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AN OXIDATIVE ROUTE TO α-TRIMETHYLSILYL KETONES BY MEANS OF RHODIUM CATALYZED DEHYDROGENATION OF β-TRIMETHYLSILYL ALCOHOLS

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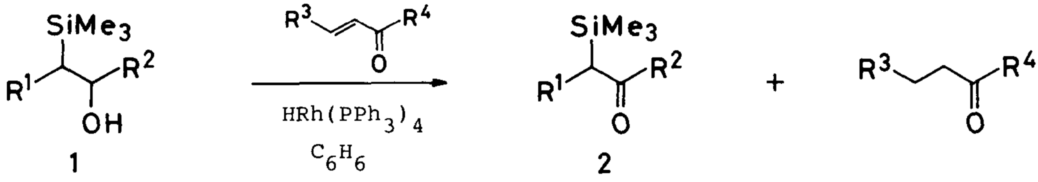
Summary: The transfer hydrogenation of β-trimethylsilyl alcohols catalyzed by $HRh(PPh_3)_4$ has been successfully applied to the efficient synthesis of α-trimethylsilyl ketones.

α-Trialkylsilyl carbonyl compounds can be utilized in a variety of synthetic transformations.[1] Especially the trialkylsilyl group plays an important role to differentiate two α-positions of unsymmetrically substituted ketones.[2] Recently we reported a novel and versatile synthetic method of α-trimethylsilyl ketones (2) resulted from the rhodium catalyzed isomerization of β-trimethylsilylallyl alcohols.[3] Although this type of reaction is not applicable to some limited cases, cyclic allyl alcohol and 3-trimethylsilyl-3-alken-2-ol, mechanistic consideration of the isomerization suggests strongly the applicability of rhodium catalyzed transfer hydrogenation.[4] Thus, we describe herein a successful dehydrogenation of β-trimethylsilyl alcohol (1) to give 2 as the result of transfer hydrogenation catalyzed by $HRh(PPh_3)_4$.

A typical procedure follows. A benzene (2.5 ml) solution of 1c (0.703g, 3.25 mmol), 2-cyclohexenone(0.556g, 5.78 mmol), and $HRh(PPh_3)_4$ (0.163g, 0.14 mmol) was heated for 30 min. at 90°C in a sealed tube. After the evaporation of volatile materials the residue was distilled [88°C (bath temp.)/0.1 mmHg] to give 2 ($R^1 = CH_3$, $R^2 = {}^nC_6H_{13}$; 0.667g, 97%).

The results are summarized in Table 1. Since the trimethylsilyl group in 2 is relatively labile, the purity of the resulting 2 depends on the combination of 1 and α,β-unsaturated ketone as a hydrogen acceptor. When 3-buten-2-one was used as a hydrogen acceptor, an appreciable amount of protode-



silylated ketone was observed (entry 1 and 3). Such an undesirable contamination was prevented completely by the use of 3-trimethylsilyl-3-buten-2-one or 2-cyclohexenone (entry 2 and 4). It is noteworthy that α-silyl aldehyde can be isolated by the present route (entry 9) despite of the indispensable use of triphenylsilyl group.

Although a similar transformation using chromic acid oxidation was already reported,[5] the present method promises the exclusion of the problems in the oxidation with chromic acid because of the instablity of 2. Thus, the regiodefined synthesis of any types of 2 can be attained by the combination of dehydrogenation of 1 and isomerization of β-trimethylsilylallyl alcohols[3] catalyzed by $HRh(PPh_3)_4$.

Table 1. Dehydrogenation of β-trimethylsilyl alcohol (1)[a]

Entry	Alcohol (1)		Hydrogen acceptor[b]	Reaction condition		Yield of 2 (%)
	R^1	R^2		time(min.)	temp.(°C)	
1	H	$^nC_7H_{15}$	A	60	90	23[c]
2	H	$^nC_7H_{15}$	B	240	105	83
3	$^nC_5H_{11}$	CH_3	A	20	90	60[c]
4	$^nC_5H_{11}$	CH_3	C	20	90	75
5	$^nC_6H_{13}$	CH_3	C	30	90	97
6	$^nC_4H_9$	$^nC_3H_7$	C	60	90	71
7	$^nC_5H_{11}$	2-Methylpropyl	C	30	100	95
8	$-(CH_2)_4-$		A	20	105	71
9	H	H	A	20	105	63[d]

a) The reaction was performed on a 3 mmol scale in benzene using 4 mol % of $HRh(PPh_3)_4$.
b) A:3-Buten-2-one, B:3-Trimethylsilyl-3-buten-2-one, C:2-Cyclohexenone.
c) Significant amount of protodesilylated ketone was obtained.
d) Triphenylsilyl group was used instead of trimethylsilyl group.

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