Communications to the Editor

Chem. Pharm. Bull.
31(8)2957—2959(1983)

NEW METHODS AND REAGENTS IN ORGANIC SYNTHESIS. 37.[1]
TRIMETHYLSILYLDIAZOMETHANE. A CONVENIENT REAGENT FOR THE PREPARATION OF VINYLSILANES FROM ALKANESULFONYL CHLORIDES

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Trimethylsilyldiazomethane reacts smoothly with alkanesulfonyl chlorides in the presence of triethylamine to give vinylsilanes.

KEYWORDS ——— trimethylsilyldiazomethane; vinylsilane ; alkanesulfonyl chloride; thermal isomerization; sulfene; episulfone

Vinylsilanes now occupy an important position as useful intermediates in organic synthesis.[2] Most methods for the preparation of vinylsilanes utilize alkynes, carbonyl compounds, or vinyl halides as starting materials.[2]

We have already reported that trimethylsilyldiazomethane (TMSCHN$_2$, (CH$_3$)$_3$SiCHN$_2$) is quite useful as a reagent for introducing a C$_1$-unit[3] and as a C-N-N synthon.[4] As an extension of these works, we now wish to report that TMSCHN$_2$ as a C$_1$-unit introducing reagent can be used for the preparation of vinylsilanes.

We have found that TMSCHN$_2$ reacts smoothly with alkanesulfonyl chlorides **1** at 0°C in tetrahydrofuran in the presence of triethylamine to give vinylsilanes **2**:

$$\underset{\mathbf{1}}{RCH_2SO_2Cl} \xrightarrow[\substack{(C_2H_5)_3N\ \text{in THF} \\ 0^\circ C,\ 1\ h}]{(CH_3)_3SiCHN_2} \underset{\mathbf{2}}{R\text{-}CH{=}CH\text{-}Si(CH_3)_3}$$

A typical experimental procedure is as follows: A solution of the alkanesulfonyl chloride (**1**, 1 mmol) in tetrahydrofuran (5 ml) was added to a stirred solution of TMSCHN$_2$[5] (1.2 mmol) and triethylamine (123 mg, 1.2 mmol) in tetrahydrofuran (5 ml) during several minutes at 0°C under argon. The mixture was stirred for 1 h at 0°C, and triethylamine hydrochloride precipitated during the reaction was filtered off. The filtrate was concentrated in vacuo, and the residue was distilled by a Kugelrohr apparatus under a reduced pressure to give the vinylsilane **2**.

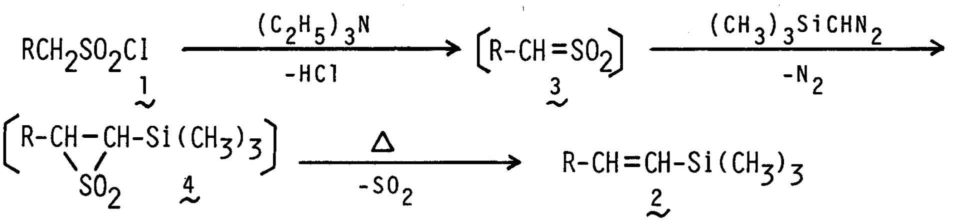
The results are summarized in Table I. Tetrahydrofuran seems to be the solvent of choice. A strong base like triethylamine is essential to conduct the reaction since no reaction occurs without triethylamine even when an excess of TMSCHN$_2$ is used and the reaction time is prolonged to 24 h. The reaction temperature does not significantly affect the yield of **2** between 0°C and -70°C. In contrast to benzylsulfonyl chloride, benzylsulfonyl fluoride was completely inactive even under the forcing reaction conditions (room temperature, overnight). The vinylsilanes **2** obtained were revealed spectroscopically to be either (E)-isomers only or an E/Z mixture in which (E)-isomers were dominant.[6] It is already known[7] that (Z)-vinylsilanes can be easily isomerized to (E)-isomers by irradiation with a sunlump in pyridine with a catalytic amount of N-bromosuccinimide.[8] Furthermore, we have found that the analogous Z to E isomerization occurs thermally. For example, when a 3/1 mixture of (E)- and (Z)-2-(4-nitrophenyl)ethenyltrimethylsilanes was heated at 190-200°C for 0.5 h, a 10/1 mixture of (E)- and (Z)-isomers was produced.

Table I. Conversion of Alkanesulfonyl Chlorides **1** to Vinylsilanes **2**

Run	R	Yield (%)	E/Z[a]	bp °C (mmHg)[b]
1	phenyl	73	13	90 (13)[c]
2	4-chlorophenyl	77	10	125 (11)
3	2-chlorophenyl	80	6	125 (11)
4	3,4-dichlorophenyl	70	E[d]	140 (20)
5	2,4-dichlorophenyl	76	9	140 (18)
6	4-nitrophenyl	80	3	100 (0.2)
7	3-nitrophenyl	55[e]	7	170-180 (20)
8	4-methylphenyl	57[e]	E[d,f]	95-105 (12)
9	D-7,7-dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl	46	E[d]	130 (0.1)[g]
10	benzyl	16	E[d,h]	100 (20)

a) See ref. 6. b) By Kugelrohr distillation. c) Lit. bp for (E)-isomer: 90-91°C/13 mm (J.J. Eisch and M.W. Foxton, J. Organometal. Chem., 11, P24 (1968)). d) (E)-Isomer only. e) The reaction time was 2 h. f) Cf. L.A. Paquette, W.E. Fristad, D.S. Dime, and T.R. Bailey, J. Org. Chem., 45, 3017 (1980). Their assignment on the configuration of this vinylsilane to be (E) should be corrected to be (Z), since the reported coupling constant (15 Hz) of the vinyl function in its NMR spectrum is too small as the (E)-isomer.[2a,6] g) $[\alpha]_D^{22}$ +19.4° (C=1, CHCl$_3$). h) Cf. F.A. Carey and J.R. Toler, J. Org. Chem., 41, 1996 (1976); A. Sekiguchi and W. Ando, J. Org. Chem., 45, 5286 (1980).

The reaction mechanism of this new preparation of vinylsilanes may be as follows: Alkanesulfonyl chlorides **1** first give sulfenes **3** with expulsion of hydrogen chloride by the action of triethylamine. Reaction of **3** with TMSCHN$_2$ gives episulfones **4** by loss of nitrogen. Evolution of sulfur dioxide from **4** thermally occurs to give vinylsilanes **2**. Similar reaction mechanism has been proposed in the alkene synthesis from alkanesulfonyl chlorides and diazomethane.[9]



Starting alkanesulfonyl chlorides **1**,[10] except D-camphor-10-sulfonyl chloride,[11] are easily prepared by the known procedure from alkyl chlorides by their reaction with sodium thiosulfate, followed by the treatment with chlorine in aqueous acetic acid. Thus the present method in combination with the preparation of **1** provides a simple three-step conversion of alkyl chlorides to vinylsilanes.

ACKNOWLEDGEMENT This work was supported by a Grant-in-Aid for Scientific Research (No. 58570882) from the Ministry of Education, Science and Culture, Japan, to which our thanks are due.

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(Received June 29, 1983)