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A FACILE SYNTHESIS OF α-TRIMETHYLSILYL KETONES AND THEIR REGIOSPECIFIC REARRANGEMENT TO TRIMETHYLSILYL ENOL ETHERS

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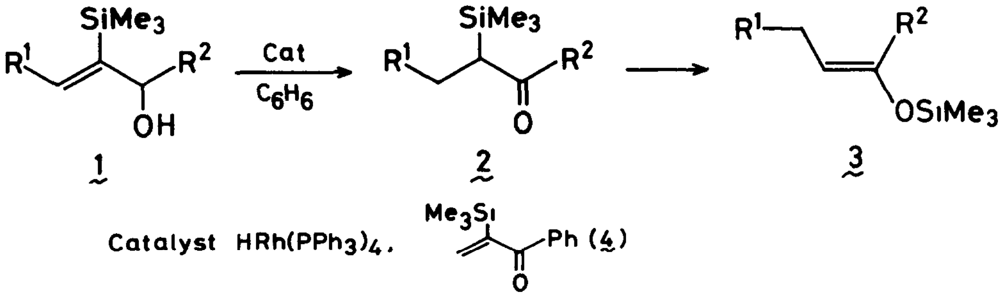
Summary The rhodium catalyzed isomerization of β-trimethylsilylallyl alcohols has been successfully applied for the stepwise and selective synthesis of α-trimethylsilyl ketones and trimethylsilyl enol ethers

Trialkylsilyl enol ethers [1] and their isomers, α-trialkylsilyl ketones [2] are versatile classes of silylated synthons capable of undergoing a variety of useful synthetic transformations A regiospecific formation of silyl enol ethers is now an interesting subject [3] On the other hand, α-silyl ketones are relatively unobtainable, since direct silylation of the corresponding ketone gives only silyl enol ethers [4, 5] Although numerous indirect methods from carboxylic acid derivatives [6] and other non-carboxylic acid derived sources [2a, 7] are presented for the selective preparation of α-silyl ketone, all of these require a rather tedious procedure because of the relatively labile silicon-carbon bond which is adjacent to a carbonyl group and are applicable to relatively limited cases We report herein a stepwise synthesis of α-trimethylsilyl ketones 2 and trimethylsilyl enol ethers 3 by the catalytic isomerization of β-trimethylsilylallyl alcohols 1 with $HRh(PPh_3)_4$ and 2-trimethylsilyl-1-phenyl-2-propen-1-one (4)

Recently we reported a regiospecific formation of trimethylsilyl enol ethers 3 derived from allyl alcohols 1 by the catalytic behavior of $HRh(CO)(PPh_3)_3$ and α,β-enone 4 [8] This transformation is composed of the



consecutive migrations of double bond and trimethylsilyl group which are not discriminative under the reaction conditions. The probable formation of α-trimethylsilyl ketone **2** in the above course prompt us to accomplish the selective migration of the double bond in **1**, since it offers a general and facile synthetic method of **2**

Although mechanistic details are uncertain in the one pot transformation of allyl alcohols **1** to **3**, the fact that the presence of α,β-enone **4** is crucial to complete reactions resembles the behavior of rhodium complex participated in transfer hydrogenation [9] Thus, $HRh(PPh_3)_4$ known as the more active catalyst in transfer hydrogenation was used in order to accelarate the first step in the equation A benzene (1 ml) solution of allyl alcohol **1b** (1.0 mmol) was heated in a sealed tube containing catalytic amounts of $HRh(PPh_3)_4$ (0 05 mmol) and **4** (0 05 mmol) at 105°C for 30 min followed by concentration and bulb to bulb distillation Through such a simple procedudre, the corresponding α-silyl ketone **2b** [10] was isolated in 90% yield with small amounts (less than 3%) of silyl enol ether **3b** In order to complete the desired reaction, temperature and time are critical factors as well as the presence of catalytic amounts of **4** No observable reaction did occur at low temperature or in the absence of **4** within the same reaction time The thermal rearrangement of α-silyl ketones **2** to silyl enol ethers **3** was recoginized at the early stage [11] We also confirmed that **2e** changed almost quantitatively to **3e** under the condition in $HRh(CO)(PPh_3)_3$ catalyzed isomerization of **1e** [8] Evidently prolonged reaction time induced the consecutive migration of double bond and trimethylsilyl group to give silyl enol ether **3b** from **1b** regiospecifically [12] The results of other allyl alcohols **1** are summarized in Table 1

The present transformation is uniformly effective both in the terminal and internal double bonds and any type of the substituents, R^2 except silyl ketone **2e** which was contaminated by silyl enol ether **3e** as the result of consecutive isomerization during the distillation (80°C/0 2 mmHg) The selective migration of the silylvinyl site to form α-trimethylsilyl α',β'-unsaturated ketone **2i** was also confirmed by the intramolecular competition in **1i** Different from the results of $HRh(CO)(PPh_3)_3$ catalysis, silyl enol ether **3** formed in the present system was not contaminated by trimethylsilyl ether of **1** of which formation could not be elucidated

It should be emphasized that the consecutive isomerization of **1** catalyzed by $HRh(PPh_3)_4$ discloses a general method to form α-trimethylsilyl ketone **2** through nonaqueous work up and a reliable methodology to differentiate both α-positions of asymmetric ketones

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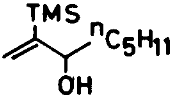
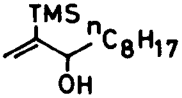
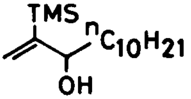
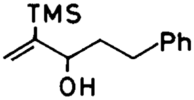
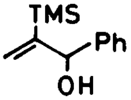
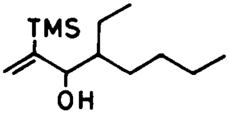
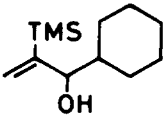
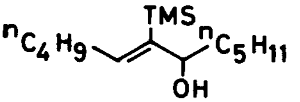
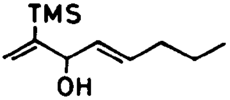
Table 1 Formation of α-trimethylsilyl ketone 2[a]

Entry	Allyl alcohol (1)	Reaction time (h)	Conversion (%)	Yield of 2[b] (%)
1	 (1a)	1	100	60
2	 (1b)	0 5	100	90
3		1 5	0	0[c]
4		20	100	0 (82)
5	 (1c)	0 25	100	96
6		20	100	0 (80)
7	 (1d)	0 5	100	94
8		20	100	0 (61)
9	 (1e)	0 08	100	56 (17)
10		20	100	0 (83)
11	 (1f)	1	100	82
12	 (1g)	0 25	100	81
13	 (1h)	1 25	100	60 (34)
14		0 5	100	87[d]
15		45	100	0 (66)
16	 (1i)	1	100	82[e]

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a) Reactions were carried out in 0 5 mmol scale at 105°C

b) Isolated yields Values in parentheses show the yield of trimethylsilyl enol ether 3

c) Reaction was carried out at 75°C

d) Ten mol % of $HRh(PPh_3)_4$ was used and filtered from the reaction mixture before distillation

e) About 7% of 2-trimethylsilyl-1-octan-3-one was included

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10 All these compounds were isolated by bulb to bulb distillation and showed correct values of analyses and corresponding i r and ^{1}H n m r spectra except **2e**. ^{1}H n m r and i r data in CCl$_4$ of **2d** are shown

I r , 1694 ($\nu_{C=O}$) and 1252 cm^{-1} ($\delta_{s\ Si-C}$)

^{1}H n m r , δ 0 00 (s, 9H, SiMe$_3$), 1 10 (d, J=7 2 Hz, 3H, C-Me), 2 29 (q, J=7 2 Hz, 1H, CH), 2 69 (t, J=4 8 Hz, 2H, CH$_2$), 2 78 (t, J=4 8 Hz, 2H, CH$_2$), and 7 17 (s, 5H, Ph)

11 A G Brook, D M MacRae, and W W Limberg, *J Am Chem Soc* , 89, 5493 (1967)

12 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 ^{1}H n m r spectra

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