Pergamon

Tetrahedron Letters 40 (1999) 711–714

TETRAHEDRON
LETTERS

Transition Metal-Catalyzed Dehydrogenative Silylation of Ketones with Amine and Halide as Cocatalysts

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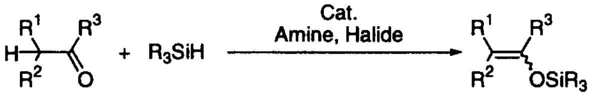
Received 22 September 1998; revised 9 November 1998; accepted 11 November 1998

Abstract

It was found that dehydrogenative silylation of ketones with hydrosilanes proceeds in the presence of a transition metal catalyst such as palladium on carbon or iridium carbonyl, with amine and halide as cocatalysts, to give the corresponding silyl enol ethers in good yields. The present reaction is applicable for a variety of ketones and hydrosilanes with complete regioselectivity.

Keywords catalysts; enol ethers; ketones; silicon and compounds; transition metals

Silyl enol ethers have been well-known as useful reagents in organic synthesis. [1] A general method for the preparation of silyl enol ethers has been the silylation of ketones with chlorosilanes in the presence of strong bases. [2,3] Although the yield of the reaction is generally high enough, the separation of silyl enol ethers from a large amount of inorganic or organic salt sometimes encounters difficulty because of the high hydrolytic reactivity of the product. The catalytic dehydrogenative silylation [4-9] of ketones with hydrosilanes, where hydrogen gas is the sole byproduct and no purification may be required, can be one exchangeable process in view of both synthetic and environmental aspects. In this paper, we report a convenient preparation of silyl enol ethers by transition metal-catalyzed dehydrogenative silylation of ketones in the presence of amine and halide as cocatalysts.



(1)

Initially, we examined the catalytic activities of transition metals and metal complexes by using cyclohexanone (**1a**) and acetophenone (**1b**) as substrates with triethylsilane in the presence of catalytic amounts of diethylamine and ethyl iodide. As shown in Table 1,

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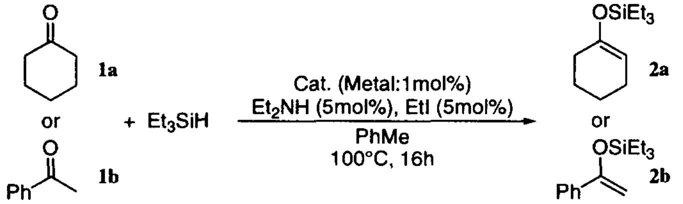
PII: S0040-4039(98)02436-8

several transition metals or metal complexes such as palladium on carbon, platinum on alumina, manganese carbonyl, and iridium carbonyl, exhibited catalytic activity for the dehydrogenative silylation. Under the optimized conditions, cyclohexanone was converted into 1-cyclohexenyloxytriethylsilane (**2a**) in 96% yield by a combination catalyst consisting of Pd/C (1 mol%), diethylamine (1 mol%), and ethyl iodide (1 mol%). A variety of amines such as *t*-butylamine, *N*-methylaniline, triethylamine, or pyridine, [8] and iodides such as methyl iodide, iodobenzene, or iodine, can be used in place of diethylamine and ethyl iodide, respectively. In the case of acetophenone, a different catalyst system consisting of $Ir_4(CO)_{12}$ (0.25 mol%), diethylamine (5 mol%), and ethyl iodide (5 mol%) yielded satisfactory results to give 1-phenylvinyloxytriethylsilane (**2b**) in 74% yield.

Typical procedure is as follows: A mixture of cyclohexanone 98.2 mg (1 mmol), triethylsilane 174.4 mg (1.5 mmol), diethylamine 0.7 mg (0.01 mmol), ethyl iodide 1.5 mg (0.01 mmol) and 5% Pd/C 21.3 mg ([Pd] = 0.01 mg-atom) in toluene (1 ml) was heated at 100 °C for 16h. GLC analysis of the reaction mixture showed the formation of 1-cyclohexenyloxytriethylsilane in 96% yield. After the reaction mixture was cooled and filtered, the filterate was concentrated under reduced pressure, and **2a** was obtained in 89% isolated yield.



(2)

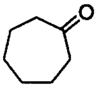
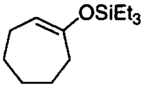
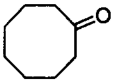
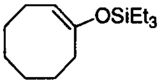
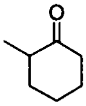
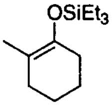
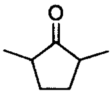
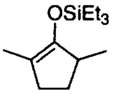
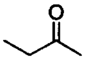
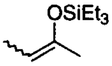
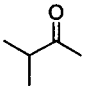
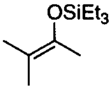
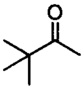
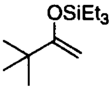
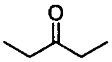
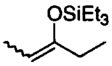
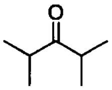
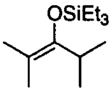
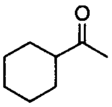
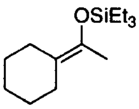
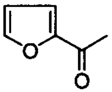
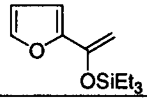
Table 1. Dehydrogenative silylation of ketones **1a** and **1b**.[a]

Entry	Ketone	Cat.	Conversion of 1[b] (%)	Product (yield[b] %)
1	**1a**	5% Pd/C	62	**2a** (59)
2[c]	**1a**	5% Pd/C	100	**2a** (96)
3	**1a**	$Ir_4(CO)_{12}$	71	**2a** (41)
4	**1a**	5% Pt/Al_2O_3	50	**2a** (38)
5	**1a**	$Mn_2(CO)_{10}$	95	**2a** (34)
6	**1b**	5% Pd/C	60	**2b** (19)
7	**1b**	$Ir_4(CO)_{12}$	79	**2b** (56)
8[d]	**1b**	$Ir_4(CO)_{12}$	99	**2b** (74)
9	**1b**	5% Pt/Al_2O_3	33	**2b** (24)
10	**1b**	$Mn_2(CO)_{10}$	75	**2b** (34)

[a] A mixture of ketone (1mmol), Et_3SiH (1mmol), Et_2NH (0.05mmol), EtI (0.05mmol) catalyst (metal=0.01mg-atom) and PhMe (1ml) was heated at 100°C for 16h under Ar atmosphere. [b] Determined by GLC analysis based on ketone. [c] Et_3SiH (1.5mmol), Et_2NH (0.01mmol) and EtI (0.01mmol) were used. [d] Et_3SiH (1.2mmol) was used.

In order to demonstrate the usefulness of the present catalytic reaction, a palladium or iridium catalyst system was applied to the dehydrogenative silylation of various ketones. The representative results are summarized in Table 2. Cyclic ketones (**1c-f**) having 5- to 8-

Table 2. Dehydrogenative Silylation of Various Ketones.

Entry	Ketone	Method[a]	Conv. of **1** (%)[b]	Product (yield[b] %)
1	 **1c**	Pd	100	 **2c** (86)
2	 **1d**	Pd	100	 **2d** (98)
3	 **1e**	Pd	100	 **2e** (98)
4	 **1f**	Pd	90	 **2f** (75)
5	 **1g**	Ir	100	 **2g** (70[c])
6	 **1h**	Pd	87	 **2h** (68)
7	 **1i**	Pd	85	 **2i** (73[d])
8[e]	 **1j**	Pd	100	 **2j** (73[f])
9[e]	 **1k**	Ir	----[g]	 **2k** (73)
10[e]	 **1l**	Pd	100	 **2l** (74)
11	 **1m**	Ir	100	 **2m** (74)

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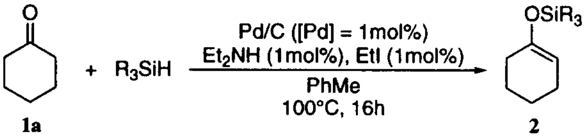
[a] Pd: A mixture of ketone (1mmol), Et_3SiH (1.5mmol), Et_2NH (0.01mmol), EtI (0.01mmol) and Pd/C ([Pd] = 0.01mg-atom) in PhMe was heated at 100°C for 16h under Ar atmosphere. Ir: A mixture of ketone (1mmol), Et_3SiH (1.2mmol), Et_2NH (0.05mmol), EtI (0.05mmol) and $Ir_4(CO)_{12}$ ([Ir] = 0.01mg-atom) in PhMe was heated at 100°C for 16h under Ar atmosphere. [b] Determined by GLC analysis based on ketone. [c] E/Z = 39/61. [d] 65% in isolated yield. [e] Heated for 40h. [f] E/Z = 24/76. [g] Not determined because of the overlap of the GLC peaks.

membered rings were converted into the corresponding silyl enol ethers in good yields by using palladium catalyst. Especially, cyclooctanone (**1d**) and 2-methylcyclohexanone (**1e**) gave the desired products in quantitative yields. Acyclic aliphatic ketones (**1g-l**) underwent the dehydrogenative silylation in good yields by using a palladium or iridium catalyst, whereas aromatic ketone (**1m**) again gave the better result on using an iridium catalyst. Unsymmetrical ketones **1e**, **1g**, **1h** and **1l**, in which two possible regioisomers can be formed, afforded the thermodynamically controlled ones exclusively. [4]

Finally, we examined the dehydrogenative silylation of cyclohexanone (**1a**) with various hydrosilanes using a palladium catalyst. The results are shown in Table 3. All hydrosilanes gave the corresponding silyl enol ethers in good to excellent yields.



(3)

Table 3. Dehydrogenative Silylation of **1a** with Hydrosilanes.[a]

Entry	Hydrosilane	Conv. of **1a**[b](%)	Yield[b](%)
1	Et_3SiH	100	96
2	$PhMe_2SiH$	100	98
3	$^tBuMe_2SiH$	90	89

[a] A mixture of cyclohexanone (1mmol), hydrosilane (1.5mmol), Et_2NH (0.01mmol), EtI (0.01mmol) and Pd/C ([Pd] = 0.01mg-atom) in PhMe (1ml) was heated at 100°C for 16h under Ar atmosphere. [b] Determined by GLC analysis based on cyclohexanone.

In conclusion, the present catalytic dehydrogenative silylation of ketones provides a facile and convenient preparation of a wide variety of silyl enol ethers with complete regioselectivity. It is remarkable that the reaction proceeds under neutral conditions and hydrogen can be formed as the sole byproduct so that neither purification nor isolation of the water-sensitive products may be required in usual organic syntheses. The mechanistic details are currently under investigation.

References

[1] Hudrlik PF. Organosilicon compounds in organic synthesis. In: Seyferth D, editor. New applications of organometallic reagents in organic synthesis. Amsterdam: Elsevier, 1976: 127-159.
[2] Stork G, Hudrlik PF. J. Am. Chem. Soc., 1968; 90: 4462-4465.
[3] House HO, Czuba LJ, Gall M, Olmstead HD. J. Org. Chem., 1969; 34: 2324-2336.
[4] Nagai Y, Uetake K, Yoshikawa T, Matsumoto H. J. Syn. Org. Chem. Jpn., 1973; 31: 759-765.
[5] Ojima I, Nagai Y. J. Organometal. Chem., 1973; 57: C42-C44
[6] Frainnet E, M-Siegfried V, Brousse E, Dedier J. J. Organometal. Chem., 1975; 85: 297-310.
[7] Frainnet E, Bourhis R. J. Organometal. Chem., 1975; 93: 309-324.
[8] Sakurai H, Miyoshi K, Nakadaira Y. Tetrahedron Lett., 1977; 18: 2671-2674.
[9] Fuchikami T, Ubukata Y, Tanaka Y. Tetrahedron Lett., 1991; 32: 1199-1202.