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Highly Regio- and Diastereoselective Synthesis of Epoxy Alcohols directly from Vinyl Silanes by Photo-oxygenation and Titanium-Catalyzed Oxygen Transfer

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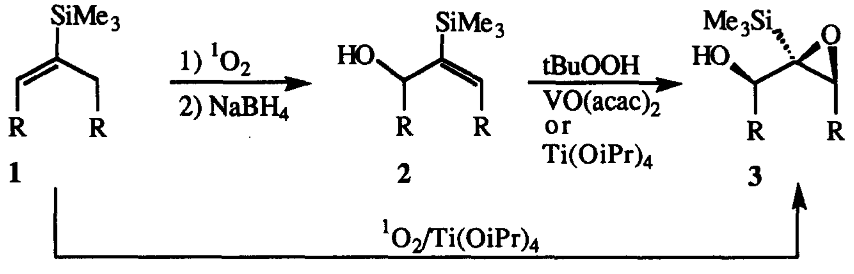
Abstract: The photooxygenation of vinyl silanes **1** in the presence of $Ti(OiPr)_4$ afforded regio- and diastereoselectively the epoxy alcohols **3**.

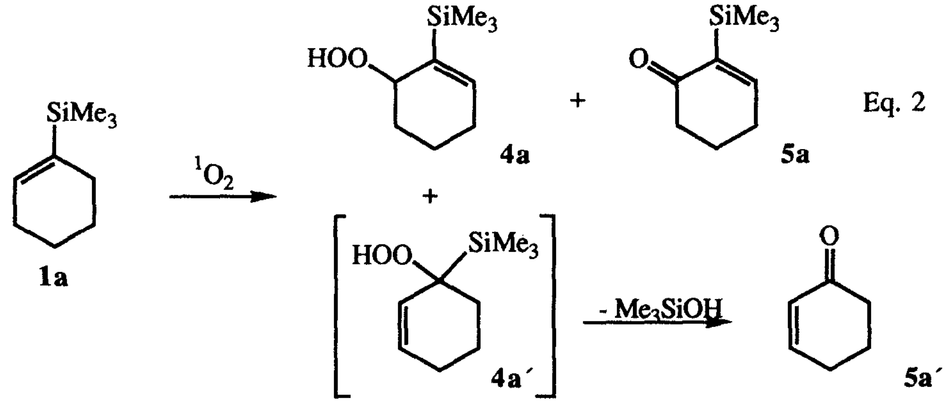
The photooxygenation of olefins in the presence of Ti(IV) catalyst has proven as a useful method for the synthesis of epoxy alcohols[1]. Unfortunately, the frequently low regioselectivity of the ene reaction of singlet oxygen with olefins[2] leads to mixtures of isomeric epoxy alcohols. However, in 1980 it was reported[3] that the photooxygenation of vinyl silanes **1** afforded after reduction regioselectively β-silyl allylic alcohols **2** (Eq. 1).



Eq. 1

Moreover, because of the steric demand of the silyl group, the metal-catalyzed epoxidation of such alcohols[4], prepared by conventional methods, resulted in the *R*S**-epoxy alcohols **3** in high diastereoselectivity (Eq. 1). Therefore, the use of vinyl silanes as substrates in the Ti(IV)-catalyzed oxyfunctionalisation[1] provides an attractive methodology to exploit the regio- and diastereoselective control exercised by the silyl group for the convenient synthesis of epoxy alcohols **3** directly from olefins by means of a "one-pot" procedure. In the following we communicate our preliminary results, in which we demonstrate the feasibility of this synthetic concept.

The photooxygenation of the vinyl silane **1a**[5] (Na lamp, MeOH, rose bengal, -10 °C, 23 h) gave in the presence of 5 mol% 2,6-di-*tert*-butyl-4-methylphenol as radical inhibitor the hydroperoxide **4a** (90%), the enone **5a**[6] (3%), and 2-cyclohexenone **5a′** (7%) , as evidenced by the ^{1}H NMR spectrum of the crude reaction mixture (Eq.2). The ene product **4a** was isolated by low temperature column chromatography (silica gel, 4:1 petroleum ether/ether , -10 °C) and characterized by ^{1}H and ^{13}C NMR, IR, MS, and elemental analysis. The formation of enone **5a′** indicates that the photooxygenation of vinyl silane **1a** is not as regioselective as reported[3], since it presumably results from the labile regioisomeric α-silyl hydroperoxide **4a′** by trimethylsilanol elimination. The photooxygenation of **1a** in the presence of 25 mol% Ti(OiPr)$_4$ (Na lamp, tetraphenylporphine, CH$_2$Cl$_2$, -10 °C, 20 h) produced directly the epoxy alcohol **3a** (Table 1) as well as **5a** and **5a′**, which could be easily separated by Kugelrohr distillation. Only one diastereomer of epoxy alcohol **3a** was formed. Its desilylation[7] (nBu$_4$NF, THF) to the known[1] 7-oxabicyclo[4.1.0]heptan-2-ol established the *cis* stereochemistry of the epoxy alcohol functionality.



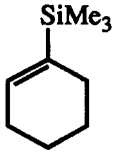
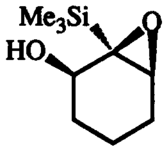
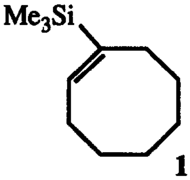
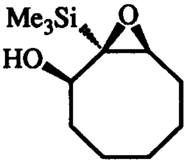
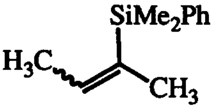
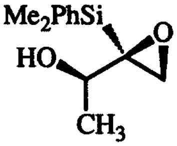
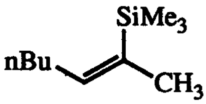
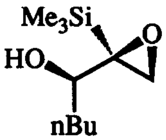
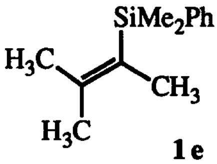
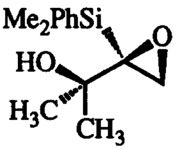
Eq. 2

Comparable results were obtained for the silanes **1b-e**[8] (Table 1). In all cases the epoxy alcohols **3** were obtained regio- and diastereoselectively in respectable yields. For the open-chain vinyl silanes **1d,e** it proved advantageous to conduct the photooxygenation and oxygen transfer steps in sequence, but the isolation of the intermediary hydroperoxides was not necessary. The yields of this "one-pot" operation need yet to be optimized.

In a typical procedure, the photooxygenation vessel [12] was charged with the vinyl silane **1d,e** (5.0 to 20.0 mmol), 30 mg of tetraphenylporphine (sensitizer) and 100 ml of dry dichloromethane. A slow stream of dry oxygen gas was allowed to purge through the solution while the mixture was irradiated with a sodium lamp (Osram Vialox NAV-TS, 250 W). When TLC showed complete conversion of vinyl silanes **1d,e** (1 to 4 h), the mixture was transferred to a round-bottomed flask, 4A molecular sieves and Ti(OiPr)$_4$ (20 mol%) were added and the flask was kept at -20 °C overnight. The liquid was decanted from the molecular sieves, ether (50 ml) and water [1 ml per mmol Ti(OiPr)$_4$] were added, and stirred for 30 min.The reaction mixture was filtered over Celite, the filtrate was dried (MgSO$_4$) and concentrated. Kugelrohr distillation afforded the epoxy alcohols **3** (Table1.).

In conclusion, the synthetically versatile silyl epoxy alcohols[13] can now conveniently be produced regio- and diastereoselectively in a "one-pot" operation directly from the readily available vinyl silanes. Thus, the synthesis of the β-silyl allylic alcohols, required for the classical Sharpless epoxidation[4], is hereby obviated.

Table 1. Yields of Epoxy Alcohols **3** Prepared from Vinyl Silanes **1**

Entry	Vinyl Silane	Epoxy Alcohol	Yield[a] (%)
1	 **1a**	 **3a**	70
2	 **1b**	 **3b**	72
3	 **1c**[b]	 **3c**	44
4	 **1d**	 **3d**[c]	59
5	 **1e**	 **3e**	67

[a] Isolated yields; the assigned structures of the epoxy alcohols **3** are in accord with the observed spectral properties (^1H, ^{13}C NMR, IR); stereochemical assignments were made by analogy to literature data [4] and for **3a,b** by desilylation; [b] a 33:67 E/Z mixture was employed; [c] see ref 4a.

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