Radical Reactions of Alkenylstannanes with *S*-Benzoyl *Se*-Phenyl Selenosulfide

Takeshi Toru,* Yoshio Yamada, Eturô Maekawa, and Yoshio Ueno
Department of Applied Chemistry, Faculty of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466

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Synopsis. Free radical reactions of allyltributylstannane or 2-butenyltributylstannane with *S*-benzoyl *Se*-phenyl selenosulfide (**1**) gave *S*-allyl benzenecarbothioate or a mixture of *S*-2-butenyl and *S*-1-methyl-2-propenyl benzenecarbothioates, respectively. The reaction of tributylvinylstannane with **1** gave an addition product, whereas the reaction of tributylstyrylstannane gave an addition–elimination product.

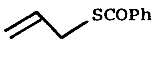
Alkyl radicals generated from alkyl halides or other radical precursors such as selenides or sulfides react with allylstannane in S_H2′ manner to give allylated compounds.[1)] The reaction of alkyl radicals with vinylstannanes affords addition–elimination products only when vinylstannanes bear an electron-withdrawing group.[2)] Heteroatom-centered radicals such as seleno or thio radicals also react with allylstannane to give allyl selenide or sulfide.[3)] Recently we have shown that *S*-benzoyl *Se*-phenyl selenosulfide [*SSe*-phenyl benzenecarbo(selenothioperoxoate)] (**1**) is a useful reagent for introducing both seleno and thioester groups by virtue of the free radical reaction with various olefins,[4)] and is also useful for substitution of mercurials with a seleno group.[5)] In order to extend the scope and limitations of reactions with selenosulfide **1** as a synthetic reagent we have examined the photo and thermal reactions of allylic and vinylic stannanes with **1**.

$PhC(=O)SSePh$

1

2a R=H

2b R=CH$_3$



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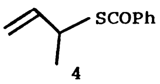

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Table 1. Reaction of Alkenylstannanes with Selenosulfide **1**

Alkenyl-stannane	Method[a)]	Reaction Time	Product (Yield,[b)] %)
2a	A	2	**3** (86)
2a	B	1.5	**3** (84)
2b[c)]	A	2	**4** and **5** (89)[d)]
2b[c)]	B	0.6	**4** and **5** (79)[e)]
6	A	7.5	**7** (92)
6	B	1	**7** (95)
8	A	3	**9** (60)
8	B	2.5	**9** (60)

a) A: Thermal reaction in the presence of AIBN. B: Photoreaction. See Experimental Section. b) Isolated yields. c) A 1 : 3 mixture of *Z*/*E* isomers was used. d) The product was obtained as a 79 : 14 : 7 mixture of **4**/(*E*)-**5**/(*Z*)-**5**. e) The product was obtained as a 77 : 17 : 6 mixture of **4**/(*E*)-**5**/(*Z*)-**5**.

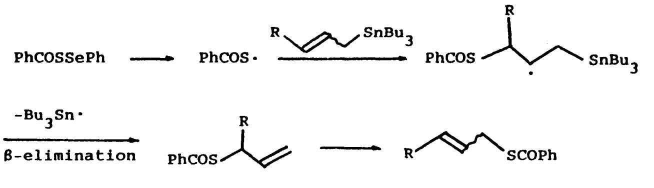
Results and Discussion

Ultraviolet irradiation of tributyl(2-propenyl)stannane[6)] (**2a**) (referred to as allyltributylstannane) and 1.8 fold excess of selenosulfide **1** in benzene for 1.5 h resulted in the formation of *S*-2-propenyl benzenecarbothioate (**3**) in 84% yield. Thermal reaction of allylstannane **2** with selenosulfide **1** in benzene in the presence of AIBN (10 mol%) also afforded benzenecarbothioate **3** in high yield. These results together with others described below are summarized in Table 1. In the above reactions we encountered some difficulty in purifying **3** by silica-gel column chromatography because of contamination of tributyl(phenylseleno)stannane formed during the reaction. Mercury(II) acetate was found to be most superior among several salts tested, including potassium fluoride that is effective to remove stannyl bromide,[7)] to separate the stannane from benzenecarbothioate **3** in the reaction mixture. Thus, isolation of **3** could be achieved by addition of a small amount of mercury(II) acetate to the reaction mixture and subsequent filtration of the resultant precipitates followed by column chromatography.

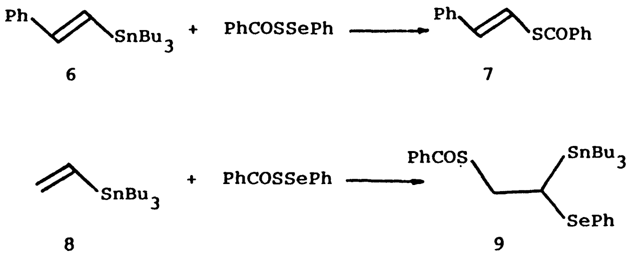
The photo and thermal reactions of 2-butenyltributylstannane[6)] (**2b**) (a 1 : 3 mixture of *Z*/*E* isomers) with selenosulfide **1** gave *S*-1-methyl-2-propenyl benzenecarbothioate[8)] (**4**) and *S*-2-butenyl benzenecarbothioate[8)] (**5**), the latter compound consisting of a mixture of the *Z*- and *E*-isomers whose ratio was 1 : 3 in the photostimulated reaction and 1 : 2 in the thermal reaction. The ratio of **4** to **5** was found to decrease as the reaction proceeded. In the photolysis monitored by the ^{1}H NMR spectroscopy it was shown that the first formed benzenecarbothioate **4** rearranged to **5** during the irradiation and reached to a mixture of **4** and **5** in the ratio 1 : 1 after about 80 min in carbon tetrachloride or in the ratio 2 : 1 after 110 min in deuterated benzene (see Table 2 in Experimental Section). This rearrangement was further verified by the irradiation of isolated benzenecarbothioate **4** which resulted in rapid and complete conversion to benzenecarbothioate **5** within 10 min. The complete conversion of **4** to **5** is probably due to the conditions without selenosulfide **1** or tributyl(phenylseleno)stannane in the reaction mixture. Similar facile rearrangement from 1-methyl-2-propenyl selenide to 2-butenyl selenide have been reported by Russell et al. in the reaction of 2-butenylstannane with diphenyl diselenide.[3)] The above overall reactions can be rationalized by the S_H2′ mechanism and subsequent interconversion of **4** to **5** as shown in Scheme 1, i.e., benzenecarbothioate **3** or **4** is formed by β-elimination of the stannyl radical from the carbon radical generated at the vicinal position to the stannyl group by the reaction of stannane **2a** or **2b** with the thiyl radical and then resulting benzenecarbothioate **4** rearranges to benzenecarbothioate **5**.

Another example of facile β-elimination of the stannyl radical was encountered in the reaction of tributyl[(*E*)-styryl]stannane[9] (**6**) with selenosulfide **1**, affording *S*-styryl benzenecarbothioate (**7**) which is apparently formed via addition of the thiyl radical to the β-olefinic carbon and subsequent β-elimination of the stannyl radical. The photoinduced reaction proceeded much faster than the thermal reaction in this case (see Table 2).

On the other hand, tributylvinylstannane[10] (**8**) reacted with selenosulfide **1** to give the addition product **9** in moderate yield after 3 h in thermal reaction and 2.5 h on irradiation. Longer reaction time in both reactions did not improve the yield but caused the decomposition of the addition product **9**. The structure of **9** was assigned by the spectral data. The ^{13}C NMR spectrum showed the signals of butyl carbons at δ 12.77, 26.53 ($^{3}J_{\text{Sn-C}}$=58.5 Hz), 28.22 ($^{2}J_{\text{Sn-C}}$=19.5 Hz), 9.67 ($^{1}J_{\text{Sn-C}}$=312.7 and 327.7 Hz) assigned to the methyl carbon, γ-carbon, β-carbon, and α-carbon to the stannane, respectively, by their coupling constants between ^{13}C and ^{117,119}Sn.[11] The methylene carbon appeared at δ 35.03 without any significant couplings, while the signal assigned to the methine carbon was observed at δ 22.70 with two sets of definitive couplings, $J_{\text{Sn-C}}$=217.6 and 227.8 Hz, and $J_{\text{Se-C}}$=90.8 Hz),[12] confirming the regiochemistry of the addition product **9**. The ^{1}H NMR spectrum showed three sets of a doublet of doublet at 3.28 (J=8.8 and 6.8 Hz), 3.47 (J=13.2 and 8.8 Hz), and 3.76 (J=13.2 and 6.8 Hz) ppm. The double resonance study of the ^{13}C NMR spectroscopy irradiated at δ 3.28, 3.47 and 3.76 confirmed the signal at δ 3.28 to correspond to the methine proton C<u>H</u>(Seph)SnBu$_3$ and the other two to the methylene protons attached to the thioester group. In addition, ^{77}Se appeared at δ 358 relative to dimethyl selenide. We have already shown that the thiyl radical generated from selenosulfide **1** adds selectively to the terminal carbon of monosubstituted olefins.[4] This high regioselectivity is derived from that the electron-deficient thiyl radical (PhCOS·) adds to the electron-rich terminal carbon.[13] It should be noted that alkyl radicals generated from alkyl halides does not react with unsubstituted and alkyl-substituted vinylstannanes.[2c] Vinylstannanes should be substituted with an electron-withdrawing group probably due to the nucleophilic nature of alkyl radicals. On the other hand, in our case the thiyl radical (PhCOS·) bearing an electron-withdrawing benzoyl group reacted readily with vinylstannane **8** as well as styrylstannane **6** because of its electrophilic nature.



Scheme 1.



Scheme 2.

Table 2. Photostimulated Reaction of **2b** with **1**

Reaction time	Ratio of **4** to **5**, **4**/**5**	
min	In CCl$_4$	In C$_6$D$_6$
10	2.5	9
20	2	4
30	1.5	3
80	1	2
100	1	2

The present reactions may serve a new synthetic method for the synthesis of thioates providing further scope of reactions with *S*-benzoyl *Se*-phenyl selenosulfide (**1**) as a synthetic reagent.[14]

Experimental

Apparatus. IR spectra were taken with a JASCO A-102 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-200 (200 MHz) or JEOL JNM-PMx60si (60 MHz) instruments. Chemical shifts are reported on the δ scale relative to Me$_4$Si as the internal standard. ^{13}C and ^{77}Se NMR spectra were obtained on a Varian XL-200 spectrometer for solutions in deuterochloroform. Microanalyses were performed by the Institute of Microanalyses, Kyoto University. All reactions were carried out under an argon atmosphere. Flash chromatography was performed using a Michael Miler column packed with Fuji Davison silica gel BW-200, equipped with FMI LAB Pump RP-G150 and FMI Pulse Damper PD-60LF, normally at a pressure of 1—2 kg cm^{-2}.

Reaction of Tributyl(2-propenyl)stannane (2a) with Selenosulfide 1. Thermal Reaction (Method A). A mixture of tributyl(2-propenyl)stannane (**2a**) (34 mg, 0.10 mmol), selenosulfide **1** (54 mg, 0.18 mmol) and AIBN (3 mg, 0.018 mmol) in degassed benzene (0.2 ml) was heated under reflux for 2 h. To the resulting yellow clear solution was added mercury(II) acetate (20 mg, 0.063 mmol) at room temperature and the mixture was stirred for 5 min when white precipitates appeared. The precipitates were filtered and the filtrate was concentrated in vacuo to leave an oil which was purified by flash column chromatography with hexane-benzene (98:2 to 8:2) to give 16 mg (86%) of *S*-2-propenyl benzenecarbothioate[8] (**3**): ^{1}H NMR (CCl$_4$) δ=3.73 (d, 2H, J=8 Hz), 5.00—5.40 (m, 2H), 5.50—6.10 (m, 1H), 7.26—8.00 (m, 5H); IR (film) 1660 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 192 (M$^+$; 2), 137 (1), 105 (100), 77 (45), 56 (22), and 51 (30).

Photostimulated Reaction (Method B). A solution of tributyl(2-propenyl)stannane (**2a**) (36 mg, 0.11 mmol) and selenosulfide **1** (57 mg, 0.19 mmol) in degassed benzene (0.2 ml) was externally irradiated in a glass tube at a distance of 15 cm with an Toshiba H-400F high-pressure Hg lamp for 1.5 h. Similar treatment of the reaction mixture to Method A and purification afforded 16 mg (84%) of *S*-2-propenyl benzenecarbothioate (**3**).

Reaction of 2-Butenyltributylstannane (2b) with Selenosulfide 1. Thermal reaction of 2-butenyltributylstannane (**2b**) (37 mg, 0.11 mmol) with selenosulfide **1** (66 mg, 0.23 mmol) in the presence of AIBN (4 mg) in benzene (0.2 ml) for 2 h and subsequent purification described above afforded a 79 : 14 : 7 mixture of **4**/(*E*)-**5**/(*Z*)-**5** (18 mg, 89%), whose ratio was determined by the ^{1}H NMR (200 MHz) spectrum.

Irradiation of a mixture of **2b** (32 mg, 0.093 mmol) and **1** (49 mg, 0.17 mmol) for 40 min afforded a 77 : 17 : 6 mixture of **4**/(*E*)-**5**/(*Z*)-**5** (14 mg, 79%).

The signals of the ^{1}H NMR spectrum were assigned as follows; for *S*-1-methyl-2-propenyl benzenecarbothioate[8] (**4**): δ=1.52 (d, 3H, J=8.0 Hz), 4.36 (ddq, 1H, J=5.0, 1.5, and 8.0 Hz), 5.08 (ddd, 1H, J=10.0, 1.5, and 1.5 Hz), 5.30 (ddd, 1H, J=17.0, 1.5, and 1.5 Hz), 5.94 (ddd, 1H, J=17.0, 10.0, and 1.5 Hz), 7.36—8.22 (m, 5H); for *S*-(*E*)-2-butenyl benzenecarbothioate[8] (*E*)-(**5**): δ=1.72 (d, 3H, J=7.2 Hz), 3.64 (d, 2H, J=5.0 Hz), 5.48 (dt, 1H, J=15.4 and 7.2 Hz), 5.70 (dq, 1H, J=15.4 and 5.0 Hz), and 7.40—8.20 (m, 5H); for *S*-(*Z*)-2-butenyl benzenecarbothioate[8] (*Z*)-(**5**): δ=1.78 (d, 3H, J=7.2 Hz), 3.71 (d, 2H, J=5.0 Hz), 5.40—5.80 (m, 2H), 7.40—8.20 (m, 5H).

Irradiation of 2-Butenyltributylstannane (2b) and 1 in a NMR Tube. The ^{1}H NMR signals (60 MHz) were monitored by the integration of a C-2 methine proton of *S*-1-methyl-2-propenyl benzenecarbothioate (**4**) at δ 4.00—4.63 and of a C-1 methylene proton of *S*-2-butenyl benzenecarbothioate (**5**) at δ 3.47—3.76. The results are shown in Table 2. The rearrangement in benzene proceeded slower than in CCl_4.

Irradiation of Benzenecarbothioate 4. The complete rearrangement of **4** to **5** in deuterated benzene was observed by the irradiation of **4**, obtained as a ca. 20 : 1 mixture of **4**/**5** by the short time thermal reaction, for 10 min as monitored by the ^{1}H NMR spectroscopy.

***S*-Styryl Benzenecarbothioate (7).** ^{1}H NMR (CCl_4) δ=6.67 (d, 1H, J=16 Hz), 7.10—8.10 (m, 11H); IR (KBr) 1665 cm^{-1}; MS (70 eV) m/z (rel intensity) 240 (M$^+$, 4), 105 (100). Found: C, 74.89; H, 5.10%. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.08%.

***S*-(2-Tributylstannyl-2-phenylselenoethyl) Benzenecarbothioate (9).** ^{1}H NMR (CCl_4) δ=0.80—1.70 (m, 27H), 3.28 (dd, 1H, J=8.8 and 6.8 Hz), 3.42 (dd, 1H, J=13.2 and 8.8 Hz), 3.76 (dd, 1H, J=13.2 and 6.8 Hz), 7.12—8.00 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=9.67 ($J_{\text{Sn-C}}$=312.7 and 327.7 Hz, $\mathrm{Sn\underline{C}H_2}$), 12.77 ($\mathrm{SnCH_2CH_2CH_2\underline{C}H_3}$), 22.70 ($J_{\text{Sn-C}}$=217.6 and 227.8 Hz, $J_{\text{Se-C}}$=90.8 Hz, $\mathrm{Sn\text{-}\underline{C}H\text{-}Se}$), 26.53 ($J_{\text{Sn-C}}$=58.5 Hz, $\mathrm{SnCH_2CH_2\underline{C}H_2}$), 28.22 ($J_{\text{Sn-C}}$=19.7 Hz, $\mathrm{SnCH_2\underline{C}H_2}$), 35.03 ($\mathrm{PhCOS\underline{C}H_2}$), 125.91, 126.26, 127.33, 127.54, 128.06, 130.64, 131.65, 132.26, 136.21 (2Ph), 190.05 (C=O): ^{77}Se NMR ($CDCl_3$) δ=358 (m) (dimethyl selenide: ν=0 ($CDCl_3$)); IR (film) 1650 cm^{-1}; MS (20 eV) m/z (rel intensity) 473 (M$^+$—PhCOS, 6), 370 (100), 290 (14), 157 (5), 105 (50), 77 (13), 51 (3). Found: C, 53.34; H, 6.61%. Calcd for $C_{27}H_{40}OSSeSn$: C, 53.13; H, 6.62%.

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