

A VERSATILE ROUTE TO SILYLSUBSTITUTED KETONES BY RHODIUM
CATALYZED ISOMERIZATION OF SILYLATED ALLYL ALCOHOLS

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Summary: The rhodium catalyzed isomerization of α -, β -, and γ -silylated allyl alcohols has been successfully applied to the selective synthesis of acylsilane, α -silyl ketones, and β -silyl ketones, respectively.

Acylsilane and α - and β -silyl ketones are versatile classes of organosilicon compounds capable of undergoing a variety of useful synthetic transformations.¹ Especially α -silyl ketones provide a reliable methodology to differentiate the two α -positions in unsymmetric ketones.²

Recently we reported a facile synthesis of α -trimethylsilyl ketones **4** by the catalytic isomerization of β -trimethylsilylallyl alcohols **1** with $\text{HRh}(\text{PPh}_3)_4$ and 2-trimethylsilyl-1-phenyl-2-propen-1-one (**2**) (Route A).³ Although this method is very reliable, it is impossible to apply to the synthesis of trimethylsilylmethyl ketones.⁴ A simple and nonaqueous work up of this type reaction is very attractive to isolate relatively labile α -trimethylsilyl ketones, since trimethylsilyl group remained intact under the reaction conditions.³ Thus, we have exploited a convenient route for obtaining **4** by the modification of allyl alcohols (Route B).

A typical experimental procedure follows. A 1,4-dioxane (10 ml) solution of **1** (5.44g, 29.2 mmol) and $\text{HRh}(\text{PPh}_3)_4$ (0.380g, 0.33 mmol) was heated for 25 min. at 105 °C in a sealed tube. The residue obtained after the evaporation of the solvent gave **4** (**5**) (4.39g, 82%) through bulb to bulb distillation (68 °C/0.15 mmHg).

Different from the isomerization of **1**, the present reaction does not need any **2** as cocatalyst and is attained in far lower concentration of $\text{HRh}(\text{PPh}_3)_4$. Turnover number of the catalyst can be increased to 450 within 1 hour. $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ is also effective in this case.⁶ Several examples are listed in Table 1. A striking feature of the reaction is the general applicability

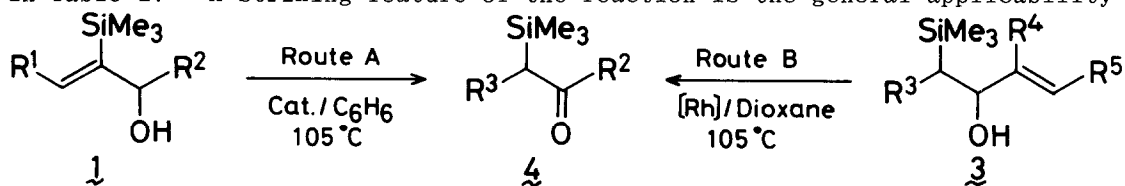
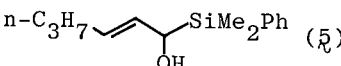
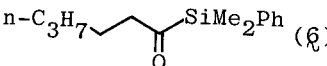
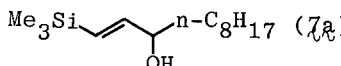
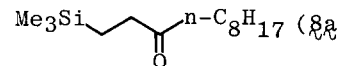
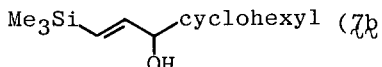
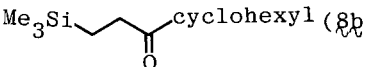


Table 1. Isomerization of silylated allyl alcohols.^a

Entry	Allyl alcohol	Reaction time (h)	Product	Yield (%) ^b
1	3a R ³ =H, R ⁴ =H, R ⁵ =H	0.5	4a	63
2	3b R ³ =H, R ⁴ =Me, R ⁵ =H	0.5	4b	65
3	3c R ³ =H, R ⁴ =H, R ⁵ =Me	0.5	4c	67
4	3d R ³ =H, R ⁴ =H, R ⁵ =n-C ₃ H ₇	0.4	4d	82
5	3e R ³ =Me, R ⁴ =H, R ⁵ =n-C ₃ H ₇	0.5	4e	60
6	3f R ³ =n-C ₅ H ₁₁ , R ⁴ =H, R ⁵ =H	0.67	4f	97
7	3g R ³ =n-C ₅ H ₁₁ , R ⁴ =Me, R ⁵ =H	0.67	4g	95
8	3h R ³ =n-C ₅ H ₁₁ , R ⁴ =H, R ⁵ =n-C ₃ H ₇	0.9	4h	94
9	n-C ₃ H ₇  (5)	13	n-C ₃ H ₇  (6)	81
10	Me ₃ Si  (7a)	16	Me ₃ Si  (8a)	83
11	Me ₃ Si  (7b)	72	Me ₃ Si  (8b)	92

a) The reaction was performed on a 10 mmol scale in 1,4-dioxane using 1 mol % of HRh(PPh₃)₄. b) Isolated yield.

to a variety of allyl alcohols. Acylsilane **6**⁵ and β-trimethylsilyl ketones **8**⁵ were also obtained as the result of HRh(PPh₃)₄ catalyzed isomerization of corresponding allyl alcohols **5**⁷ and **7**.

The present rhodium catalyzed isomerization of allyl alcohols discloses a versatile methodology introducing a silyl group at a specific position of ketones.

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