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

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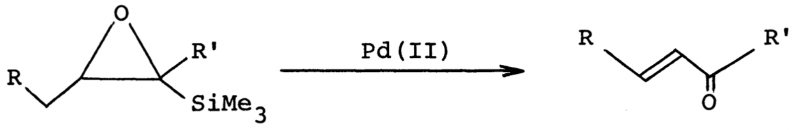
Treatment of α,β-epoxysilanes with palladium(II) salt in DMF affords α,β-unsaturated carbonyl compounds, in which the carbonyl group appears on the carbon originally bearing the silyl group.

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



1 **2**

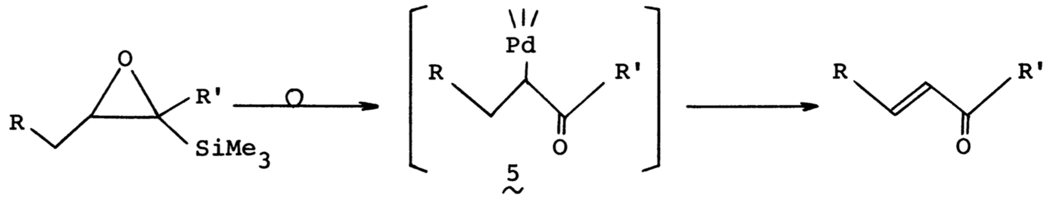
Typical procedure is as follows. To a solution of palladium acetate (1 mmol) in DMF (4 ml) was added (Z)-1-trimethylsilyl-1-hexene oxide[3] (**1a**, 1 mmol) at room temperature. The resultant mixture was stirred at 60°C for 7 h under nitrogen. The reaction proceeded with deposition of metallic palladium. 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 $PdCl_2(PhCN)_2$ instead of $Pd(OAc)_2$ gave a moderate yield of 2a, being contaminated with hexanal (3a) and 1-chloro-1-trimethylsilyl-2-hexanol (4a). The cationic palladium complex, $[Pd(acac)(1,5\text{-}COD)]BF_4$, 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 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 1a~1d.

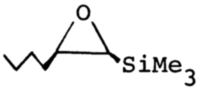
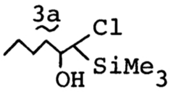
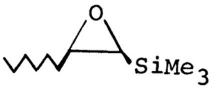
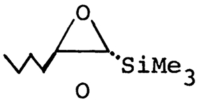
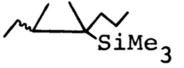
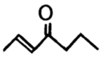
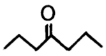
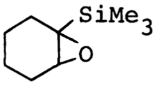
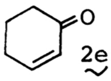
A catalytic process of the present transformation was attempted by adding $CuCl_2$ into the mixture of 1a and a catalytic amount of $Pd(OAc)_2$ in DMF, but the product obtained was the α-chloro-β-hydroxysilane 4a (62%). The reaction only in the presence of $CuCl_2$ also gave 4a (80%), which corresponds to the product in magnesium bromide assisted rearrangement of α,β-epoxysilanes.[5)] Reoxidation of the reduced Pd(0) was performed by using Ag_2O as an oxidant. The reaction of 1a was carried out in the presence of $Pd(OAc)_2$ (0.1 equiv.) and Ag_2O (1 equiv.) at 60°C for 20 h to produce 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 5[6)], which is subjected to β-elimination of Pd-H species to give the α,β-unsaturated carbonyl compound 2.



α,β-Epoxysilanes are easily prepared by oxidation of vinylsilanes or homologation[7)] 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-Epoxysilanes with Palladium Salt

1	Palladium Salt	Solv.	Reaction Temp.	Reaction Time	Products[a]	(%)
 1a	$Pd(OAc)_2$	DMF	60°C	7 h	 2a	90 (76)[b]
	$Pd(OAc)_2$	DMF	rt	3 days	2a	71
	$Pd(OAc)_2$	CH_3CN	rt	3 days	2a	10
	$Pd(OAc)_2$	DMSO	rt	4 days	————[c]	
	$PdCl_2(PhCN)_2$	DMF	rt	2.5 h	2a	40
					 3a	27
					 4a	21
	$PdCl_2(PhCN)_2$	CH_3CN	80°C	3.5 h	2a	trace
					4a	38
	$Pd(NO_3)_2$	DMF	rt	3 h	2a	58
					3a	7
	$[Pd(acac)(1,5\text{-}COD)]BF_4$	DMF	rt	3 h	2a	47
 1b	$Pd(OAc)_2$	DMF	60°C	7 h	 2b	80
 1c	$Pd(OAc)_2$	DMF	60°C	1 h	2a	98
 1d	$Pd(OAc)_2$	DMF	100°C	38 h	 2d	20
					 3d	20
	$PdCl_2(PhCN)_2$	DMF	60°C	7 h	2d	32
					3d	30
 1e	$Pd(OAc)_2$	DMF	100°C	15 h	 2e	20

a. Yields were determined by glc. b. Isolated yield. c. Formation of 2a was not observed.

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References

1) P. F. Hudrlik, D. Peterson, and R. J. Rona, J. Org. Chem., 40, 2263 (1975); P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, J. Am. Chem. Soc., 99, 1993 (1977); M. C. Croudace and N. E. Schore, J. Org. Chem., 46, 5357 (1981).

2) a) G. Stork and E. Colvin, J. Am. Chem. Soc., 93, 2080 (1971); b) R. K. Boeckman and K. J. Bruza, Tetrahedron Lett., 1974, 3365; c) P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra, and R. J. Rona, ibid., 1977, 591.

3) (Z)-α,β-Epoxysilanes were prepared by the Cp_2TiCl_2-catalyzed Grignard exchange reaction with trimethylsilylacetylenic compounds, followed by oxidation with MCPBA; F. Sato, H. Ishikawa, and M. Sato, Tetrahedron Lett., 22, 85 (1981).

4) C. M. Robbins and G. H. Whitham, J. Chem. Soc., Chem. Commun., 1976, 697.

5) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, Tetrahedron Lett., 1976, 1453.

6) Y. Ito, T. Hirao, and T. Saegusa, J. Org. Chem., 43, 1011 (1978).

7) C. Burford, F. Cooke, E. Ehlinger, and P. Magnus, J. Am. Chem. Soc., 99, 4536 (1977).

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