Preliminary Communication

Studies on organosilicon chemistry

CXXII. * Reaction of 2-oxiranylallylsilanes with acetals. Direct introduction of a vinyloxirane moiety

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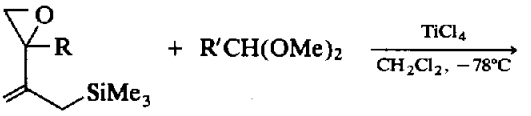
Abstract

Direct 2-oxiranylallylation to acetals can be attained using 2-oxiranyl-2-propenyltrimethylsilanes. These are a new type of nucleophiles incorporating a vinyloxirane moiety as an electrophilic functionality.

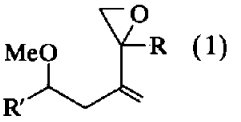
Key words: Silane; Vinyloxirane; Acetal; Allylation; Allylsilane

The versatile and regiospecific reactivities of allylsilanes as an allylating reagent have been well established by us and others in organic synthesis [2]. During the course of our investigations aimed at allylation by use of allylsilanes bearing labile functional groups, we have recently reported the reaction of 2-cyclopropyl-2-propenyltrimethylsilane with electrophiles, in which the transient cyclopropylcarbinyl cations are remarkably stabilized by the β-trimethylsilyl group owing to σ–π conjugation [3], and thus allow the 2-cyclopropylallylation to yield no rearranged products [4].

2-Oxiranylallylsilanes possess a vinyloxirane moiety, and have become important and interesting nucleophilic reagents in organic synthesis when the product also has the vinyloxirane function after the reaction with a certain electrophile, similarly to an ordinary allylsilane. Now we wish to report on the synthesis and reaction of 2-oxiranyl-2-propenyltrimethylsilanes **1** with acetals (eqn. (1)).



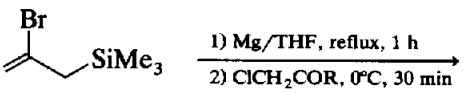
1a: R = H
1b R = Me



(1)

2

2-Oxiranylallylsilanes **1** were readily prepared from the Grignard reagent of 2-bromoallylsilane [5] and α-chloro aldehyde or α-chloro ketone in a one-pot operation as shown in eqn. (2) [6*].



(2)

$TiCl_4$ was the effective Lewis acid for the reaction of oxiranylallylsilane **1** with acetals, −78°C in CH_2Cl_2 in our setup. The results are summarized in Table 1 [7*]. A typical procedure is as follows: valeraldehyde dimethylacetal (0.5 mmol) and dichloromethane (1 ml) were mixed under nitrogen and the mixture was cooled to −78°C. $TiCl_4$ (0.5 mmol) and oxiranylallylsilane **1b** (0.55 mmol) were added to the mixture. After stirring at −78°C for 1 h, saturated aq. $NaHCO_3$ was added to the reaction mixture. Extraction with ether from the aqueous layer, washing with brine of the combined organic layer, drying with Na_2SO_4, and evaporation of the solvent from the organic layer gave a crude product. Purification by column chromatography (R_f = 0.5; silica gel, hexane/ethyl acetate = 4/1) gave **2** (R = Me, R' = Bu) as a mixture of diastereomers (1:1, 73%). These results deserve the following comments. The reactions proceed under mild conditions with acetals of structural variety in moderate yields. Although vinyloxiranes are well known to be very reactive towards both nucleophiles and Lewis acids [8], the reagent **1** indeed serves as a nucleophile, not as an electrophile,

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* For Part CXXI see ref. [1].

* Reference number with asterisk indicates a note in the list of references.

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TABLE 1. Reaction of 2-oxiranylallylsilanes **1** with acetals

Entry	Allyl-silane	Acetal	Conditions [a]	Yield [b] (%)
1	**1a**	$BuCH(OMe)_2$	−78°C, 3 h	58
2	**1b**	$BuCH(OMe)_2$	−78°C, 1 h	73
3	**1b**	$EtCH(OMe)_2$	−78°C, 1 h	47
4	**1a**	c-$HexCH(OMe)_2$	−78°C, 3 h	43
5	**1b**	c-$HexCH(OMe)_2$	−78°C, 1 h	65
6	**1a**	$Ph(CH_2)_2CH(OMe)_2$	−78°C, 3 h	33
7	**1b**	$Ph(CH_2)_2CH(OMe)_2$	−78°C, 1 h	70
8	**1a**	$PhCH(OMe)_2$	−78°C, 7 min	64
9	**1b**	$PhCH(OMe)_2$	−78°C, 1 h	72

[a] General reaction conditions: to a solution of acetal (0.5 mmol) and $TiCl_4$ (0.5 mmol) in dichloromethane (2 ml) was added allylsilane **1** (0.5–0.55 mmol) at −78°C and the mixture was stirred for a period shown in the table.
[b] Isolated yield based on the acetal.

and $TiCl_4$ selectively activates only to an oxygen atom of acetals, not of oxiranes. It is important and interesting to note that the vinyloxirane moiety remains intact through this operation.

In conclusion, oxiranylallylation to acetals can be attained using oxiranylallyltrimethylsilanes, which are a new type of nucleophiles incorporating an electrophilic functionality in itself. Since alkenyloxiranes are known to be important intermediates in organic synthesis and various methods have been developed [9], the present work provides new and easy entry to introducing a vinyloxirane moiety in a nucleophilic process. Further work on these reactions, but with other electrophiles and introduction of other functionalities to the allylsilane skeleton, is currently in progress.

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References and notes

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6 **1a**: 50% yield; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.03 (s, 9 H), 1.39 (d, J = 14.0 Hz, 1 H), 1.64 (d, J = 14.0 Hz, 1 H), 3.48 (dd, J = 7.9, 11.2 Hz, 1 H), 3.69 (dd, J = 3.0, 11.2 Hz, 1 H), 4.12–4.15 (m, 1 H), 4.80 (brs, 1 H), 5.03 (brs, 1 H); ^{13}C NMR ($CDCl_3$, 67.7 MHz) δ −1.4 (q), 23.0 (t), 49.1 (t), 75.0 (d), 109.5 (t), 145.4 (s). **1b**: 42% yield; b.p. 90°C (2 mmHg); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.37 (s, 9 H), 1.35 (s, 3 H), 1.50 (d, J = 13.5 Hz, 1 H), 1.58 (d, J = 13.5 Hz, 1 H), 3.52 (d, J = 11 Hz, 1 H), 3.68 (d, J = 11 Hz, 1 H), 4.78 (s, 1 H), 4.97 (s, 1 H), 5.03 (brs, 1 H); ^{13}C NMR ($CDCl_3$, 67.7 MHz) δ −0.8 (q), 21.1 (t), 25.2 (q), 53.9 (t), 74.7 (t), 109.3 (t), 149.4 (s).
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