Synthesis of α,β-Unsaturated Carbonyl Compounds by Successive Rearrangement and Peterson Olefination of β′-Hydroxy-α,β-epoxysilanes

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The reaction of β′-hydroxy-α,β-epoxysilanes with boron trifluoride–diethyl ether results in rearrangement of the epoxysilane skeleton followed by Peterson olefination, leading to α,β-unsaturated carbonyl compounds.

Rearrangement reactions of α,β-epoxysilanes and 1,2-elimination reactions of β-functionalized organosilanes have been extensively studied and widely applied to organic synthesis.[1] However, there are few investigations of the chemistry of β′-functionalized α,β-epoxysilanes which contain both an α,β-epoxysilane and a β-functionalized organosilane skeleton adjoining each other. The only reactions so far reported are the 1,2-elimination reaction of β′-chloro-α,β-epoxysilanes by fluoride ion which leads to allene oxides,[2] and the fluoride-induced protodesilylation of β′-hydroxy-α,β-epoxysilanes.[3]

Table 1. Reaction of complexes (2) with $BF_3 \cdot OEt_2$.[a]

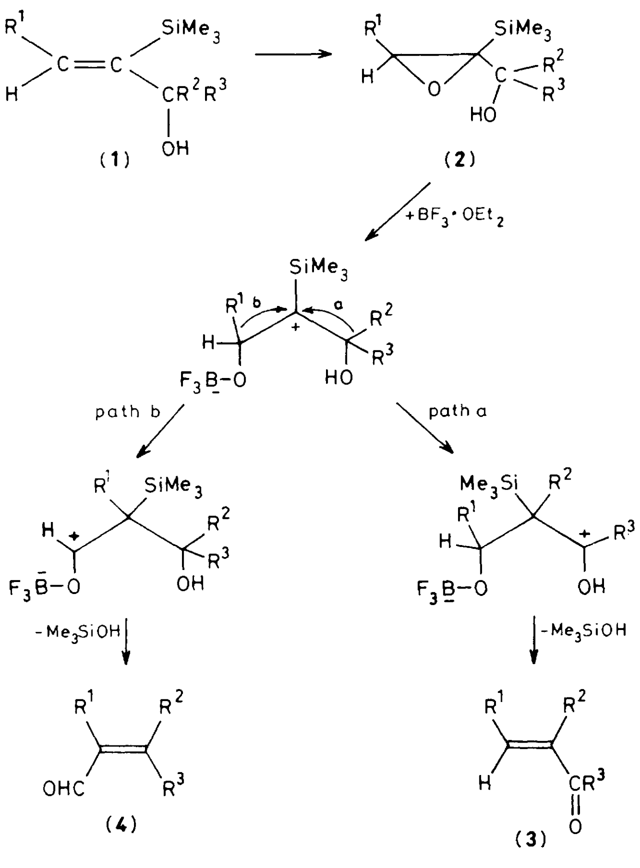
	Complex (2)[b] $R^1 = Bu^n$	Products [c,d]	Yield[e] (%)
a;	$R^2 = R^3 = H$	(**3a**)[f]	58
b;	$R^2 = Me, R^3 = H$	(**3b**), (**4b**) (1 : 1)[g]	83[h]
c;	$R^2 = Bu, R^3 = H$	(**3c**)	82
d;	$R^2 = Ph, R^3 = H$	(**3d**)[f]	85
e;	$R^2 = R^3 = Me$	(**3e**), (**4e**) (3 : 1)[g]	90[h]
f;	$R^2–R^3 = -[CH_2]_5-$	(**3f**)[f]	75

[a] $BF_3 \cdot OEt_2$ (3 equiv.) was added to a methylene chloride solution of (**2**) at room temperature and stirred for 15 min at that temperature. [b] Prepared by hydromagnesiation of 1-trimethylsilylhex-1-yne followed by treatment with the corresponding aldehyde or ketone. [c] Identified by comparison of ^1H n.m.r. spectra and g.l.c. retention times with those of authentic samples. [d] All products have (*E*)-configuration (by ^1H n.m.r.). [e] Isolated by distillation under reduced pressure. [f] >98% pure (by g.l.c. and ^1H n.m.r.). [g] Determined by g.l.c. [h] Combined yield.

Recently we reported a general and convenient method for the preparation of β-hydroxyvinylsilanes (**1**) which was based on hydromagnesiation of silylacetylenes followed by treatment with aldehydes or ketones.[4] Since the componds (**1**) are readily epoxidized to β′-hydroxy-α,β-epoxysilanes (**2**) with *m*-chloroperbenzoic acid or $VO(acac)_2$–t-butyl hydroperoxide (acac = pentane-2,4-dione),[5] we were interested in the behaviour of (**2**) under the conditions which would cause both rearrangement and 1,2-elimination.

We have now found that when compounds (**2**) are treated with boron trifluoride–diethyl ether in methylene chloride, α,β-unsaturated carbonyl compounds (**3**) [and (**4**)] are obtained in good to excellent yields (Table 1). The production of (**3**) [and (**4**)], though rather strange at first glance, can be explained by assuming that rearrangement of the α,β-epoxysilane skeleton occurs prior to (and does not compete with) the 1,2-elimination reaction, as shown in Scheme 1. The stepwise pathway for the rearrangement process, which involves preliminary ring opening is shown in Scheme 1, but the concerted process could be an alternative.[6]

The structure of the products (**3**) [and (**4**)] indicated that the regio-chemistry of the rearrangement step was strongly



Scheme 1

dependent on the substituents R^1, R^2, and R^3 in (**2**) individually, as well as in combination. With some compounds (**2**), a migration from C(β') to C(α) occurred predominantly, thus making the reaction useful for the preparation of α,β-unsaturated carbonyl compounds such as (**3a**), (**3c**), (**3d**), and (**3f**). In other cases, the rearrangement involved the migration of R groups from both C(β) and C(β') to C(α), to form the mixtures of products (**3b**) and (**4b**), (**3e**) and (**4e**). However, in every case, no migration of H from C(β) to C(α) was observed. It is also noteworthy that the products (**3**) [and (**4**)] thus obtained have (*E*)-configuration predominantly.

Received, 7th June 1983; Com. 736

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