

PALLADIUM-PROMOTED TRANSFORMATION OF α, β -EPOXYSILANES
TO α, β -UNSATURATED CARBONYL COMPOUNDS

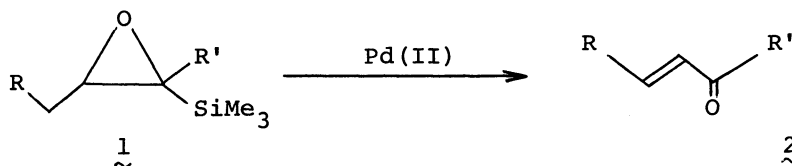
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Treatment of α, β -epoxysilanes with palladium(II) salt in DMF affords α, β -unsaturated carbonyl compounds, in which the carbonyl group appears on the carbon originally bearing the silyl group.

α, β -Epoxy silanes have been used as versatile intermediates in organic synthesis.¹⁾ Open chain α, β -epoxy silanes are hydrolyzed in acid to give aldehydes or ketones,²⁾ which indicates α, β -epoxy silane is a synthetic equivalent to aldehyde or ketone. Herein, we wish to describe a novel transformation of α, β -epoxy silanes to α, β -unsaturated carbonyl compounds with palladium(II) salt.



Typical procedure is as follows. To a solution of palladium acetate (1 mmol) in DMF (4 ml) was added (Z)-1-trimethylsilyl-1-hexene oxide³⁾ (1a, 1 mmol) at room temperature. The resultant mixture was stirred at 60°C for 7 h under nitrogen. The reaction proceeded with deposition of metallic palladium. After removing the deposit, aqueous saturated sodium chloride solution was added to the filtrate, which was extracted with ether. The combined extract was washed with aqueous saturated sodium chloride solution and concentrated. The residue was chromatographed on a silica gel column to give (E)-2-hexenal in 76% yield. Formation of the Z isomer was not observed in the NMR spectrum of the crude product.

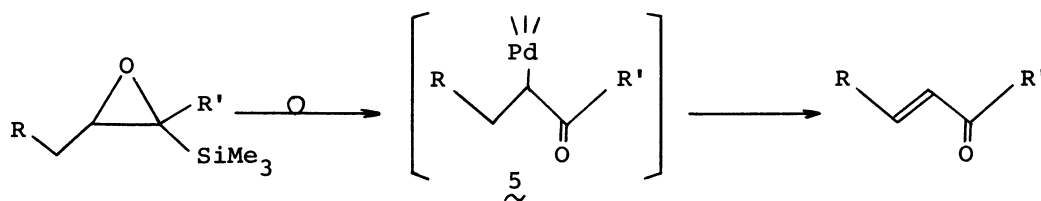
The reaction of 1a at room temperature also produced (E)-2-hexenal. The

transformation was well achieved only in DMF, and the reaction in acetonitrile gave a poor result. Use of $\text{PdCl}_2(\text{PhCN})_2$ instead of $\text{Pd}(\text{OAc})_2$ gave a moderate yield of $\underline{2a}$, being contaminated with hexanal ($\underline{3a}$) and 1-chloro-1-trimethylsilyl-2-hexanol ($\underline{4a}$). The cationic palladium complex, $[\text{Pd}(\text{acac})(1,5\text{-COD})]\text{BF}_4$, also promoted the present reaction. The results are shown in Table 1.

Similarly, (Z)-1-trimethylsilyl-1-hexene oxide was converted to (E)-2-hexenal in 98% yield. In the case of internal α,β -epoxysilanes, the yield of $\underline{2}$ was decreased. The reason might be explained by the difficulty of their hydrolysis.^{2c,4)} It is of interest that only (E)- α,β -unsaturated carbonyl compounds were produced selectively regardless of the stereochemistry of α,β -epoxysilanes $\underline{1a}\sim\underline{1d}$.

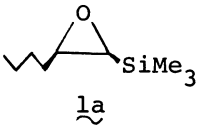





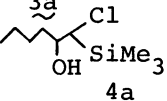





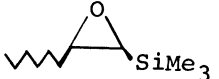


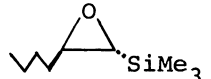

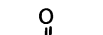
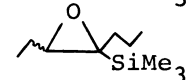
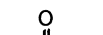



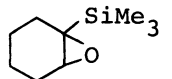
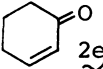
A catalytic process of the present transformation was attempted by adding CuCl_2 into the mixture of $\underline{1a}$ and a catalytic amount of $\text{Pd}(\text{OAc})_2$ in DMF, but the product obtained was the α -chloro- β -hydroxysilane $\underline{4a}$ (62%). The reaction only in the presence of CuCl_2 also gave $\underline{4a}$ (80%), which corresponds to the product in magnesium bromide assisted rearrangement of α,β -epoxysilanes.⁵⁾ Reoxidation of the reduced $\text{Pd}(0)$ was performed by using Ag_2O as an oxidant. The reaction of $\underline{1a}$ was carried out in the presence of $\text{Pd}(\text{OAc})_2$ (0.1 equiv.) and Ag_2O (1 equiv.) at 60°C for 20 h to produce $\underline{2a}$ in 31% yield.

The present reaction involves a carbon-silicon bond cleavage. Although the reaction path has not been clarified, the bond cleavage might be induced by palladium(II) salt. The epoxy ring undergoes rearrangement to form the palladium complex $\underline{5}$ ⁶⁾, which is subjected to β -elimination of Pd-H species to give the α,β -unsaturated carbonyl compound $\underline{2}$.



α,β -Epoxysilanes are easily prepared by oxidation of vinylsilanes or homologation⁷⁾ of ketones or aldehydes with α -chloro- α -trimethylsilyl carbanion. Combination of this homologation reaction and the present palladium(II)-promoted transformation provides a versatile process for the preparation of α,β -unsaturated aldehydes.

Table 1. Reaction of α,β -Epoxyasilanes with Palladium Salt

$\underline{1}$	Palladium Salt	Solv.	Reaction		Products ^a (%)	
			Temp.	Time		
 $\underline{1a}$	Pd(OAc) ₂	DMF	60°C	7 h	 $\underline{2a}$	90 (76) ^b
	Pd(OAc) ₂	DMF	rt	3 days	 $\underline{2a}$	71
	Pd(OAc) ₂	CH ₃ CN	rt	3 days	 $\underline{2a}$	10
	Pd(OAc) ₂	DMSO	rt	4 days	— ^c	
	PdCl ₂ (PhCN) ₂	DMF	rt	2.5 h	 $\underline{2a}$	40
					 $\underline{3a}$	27
					 $\underline{4a}$	21
	PdCl ₂ (PhCN) ₂	CH ₃ CN	80°C	3.5 h	 $\underline{2a}$	trace
					 $\underline{4a}$	38
					 $\underline{2a}$	58
[Pd(acac)(1,5-COD)]BF ₄	DMF	rt	3 h	 $\underline{2a}$	47	
				 $\underline{3a}$	7	
 $\underline{1b}$	Pd(OAc) ₂	DMF	60°C	7 h	 $\underline{2b}$	80
					 $\underline{2a}$	98
 $\underline{1c}$	Pd(OAc) ₂	DMF	60°C	1 h	 $\underline{2a}$	98
					 $\underline{2d}$	20
 $\underline{1d}$	Pd(OAc) ₂	DMF	100°C	38 h	 $\underline{2d}$	20
					 $\underline{3d}$	20
					 $\underline{2d}$	32
					 $\underline{3d}$	30
 $\underline{1e}$	Pd(OAc) ₂	DMF	100°C	15 h	 $\underline{2e}$	20

a. Yields were determined by glc. b. Isolated yield. c. Formation of $\underline{2a}$ was not observed.

Acknowledgement

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