# Lewis Acid-catalyzed Coupling Reactions of Allylsilanes with Tris(phenylchalcogeno)methane. Synthesis of Homoallylchalcogenoacetals.

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*Abstract: Reaction of allylsilanes with tris(phenylseleno)methane or tris(phenylthio)methane in the presence of a Lewis acid furnishes the corresponding homoallylchalcogenoacetals in moderate to good yields.*
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There has been considerable interest in the development of new synthetic methods employing onganoselenium intermediates.[1] In this way, phenylseleno stabilized carbocations have been applied to the regiospecific formation of new carbon-carbon bonds, by reactions with silyl enol ethers,[2,3] alkenes,[4,5] arenes[6] and allylsilanes.[3,4,6b,7,8] Previous reports using allylsilanes described their reaction with selenoacetals,[7] O/Se-heteroacetals[8] and α-sulphonyl selenides[4] mediated by a Lewis acid, furnishing homoallyl selenides.[7,8]

As a part of our interest on chalcogeno stabilized carbocations we studied the reaction of tris(phenylseleno)methane 1 and tris(phenylthio)methane 2 with allylsilanes 3a-f. These reactions furnished the homoallylseleno 4a-e and the homoallylthioacetals 5a-f with yields indicated in Table 1 (Schemes 1 and 2).
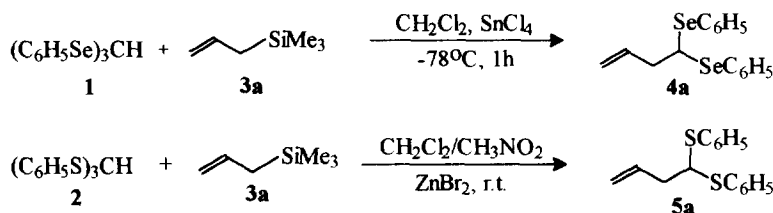


**Scheme 1**

Treatment of allyl trimethylsilane 3a (2.5 mol eq.) with 1 and SnCl$_4$ in CH$_2$Cl$_2$ at -78°C, results in formation of homoallyl phenylselenoacetal 4a in 72%, and reaction of 3a with 2 in a mixture of CH$_2$Cl$_2$/CH$_3$NO$_2$ and ZnBr$_2$ at room temperature afforded the adduct 5a in 55% yield after column chromatography purification (entry 1, Table 1). Reactions of 3b-f with 1 or 2 gave similar results with yields ranging from 58 to 83% or 35 to 73% , respectively (columns 5 and 8, entries 2-5, Table 1). All reactions of allylsilanes and 1 were observed to be completed in one hour or less, while the phenylthio derivative 2 reacts

slower (4.5h to 24h) than the corresponding phenylseleno derivative **1** as indicated in Table 1. In all cases studied on the reaction of allylsilanes with **1**, SnCl₄ was the most effective catalyst and CH₂Cl₂ was used as solvent. On the other hand, for the sulfur **2** analogue ZnBr₂ was the best catalyst and the use of nitromethane as a co-solvent was more effective.

In the case of reaction with the 2-(methyltrimethylsilyl)heptene **3b** (Table 1, entry 2; Scheme 2), the homoallyl selenoacetal **4b** obtained was easily identified by the $^1$H NMR spectrum, in which a triplet at 4.54 ppm (J 7.4 Hz, selenoacetal 1H) and a doublet at 2.67 ppm (J 7.4 Hz, allylic 2H) are seen. In this reaction, a new compound was also formed and identified as the isomer **6** by a doublet at 4.47 ppm (J 5.7 Hz, selenoacetal H) and a broad singlet at 1.72 ppm of the allylic methyl group. A variable ratio on the formation of **4b** and **6** was observed, ranging from 2:1 to 5:1 depending on the reaction conditions. The same type of products were observed in the reaction of **3b** with sulfur derivative **2**. However, in this case isomerization occurs to a lower extent (10% of 7 was formed as determined by GC/MS analysis). In all other cases studied, no such isomerization was observed.
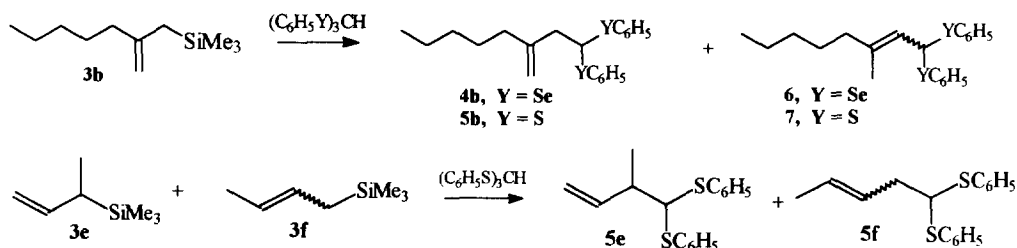


**Scheme 2**

Along with homoallylselenoacetals, small amounts of the corresponding allylmonoselenides were formed, which were easily separated by column chromatography. The formation of these compounds occurs probably by reaction of the allylsilane with a phenylselanyl species formed in the reaction media. This is in accordance with previous[9] reports that allylsilanes react with C₆H₅SeCl (AlCl₃ or ZnBr₂) to give allylselenides. In reactions of **3a-f** with **2** the formation of allylsulfides was not observed.

In all examples under our reaction conditions any further reaction of the homoallyl selenoacetals formed with another equivalent of allylsilane present in the reaction media was not observed. This reaction could produce the bis(homoallyl)selenide in aggrement with results recently described by Hermans and Hevesi[7] on the reaction of selenoacetals with allylsilanes.

Reaction of allylsilanes **3e** and **3f** (a 1:1 mixture of isomers) with **1** gave only the product **4e** derived from the reaction of allylsilane **3f** (entry 5, Table 1), that seems to be more reactive than **3e**. Reaction of the same mixture with **2** results in formation of the isomeric homoallylphenylthioacetals **5e** and **5f** in a ratio of 1:4 (scheme 2, Table 1).

**Table 1.** Homoallylchalcogenoacetals obtained.

| Entry | Allylsilane | Product[a] | t (h) | Yield[f] (%) | Product[a,c] | t (h) | Yield[e,f] (%) |
|---|---|---|---|---|---|---|---|
| 1 | **3a** | **4a** | 1 | 72[b] | **5a** | 24 | 55 |
| 2 | **3b** | **4b** | 1 | 58[b](73)[c] | **5b** | 4.5 | 73[d] |
| 3 | **3c** | **4c** | 1 | 65[b](75)[c] | **5c** | 20 | 59 |
| 4 | **3d** | **4d** | 1 | 81[b](83)[c] | **5d** | 7 | 65 |
| 5[e] | **3e** + **3f** | **4e** | 1 | 54[b](69)[c] | **5e** + **5f** | 24 | 35 |

[a] All products were fully characterized by $^1$H NMR, $^{13}$C NMR, IR, GC/MS and gave correct elemental analysis. [b] 2.5 eq of allylsilane [c] 4 eq of allylsilane [d] 10% isomerized product (see text) [e] 1 : 1 mixture of allylsilanes [f] Isolated yield.

Tris(phenylchalcogeno)methanes were easily prepared on half-mole scale by the reaction of thiophenol or selenophenol with trialkylorthoformiate and $BF_3 \cdot OEt_2$ as the catalyst.[10] The allylsilanes were prepared by reaction of the allylic Grignard reagents with $ClSiMe_3$[11] or by Pd-catalyzed coupling of vinyl iodides[12] with the Grignard reagent derived from $ClCH_2SiMe_3$.[13]

In conclusion, the reaction[14,15] of allylsilanes with tris(phenylchalcogeno)methanes makes the synthesis of the very useful homoallyl chalcogenoacetals particularly easy. The compounds obtained in this paper could be used in several ways as interesting intermediates in organic synthesis. For example, oxidative elimination of one phenylchalcogeno group results in formation of chalcogeno-1,4-butadiene and hydrolysis of the same compounds could form the corresponding β-γ-unsaturated aldehydes since the chalcogenoacetal group is a masked aldehyde group.

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14)  **Typical procedure**: To a solution of HC(SePh)$_3$ (0.24g; 0.5 mmol) and allylsilane **3a** (0.057g, 0.5 mmol) in CH$_2$Cl$_2$ (2 mL), cooled to -78°C under nitrogen, was added dropwise SnCl$_4$ (0.12 mL, 1 mmol). After 15, 30 and 45 min of reaction more allylsilane (0.25 mmol each time) was added. After 1 h of reaction at -78°C water (1 mL) and sat aq NaHCO$_3$ was added and extracted with ethyl acetate. The organic phase was dried (MgSO$_4$), filtered and the solvent removed under vacuo. The residual oil was purified by column chromatography of silicagel, eluting with hexanes. Yield : 0.265g (72%). **4a**: $^1$H NMR δ 2.71(t, J=6.4Hz, 2H), 4.49(t, J=6.4Hz, 1H), 4.9-5.08(m, 1H), 5.17 (br s, 1H), 5.7-6.2(m,1H), 7.14-7.64 (m, 10H); $^{13}$C NMR δ 40.9, 42.3, 117.6, 127.9, 128.9, 130.1, 134.6, 135.2; GC/MS, m/z : 368 (M$^+$), 211(100%), 157, 131, 77; *Anal.* calcd. for C$_{16}$H$_{16}$Se$_2$ : C, 52.48; H, 4.40; found C, 52.10; H, 4.31.

15)  **Selected spectral and analytical data** ($^1$H NMR were taken at 80 MHz in CDCl$_3$).
     **4d**: $^1$H NMR δ 1.18-2.34(m, 8H), 2.40-2.68(m, 1H), 4.68(d, J=6Hz,1H),4.77 (s, 2H), 7.03-7.59(m, 10H), $^{13}$C NMR (20 MHz) δ 23.3, 27.3, 31.0, 34.2, 48.6, 48.7, 107.9, 126.9, 127.0, 128.1, 129.2, 133.7, 133.8, 148.2; GC/MS m/z : 265 (M$^+$ - SePh), 183, 157, 107, 79(100%), 77; *Anal.* calcd. for C$_{20}$H$_{22}$Se$_2$ : C, 57.15; H, 5.28; found C, 56.77; H, 5.24. **5a**: $^1$H NMR δ 2.60 (t, J=6.8Hz, 2H), 4.43 (t, J=6.8Hz, 1H), 4.96-5.1 (m, 1H), 5.2 (d, J=1.0Hz, 1H), 5.73-6.24 (m, 1H), 7.19-7.56 (m, 10H); $^{13}$C NMR (20 MHz) δ 39.8, 57.5, 117.9, 127.6, 128.8, 132.7, 134.0, 134.11; GC/MS m/z : 163 (100%, M$^+$ - SPh), 135, 109; *Anal.* calcd. for C$_{16}$H$_{16}$S$_2$ : C, 70.57; H, 5.93; found C, 69.93; H, 5.81. **5c**: 0.68-2.0 ( m, 11 H), 2.31-2.67 (m, 1H), 4.45 (d, J=3.5Hz,1H), 5.04 (dd, J=16.5, 2.1 Hz, 1H), 5.16 (dd, J=10.5, 2.1 Hz, 1H), 5.89 (ddd, J=16.5, 10.5, 8.4 Hz, 1H), 7.06-7.47 (m, 10H); $^{13}$C NMR (20 MHz) δ 13.9, 22.4, 26.8, 30.9, 31.5, 48.6, 65.1, 117.3, 127.3, 127.4, 128.8, 132.3, 132.4, 135.1, 135.2, 138.4; GC/MS m/z : 233 (100%, M$^+$ - SPh), 153, 135, 123, 109; *Anal.* calcd. for C$_{21}$H$_{26}$S$_2$ : C, 73.65; H, 7.66; found C, 73.22; H, 7.66.