

## Palladium(0)-Catalyzed Rearrangement of Silicon Substituted Vinyloxiranes. Enantiocontrolled Preparation of $\alpha$ -Tertiobutyldimethylsilyl- $\beta,\gamma$ -Unsaturated Aldehydes.

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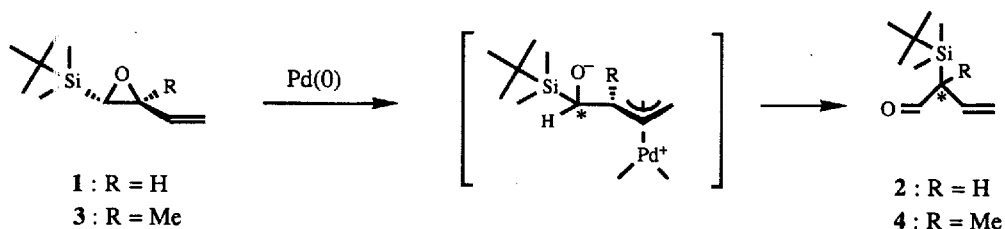
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**Key Words :** *Palladium(0)-catalyzed reaction / Silicon substituted vinyloxiranes / Migration of silicon / Enantiocontrolled reaction / Sharpless epoxidation.*

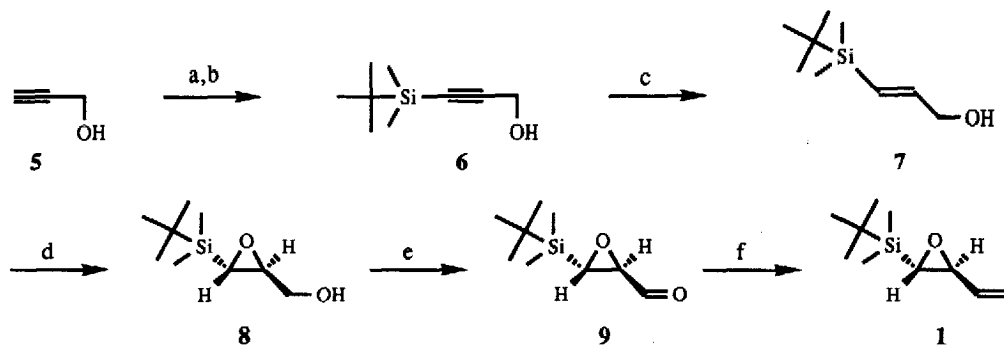
**Abstract :** *Palladium(0)-catalyzed rearrangement of silicon substituted vinyloxiranes occurred with a high stereoselectivity and in a very good chemical yield.*

Vinyloxirane derivatives have been extensively studied in the presence of palladium (0)<sup>1</sup> and are of great interest in organic chemistry. Moreover, homochiral ( $\pi$ -allyl)palladium complexes are very useful for the synthesis of optically active molecules. Surprisingly, reactivity of vinyloxirane bearing trialkylsilyl group like **1** with palladium (0) has never been studied.

In this letter, we describe our preliminary results in this field. Reaction of **1** with a catalytic amount of zerovalent palladium generated from 5 mol % Pd(OAc)<sub>2</sub> and 20 mol % P(OiPr)<sub>3</sub> in tetrahydrofuran, at -78°C, afforded instantaneously aldehyde **2** in a very good chemical yield (85 %). Its formation can only be explained by a rearrangement where an intramolecular migration of silicon occurs.<sup>2</sup>



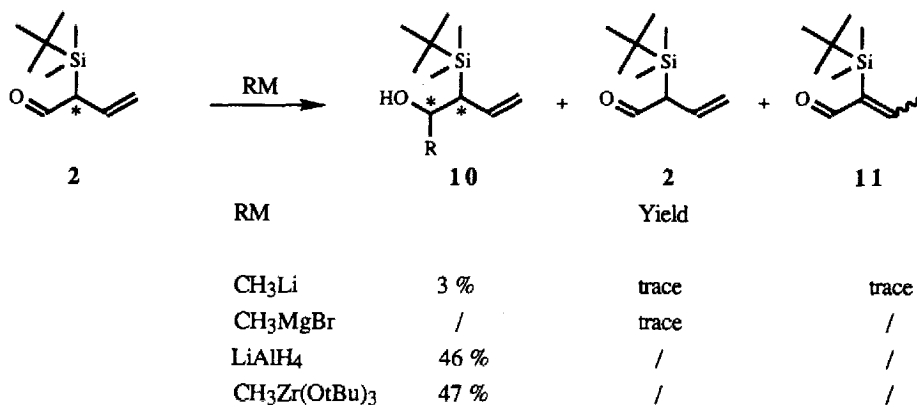
Vinylepoxyde **1**<sup>3</sup> ( $[\alpha]_D^{20} = -5,2$  [ $c = 10,30$  ; EtOH]) was readily prepared in five steps from the commercially available propargylic alcohol in 43% overall yield. Chirality was introduced *via* an enantioselective modified Sharpless epoxidation<sup>4</sup> (**8** : e.e.  $\geq 98\%$   $[\alpha]_D^{20} = -26,9$  [ $c = 11,85$  ; CHCl<sub>3</sub>]).



a) *n*BuLi, TBDMSCl, THF ; b) AcOH, 100 % ; c) RedAlH, Et<sub>2</sub>O, 85 % ; d) L-(+)-DET, Ti(O*i*Pr)<sub>4</sub>, *t*BuOOH, CH<sub>2</sub>Cl<sub>2</sub>, 75 % ; e) DMSO, (COCl)<sub>2</sub>, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 87 % ; f) *t*AmONa, Ph<sub>3</sub>P<sup>+</sup>-CH<sub>3</sub>, Br<sup>-</sup>, PhH, 78 % .

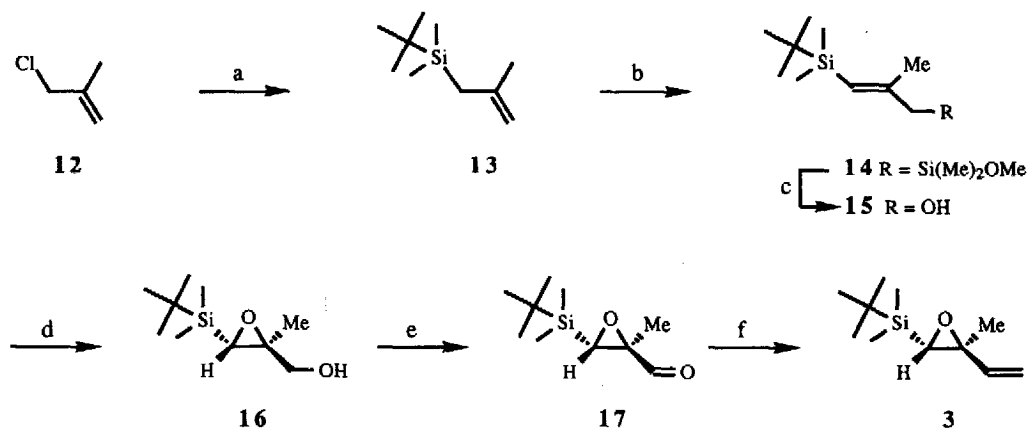
It should be pointed out that all of the four stereoisomers could be obtained from the C-silylated propargylic alcohol **6**. Indeed, reduction of the triple bond with Red-Al led stereoselectively to the *E* vinylsilane allylic alcohol **7**<sup>5</sup> while the use of cristal clear solution of LAH produced the *Z* isomer.<sup>6</sup> Sharpless asymmetric epoxidation using (+) DET or (-) DET provided each corresponding epoxide.

Aldehyde **2**<sup>7</sup> ( $[\alpha]_D^{20} = -40,8$  [ $c = 6,05$  ; EtOH]) is optically active meaning the migration of the silicon group proceeded with some degree of stereoselectivity. But this kind of compound is relatively sensitive to racemization which is confirmed by our preliminary studies involving its use in asymmetric synthesis. Indeed, organolithium and Grignard reagents acted as bases and only enolized **2** (as evidenced by the formation of **11**) which finally decomposed on a longer reaction time. Hydride such as LAH gave 46 % of the corresponding primary alcohol. Interestingly, use of nucleophiles such as organozirconium reagents allowed us to achieve an addition on the carbonyl group, due to their low basicity and high carbonylophilicity.<sup>8</sup> Moreover, this addition arose in a high diastereoselectivity.



Because of this problem of partial racemization, attempts to determine the exact degree of chirality transfer in the 1,2-silicon shift were unsuccessful. In order to circumvent this difficulty, we decided to study the migration of the silicon group with substrate **3**, having a quaternary center.

Following the same procedure, vinyloxyde **3** was obtained from glycidol **16** (**16**: e.e.  $\geq 98\%$  [ $\alpha_D^{20} = -24,9$  [ $c = 9,55$ ;  $\text{CHCl}_3$ ]). While a few useful methods for the synthesis of *E* and *Z* trisubstituted vinylsilane allylic alcohols have been recorded,<sup>9</sup> they have never been applied to the preparation of *E*-3-trialkylsilyl-2-methyl-2-propen-1-ol like **15**. Herein, we report a short and efficient preparation of **15**: firstly, the silylallyl carbanion, generated from (2-methylallyl)tert-butyl-dimethylsilane **13**,<sup>10</sup> reacted with alkoxychlorosilane to afford regioselectively **14** as the pure *E* isomer. Finally, chemoselective Tamao oxidation<sup>11</sup> furnished **15** in 73% overall yield.



a) TBDMSCl, Mg, THF, 62%; b)  $n\text{BuLi}/t\text{BuOK}$ ,  $\text{ClSi}(\text{Me})_2\text{OMe}$ ,  $\text{Et}_2\text{O}$ ; c)  $\text{H}_2\text{O}_2$ ,  $\text{KHCO}_3$ ,  $\text{MeOH}$ , THF, 73%; d) L-(+)-DET,  $\text{Ti}(\text{OiPr})_4$ ,  $t\text{BuOOH}$ ,  $\text{CH}_2\text{Cl}_2$ , 78%; e) DMSO,  $(\text{COCl})_2$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ , 67%; f)  $t\text{AmONa}$ ,  $\text{Ph}_3\text{P}^+\text{-CH}_3$ ,  $\text{Br}^-$ ,  $\text{PhH}$ , 81%.

Then, vinyloxirane **3** ( $[\alpha_D^{20} = -6,8$  [ $c = 8,05$ ;  $\text{EtOH}$ ]) was subjected to the palladium-catalyzed reaction as described above. The generated ( $\pi$ -allyl)palladium complex produced aldehyde **4** ( $[\alpha_D^{20} = +42,1$  [ $c = 10,20$ ;  $\text{EtOH}$ ]) in 87% yield.

Once again, we observed a very fast 1,2-silicon shift. This migration occurred in 77% enantiomeric excess which was determined by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR analyses of Mosher's ester obtained from the primary alcohol derivative of aldehyde **4**.

Besides, vinyloxirane **3** was transformed to aldehyde **4** using a catalytic amount of  $p\text{TsOH}$  in dichloromethane, the optical antipode ( $[\alpha_D^{20} = -36,9$  [ $c = 6,05$ ;  $\text{EtOH}$ ]) was obtained as the major enantiomer.

Active work is dedicated to the establishment of the absolute configuration of chiral center and thus to gain insight on the reaction mechanism.

Furthermore, very promising stereoselective synthetic transformations could be achieved in view of the ambident character of aldehydes **2** and **4**. Current efforts in our laboratory are devoted to this goal.

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- 3 Description of **1** : IR (neat) : 3080, 2920, 2850, 1640, 1470, 1360, 1250, 910, 830, 790 cm<sup>-1</sup> ;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) : -0.07 (s, 3H), -0.01 (s, 3H), 0.93 (s, 9H), 2.18 (d, *J* = 3.5 Hz, 1H), 3.13 (dd, *J* = 7.0, 3.5 Hz, 1H), 5.21 (dd, *J* = 9.0, 2.2 Hz, 1H), 5.42 (dd, *J* = 17.0, 2.2 Hz, 1H), 5.55 (ddd, *J* = 17.0, 9.0, 7.0 Hz, 1H) ;  
<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz) : -8.5, -8.0, 17.0, 26.0, 51.0, 56.0, 118.0, 138.0.
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- 7 Description of **2** : IR (neat) : 3080, 2970, 2860, 2820, 2710, 1700, 1630, 1470, 1380, 1250, 950, 860, 770 cm<sup>-1</sup> ;  
<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz) : -0.10 (s, 6H), 0.79 (s, 9H), 3.02 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.78 (dd, *J* = 17.0, 1.2 Hz, 1H), 4.88 (dd, *J* = 10.0, 1.2 Hz, 1H), 6.12 (dt, *J* = 17.0, 10.0 Hz, 1H), 9.52 (d, *J* = 3.0 Hz, 1H) ;  
<sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz) : -7.0, -6.0, 18.0, 28.0, 55.0, 115.0, 133.0, 198.0.
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