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A ROUTE TO 1,1-DIORGANOMETALLIC SPECIES VIA THE CLAISEN REARRANGEMENT OF FUNCTIONALIZED γ-HYDROXYVINYLSTANNANES

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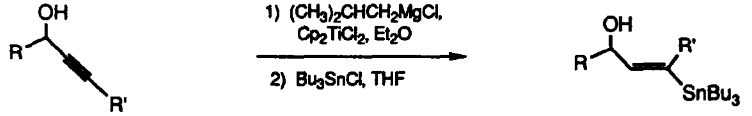
Abstract: A variety of γ-hydroxyvinylstannanes were subjected to the Eschenmoser Claisen rearrangement to produce allylstannanes including those bearing a silicon and tin on the same carbon.

Allylsilanes and stannanes have proven to be be useful intermediates for a variety of organic transformations.[2] For example, allylstannanes undergo highly regio- and stereoselective carbonyl addition processes,[3b] displacement reactions and a variety of radical or metal-catalyzed coupling reactions.[3] Allylsilanes show similar reactivity patterns though there is no data available on the reactivity of compounds bearing both functional groups to determine whether differential reactivity can be achieved.

Ritter has recently shown that the Claisen rearrangement of hydroxyvinylstannanes represents a useful method for the synthesis of simple allyl- or vinylstannanes.[4] The principal limitation associated with this methodology is the difficulty encountered in the synthesis of highly substituted stannylated starting materials. Known methods for the introduction of tin into propargyl alcohols include 1) the radical hydrostannylation process,[5] 2) the hydroalumination-stannylation reaction[6] or 3) a palladium-catalyzed silylstannylation.[7]

We have recently reported the stereospecific synthesis of highly substituted γ-hydroxyvinylstannanes via the titanium catalyzed hydrometallation of propargyl alcohols (the Sato reaction[8]) followed by trapping of the resulting vinylorganometallic species with tributyltin chloride, eq. 1.[9] We have shown that a wide range of substituents are tolerated on the acetylenic carbon including alkyl and aryl groups, silanes and stannanes. In this publication we report the facile preparation of highly functionalized allylstannanes via a Claisen rearrangement of these materials. In particular, a simple entry into the synthesis of 1,1-diorganometallic compounds is described.[10]

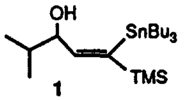
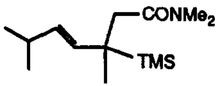
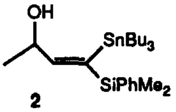
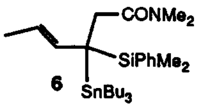
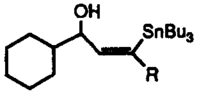
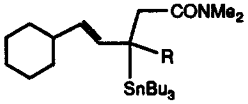
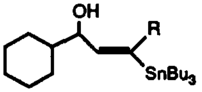
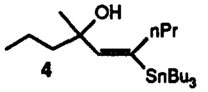


(1)

We were particularly interested in preparing allyl stannanes bearing a second organometallic group (i.e. R'= tin or silicon) on the same carbon. The Eschenmoser variation[11] of the Claisen rearrangement proved to be ideal since the reaction is carried out under nearly neutral conditions insuring the survival of the allyl diorganometallic products which we suspected to be extremely sensitive toward acidic conditions.

The results in Table 1 show that a variety of secondary alcohols undergo rearrangement when heated with N,N-dimethylacetamide dimethyacetal in cyclohexane or toluene.[12] High olefin selectivity (trans:cis>10:1) was apparent from the ^1H NMR spectra of the crude products. Substrates bearing a tin and a silicon on the

Table 1 Claisen Rearrangement of γ-Hydroxyvinylstannanes

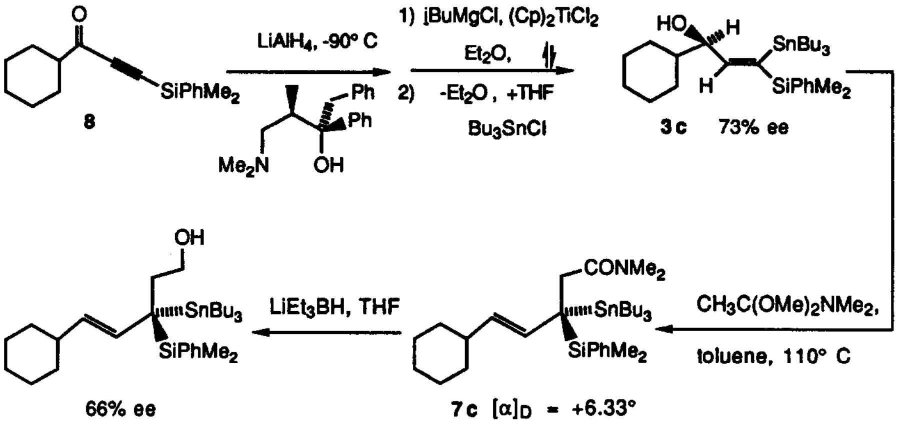
Entry	Propargyl Alcohol[1]	Time[2]	Product	Yield[3]
1	 1	36 h,B	 5	85%
2	 2	16 h, B 36h, A	 6	66%[4] 60%
3				
	3 a R=TMS	16h, B	7 a R=TMS	79%
	b R=SiPhMe 2	24h, B	b R=SiPhMe 2	79%
	c R=SnBu 3	16h, B	c R=SnBu 3	84%
				
	d R=n-Bu	16h, A	d R=n-Bu	86%
	e R=Ph	16h, B 24h, A	e R=Ph	53%[5] 70%[6]
4	 4		N.R.	

1. Vinylstannanes prepared by the titanium catalyzed hydrostannylation, see ref. 9. 2. Reaction time using 3-5 eq. of $CH_3C(OMe)_2NMe_2$ at A= 80° C in cyclohexane or B=110° C in toluene. 3. Yield after purification by flash chromatography. 4. The regioisomeric allylstannane was isolated in 33% yield, see text. 5. The regioisomeric allylstannane was isolated in 13% yield, see text. 6. Less than 5% of the isomeric stannane

olefinic carbon required higher reaction temperatures and longer reaction times to give complete reaction. Ritter has shown a similar trend for the rearrangement of the E vs. Z terminal vinylstannanes. Tertiary alcohols did not react under these conditions, entry 4. We noted that with substrates 2 and 3e, selective metallotropic rearrangement of the tin moiety occurred when the Claisen reaction was carried out at temperatures above 95° C. This result was surprising since 2,3a,b were stable at 110° C. It appears as if the tin is more likely to undergo metallotropic shift if the difference in steric environment is large or if rearrangement would lead to increased conjugation. Allyldistannane 7c was rather sensitive to chromatography requiring rapid purification on a short plug of silica gel but the other compounds were all stable to standard purification conditions. Adducts 5,6, 7a-c are particularly interesting as they contain a carbon bearing two tins or a tin and silicon in the same molecule in allylic orientations.[13] This combination of functional groups is quite rare and their chemistry is totally unexplored. These molecules are currently being assessed as synthons of either a 1,1 allyl dianion or a 1,3-allyl dianion.

In light of the particular interest in the preparation of optically active allyl organometallics we have carried out preliminary investigations on the utility of the hydrostannylation-rearrangement to address this challenge, Scheme 1. Reduction of ketone 8 with Darvon alcohol[14] and $LiAlH_4$ gave the propargyl alcohol in 98% yield and 73% ee as measured by conversion to the Mosher ester.[15] Hydrostannylation under the standard conditions gave 3c in 79% yield with no change in the ee. Finally, Claisen rearrangement in toluene at 110° C for 16h gave 7c in 74% yield. While 7c had an optical rotation of +6.33° we were unable to determine the degree of chirality transfer since the use of chiral shift reagents failed to resolve any signals in the ^{1}H NMR spectrum. However, following reduction of the amide to the primary alcohol (Super Hydride™, THF),[16] conversion to the Mosher ester indicated an enantiomeric excess of 66%, i.e. ca. 90% chirality transfer. The stereochemistry at C-3 is assumed to be (*S*) on the basis of a chair-like transition state for the rearrangement. With improved methods for the synthesis of optically pure alcohols emerging,[17] we feel that the synthesis of highly enriched chiral allyl diorganometallic compounds is now possible using the methodology reported herein. Further increases in levels of chirality transfer may be possible using other variations of the Claisen rearrangement which occur at lower temperatures.[18]

Scheme 1



In conclusion, we have shown that the preparation of allylstannanes with additional metalloid substituents on the carbon bearing the tin is quite simple using substrates prepared by hydrometallation-rearrangement reactions.

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12. A typical experimental procedure is as follows: The allylic alcohol (0.2 mmol) was dissolved in toluene or cyclohexane (0.75 mL) to which was added N,N-dimethylacetamide dimethylacetal (3-5 equiv.). The reaction was heated to reflux for the indicated time then poured into a separatory funnel containing ether and brine. After removal of the volatiles, the crude mixture was passed through a short plug of silica gel yielding the pure products. Satisfactory NMR, IR, and mass spectra and/or combustion analyses were obtained for all new compounds.

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