A New Stereoselective Synthesis of (Z)-Vinylstannyl Allylic Alcohol

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Vinylstannanes which can lead to carbon-carbon bond formation under a variety of conditions are of increasing importance as intermediates in synthetic organic chemistry.¹ Indeed, vinylstannanes can be condensed with a large number of electrophiles including carbonyl compounds, enones, acyl chlorides, vinyl, aryl, and benzyl halides or triflates. In these reactions, vinylstannanes may be used as they are, in conjunction with palladium catalysts,¹² or as some other organometallic species by prior in situ transmetallation reaction (usually the vinyllithium or vinylvopper (I)).¹³⁻¹⁴

In connection with several projects currently under investigation in our laboratory, it is required to develop a fast and general route of (Z)-phenylthio substituted vinylstannane (1, Fig. 1). According to the early works in our lab, (Z)-phenylthio iodoolefin (2) could be prepared by a modification of the Corey reductive halogenation in acceptable yield.⁵ Although this iodoolefin (2) is equivalent to the corresponding vinylstannane (1) from a view point of synthetic chemistry, still efficient synthetic method for the compound 1 is not reported and our pure chemical interest lead us to focus on searching a new methodology. Recently, successful 1,4-silyl migration reactions on allyl silyl ether were reported (Eq. 1).⁶ Our group decided to test a feasibility of application of the 1,4-silyl migration reaction by substitution of silyl group to stannane (Eq. 2).

The required allyl stannane ether (6) was prepared from the corresponding (Z)-iodoalcohol (2, Eq. 3).⁵ The synthesis of (Z)-iodoalcohol (2) was accomplished from phenyl vinyl sulfide (7)⁷ as described in Scheme 2. With a (Z)-iodoalcohol (2) in hand, allyl stannane ether (6) was prepared by the following procedure.⁸

![Fig. 1.](image-url)
migration reaction without purification. Since the allyl stannane ether (6) is very sensitive to moisture, the reaction was monitored by NMR with Et₃N pre-treated (trace amount) CDCl₃. The product to the remaining starting compound ratio was calculated from the integration of allylic hydrogens. The best ratio between the product to starting compound was 13 to 1. Use of K₂CO₃ or K₂CO₃/MgSO₄ mixture as a dehydration agent did not show any improvement in the product yield.

The experimental procedure for the 1,4 O→C stannane migration reaction is described as follows (Eq. 2). The crude allyl stannane ether (6) obtained from the above reaction (assumed 0.267 mmol) dissolved in 1 mL of freshly distilled THF was added to a suspension of CeCl₃ (96 mg of CeCl₃·7H₂O, 0.267 mmol, pre-dried at 140°C for 3 h) in 3 mL of THF at room temperature. The solution was cooled to −78°C, treated with tert- BuLi (0.35 mL, 1.7 M in pentane, about 2 equiv), and stirred for 30 min at that temperature. The reaction mixture was then allowed to warm up to room temperature, stirred overnight, quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous MgSO₄, concentrated under reduced pressure then purified by flash column chromatography (30% diethyl ether/70% hexane) to afford the phenylthio substituted vinyl stannane (1) in 60% overall yield from the starting (Z)-iodoalcohol (2). Destannylated phenylthio allyl alcohol (3, Fig. 1) was also detected as a major byproduct and subsequently isolated.

Regiochemical and stereochemical assignments of vinyl stannane (1) structure was made based on the vinylic hydrogen (t, 6.12) coupling constant (¹H NMR) of 5.1 Hz (allylic hydrogen) and 194.4 Hz (trans Sn¹¹⁷/Sn¹¹⁹) respectively.³

Although the reaction was quite successful, each
of the reaction steps should be carried out under extreme caution since most of reagents and intermediate were very moisture sensitive. The mechanism of the stannane migration reaction is presumed to follow an intramolecular pathway through an intermediate of penta-coordinated stannate based on the results of silicon version of the reaction. This explanation implicate that the equilibrium between stannated vinyl carbanion and allylic alkoide is expected to be lifted according to the stability of each species but this idea is await for experimental verification. Further application of the intramolecular delivery concept on related \( \gamma \)-stannated allylic alcohols are the subject of our current studies.

REFERENCES

9. The average coupling constant for cis vinyllic hydrogen-Sn\(^{117}\)/Sn\(^{119}\) in the (E) diasteromer of 5 is 48.5 Hz.