CHEMISTRY LETTERS, pp. 1457-1458, 1983. 1983

A NEW STEREOSELECTIVE SYNTHESIS OF VINYLSILANES UTILIZING VINYL SULFONES

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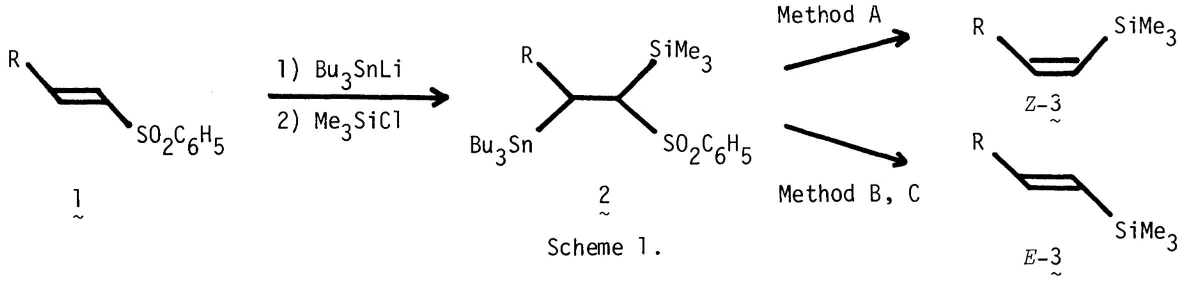
Vinylsilanes 3 were prepared stereoselectively from vinyl sulfones *via* the formation of β-tributylstannyl sulfones 2. The stereochemistry of 3 was controlled by the choice of the method for the destannylsulfonation of 2.

The reaction of vinylsilanes with a wide variety of electrophiles has been shown to be highly stereoselective and applicable.[1] Hence it became very important to develop a method for the stereoselective synthesis of vinylsilanes. Actually some methods have been reported: hydrosilylation of alkynes,[2] hydrometallation of alkynylsilanes followed by the proto- or carbo-demetallation,[3] and silyl-Wittig-Peterson reaction.[4] In this paper we wish to report a new stereoselective method for the synthesis of *E*- and *Z*-vinylsilanes 3 utilizing vinyl sulfones 1. The whole reaction sequence is shown in Scheme 1, in which the stereochemistry of the product 3 was affected by the method for the destannylsulfonation of α-silyl-β-stannyl sulfone 2 prepared from 1.



Scheme 1.

Michael addition of tributylstannyllithium to *E*-vinyl phenyl sulfone 1a ($R=C_8H_{17}$) in tetrahydrofuran at -78°C for 20 min under nitrogen followed by the treatment with trimethylsilyl chloride at -78°C for 1h and at room temperature for 12h afforded the α-silyl-β-stannyl sulfone 2a ($R=C_8H_{17}$) smoothly. The destannylsulfonation[5] of 2a was carried out by the following three different ways. When the sulfone 2a was treated with silica gel (Merck silica gel 60, 70-230 mesh) in chloroform at room temperature (Method A), *Z*-vinylsilane 3a ($R=C_8H_{17}$) was obtained stereoselectively in 83% yield (isomeric purity; > 98%) on the basis of the vinyl sulfone precursor 1a. On the other hand *E*-3a was produced in 74% yield by the reaction with finely powdered silica gel (Merck silica gel 60, 230-400 mesh) in chloroform at reflux (Method B). In this reaction, isomerization of the initially formed *Z*-3a to the thermodynamically more stable *E*-3a was observed. The active reagent for the isomerization of *Z*-3a was found to be benzenesulfinic acid [6] which was produced in the silica gel catalyzed destannylsulfonation of 2a. Thus *Z*-3a was isomerized to *E*-isomer in 95% yield (isomeric purity; 97%), by the reaction with benzenesulfinic acid and silica gel in refluxing chloroform. Thermal destannylsulfonation of 2a in benzene-d_6 at 85 °C in a sealed tube (Method C) for 30 h afforded the *E*-3a as a major product. The results are summarized in Table 1.

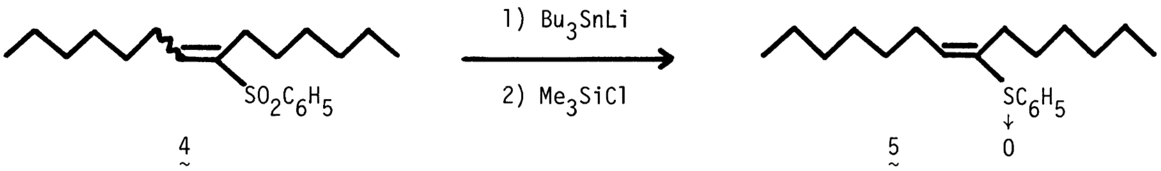
Table 1. Stereoselective Synthesis of *E*- and *Z*-Vinylsilanes **3**

Run	Vinyl sulfone **1**			Destannylsulfonation Method	Time/h	Product **3**	*E* : *Z*	Yield/%[a]
1	R=C_8H_{17}	**1a**	(*E*)	A	7.5	**3a**	< 2 : > 98	83
2	**1a**		(*E*)	B	27	**3a**	> 98 : < 2	74
3	**1a**		(*E*)	C	30	**3a**	88 : 12	(100)[b]
4	**1a**		(*Z*)	A	16	**3a**	< 2 : > 98	60
5	**1a**		(*Z*)	B	49	**3a**	> 98 : < 2	69
6	**1a**		(*Z*)	C	30	**3a**	88 : 12	(97)[b]
7	R=$C_{10}H_{21}$	**1b**	(4 : 1)[c]	A	17	**3b**	4 : 96	85
8	**1b**		(4 : 1)[c]	B	21	**3b**	98 : 2	78
9	**1b**		(4 : 1)[c]	C[d]	21	**3b**	95 : 5	(64)
10	R=$C_6H_5(CH_2)_2$	**1c**	(6 : 1)[c]	A	7	**3c**	3 : 97	(55)
11	**1c**		(6 : 1)[c]	B	52	**3c**	97 : 3	(56)
12	**1c**		(6 : 1)[c]	C[d]	19	**3c**	96 : 4	(47)

a) Isolated yield based on **1** (GLC yield). b) Yield based on 2a. The compound 2a was isolated by flash column chromatography in 39 and 43% yields from *E*- and *Z*-**1a**, respectively. c) *E* : *Z* Ratio. d) Destannylsulfonation was carried out in refluxing toluene.

The stereochemistry of vinylsilanes **3** was shown to be not affected by that of vinyl sulfones **1** used. Thus sulfone **2a** prepared from *Z*-**1a** in a similar manner gave rise to *Z*- or *E*-**3a** stereoselectively by its destannylsulfonation using Method A or B and C, respectively (Runs 4-6). A mixture of stereoisomers of vinyl sulfones **1b** (R=$C_{10}H_{21}$) and **1c** [R=$C_6H_5(CH_2)_2$] afforded the corresponding vinylsilanes **3** in a highly stereoselective manner (Runs 7-12).

α,β-Disubstituted vinyl sulfone **4** on treatment with tributylstannyllithium and then with trimethylsilyl chloride resulted in the formation of reduction product unexpectedly. *E*- and *Z*-Vinyl sulfones **4** produced the *E*-vinyl sulfoxide **5** in 38 and 44% yields, respectively.



4 **5**

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(Received July 13, 1983)