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A NEW SYNTHESIS OF γ-HYDROXYVINYLSTANNANES AND SILANES UTILIZING β-STANNYLVINYL AND β-SILYLVINYL SULFONES

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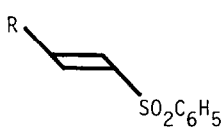
Summary: β-Stannylvinyl sulfone 1 (new compound) and β-silylvinyl sulfone 2 on sequential treatment with Bu_3SnLi and aldehydes afforded γ-hydroxyvinylstannanes 6 and silanes 7, respectively, in good yields. From β-chlorovinyl sulfones 9 and 10 stannanes 11 were prepared. The stannanes 11 were shown to be useful for the synthesis of α,β-unsaturated γ-lactones 12.

A useful synthesis of the substituted allyl alcohols has been required strongly, because of their wide distribution in the molecules of biologically active natural products. For the synthesis of such a synthon, vinylstannanes and vinylsilanes seem to be promising intermediates, because their transformations such as substitution reaction by electrophilic reagents[1] and transmetalation[2,3] occur smoothly and are highly applicable. In fact, prostaglandin E_2 was prepared by the conjugate addition to cyclopentenones of the mixed cuprate derived from the O-protected γ-hydroxyvinylstannane.[4] We wish to report a new approach for the stereoselective synthesis of γ-hydroxyvinylstannanes and silanes utilizing a Michael addition of tributylstannyllithium to β-stannyl and β-silyl substituted vinyl sulfones.

E-1-Phenylsulfonyl-2-(tributylstannyl)ethylene (1), a key compound for the synthesis of γ-hydroxyvinylstannanes 6, was prepared from β-chlorovinyl sulfone 3 stereoselectively. The chloride 3 was obtained from acetylene by treatment with benzenesulfenyl chloride followed by the oxidation (*m*-CPBA), according to the Montanari's procedure.[5] The conjugate addition of Bu_3SnCu[6] to 3 took place in THF at -78°C with concomitant loss of chloride, and the vinylstannane 1 was given in 55% yield.[7] Its *E*-stereochemistry was determined by the large coupling constant (18 Hz) between two vinylic protons.



1 R = Bu_3Sn
2 R = Me_3Si
3 R = Cl

Addition of Bu_3SnLi[8] to sulfone 1 in THF or hexane at -78°C followed by the treatment with aldehyde afforded the desired vinylstannane 6 directly in good yield. The results are

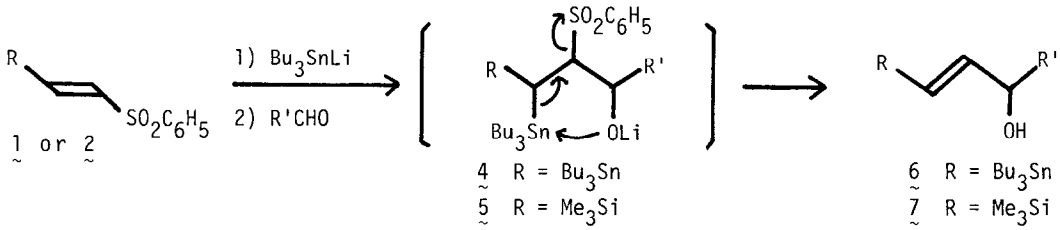
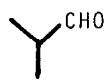
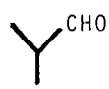


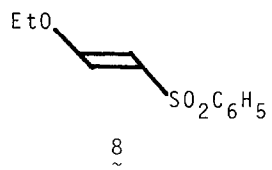
Table Synthesis of γ-hydroxyvinylstannanes 6 and silanes 7[a]

Run	R'CHO	Vinyl Sulfone	Solvent	Product	Ratio *E* : *Z*	Yield, %[b]
1		1	THF	6a[c]	85 : 15	82
2	"	1	hexane	6a	66 : 34	92
3		1	THF	6b[c]	61 : 39	69
4	"	1	hexane	6b	35 : 65	85
5		1	THF	6c[c]	63 : 37	89
6	"	1	hexane	6c	30 : 70	89
7		2	THF	7a	100 : 0	85
8		2	THF	7b	100 : 0	93
9		2	THF	7c	100 : 0	77

a) To a solution of sulfone 1 or 2 in THF or hexane was added dropwise a solution of Bu_3SnLi (1.2 equiv.) in THF at -78°C under nitrogen. After being stirred for 10 - 20 min, aldehyde (1.2 equiv.) was added to the resulting red solution at -78°C. The reaction temperature was finally raised to room temperature. The mixture was poured into brine and extracted with dichloromethane. Concentration of the dried (Na_2SO_4) extracts and purification by flash column chromatography or preparative TLC afforded the product. b) Isolated yield. c) a: R' = C_5H_{11}; b: R' = $C_6H_5(CH_2)_2$; c: R' = $(CH_3)_2CH$.

summarized in Table (Runs 1-6). The reaction seems to proceed *via* the destannylsulfonation[9] of the initially formed β,β-bis(tributylstannyl) sulfone 4. The intramolecular attack of oxygen anion to one of its two tin atoms may play an important role in the destannylsulfonation of 4. The ratio of stereoisomers in product 6 was highly dependent on the solvent. The *E*-isomer of 6

was obtained as the major product in THF. Thus the stannane 6a was shown to consist of 85% of the *E*-isomer, a potent intermediate for prostaglandin E_2 (Run 1). In hexane, however, *Z*-isomers of 6b and 6c were the major products. Such a solvent effect can be reasonably explained by considering a more tight coordination between oxygen and tin atoms of 4 in hexane than in THF, which may be one of the most important factors controlling the stable conformation of 4. Vinylstannane 6a was also obtained directly from *E*-β-ethoxyvinyl sulfone 8 *via* the *in situ* formation of β-stannylvinyl sulfone 1: 8 on treatment with 2.6 equiv. of Bu_3SnLi and 2 equiv. of hexanal in THF gave the stannane 6a (*E* : *Z* 91 : 9) in 74% yield.[10]



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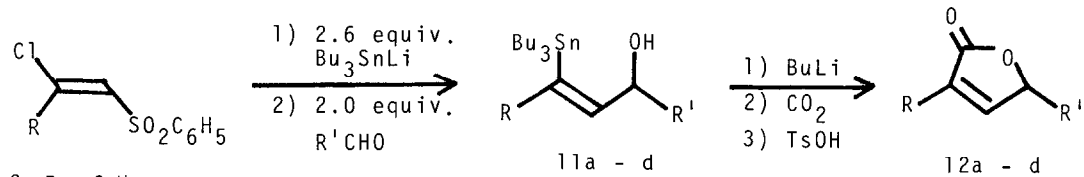
In contrast to the above results, β-trimethylsilylvinyl sulfone 2[11] on similar treatment with Bu_3SnLi and aldehydes in THF afforded *E*-γ-hydroxyvinylsilanes 7 in a completely stereoselective manner (Table, Runs 7-9). In the reaction an alternative pathway yielding vinylstannanes 6 by the desilylsulfonation of the possible intermediates 5 should be considered, but the formation of 6 was not observed. Compared with the report of Gröbel and Seebach,[12] in which deoxysilylation of the lithium salt of β-silyl-β-stannyl alcohol was shown to be a preferred reaction pathway over its deoxystannylation, the above results are very interesting.

γ-Hydroxyvinylstannanes 11 were also prepared from β-chlorovinyl sulfones[13] 9 and 10 in THF. The major products isolated by preparative TLC were found to be *Z*-isomers of 11. Their stereochemistry was determined by the coupling constant between tin and vinylic proton: for example, the observed coupling constants, J(Sn-H), of *E*- and *Z*-isomers of 11a were 70 and 129 Hz, respectively.[14] As one of the synthetic applications of γ-hydroxyvinylstannane, *Z*-isomers of 11 were converted to the α,β-unsaturated γ-lactones 12 by the following reaction sequence: i) an excess BuLi in THF, ii) carbon dioxide, and iii) *p*-toluenesulfonic acid in refluxing benzene. The results reconfirmed the *Z*-stereochemistry for the major isomers of 11.

Thus we developed a new convenient method for the synthesis of γ-hydroxyvinylstannanes and silanes.



9 R = C_6H_{13}
10 R = $C_6H_5(CH_2)_2$

11a - d

12a - d

		Yield of 11	Ratio (*E* : *Z*)	Yield of 12 (from *Z*-11)
a	R = C_6H_{13}, R' = C_5H_{11}	11a 57%	17 : 83	12a 97%
b	R = C_6H_{13}, R' = $C_6H_5(CH_2)_2$	11b 56%	11 : 89	12b 66%
c	R = $C_6H_5(CH_2)_2$, R' = C_5H_{11}	11c 73%	18 : 82	12c 54%
d	R = R' = $C_6H_5(CH_2)_2$	11d 72%	16 : 84	12d 64%

References and Notes

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7. 1; IR($CHCl_3$) 1590, 1470, 1450, 1315, 1150, 1090, 980, 870, 635, 560, 540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6 - 1.9 (27H), 6.65 (d, J = 18 Hz, 1H), 7.3 - 7.6 (m, 3H), 7.72 (d, J = 18 Hz, 1H), 7.75 - 7.9 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) δ 148.0, 142.6 (each d), 140.3 (s), 133.2, 129.2, 127.8 (each d), 28.8, 27.1(each t), 13.6 (q), 10.1 (t) ppm; MS (m/e) 401 (M^+-Bu), 345, 289, 197, 177, 125.
8. Bu_3SnLi was prepared from tributyltin chloride and an excess amount of granular lithium in THF: (a) K. Kobayashi, M. Kawanisi, T. Hitomi, and S. Kozima, *J. Organomet. Chem.*, 233, 299 (1982); (b) C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, 28, 237 (1963).
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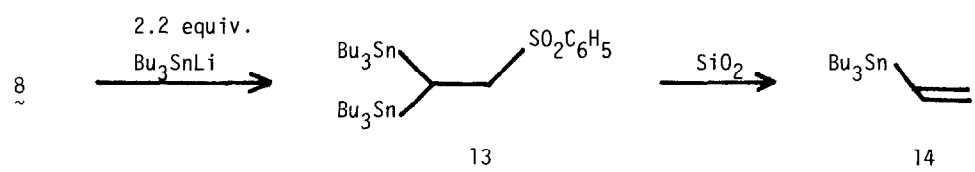
10. Michael addition of Bu_3SnLi to 8 afforded the sulfone 13, which on treatment with silica gel in chloroform at 50°C produced vinylstannane 14 in good yield.



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13. Prepared by the copper-catalyzed addition of benzenesulfonyl chloride to acetylenes: Y. Amiel, *J. Org. Chem.*, 36, 3691 (1971).
14. It has been known that | J(Sn-Htrans) | is about two times as large as | J(Sn-Hcis) |: A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, 9, 285 (1967).

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