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Novel diastereoselective synthesis of (*E*)- and (*Z*)-allylsilanes via organoboranes

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Abstract—A simple, novel diastereoselective synthesis of both (*E*)- and (*Z*)-allylsilanes via organoboranes is developed. (*E*)-1-Alkenylboronate esters easily prepared from the corresponding terminal alkynes via hydroboration with dibromoborane-methyl sulfide complex followed by treatment with 1,3-propane diol readily react with trimethylsilylmethyllithium at −78 °C in methanol followed by reaction with iodine in methanol to produce the corresponding (*Z*)-allylsilanes in high yields (72–80%) and in high stereochemical purities (98% as evidenced by CMR spectral data). Similarly, the (*Z*)-1-alkenylboronate esters react with trimethylsilylmethyllithium at −78 °C in methanol followed by treatment with iodine in methanol to produce the corresponding (*E*)-allylsilanes in moderate yields (57–65%) in high stereochemical purities (>98% as revealed by CMR spectral data).

1. Introduction

Organosilanes are extremely useful in organic synthesis due to the large number of transformations the C–Si bond is capable of undergoing. Among the organosilanes, a considerable degree of importance has been placed on allylsilanes because of their roles as synthetic intermediates.[1] Allylsilanes are versatile compounds that are thermally stable and remain unreactive when in the presence of water or oxygen, requiring no special precautions for storage of allylsilanes. It is in part due to this high level of stability that allows such high degrees of regioselectivity and stereoselectivity when running reactions that involve allylsilanes.[2,3]

Examples of the uses for allylsilanes include being an important intermediate for a variety of stereocontrolled C–C bond formation, carbocyclic ring forming reaction[4] and participation as a starting compound for rhenium-catalyzed coupling reactions with propargyl alcohols.[5] Along with the synthetic importance of allylsilanes, some of these compounds are also incorporated in the reaction schemes of natural products such as Apicularen A, which has demonstrated a number of medicinally important applications such as to act as a strong antitumor agent.[6] Within natural synthesis, allylsilanes are seen as important because they are highly nucleophilic π-systems that are relatively inert toward a wide range of reactants and are also resistant to functional group manipulations such as saponifications, oxidations, and reductions. While they are extremely stable under normal conditions, allylsilanes can be made active with electrophiles that are generated in situ by the addition of a Lewis acid.[7]

Due to the value of allysilanes in organic synthesis, several methods for their synthesis have been developed. Such methods include its preparation via reductive lithiation of thioethers[8] or via silylcupration of C–C multiple bonds.[9] Stereoselective preparations of allylsilanes, however, are necessary when the synthesis reactions they participate in need to be of specific configuration. It has been shown that the presence of minor isomers in the product generally inhibit biological activity, therefore stereospecific synthesis of the most active isomer is of great scientific importance.[10] Methods of stereoselective preparations of allylsilanes in the past include a general route of cobalt-catalyzed mono-coupling of R_3SiCH_2-MgCl with 1,2-dihalogenoethylene[11] and coupling reactions of dienes and aldehydes using a nickel complex bearing PPh_3 or *N*-heterocyclic carbene.[12]

The method presented here, however, is unique in its usage of organoboranes for the synthesis of (*E*)-allylsilanes. These boron containing organic compounds have been proven to be of significant use as intermediates in

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various other organic synthetic reactions such as the enantioselective synthesis of α-amino acid derivatives,[13] the selective oxidation of zirconocyclopentenes,[14] and the catalytic ring-opening of polymerization of propylene oxide.[15] In this report, we investigate a novel synthesis of stereospecific allyltrimethylsilanes utilizing organoboranes. The purpose of producing stereospecific allylsilanes using organoboranes is to provide an alternate route of synthesis for a compound widely used as both starting material and as an intermediate in various organic synthetic reactions. Allylsilanes can also be used for non-synthetic purposes such as acting as a binding functional group in silica gel for affinity chromatography.[16]

2. Results and discussion

2.1. Synthesis of α-bromo-(*Z*)-1-alkenylboronate esters

Before the synthesis of the allylsilane could begin, the organoborane first needed to be synthesized. As reported by Brown et al.,[17] 1-alkynes will react with *n*-butyllithium followed by bromine to afford the corresponding 1-bromo-1-alkynes. The alkynes are then subsequently converted to (*Z*)-1-bromo-1-alkenylboronate esters when it is hydroborated with dibromoborane-methylsulfide complex followed by the reaction with 1,3-propanediol.

2.2. Synthesis of (*Z*)-1-alkenylboronate esters

In order to convert the above compound into the needed (*Z*) isomer, the product was then reacted with potassium tri-isopropoxyborohydride (KIPBH) as reported by Brown et al.[18] causing the replacement of the bromide in the ester with a hydrogen. The ability for the ester to maintain the (*Z*) configuration is of paramount importance in the stereoselective synthesis of the (*E*)-allylsilane. With separate stockpiles of (*Z*) and (*E*) *1-alkenylboronate esters*, the compounds can be reacted in a parallel reaction scheme with the same procedure to give the corresponding (*Z*) and (*E*)-allylsilanes with high stereo-purity.

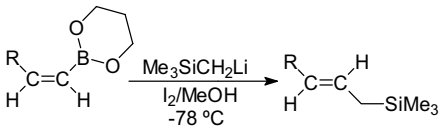
2.3. Synthesis of the (*Z*) and (*E*) allylsilanes

The following procedure will deal with formation of the (*E*)-allylsilane. With a supply of (*Z*) 1-alkenylboronate esters, the (*E*)-allylsilanes were then synthesized via treatment with trimethylsilylmethyllithium in the presence of iodine and methanol at −78 °C (Eq. 1). The slight polarity between the C–Li bond of trimethylsilylmethyllithium causes an attraction to the empty orbital of the boron in the ester, creating an 'ate' complex. This complex then reacted with the iodine in methanol to produce the (*E*)-allyltrimethylsilane.[19] The same reaction with (*E*) 1-alkenylboronate esters yielded (*Z*)-allyltrimethylsilanes (Eqs. 1 and 2).

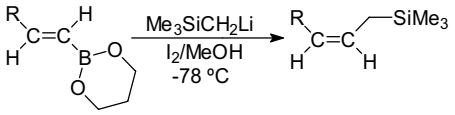
Table 1. Diastereoselective synthesis of (*E*)- and (*Z*)-allylsilanes (Eqs. 1 and 2)

Entry	R	Percent yield (*Z*)[a,b] (%)	Percent yield (*E*)[a,b] (%)
1	$-C(CH_3)_3$	57	80
2	n-C_5H_{11}	65	78
3	$-(CH_2)_3Ph$	61	—
4	$-(CH_2)_3Cl$	60	74
5	n-C_6H_{13}	64	73
6	n-C_4H_9	57	74
7	$-(CH_2)_2Ph$	—	72

[a] All of the reactions were carried out on 5 mmol scale.
[b] Isolated yields. The stereochemical purities[20] were established by NMR spectral data.



(1)



(2)

This procedure was repeated with 1-alkynes containing different R groups (Table 1).

3. Conclusions

A novel synthesis of stereospecific allylsilanes was effectively developed. By synthesizing (*E*)-1-alkenylboronate esters as described in the literature[16] and then replacing the boron with trimethylsilylmethyl group via reaction with trimethylsilylmethyllithium followed by iodine in methanol, the stereoselective synthesis of (*Z*)-allylsilanes was accomplished. Similarly, the reaction of trimethylsilylmethyllithium with (*Z*)-1-alkenylboronate esters followed by reaction with iodine in methanol produced the corresponding (*E*)-allylsilanes. We are currently engaged in extending this methodology with other stereodefined alkenylboronate esters.

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19. The synthesis of 5-phenyl-2-(*E*)-pentenyl-1-trimethylsilane is representative: The α-bromo-(*Z*)-1-alkenylboronate ester was prepared as described by Brown et al.[17] To 10 mmol of α-bromo-(*Z*)-4-phenyl-1-butyl boronate ester (1.9 mL) was added KIPBH[18] (12 mmol, 12 mL) at 0 °C in a nitrogen-fixed 100 mL round-bottomed flask equipped with magnetic stir bar. The mixture was allowed to stir overnight, then reacted with excess water to remove byproduct triisopropoxyborane. The product was then extracted with 75 mL ether and 100 mL water, then washed twice with 25 mL water. Evaporation and subsequent vacuum pump were applied to remove excess ether. To the resulting solution were added 50 mL pentane and 1 mL 1,3-propanediol and stirred for an hour. The product was decanted and washed with pentane, and the excess solvent removed through evaporation and vacuum pump again. The crude product was further purified by column chromatography using alumina and pentane. NMR and IR analyses confirmed the synthesis of (*Z*)-1-alkenylboronate ester.
(Z)-4-Phenyl-1-butenyl boronate ester: PMR ($CDCl_3$/TMS): δ 1.96–3.19 (*m*, 6H), 4.05 (*m*, 4H), 5.34 (*m*, 1H), 6.69 (*m*, 1H) and 7.28 ppm (*m*, 5H). CMR ($CDCl_3$/TMS): δ 27.51, 33.56, 36.28, 61.67, 61.82, 76.85, 77.27, 77.69, 125.83, 128.35, 128.69, 142.34, and 151.38 ppm. The newly synthesized (*Z*)-4-phenyl-1-butenyl boronate ester was redissolved in 10 mL of ether and allowed to stir with 10 mmol trimethylsilylmethyllithium at −78 °C in a 100 mL round-bottomed flask for a few hours. To the resulting solution was added 10 mmol iodine dissolved in methanol and allowed to stir overnight. Workup followed by purification over column chromatography provided the corresponding (*E*)-allyltrimethylsilane. The spectral data confirmed its identity.
5-Phenyl-2-(E)-pentenyl-1-trimethylsilane: PMR ($CDCl_3$/no TMS): δ 0.058 (*s*, 9H), 1.44–2.82 (*m*, 6H), 5.45 (*m*, 1H), 6.27 (*m*, 1H) and 7.33 ppm (*m*, 5H). CMR ($CDCl_3$/no TMS): δ −1.81, 22.00, 34.22, 36.53, 126.24, 128.37, 128.60, and 140.377 ppm. IR: υ 1495 (aromatic region) and 1603 cm^{-1} (C=C).
20. In a mixture of isomers, the vinylic carbons of the (*Z*)-alkenes can be distinguished from the corresponding carbons of (*E*)-alkenes. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem* **1971**, *36*, 2757.