

NOVEL PREPARATION OF SILYL ENOL ETHERS FROM ALLYL ALCOHOLS

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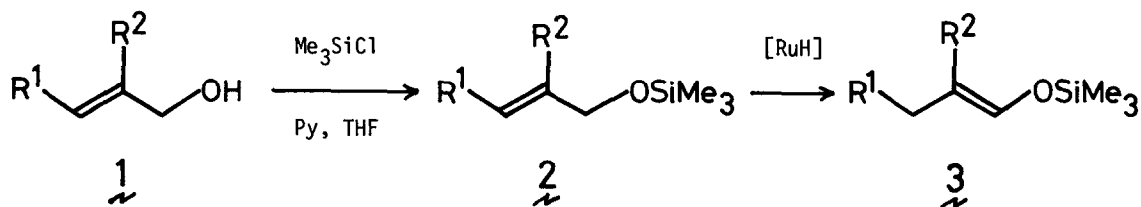
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Abstract: A novel synthetic method for silyl enol ethers from allyl alcohols was developed using ruthenium hydride catalyst.

In recent years, utilization of silyl enol ethers has increased greatly in various synthetic transformations. The most widely used method for the preparation of silyl enol ethers has involved either the reaction of enolates with chlorosilanes or the hydrosilylation of unsaturated carbonyl compounds.¹⁾ Although some new procedures and modifications of the original method have been reported, carbonyl compounds have been generally used as the starting materials in every synthetic method for silyl enol ethers so far as reported. We wish to report here a novel and elegant synthetic method for silyl enol ethers from allyl alcohols using transition metal complexes as catalyst.

Our method consists in double bond migration of allyl silyl ethers which are easily derived from allyl alcohols (1) and chlorotrimethylsilane. The studies of double bond migration of allylic compounds to the corresponding vinylic ones



have been developed using transition metal complexes by many groups.²⁾ Sasson³⁾ and Strohmeier⁴⁾ reported the conversion of allyl alcohols to aldehydes and ketones by ruthenium hydride complexes. We found that application of ruthenium hydride complexes to allyl silyl ethers (2) resulted in selective migration of double bond and gave the corresponding silyl enol ethers (3) as the sole product (eq. 1).

Table 1. Isomerization of Allyl silyl Ether to Silyl Enol Ether Catalyzed by $H_2Ru(PPh_3)_4$ ^{a)}

	Allyl Silyl Ether		Reaction Conditions			Yield (%)	Silyl Enol Ether	
	R ₁	R ₂	Solvent	Temp(°C)	Time(hr)		(Z)	: (E)
<u>2a</u>	CH ₃	H	benzene	150	20	100	55	45
			O-xylene	rfx	10	61	56	44
<u>2b</u>	H	CH ₃	benzene	150	17	92		
<u>2c</u>	Ph	H	benzene	150	13	71	68	32
			O-xylene ^{b)}	rfx	20	68	61	39
<u>2d</u>	CH ₂ =CH-	H	benzene	150	17	85 ^{c)}	-	- ^{d)}
<u>2e</u>	Me ₃ SiOCH ₂ -	H	benzene	150	1.5	100	55	45
			THF	110	1	100	58	42
			none	140	4	100	63	37
<u>2f</u> ^{b)}	geranyl silyl ether		O-xylene	rfx	23	27	-	- ^{d)}
<u>2g</u> ^{b)}	neryl silyl ether		benzene	150	72	58	64	36

a) The yield and isomer ratio were determined on the basis of nmr spectra. Unless otherwise noted, the ratio of allyl silyl ether to catalyst was adjusted as $[allyl\ silyl\ ether]/[H_2Ru(PPh_3)_4] = 500$.

b) $[Allyl\ silyl\ ether]/[H_2Ru(PPh_3)_4] = 50$.

c) The product is  OSiMe₃.

d) Undetermined.

Thus, the primary allyl alcohols offer the potential as synthetic aldehyde equivalents.

A typical procedure is described for the reaction of crotyl silyl ether (2a) with dihydrido tetrakis(triphenylphosphine)ruthenium, $H_2Ru(PPh_3)_4$. To 3 ml of dry benzene were added 480 mg (3.3 mmol) of 2a and 20 mg (0.0068 mmol) of $H_2Ru(PPh_3)_4$. The reaction mixture was sealed in pyrex tube (20 ϕ) and heated at 150°C for 20 hr. After cooling, solvent removal left the isomeric mixture of (Z)-1-butenyl silyl ether [(Z)-3a] and (E)-1-butenyl silyl ether [(E)-3a] (isomer ratio; Z/E = 55/45) as the yellow oily liquid in quantitative yield. Starting allyl silyl ether was completely consumed and no products other than (Z)-3a and (E)-3a were detected. The generality of the reaction was demonstrated for the silyl ethers of methallyl alcohol (2b), cinnamyl alcohol (2c), 2,4-pentadienyl alcohol (2d), 4-trimethylsiloxy-2-buten-1-ol (2e), geraniol (2f), and nerol (2g), all of which could be converted to the corresponding silyl enol ethers. The results of the isomerization of various allyl silyl ethers catalyzed by $H_2Ru(PPh_3)_4$ was summarized in Table 1.

Evidently the observed yield of each silyl enol ether depends on both the reaction rate of the starting allyl silyl ether and the thermodynamic equilibrium between the reactant and the product. The isomerizations of the conjugated allyl silyl ethers (2c and 2d) or the sterically hindered ones (2f and 2g) were incomplete under the conditions adopted in the experiments. Even in these cases, no other products were detected and the unconverted starting materials were recovered after the reaction. Use of a large amount of catalyst and a prolonged reaction time did not improve the yield of 2c. Application of higher temperatures resulted in the decomposition of both reactant and product. Other hydride complexes of ruthenium, such as $H_2Ru(PPhMe_2)_4$, $H_2Ru(PPh_2H)_4$, and $H_2Ru(PPh_2Me)_4$ were also tested and were found to be catalytically active. However, in spite of different basicity and bulkiness of the ligand, they did not bring any drastic change of the isomer ratio (Z/E) of the products.

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