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A REGIOSPECIFIC SYNTHESIS OF TRIMETHYLSILYL ENOL ETHERS USING RHODIUM CATALYZED ISOMERIZATION OF β-TRIMETHYLSILYLALLYL ALCOHOLS

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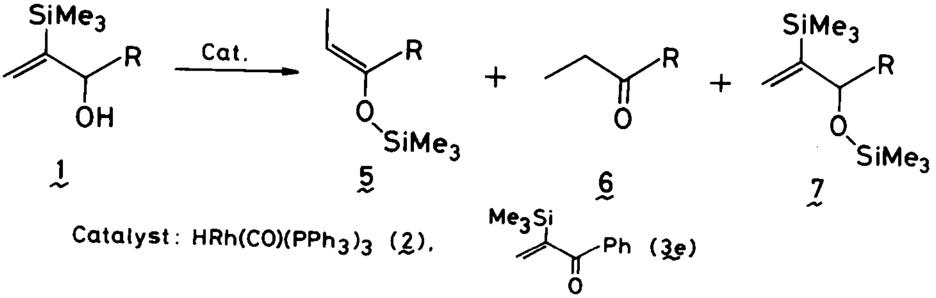
Summary: The rhodium catalyzed isomerization of β-trimethylsilylallyl alcohols has been successfully applied for the regiospecific synthesis of trimethylsilyl enol ethers.

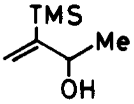
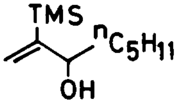
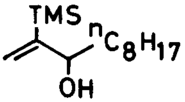
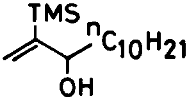
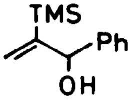
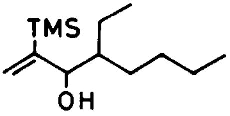
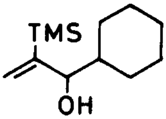
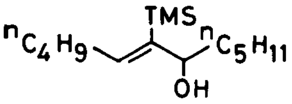
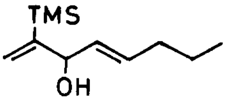
Trimethylsilyl enol ethers have become extremely important intermediates in synthetic organic chemistry.[1, 2] Although the numerous methods for the regioselective synthesis of them are reported, most approaches depend on the energy difference between the kinetically and thermodynamically controlled forms.[3] Michael type addition of triethylsilane to α,β-enones[4] and the oxygenative conversion of vinylsilanes[5] provide unambigous routes for the regiospecific synthesis of silyl enol ethers, however, these methods are suffered from the relatively restricted starting materials. On the other hand, ruthenium catalyzed isomerization of allyl silyl ethers to silyl enol ethers is also limited to aldehyde enolates.[6] We describe herein a successful regiospecific synthesis of trimethylsilyl enol ethers (**5**) from β-trimethylsilylallyl alcohols (**1**) using $HRh(CO)(PPh_3)_3$ (**2**) and 1-phenyl-2-trimethylsilyl-2-propen-1-one (**3e**) as catalysts.

The present method is achieved by the successive migration of double bond and trimethylsilyl group in allyl alcohols (**1**) which are readily prepared from aldehydes and α-trimethylsilylvinyl magnesiumbromide. When a benzene solution of **1c**, **2**, and **3e** was heated in a sealed tube, allyl alcohol, **1c** was consumed completely to give (E)-silyl enol ether, **5c**[7] accompanied with small amounts of



ketone, 6c and allyl silyl ether, 7c. No regioisomer of 5c was detected at all in G. C. analysis. Different from the reported isomerization of allylic

Table 1. Catalytic isomerization of β-trimethylsilylallyl alcohols (1).[a]

Entry	Allyl alcohol (1)		Reaction time (h)	Conversion (%)	Product selectivity (%)[b]		
					5	6	7
1		(1a)	65	21	38	12	50
2		(1b)	20	77	96	2	2
3			98	100	95	1	4
4		(1c)	20	100	81	12	5[c]
5			62	100	91	4	3[c]
6		(1d)	20	100	88	3	9
7		(1e)	20	100	78	7	15
8		(1f)	20	89	96	2	2
9			63	100	99	0.5	0.5
10		(1g)	20	100	98	0	2
11		(1h)	20	100	49	2	6[d]
12			113	100	92	1	7
13		(1i)	20[e]	100	87	4	2[f]

a) Reactions were carried out at 105°C in a sealed tube including benzene (0.5 ml) solutions of allyl alcohols 1 (2 mmol), 2 (0.1 mmol), and 3e (0.1 mmol). After the reaction products were collected by Kugelrohr distillation.
b) Determined by GLC (PEG-20M). c) Two percent of 1-dodecen-3-one was detected.
d) The remaining product was 4h. e) 1,4-Dioxane was used as a solvent.
f) The remaining product was 2-trimethylsilyl-1-octen-3-one.

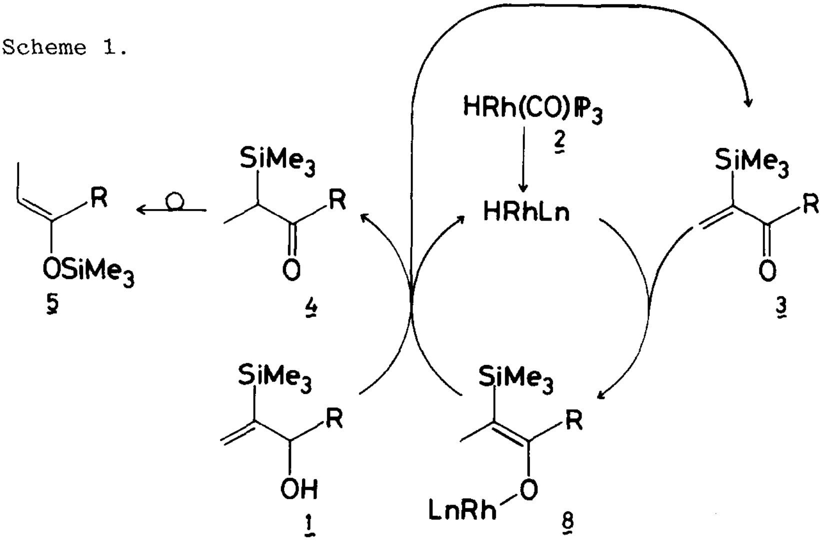
compounds catalyzed by transition metal complexes,[6, 8] the presence of both **2** and α,β-enone, **3e** is crucial to give silyl enol ether, **5c** selectively. In fact, replacement of **3e** by **3a** (R=Me), 1-phenyl-2-propen-1-one, 1,3-diphenyl-2-propen-1-one, 3-buten-2-one, or *p*-quinone as the cocatalyst causes a sharp drop in the selectivity of **5c**. The effect of transition metal species is also remarkable. Other rhodium complexes, $ClRh(PPh_3)_3$, $ClRh(CO)(PPh_3)_3$, and $[(COD)Rh(Diphos)]^+ClO_4^-$ did not show any catalytic effect. Ruthenium complex, $H_2Ru(PPh_3)_4$ gave only desilylated ketone **6c**. The scope of the reaction was demonstrated for various types of allyl alcohols, which could be transformed to the corresponding silyl enol ethers regiospecifically.[7] The only unsatisfied result was given in the case of **1a**. The results are summarized in Table 1.

The resultant enolate forms are unequivocally directed to the carbon originally bearing trimethylsilyl group in all cases and does not isomerize during the prolonged reaction time. In addition to the terminal double bond, the internal one also migrates smoothly, however, the subsequent migration of the trimethylsilyl group is considerably retarded. The supposed intermediate α-trimethylsilylketone **4h** which completely isomerized to **5h** in the longer heating was obtained as the mixture including almost equal amounts of **5h** in the short reaction time (Entries 11 and 12 in Table 1).

It should be emphasized that the present transformation discloses a novel methodology to differentiate both α-positions of asymmetric ketones. The selective migration of the silylvinyl site to form silyl enol ether **5i** is also confirmed by the intramolecular competition in **1i**. It provides an alternative route to 2-trimethylsiloxy-1,3-diene derivatives.[9]

Scheme 1 illustrates the mechanistic rationale for the present

Scheme 1.



transformation. Rhodium complex **2** enters the catalytic cycle which is initiated by the reaction with **3** to form alkoxy complex **8**. This intermediate **8** interacts with **1** to give α-silylketone **4** along with simultaneous regeneration of **3** and active rhodium complex. Further rearrangement of **4** leads to silyl enol ether **5**. The authentic silylketone **4c**[10] rearranged completely to **5c** under the reaction conditions.

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7. The regiochemical purity was checked by the comparison of the G. C. spectra with the authentic mixture of the regioisomers. All silyl enol ethers gave the correct N. M. R. spectra, which showed almost pure E-form in the stereochemistry.
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10. Silylketone **4c** was derived from **1c** by Collins oxidation and the subsequent selective hydrogenation catalyzed by $ClRh(PPh_3)_3$.

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