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Lewis Acid Mediated Reaction of Trimethylstyrylsilanes with Thioacetal Derivatives

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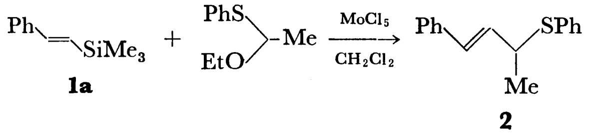
Synopsis. Treatment of trimethylstyrylsilanes with 1-ethoxy-1-(phenylthio)ethane or 2-ethoxy-1,3-dithiolane in the presence of Lewis acid gives the corresponding (*E*)-allyl sulfide or (*E*)-2-styryl-1,3-dithiolane, respectively. In both cases, a carbon-oxygen bond of thioacetal derivatives is cleaved selectively.

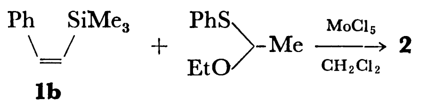
Electrophilic substitution reaction of vinylsilanes provides a versatile method for stereospecific and regioselective carbon–carbon bond formation.[1] However, electrophiles are limited to acid chloride,[2,3a] and α-chloro ether.[3] We previously found that acetal acts as an electrophile in the presence of Lewis acid, especially $MoCl_5$.[4] This methodology was used in the intramolecular reaction by Tius[5] and dithioacetal has been shown to be an electrophile in the cyclization reaction.[6] Now, we wish to report the Lewis acid mediated reaction of trimethylstyrylsilanes with monothioacetal.

Treatment of (*E*)-trimethylstyrylsilane (**1a**) with 1-ethoxy-1-(phenylthio)ethane in the presence of $MoCl_5$ at up to −20 °C gave the 1:1 adduct, (*E*)-1-phenyl-3-phenylthio-1-butene (**2**), in 42% yield exclusively.



The reaction at −78 °C decreased the yield of **2**, as shown in Table 1. $TiCl_4$ was less effective than $MoCl_5$, as observed in the reaction with acetal.[4] A fission of a carbon-oxygen bond occurred selectively, and the product derived from the attack of $EtOC^{+}HMe$ was not detected. This finding exhibits a contrast to the reaction of trimethylstyrylsilanes with benzaldehyde diethyl acetal. In the latter case, both ethoxyl groups participate in the reaction to produce the 1,4-pentadiene derivatives selectively.

(*Z*)-Trimethylstyrylsilane (**1b**) was also allowed to react with 1-ethoxy-1-(phenylthio)ethane in the presence of $MoCl_5$ to yield the same allyl sulfide **2** (53%)



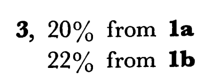
exclusively. The stereochemistry of **1b** is not retained, which might be due to the Lewis acid catalyzed isomerization of the (*Z*)-allyl sulfide into the stable *E*-isomer as reported in the reaction of dichloromethyl methyl ether.[3d] This result strikingly contrasts with the stereospecific reaction of trimethylstyrylsilanes with acetal.

2-Ethoxy-1,3-dithiolane was subjected to the substitution reaction with trimethylstyrylsilanes in the presence of $BF_3 \cdot OEt_2$ to give the 1:1 adduct, (*E*)-2-styryl-1,3-dithiolane (**3**), though the yield was not high. Lewis acid such as $MoCl_5$ or $TiCl_4$ appeared to decompose 2-ethoxy-1,3-dithiolane giving none of the adduct. A carbon-oxygen bond of 2-ethoxy-1,3-dithiolane was cleaved selectively and the *E* product **3** was formed regardless the configuration of the starting vinylsilanes **1**, as mentioned in the reaction with monothioacetal.

TABLE 1. REACTION OF (*E*)-TRIMETHYLSTYRYLSILANE (**1a**) WITH 1-ETHOXY-1-(PHENYLTHIO)ETHANE[a]

Lewis acid	Reaction temp/°C	Isolated yield/% of **2**
$MoCl_5$	−78	28
	−78→−20	42
$TiCl_4$	−78	10
	−78→−20	24

a) Reaction time, 4 h.



3, 20% from **1a**
22% from **1b**

We showed a new carbon–carbon bond formation with trimethylstyrylsilanes, but it is disappointing to find that the other vinylsilanes such as 1-trimethylsilyl-1-hexene and -cyclohexene were not so reactive as trimethylstyrylsilanes.

Experimental

^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-PMX 60 or JNM-FX 90Q with tetramethylsilane as an internal standard, respectively. IR spectra were recorded with a JASCO IRA-I spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer. Commercially available reagents were used unless otherwise noted. (*Z*)- and (*E*)-Trimethylstyrylsilanes,[7] 1-ethoxy-1-(phenylthio)ethane,[8] and 2-ethoxy-1,3-dithiolane[9] were prepared by the reported methods.

*Reaction of **1a** with 1-Ethoxy-1-(phenylthio)ethane.* To a suspension of $MoCl_5$ (0.273 g, 1.0 mmol) in dichloromethane (4 ml) was added (*E*)-trimethylstyrylsilane (**1a**; 0.176 g, 1.0 mmol) and 1-ethoxy-1-(phenylthio)ethane (0.182 g, 1.0 mmol) in dichloromethane (4 ml) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 2.5 h, and then warmed to −20 °C. At this temperature, the mixture was stirred for 1.5 h, and quenched with 50% aqueous methanol. The resultant mixture was warmed to 0 °C, and poured into saturated aqueous Na_2CO_3 solution (5 ml), which was extracted with ether (3×10 ml). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on a silica-gel column to give 0.101 g (42%) of (*E*)-1-phenyl-3-phenylthio-1-butene (**2**) and 0.0541 g of 1,1-bis(phenylthio)ethane. **2**: ^{1}H NMR ($CDCl_3$) δ 1.44 (d, 3H, J=7.1 Hz), 3.85 (qdd, 1H, J=7.1, 6.6, 0.2 Hz), 6.11 (dd, 1H, J=15.7, 6.6 Hz), 6.17 (dd, 1H, J=15.7, 0.2 Hz), 6.8—7.6 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 20.7, 46.4, 126.3, 127.2, 127.3, 128.4, 128.6, 129.9, 131.6, 133.2, 134.7, 136.9; IR (neat) 1575, 960 cm^{-1}; MS *m/e* 240 (M^+).

*Reaction of **1b** with 1-Ethoxy-1-(phenylthio)ethane.* The reaction was carried out in the same way as mentioned above. The allyl sulfide **2** was produced in 53% yield.

*Reaction of **1a** with 2-Ethoxy-1,3-dithiolane.* To a solution of $BF_3 \cdot OEt_2$ (0.13 ml, 1.0 mmol) in dichloromethane (2 ml) was added (*E*)-trimethylstyrylsilane (**1a**; 0.176 g, 1.0 mmol) in dichloromethane (1 ml) at 0 °C under nitrogen. Then, 2-ethoxy-1,3-dithiolane (0.150 g, 1.0 mmol) in dichloromethane (2 ml) was added dropwise to the mixture at 0 °C for 30 min. The resultant solution was stirred at room temperature for 5 h. Saturated aqueous Na_2CO_3 solution (5 ml) was added to the mixture, which was extracted with ether (3×10 ml). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on a silica-gel column to give 0.0416 g (20%) of (*E*)-2-styryl-1,3-dithiolane (**3**). Mp 67 °C (uncorrected); ^{1}H NMR ($CDCl_3$) δ 3.25 (broad s, 4H), 5.18 (d, 1H, J=7.6 Hz), 6.12 (dd, 1H, J=15.4, 7.6 Hz), 6.50 (d, 1H, J=15.4 Hz), 7.1—7.5 (m, 5H); IR ($CHCl_3$) 950 cm^{-1}; MS *m/e* 208 (M^+).

*Reaction of **1b** with 2-Ethoxy-1,3-dithiolane.* The reaction was carried out in the same way as mentioned above. (*E*)-2-Styryl-1,3-dithiolane (**3**) was produced in 22% yield.

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