LEWIS ACID MEDIATED REACTIONS OF 2-STANNYL-3-SILYLPROPENE WITH ACID CHLORIDES. FORMATION OF VINYLSILANES VIA 1,2-SILYL MIGRATION AND DESTANNYLATION.

Kyung-Tae Kang, Jae Chul Lee, and Jong Sun U. Department of Chemistry, Pusan National University, Pusan 609-735, Korea

Reactions of 2-stannyl-3-silylpropene with acid chlorides in the presence of Lewis acid afford vinylsilanes via 1,2-silyl migration followed by destannylation.

The bismetallic reagent, 2-stannyl-3-silylpropene 1 should be a versatile intermediate since both the vinylstannane and allylsilane moieties might be independently and sequentially manipulated for the construction of more complex and usefully funtionalized molecules. Indeed, by modifying the vinylstannane moiety of 1 via the palladium-catalyzed cross-coupling with organic halides, various funtionalized allylsilanes could be obtained in good yields.¹ Thus obtained α -trimethylsilylmethyl-substituted divinyl ketones were useful acyclic precursors of α -methylenecyclopentanones via silicon-directed Nazarov reaction.²

In continuation of our studies on exploring synthetic application of 1, we performed the Lewis acid promoted reactions of 1 with acid chlorides in order to prepare vinylstannanes 4 by manipulating the allylsilane moiety of 1.³ Unexpectedly, vinylsilanes 3 were produced instead of vinylstannanes 4.



In a typical procedure, a dichloromethane (5 ml) solution of benzoyl chloride (142 mg, 1.0 mmol) was added to $AlCl_3$ (139 mg, 1.0 mmol) at -78 °C under argon atmosphere. After 10 min, 1a (276 mg, 1.0 mmol) in dichloromethane (1 ml) was added. The resulting solution was stirred for 2 hours at -78 °C, and the reaction was quenched by adding 3 M HCl and ether. The etheral extract was washed with sat. aq NaHCO₃ solution, dried over Na₂SO₄, and concentrated in vacuo. Purification by preparative TLC (silica gel, hexane/ether = 3 : 1) gave 196 mg (90%) of vinylsilane **3h**.

Entry	Acid chloride 2	Reaction Conditions ^a	Vinylsilane 3	Yield ^b %
a	CI	1 h	SiMe _{3 O}	85
b		2 h	SiMe ₃	89
с	Ph	2 h	SiMe _{3 O} Ph	90
d	Ci	2 h	Sille _{3 O}	76
e	S CI	3 h	SiMe ₃ O	96
f	CI CI	2 h	SiMe ₃ O	71
9	CI	0 ºC, 6h	SiMe ₃	52
h		2 h	SiMe ₃	90
		AlCl ₃ ^c , 2h	- 🗸 'Ph	90 20
		EtAICl ₂ °, 2h TiCl4 [°] , 1h		90 85

Table 1. Reaction of 1 with Acid Chlorides in the Presence of Lewis Acid.

^aReactions were carried out with the use of **1a** and $AICI_3$ at -78 ^{o}C in CH_2CI_2 , unless otherwise noted. ^bIsolated yield. ^c**1b** was used.

As indicated by Table 1, reactions of 2-trimethylstannyl-3-trimethylsilylpropene 1a with a variety of acid chlorides in the presence of AlCl₃ proceeded smoothly at -78 °C to furnish vinylsilanes 3 in good yields. The structure of products were established by spectral characterizations.⁴

When 2-tributylstannyl-3-trimethylsilylpropene **1b** was allowed to react with benzoyl chloride in the presence of $AlCl_3$, vinylsilane **3h** was also produced in 90% yield. We investigated the effect of Lewis acid on reaction of **1b** with benzoyl chloride. Ethylaluminum dichloride (EtAlCl₂) and TiCl₄ were also effective to produce **3h** (entry h). When $SnCl_4$ or BF_3 -etherate was used the reaction did not occur at all even at room temperature.

The formation of vinylsilane 3 could be rationalized as depicted in Scheme 1. An acylium ion is generated in situ from an acid chloride and $AICI_3$. It adds to C-1 of 2-stannyl-3-silylpropene 1 to produce carbocation I, which rapidly rearranges to the isomeric cation II. The cation II undergoes chloride-initiated destannylation to give vinylsilanes 3. Vinylstannane 4 would be expected from the desilylation of both cation I and II. However, no desilylated product 4 was detected. This indicates that the rearrangement of cation I to II is an irreversible process and the destannylation from cation II occurs exclusively over the desilylation.⁵ Such a high migratory aptitude of the silyl group can be attributed to the different stability of cation I and II. The cation I, though a generally more stable secondary carbocation, is largely destabilized by the α -stannyl group. On the contrary, the cation II is stabilized by interaction with the adjacent carbon-silicon and carbon-tin bonds.⁶





Catioinic 1,2-silyl migration has been observed in several systems.⁷ Danheiser and his coworkers observed 1,2-silyl migration in the β -silylvinyl cations generated from Lewis acid promoted reactions of allenylsilanes with electrophiles.⁸ This 1,2-silyl migration in [3 + 2] cycloaddition reactions was exploited for the preparation of several classes of five-membered carbocycles and heterocycles. More recently, 1,2-silyl shift across the single carbon-carbon bond of carbocations was also reported.⁹

To our knowledge, this is the first example of a transformation of vinylstannane to vinylsilane via 1,2-silyl migration followed by destannylation. Further study on the scope and synthetic applications of this reaction is in progress.

Acknowledgment : This work was supported by the Korea Science and Engineering Foundation through the Organic Chemistry Research Center. We also acknowledge Mr. Chi Hyo Park of Lucky Ltd., for GC-MS and NMR spectra.

References and Notes

- 1. Kang, K. -T.; Kim, S. S.; Lee, J. C. Tetrahedron Lett. 1991, 32, 4341.
- 2. Kang, K. -T.; Kim, S. S.; Lee, J. C.; U, J. S. Tetrahedron Lett. in press.
- 3. Pilot, J. P.; Deleris, J.; Calas, R. J. Org. Chem. 1979, 44, 3397, and references therein.
- 4. Spectral data for the selected vinylsilanes are given below.
 - **3b**: ¹H-NMR (CDCI₂) δ 0.08 (s. 9H), 1.88 (d. 3H, J = 1.2 Hz), 2.14 (d. 3H, J = 1.2 Hz), 3.21 (s. 2H), 5.50-5.54 (m, 1H), 5.63-5.67 (m, 1H), 6.07-6.11 (m, 1H); ¹³C-NMR δ-1.61, 20.69, 27.64, 52.01, 123.35, 128.45, 146.22, 155.39, 199.15; MS m/z 181 (M* - CH₃, 12), 83 (100), 73 (17%). 3d: 1H-NMR & 0.09 (s, 9H), 1.55-1.70 (m, 4H), 2.20-2.27 (m, 4H), 3.46 (s, 2H), 5.48 (s, 1H), 5.55 (s, 1H), 6.85-6.92 (m, 1H); ¹³C-NMR δ -1.54, 21.51, 21.94, 23.21, 26.06, 44.60, 127.52, 139.08, 140.36,146.94, 200.10; MS m/z 222 (M⁺, 1), 207 (32), 109 (100), 81 (82), 79 (68), 73 (59%). 3e: 1H-NMR & 0.12 (s, 9H), 3.72 (s, 2H), 5.56 (s, 1H), 5.70 (s, 1H), 7.10-7.15 (m, 1H), 7.63 (d, 1H, J = 4.9 Hz), 7.71 (d, 1H, J = 3.6 Hz); ¹³C-NMR δ -1.54, 46.87, 128.03, 128.59, 132.20, 133.56, 144.22, 145.80, 191.68; MS m/z 224 (M*, 2), 209 (61), 111 (100), 83 (19), 73 (42%). 3f: ¹H-NMR δ 0.16 (s, 9H), 3.69 (s, 2H), 5.56 (s, 1H), 5.66 (s, 1H), 7.28-7.33 (m, 1H), 7.54 (d, 1H, J = 4.9 Hz), 8.05 (d, 1H, J = 1.8 Hz); ¹³C-NMR δ -1.53, 47.46, 126.19, 127.20, 128.47, 132.17, 142.17, 146.00, 193.24; MS m/z 224 (M*, 3), 209 (65), 111 (100), 83 (36), 73 (51%). 3g: ¹H-NMR & 0.11 (s, 9H), 3.64 (s, 2H), 5.55 (s, 1H), 5.69 (s, 1H), 6.50-6.55 (m, 1H), 7.18-7.30 (m, 1H), 7.57-7.59 (m, 1H); ¹³C-NMR δ -1.62, 45.53, 112.20, 117.25, 128.60, 145.29, 146.22, 152.64, 187.79; MS m/z 193 (M⁺ - CH₂, 100), 95 (78), 75 (78), 73 (72%). 3h: ¹H-NMR δ 0.12 (s, 9H), 3.78 (s, 2H), 5.55 (s, 1H), 5.63 (s, 1H), 7.4-7.6 (m, 3H), 7.9-8.0 (m, 2H); ¹³C-NMR δ -1.54, 45.95, 128.41, 128.46, 128.53, 132.93, 136.91, 146.16, 199.17; MS m/z 218 (M⁺, 3), 217 (8), 203 (80), 105 (99), 77 (100), 73 (37%).
- Exclusive destannylation over desilylation was also found in the Lewis acid promoted . reactions of 1-silyl-3-stannylpropene with aldehydes. Yamamoto, Y.; Saito, Y.; Maruyama, K. J. Organomet. Chem. 1985, 292, 311.
- For β-tin stabilization of carbocation, see: Alvanipour, A.; Eaborn, C.; Walton, D. R. M. J. Organomet. Chem. 1980, 201, 233.
- For a review of 1,2-cationic rearrangements in organosilicon compounds, see: Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, **1980**; Vol.II, p 190-192.
- (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1980**, *102*, 6311. (b)
 Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407, and references therein.
- 9. Yamazaki, S.; Katoh, S.; Yamabe, S. J. Org. Chem. 1992, 57, 4.

(Received in Japan 23 March 1992)