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Concise Allene Synthesis from Propargylic Alcohols by Hydrostannation and Deoxystannylation: A New Route to Chiral Allenes

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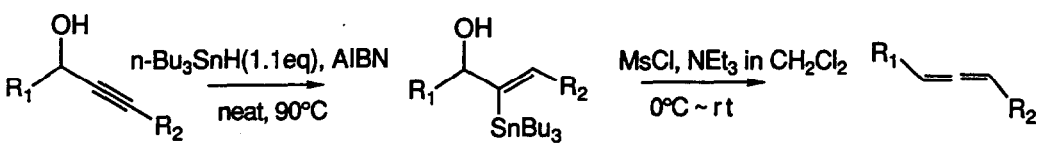
Abstract: Propargylic alcohols were converted to allenes in a two-step one-pot process comprised of hydrostannation of propargylic alcohols and subsequent deoxystannylation. Chiral (*S*)-2,3-decadiene of high enantiomeric excess (ee) can be prepared in a similar way.

Allenes have become extremely versatile intermediates in organic synthesis,[1] and 1,3-disubstituted allenes, which are chiral in nature, can serve as synthons in the preparation of chiral molecules. Propargylic alcohols have proven to be useful precursor for allene synthesis. The most frequently employed method is the S_N2' type reaction of propargylic derivatives with organometallics or hydride reagents. Chiral allenes can be prepared from chiral propargylic alcohols,[2] but obtaining high levels of chirality induction is difficult.

In considering the allene structure, β-elimination from a suitably substituted allylic alcohol was expected to offer an alternative approach to the construction of allenes. Here we describe this type of allene synthesis from propargylic alcohols, based on the use of tin chemistry,[3] in a conceptually different manner from conventional allene syntheses.



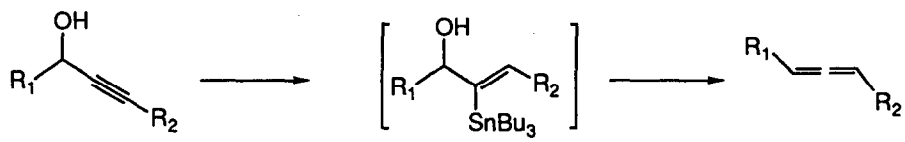
1 2 3

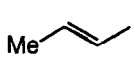
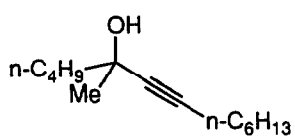
Our synthesis utilizes the radical hydrostannation of propargylic alcohols **1** and subsequent deoxystannylation of the resultant stannyl allylic alcohols **2**. The results are summarized in Table 1,[4] which shows how a variety of propargylic alcohols can be converted into allenes **3**.[5] Our first step focused on the

addition of tributyltin hydride on propargylic alcohols in the presence of a catalytic amount of AIBN. Several of our findings are noteworthy although there have been many studies on the hydrostannation of acetylenic alcohols. Propargylic alcohols of non-terminal acetylenes led exclusively to allylic alcohols stannylated at the 2-position.[6] Alkyl-substituted acetylenes gave the *Z* isomer with very high selectivity (>95%),[7] in contrast, phenyl- or alkenyl-substituted ones (entry 4, 5) gave a mixture of *Z* and *E* isomers (1:1). The stereochemistry of the addition was apparent from the ^{1}H NMR spectra by examination of the ^{117}Sn-H coupling constant; when the proton and tin were cis, J = 50-80 Hz and when they were trans, J = 95-155 Hz.[8] Propargylic alcohols bearing an sp^2 substituent at the α-position (entry 6, 7) and a tertiary propargylic alcohol (entry 8) required moderate excess (1.5 eq.) of tin hydride to give a complete reaction, and the yields of hydrostannation were modest. These stannylated alcohols were sensitive to silica gel chromatography and used without purification for the second step.

The second step is the deoxystannylation of the resulting β-stannyl allylic alcohols **2**. The deoxystannylation by the β-elimination of stannyl alcohols was executed quite effectively just by treatment with methanesulfonyl chloride and triethylamine to give allenes **3**. An allylic methanesulfonate was presumed to be an

Table 1. Formation of Allenes from Propargylic Alcohols via Stannyl Allylic Alcohols

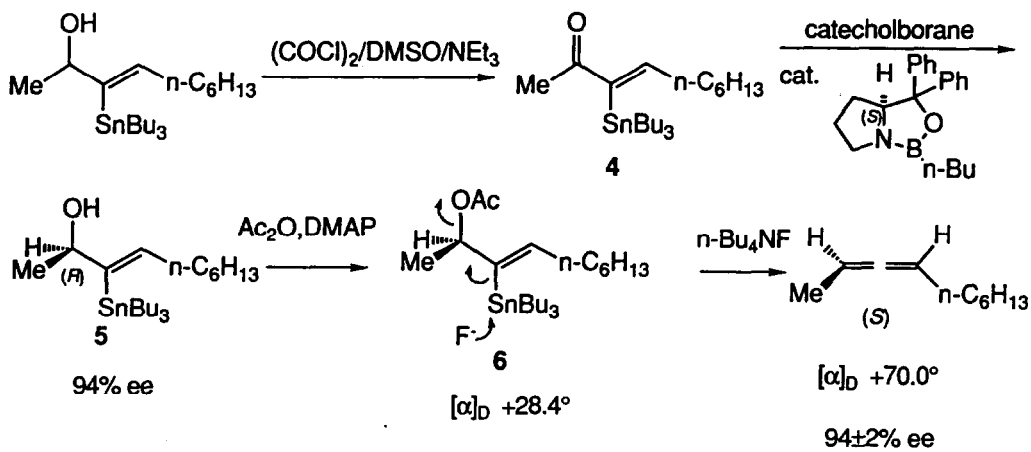


entry	Propargylic Alcohol[c]		Allene, % yield[d]
	R_1	R_2	
1	Me	n-C_6H_{13}	81
2	Et	n-C_6H_{13}	71
3		n-C_4H_9	75
4	Et	Ph	85[a]
5	Me		72[a]
6		n-C_6H_{13}	40[b]
7	Ph	-CH_2OTBDMS	43[b]
8			59[b]

a) A mixture of *E*- and *Z*-vinyltin was obtained by hydrostannation.
b) 1.5 eq of n-Bu_3SnH was used.
c) Propargylic alcohols were prepared by addition of acetylide (EtMgBr, 0°C to room temperature) to the corresponding aldehyde or ketone.
d) Yield after purification by chromatography and/or distillation.

intermediate but was not detected because β-elimination of stannyl methanesulfonate was rapid under the reaction conditions. Our deoxystannylation conditions are very mild and should be useful in organic synthesis as β-stannyl alcohols are olefin precursors[9] and the related deoxystannylation[10] of stannyl alcohols has been used in organic synthesis. Chan[11] reported the Peterson-type[12] allene synthesis based on the high affinity of silicon and fluorine, which has only limited synthetic utility. Our allene synthesis is simple and concise and can be performed in one-pot two-step process under mild conditions without the need to isolate or purify the intermediate stannyl allylic alcohols.

In light of the interest in the preparation of chiral allene, we carried out a preliminary investigation on the utility of the deoxystannylation of a chiral stannyl allylic alcohol. Ketone **4**[13] was prepared by oxidation[14] of racemic (*Z*)-3-tributylstannyl-3-decene-2-ol, and reduction of **4** under Corey's condition[15] gave the optically active (*R*)-(*Z*)-3-tributylstannyl-3-decene-2-ol **5** in 78% yield and 94% ee as measured by the conversion to the Mosher ester.[16] It was converted to (*S*)-2,3-decadiene of 51% ee by treatment of methanesulfonyl chloride-triethylamine. The relationship between the absolute configuration of the starting allylic alcohol and the allene shows that the deoxystannylation proceeded in the anti-β-elimination process with a slight loss of specificity. Finally, (*S*)-2,3-decadiene of higher ee was prepared by the two-step process. Alcohol **5** was converted to acetate **6** in 81% yield and this was treated with tetrabutylammonium fluoride to give (*S*)-2,3-decadiene in 42% yield in 94±2% ee as measured by ^{1}H-NMR with chiral shift reagent,[17] ([α]$_D$ 70°, *c* 1.3 in methanol)[18]. This demonstrated the essentially complete anti-specificity of β-elimination.



In conclusion, we have shown that the preparation of allenes from propargylic alcohols is quite simple and can be used to obtain chiral allenes.

References and Notes

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4. A typical experimental procedure is as follows: A mixture of propargylic alcohols (10 mmol) and tributyltin hydride (11 mmol) was heated under nitrogen atmosphere with a catalytic amount of AIBN. After 10 ml of dichloromethane was added to dilute the mixture, triethylamine (20 mmol) and methanesulfonyl chloride (15 mmol) were added under ice cooling. The reaction temperature was allowed to rise to room temperature and stirring was continued for 30 min. The mixture was poured into diluted aqueous hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with an aqueous solution of sodium bicarbonate and dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The residue was purified by silica gel chromatography and/or distillation under reduced pressure.
5. Satisfactory ^{1}H- and ^{13}C-NMR, IR, mass spectra and/or elemental analysis were obtained for all the new compounds.
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13. ^{1}H NMR ($CDCl_3$) δ 7.17(t, 1H, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{SnH}$ = 116.8/111.8 Hz), 2.27(s, 3H), 2.3-2.1(m, 2H), 1.6-1.2(m, 20H), 1.0-0.8(m, 18H)
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