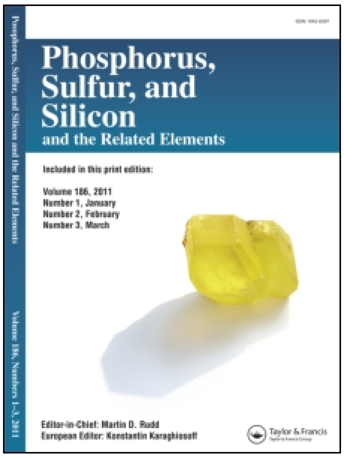

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SYNTHESIS OF PHENYLETHYNYLDIBENZOSELENOPHENIUM SALT AND ITS REACTIONS WITH NUCLEOPHILES

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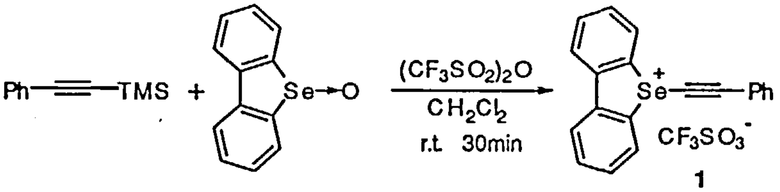
5-Phenylethynyldibenzoselenophenium triflate **1** was prepared from dibenzoselenophene 5-oxide and phenyltrimethylsilylacetylene in the presence of triflic anhydride. The FAB mass spectrum exhibited an (M^{+}+1) peak at *m/z* 483, and the X-ray crystallographic data showed that two C-Se bonds occupied equatorial positions, and the acetylenic bond and the triflate take an apical array with a bond angle of 172.1°. Namely, the compound **1** had a distorted trigonal bipyramid structure. Reactions of **1** with sodium benzenesulfinate in an alcohol gave Z-alkoxyvinylsulfone **2** and dibenzoselenophene **3** in moderate yields, whereas the compound **1** did not react with benzenesulfinic acid.

Keywords: selenonium salt; dibenzoselenophene; X-ray diffraction analysis; selenurane; sodium benzenesulfinate

It is an interesting topic in the chemistry of organoselenium compounds whether selenonium salts have tetrahedral structures or trigonal bipyramidal structures as selenuranes[1]. Selenuranes are usually produced by the selenophilic attack of a nucleophile on selenonium salts. σ-Selenuranes bearing electronegative ligands such as oxygen or halogen atoms were stable and isolated as crystals[2], while the selenuranes with four carbon-selenium bonds were unstable and have not been isolated except bis(2, 2'-biphenylene)selenurane[3]. Dibenzoselenophene would be a useful skeleton for the construction of trigonal bipyramidal structures, because the selenophene ring is rigid but two C-Se bonds can take two equatorial bonds or apical and equatorial bonds. There are few reports on the selenonium salts with the dibenzoselenophene skeleton and their detailed structural analyses have not been done[3a], [4]. Here we report synthesis, X-ray analysis and reactions of the alkynyldibenzoselenophenium salt compared with those of diphenyl(phenylethynyl)selenonium triflate[5].

5-Phenylethynyldibenzoselenophenium triflate **1** was synthesized by the reaction of phenyltrimethylsilylacetylene and dibenzoselenophene 5-oxide with triflic anhydride in dichloromethane in 57% yield(Scheme 1). The structure of this compound was identified by the elemental and spectral analysis[6]. Selenonium salts usually showed only fragment ion peaks rising from the cation moieties, but this compound interestingly showed an (M^{+}+1) peak at *m/z* 483 and an (M-TfO)$^{+}$ peak at *m/z* 333 in the FAB mass spectrum. The crystal structure of **1** by X-ray diffraction analysis is shown in Figure 1[7]. The Se-O distance is 2.711Å, which is shorter than the sum of the van der Waals radii (3.40Å), although it is slightly longer than those of the selenuranes with halogen and oxygen ligands. The O-Se-C (acetylenic) bond angle of 172.1° is approximately collinear. Namely, the compound **1** has a distorted trigonal bipyramid structure in which the acetylenic bond and the triflate take an apical array.



SCHEME 1

Reactions of the selenonium salt **1** with sodium benzenesulfinate were accomplished in the following manner. One equivalent of sodium benzenesulfinate was added to the selenonium salt **1** in an alcohol and the mixture was stirred at room temperature for 3 hours under Ar_2 (Scheme 2). A (Z)-alkoxyvinylsulfone **2** and dibenzoselenophene **3** were obtained in good yields (Table 1).

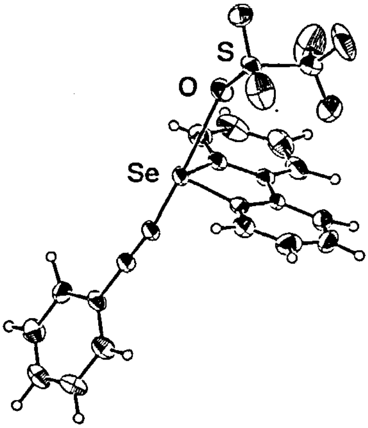
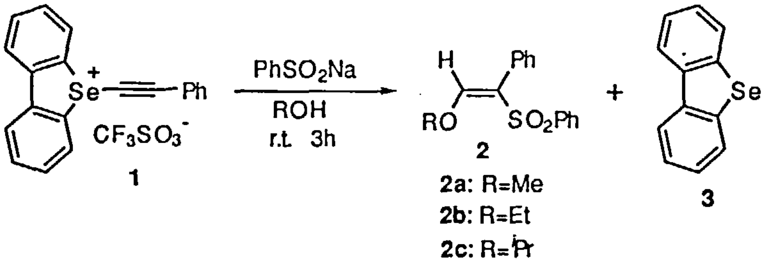


FIGURE 1
ORTEP drawing of **1**

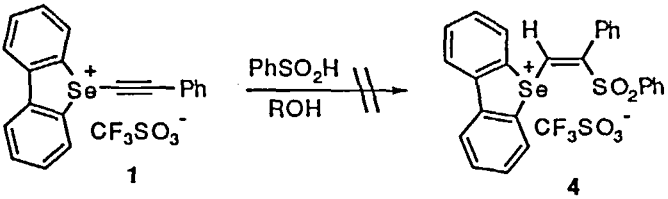


SCHEME 2

TABLE 1

Entry	ROH	Products (%Yield)	
1	MeOH	2a (65)	3 (91)
2	EtOH	2b (77)	3 (94)
3	*i*-PrOH	2c (51)	3 (87)

We attempted to prepare the vinyl selenonium salt **4** by the reaction of **1** with benzenesulfinic acid in an alcohol (Scheme 3). However, the reaction did not proceed in methanol or 2-propanol at room temperature, or under reflux in methanol. This result was much different from that of diphenyl(phenylethynyl) selenonium triflate[5] and would be attributable to the difference in the nature of the Se-O_3SCF_3 bonds in **1** and the diphenyl derivative.



SCHEME 3

Acknowledgments

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[6.] **1**: m.p. 100-117°C; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.26 (2H, t, ArH), 7.37 (1H, d, ArH), 7.45 (2H, d, ArH), 7.60 (2H, t, ArH), 7.75 (2H, t, ArH), 8.02 (2H, d, ArH), 8.31 (2H, d, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 67.0 (s), 104.5 (s), 118.5 (s), 120.5 (q), 124.8 (d), 128.5 (d), 129.8 (d), 131.4 (d), 132.9 (d), 133.6 (d), 135.1 (d), 141.2 (s); FABMS (*m/z*): 483 (M$^+$+H), 335 (M-TfO)$^+$; Anal. Calcd for $C_{21}H_{13}F_3O_3SSe\cdot 1/2H_2O$: C, 51.44; H, 2.89. Found: C, 51.64; H, 2.78.

[7.] Crystallographic data for **1**: $C_{21}H_{13}F_3O_3SSe$, MW=481.35, monoclinic, space group p2$_1$/c (#14), a=8.516 (3) Å, b=19.957 (2) Å, c=11.856 (2) Å, β=92.55 (2)°, V=2013.2 (7) Å^3, Z=4, D$_{calcd}$=1.588 g/cm^3, μ(MoK$_\alpha$)=19.89 cm^{-1}, R=4.6%, R$_W$=4.6%.