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TRIMETHYLSILYLDIAZOMETHANE: A CONVENIENT REAGENT FOR THE PREPARATION OF (E)-1-TRIMETHYLSILYL-1-ALKENES[1]

Toyohiko Aoyama* and Takayuki Shioiri

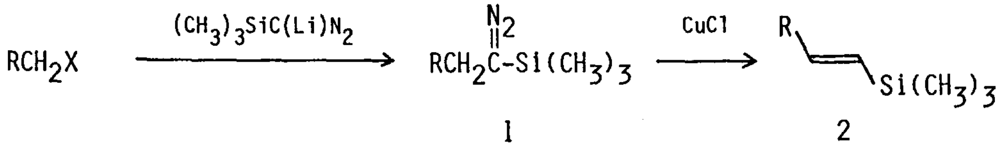
Faculty of Pharmaceutical Sciences, Nagoya City University
Tanabe-dori, Mizuho-ku, Nagoya 467, JAPAN

Abstract: The cuprous chloride-catalyzed decomposition of α-trimethylsilyldiazoalkanes gives (E)-1-trimethylsilyl-1-alkenes in high yields.

Vinylsilanes have been well recognized as versatile intermediates in organic synthesis.[2] Most of methods for the preparation of (E)-1-trimethylsilyl-1-alkenes utilize alkynes and vinyl halides as starting materials.[2]

We have already revealed that trimethylsilyldiazomethane (TMSCHN$_2$, $(CH_3)_3SiCHN_2$), which is quite useful as a reagent for introducing a C$_1$-unit,[3] smoothly reacts with benzylsulfonyl chlorides in the presence of triethylamine to give (E)-2-aryl-1-trimethylsilylethylenes in good yields.[4] This reaction, however, is not effective for the preparation of (E)-2-alkyl-1-trimethylsilylethylenes since the yields are low. Recent reports[5] involving the use of aldehydes have prompted us to report our results.

Our continued interest in the use of TMSCHN$_2$ in vinylsilane synthesis has revealed that (E)-1-trimethylsilyl-1-alkenes can be easily prepared in 2 steps from alkyl halides by alkylation of the lithium salt of TMSCHN$_2$,[6] followed by decomposition with cuprous chloride.

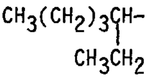
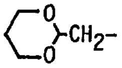
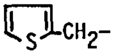


A typical experimental procedure is as follows: A solution of **1**[6] (1 mmol) in dry benzene (3 ml) was added dropwise over 2 min to a boiling suspension of cuprous chloride (5 mg, 5 mol%) in dry benzene (7 ml) under argon. The mixture was stirred at reflux for 30 min, and the catalyst was removed by short column chromatography on silica gel (hexane : benzene = 1 : 1). The eluate was concentrated, and the residue was purified by distillation to give **2**.

The results are summarized in Table. Decomposition of various **1** with cuprous chloride smoothly proceeds to give **2** with high stereoselectivity. Cuprous chloride seems to be the catalyst of choice, though copper sulfate can also be used.

The present method using commercially available $TMSCHN_2$ makes possible the conversion of alkyl halides to homologous (E)-1-trimethylsilyl-1-alkenes, and will provide an added flexibility in the vinylsilane synthesis.

Table[a] Preparation of (E)-1-Trimethylsilyl-1-alkenes (2)

Run	R	Yield(%)	E/Z	bp(°C)/mmHg[b]
1	$PhCH_2-$	89	95/5[c]	80-90/7
2	$CH_3(CH_2)_8-$	96	95/5[d]	80-85/1
3	 $CH_3(CH_2)_3CH(CH_2CH_3)-$	86	96/4[c]	90-95/20
4	$CH_2{=}CH(CH_2)_8-$	96	93/7[d]	65-70/0.1
5	$CH_3(CH_2)_2C{\equiv}CCH_2-$	87	97>[d]	65-70/5
6		82	95/5[d]	100-105/15
7	Ph-	89	94/6[c]	110-115/25
8		91	95/5[d]	100-105/13

a) All products gave satisfactory spectral data and elemental analysis. b) By Kugelrohr distillation. c) Determined by GLC. d) Determined by ^1H-NMR.

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6. α-Trimethylsilyldiazoalkanes (**1**) were easily prepared from alkyl halides and lithium trimethylsilyldiazomethane. See ref. 3b.

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