CHEMISTRY LETTERS, pp. 1457-1458, 1983.

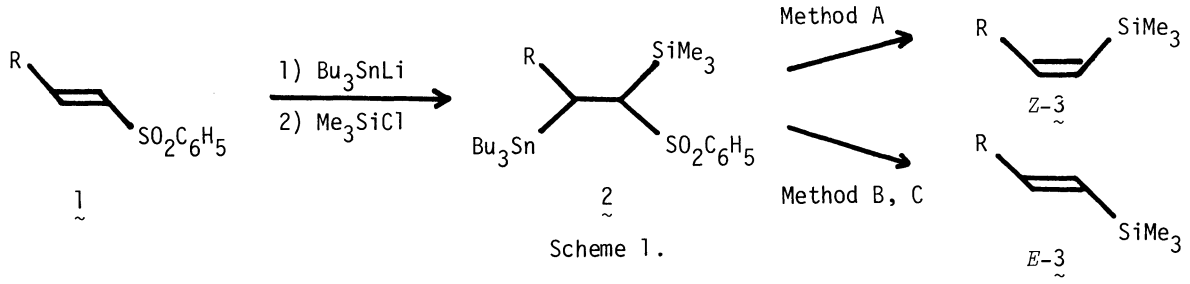
A NEW STEREOSELECTIVE SYNTHESIS OF VINYLSILANES UTILIZING VINYL SULFONES

Masahito OCHIAI, Tatsuzo UKITA, and Eiichi FUJITA*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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.

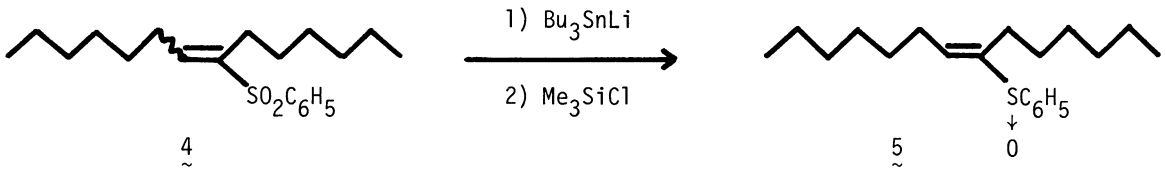
Table 1. Stereoselective Synthesis of *E*- and *Z*-Vinylsilanes 3

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

References

1) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983), p. 79. 2) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, J. Am. Chem. Soc., 83, 4385 (1961); K. Tamao, N. Miyake, Y. Kiso, and M. Kumada, *ibid.*, 97, 5603 (1975); H. Matsumoto, S. Nagashima, T. Kato, and Y. Nagai, Angew. Chem., Int. Ed. Eng., 17, 279 (1978). 3) J. J. Eisch and M. W. Foxton, J. Org. Chem., 36, 3520 (1971); K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, 41, 2215 (1976). 4) B.-T. Gröbel and D. Seebach, Chem. Ber., 110, 852 (1977). 5) M. Ochiai, S. Tada, K. Sumi, and E. Fujita, Tetrahedron Lett., 23, 2205 (1982); M. Ochiai, T. Ukita, and E. Fujita, J. Chem. Soc., Chem. Commun., 1983, 619. 6) Protodesilylation of vinylsilanes using p-toluenesulfinic acid has been reported; G. Büchi and H. Wüest, Tetrahedron Lett., 1977, 4305.

(Received July 13, 1983)