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Stereocontrolled Rearrangement of Silylated Vinyloxiranes into α-Trialkylsilyl-β,γ-Unsaturated Aldehydes.

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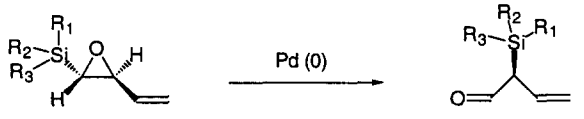
Abstract : Silylated vinyloxiranes **1**, substituted on the double bond, have been synthesized and reacted under very mild conditions in the presence of a catalytic amount of palladium (0). They rearrange into α-silylated-β,γ-unsaturated aldehydes **2**, not only with complete chirality transfer but also with total retention of the double bond stereochemistry. © 1997 Published by Elsevier Science Ltd.

We previously reported[1,2] a zerovalent palladium catalyzed rearrangement of vinyloxiranes **1** into highly functionalized α-silylated-β,γ-unsaturated aldehydes **2** (Scheme 1).



1 **2**

Scheme 1

This 1,2-silicon migration proceeds under smooth conditions and yields stereoselectively versatile ambident compounds. As part of our study of this reaction, we checked how silylated vinyloxiranes, with a substituted double bond, are transformed *via* this palladium(0) catalysis.

Vinylepoxides **1** are synthesized from epoxyaldehydes **3** (Scheme 2, Table1) by a Horner-Wadsworth-Emmons reaction. In case of **1a** and **1f**, we used lithium chloride and an amine (DBU) as a mild olefination procedure which led easily to the (*E*)vinyloxirane.[3] In order to synthesize (*Z*)-α,β-unsaturated esters **1b** and **1e**, methyl-bis(trifluoroethyl)phosphonoester[4] was chosen as the Horner-Emmons reagent. Epoxyaldehydes **3** are prepared in five steps from commercially available propargylic alcohol.[5] They could be obtained either as a racemic mixture or *via* a Sharpless enantioselective epoxidation step.[6]

3a : R_1=R_2=Ph R_3=*t*-Bu
3b : R_1=R_2=Me R_3=*t*-Bu

1a-f

Scheme 2

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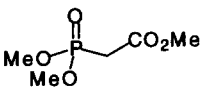
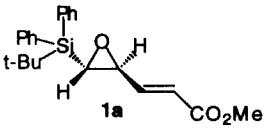
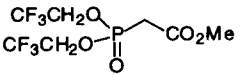
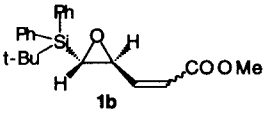
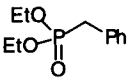
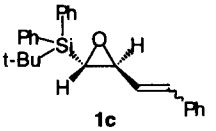
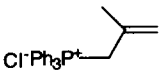
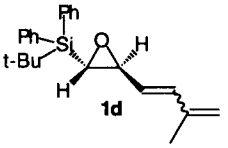
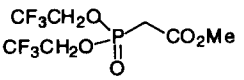
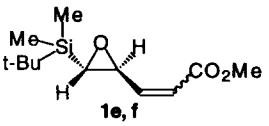
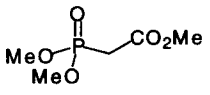
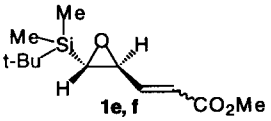
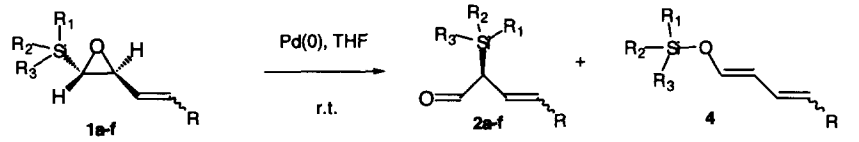
Table 1. Preparation of α,β-Unsaturated Vinyloxiranes.

Epoxyaldehydes	Conditions	Yield (%)	Products	*Z*/*E*
3a[a]	 *i*	99	 **1a**	0 / 1
3a[b]	 *j*	60	 **1b**	17 / 3
3a[b]	 *k*	42	 **1c**	1 / 9
3a[b]	 *l*	86	 **1d**	1 / 1
3b[c]	 *j*	(*Z*)-**1e**= 54[d] (*E*)-**1f**= 27	 **1e, f**	2 / 1[d]
3b[c]	 *i*	(*Z*)-**1e**= 10 (*E*)-**1f**= 68	 **1e, f**	1 / 6.5

a) ee = 85%, b) racemic mixture, c) ee = 98%, d) *E* and *Z* stereomers were separated on silica gel flash chromatography eluted by petroleum ether (98%) and ether (2%). *i*) : LiCl, DBU, CH_3CN, r.t., 0.5h. *j*) : Crown-ether[18-C-6], KHMDS, THF, -78°C. *k*) : NaH, $PhCH_3$, 105°C., 0.5h. *l*) : $C_2H_5(CH_3)_2CONa$, PhH, reflux, 0.5h.

1a-f rearranged in the presence of a catalytic amount of zerovalent palladium generated *in situ* from $Pd(OAc)_2$ and $P(iOPr)_3$ or $P(OPh)_3$[7] in tetrahydrofuran at room temperature (Scheme 3, Table 2). Except in case of **1a**, we detected no trace of conjugated silylenolether **4**, resulting from a 1,2 shift of silicon from carbon to oxygen. The absence of Brook[8] rearrangement in the case of **1c-f** can be rationnalized according to our previous study[5] of the influence of silicon substituents on the rearrangement products.



Scheme 3

Table 2. Rearrangement of Vinyloxiranes into α-Silylated β,γ-Unsaturated Aldehydes.

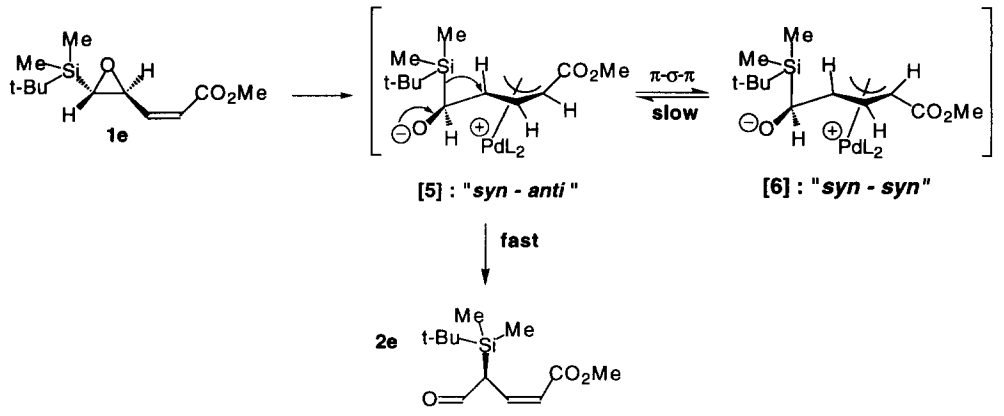
Vinyloxiranes	Conditions[a]	**2a-f** (*Z* / *E*)	Yields (%)
(*E*)-**1a**	A	(*E*)-**2a**	63[c]
1b (*Z* / *E* = 17 / 3)	A	**2b** (*Z* / *E* = 17 / 3)	10[b]
1c (*Z* / *E* = 1 / 9)	A	**2c** (*Z* / *E* = 1 / 9)	90
1d (*Z* / *E* = 1 / 1)	A	**2d** (*Z* / *E* = 1 / 1)	86
(*Z*)-**1e**	B	(*Z*)-**2e**	30[b]
(*Z*)-**1e**	C	(*Z*)-**2e**	76
(*E*)-**1f**	C	(*E*)-**2f**	27

a) A : 5% $Pd(OAc)_2$, 20%$P(O\textit{i}Pr)_3$. B : 20%$Pd(OAc)_2$, 80%$P(O\textit{i}Pr)_3$. C : 5%$Pd(OAc)_2$, 20%$P(OPh)_3$. b) unoptimized, c) **4a** is obtained with 10% yield.

When *Z* and *E* vinyloxiranes could not be separated, their mixtures (Table 2 : entries **1a-d**) were exposed to zerovalent palladium in catalytic amount and a mixture of *Z* and *E* aldehydes **2a-d** was isolated in an equal ratio of *Z* to *E* as the starting vinyloxirane mixture.

When only one stereomer was transformed (**1e-f**)[9a-b] only one aldehyde (**2e-f**)[9c-d] was obtained in the pure stereomeric form (*Z*)-**2e** from (*Z*)-**1e**, and respectively (*E*)-**2f** from (*E*)-**1f**, with no trace of the other stereomer. Therefore we establish that the rearrangement of vinyloxiranes into α-silylated-β,γ-unsaturated aldehydes occurs with retention of the double bond configuration.

These results indicate that silicon migration takes place before the *syn-anti* isomerization[10,11] of π-allyl palladium reaches the equilibrium state. According to former studies, we can suppose that the most stable form for the disubstituted π-allylic palladium complex [**5**], obtained from vinyloxirane (*Z*)-**1e**, is the *syn-syn* isomer [**6**]. Our results stress that the equilibrium rate between [**5**] and [**6**] is slower than the 1,2 silicon shift (scheme 4), leading to the aldehyde **2e**. This explains that no trace of the (*E*)-**2f** stereomer could be isolated.



Scheme 4

In conclusion, our results lead to a better understanding of this unusual 1,2 silicon shift from carbon to carbon *via* a π-allylic palladium complex. The rearrangement of vinyloxiranes substituted on the double bond, show total retention of the double bond configuration. These results make vinyloxiranes **1e-f** and their rearranged aldehydes **2e-f**, substituted with an electron-withdrawing ester group, powerful synthons for further stereoselective syntheses.

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9a. (**Z**)-**1e** : ^{1}H-NMR (400MHz,$CDCl_3$) δ 5.92 (d, *J* =11.7 Hz, 1H), 5.75 (dd, *J* = 11.7, 8.2 Hz, 1H), 4.40 (dd, *J* = 3.4, 8.2 Hz, 1H), 3.73 (s, 3H), 2.23 (d, *J* = 3.4 Hz, 1H), 0.95 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 166.4, 149.4, 122.3, 51.4, 51.2, 50.6, 29.7, 26.5, -8.2, -8.5.

9b. (*E*)-**1f** : ^{1}H-NMR (400MHz,$CDCl_3$) δ 6.58 (dd, *J* = 7.6, 15.5 Hz, 1H), 6.12 (d, *J* = 15.5 Hz, 1H), 3.70 (s, 3H), 3.21 (dd, *J* = 7.6, 3.1 Hz, 1H), 2.25 (d, *J* = 3.4 Hz, 1H), 0.99 (s, 9H), 0.00(s, 3H), -0.04 (s, 3H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 166.1, 147.4, 122.8, 53.5, 52.3, 51.7, 29.7, 26.4, -8.2, -8.5.

9c. (*Z*)-**2e** : ^{1}H-NMR (400MHz,$CDCl_3$) δ 9.74 (d, *J* = 2.0 Hz, 1H), 6.81 (t, *J* = 11.2, 11.7 Hz, 1H), 5.79 (d, *J* = 11.7 Hz, 1H), 5.29 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.71 (s, 3H), 1.00 (s, 9H), 0.12, (s, 3H), 0.09 (s, 3H);); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 198.0, 166.9, 143.7, 116.5, 52.5, 51.2, 29.8, 27.0, -5.8, -6.5.

9d. (*E*)-**2f** : ^{1}H-NMR (400MHz,$CDCl_3$) δ 9.73 (d, *J* = 3.2Hz, 1H), 7.34 (dd, *J* = 15.8, 10.2 Hz, 1H), 5.84 (d, *J* = 15.8 Hz, 1H), 3.74 (s, 3H), 3.62 (dd, *J* = 10.2, 3.2 Hz, 1H), 0.95 (s, 9H), 0.08 (s, 6H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 197.5, 167.2, 142.5, 119.6, 54.5, 51.7, 29.8, 26.9, -6, -6.3.

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