield. Therefore, the addition-elimination mechanism is most plausible for formation of **6** and **7**. Investigation on the precise reaction is now in progress.



13 **14** **15** **16**

Reference and Notes:

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2. Gosselck, J.; Peress, L.; Schenk, H.; Schmidt, G. *Angew. Chem.* **1965**, *77*, 1440.
3. **2**: m.p. 134-136°C; ^{1}H NMR (400 MHz, CD_3CN) δ: 3.15 (6H, s, Me), 7.46-7.65 (5H, m, ArH); ^{13}C NMR (100 MHz, CD_3CN) δ: 29.0 (q), 65.3 (s), 104.8 (s), 119.6(s), 129.9 (d), 132.8 (d), 133.5 (d); FABMS (*m/z*): 211 $(M\text{-}BF_4)^+$; Anal. Calcd for $C_{10}H_{11}BF_4Se$: C, 40.15; H, 3.73. Found: C, 40.34; H, 3.37. **5**: m.p. 117°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-8.05 (15H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 64.7 (s), 110.9 (s), 118.1 (s), 120.9 (q), 128.5 (s), 129.3 (d), 130.2 (d), 130.8 (s), 131.8 (d), 132.7 (d), 133.4 (d), 133.8 (d); FABMS (*m/z*): 335 $(M\text{-}TfO)^+$; Anal. Calcd for $C_{21}H_{15}F_3O_3SSe$: C, 52.18; H, 3.13. Found: C, 52.08; H, 3.24.
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6. Compounds **6a-c** were fully characterized by spectroscopic means. Selected spectral data are : **6a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.20 (3H, t, *J*=7.3Hz,Me), 3.99 (2H, q, *J*=7.3Hz, CH_2) 6.60 (1H, s, CH), 7.28-7.38 (5H, m, ArH), 7.43.7-7.92 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.8 (q), 71.3 (t), 121.2 (s), 127.4 (d), 127.9 (d), 128.0 (d), 128.2 (d), 130.6 (d), 131.5 (s), 132.5 (d), 142.4 (s), 154.7 (d); MS (*m/z*): 288 (M^+).
7. **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.97 (1H, d, *J*=2.5Hz,CH), 7.20-7.67 (10H, m, ArH), 10.0 (1H, d, *J*=2.5, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 80.3 (d), 126.6 (d), 129.0 (d), 129.1 (d), 129.8 (d), 130.5 (d), 130.7 (s), 134.5 (d), 137.1 (s), 190.7 (d); MS (*m/z*): 260 (M^+).
8. **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29 (3H, t, *J*=7.3Hz,Me), 4.11 (2H, q, *J*=7.3Hz, CH_2), 7.18-7.67 (10H, m, ArH), 7.73 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.2 (q), 63.4 (t), 120.6 (s), 127.6 (d), 128.1 (d), 128.4 (d), 128.6 (d), 128.9 (s), 130.7 (d), 132.6 (d), 140.7 (s), 156.1 (d); MS (*m/z*): 288 (M^+).
9. **11**: m.p. 176-178°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.17 (6H, s, Me), 7.08 (1H, s, CH), 7.26-7.73 (10H, m, ArH); ^{13}C NMR (100 MHz, CD_3CN) δ: 26.2 (q), 129.3 (d), 129.6 (d), 129.7 (d), 130.1 (d), 130.6 (d), 131.4 (d), 131.9 (d), 136.3 (d), 136.7 (s), 153.5 (s); FABMS (*m/z*): 353 $(M\text{-}BF_4)^+$; Anal. Calcd for $C_{16}H_{17}BF_4O_2SSe$: C, 43.76; H, 3.90. Found: C, 43.69; H, 3.90. **12**: m.p. 106-107°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (1H, s, CH), 7.27-7.85 (20H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 120.7 (q), 127.2 (d), 129.0 (d), 129.4 (d), 129.5 (d), 129.6 (d), 129.9 (s), 130.5 (d), 131.2 (d), 131.5 (d), 131.6 (s), 133.2 (d), 134.9 (s), 135.2 (d), 155.0 (s); FABMS (m/z): 477 $(M\text{-}TfO)^+$; Anal. Calcd For $C_{27}H_{21}F_3O_5S_2Se$: C, 51.84; H, 3.38. Found: C, 51.78; H, 3.56.
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