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Dehydrogenative silylation of terminal alkynes by iridium catalyst

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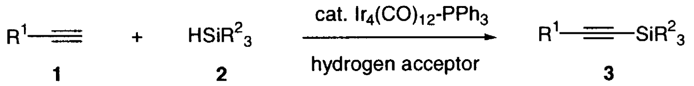
Abstract

Dehydrogenative silylation of terminal alkynes with hydrosilanes proceeds in the presence of iridium catalyst to afford the corresponding silylacetylenes. When phenylacetylene and triethylsilane were heated in dry DME in the presence of $Ir_4(CO)_{12}$–PPh_3, (2-phenylethynyl)triethylsilane was obtained in 96% yield with little of hydrosilylated products. The present method is applicable for a variety of terminal alkynes and hydrosilanes to give the corresponding silylacetylenes in good yields with high selectivities. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: iridium; iridium compounds; silicon; silicon compounds; alkynes; dehydrogenation; catalysis.

Hydrosilylation of carbon–carbon multiple bonds has been one of the most important laboratory and industrial methods for the formation of silicon–carbon bonds, and many transition-metal catalysts have been found to be effective for these reactions.[1,2] On the other hand, there have been only a few reports on transition-metal catalyzed dehydrogenative silylation of terminal alkynes with hydrosilanes to afford the corresponding alkynylsilanes, selectively. For example, some cationic iridium complexes were reported to have some catalytic activities toward this reaction, where a lot of the undesired alkenylsilanes were formed together.[3–5] Murai et al. also reported that a dehydrogenatively silylated compound was obtained as a by-product in iridium catalyzed hydroformylation of terminal alkyne with hydrosilane under CO pressure.[6]



(1)

Here, we wish to report that dehydrogenative silylation of terminal alkynes with hydrosilanes proceeds in the presence of iridium catalysts to afford the corresponding silylacetylenes in good yields with high selectivities (Eq. (1)).

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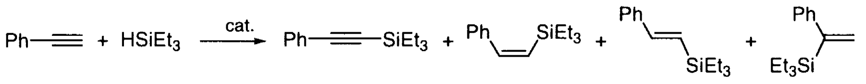
First, we examined the reaction of phenylacetylene (**1a**) and triethylsilane (**2a**) (Eq. (2) and Table 1). When phenylacetylene (**1a**; 1.00 mmol) and triethylsilane (**2a**; 1.00 mmol) were heated in DME in the presence of $Ir_4(CO)_{12}$ (1 mol%) at 100°C for 24 h, (2-phenylethynyl)triethylsilane (**3aa**) was obtained only in 5% yield, in addition to a mixture of (phenylethenyl)triethylsilanes in 55% yield.[7] $[IrCl(cod)]_2$, $IrCl(CO)(PPh_3)_2$, $IrH(CO)(PPh_3)_3$, Rh/C, and $Rh_6(CO)_{16}$ were less effective for the present dehydrogenative silylation. When the reaction was carried out in the presence of $Ir_4(CO)_{12}$–PPh_3 catalyst, **3aa** was obtained in good selectivity, with little of the hydrosilylated products. In this reaction, the formation of styrene was also observed as a by-product, which indicates that phenylacetylene acts as a trapping agent of hydrogen generated in situ. The employment of 2 equiv. of acetylene **1a** in the presence of $Ir_4(CO)_{12}$ (1 mol%)–PPh_3 (12 mol%) gave the corresponding silylacetylene in 96% yield, as shown in Table 1 (run 1). When decreasing the amount of additive phosphine, both yields and selectivities of the desired **3aa** were lower (runs 2 and 3). The silylated acetylene **3aa** was obtained in excellent yields not only in DME but also in hexane, toluene, THF, acetonitrile, and 1,2-dichloroethane as a solvent. The reaction proceeded more slowly without any solvent.



1a **2a** **3aa** **4aa** **5aa** **6aa**

(2)

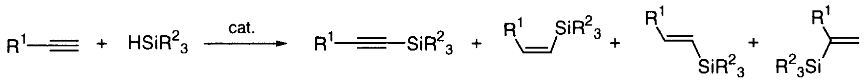
Table 1
Dehydrogenative silylation of phenylacetylene (**1a**) with triethylsilanes (**2a**)[a]

Run	cat. (mol%)		Yields[b] (%)				Ratio[c]
	$Ir_4(CO)_{12}$	PPh_3	**3aa**	**4aa**	**5aa**	**6aa**	
1	1	12	96	1	1	1	97/3
2	1	4	73	8	7	trace	83/17
3	1	-	18	39	24	7	20/80
4[d]	1	12	66 (96)	trace	2	trace	95/5
5[e]	1	12	90	1	1	1	97/3
6[f]	1	12	93 (95)	1	2	trace	95/5

[a] All reactions were carried out with phenylacetylene (**1a**; 2.30 mmol), triethylsilane (**2a**; 1.00 mmol), iridium carbonyl (0.01 mmol, 1 mol%) and triphenylphosphine in dry DME (1.0 ml) at 100°C for 24 h unless otherwise noted. [b] Determined by GLC based on employed **2a**. Conversion yields were shown in parentheses. [c] Ratio= **3aa**/ (**4aa** + **5aa** + **6aa**). [d] Reaction without any solvent. **2a** (31%) was recovered. [e] Toluene was employed as a solvent instead of DME. [f] Hexane was employed as a solvent instead of DME.

The present method is applicable for a variety of terminal alkynes and hydrosilanes to give the corresponding silylacetylenes with good to excellent results as summarized in Table 2 and Eq. (3). When *tert*-butyldimethylsilane (**2c**), possessing a bulky *tert*-butyl group on the silicon atom, was employed as a hydrosilane, a higher reaction temperature and greater amounts of catalyst were required (Table 2, run 2). Siloxy- and alkoxysilanes were also able to be submitted to this reaction (runs 3 and 4). Aliphatic acetylenes also gave good to excellent results. Thus, 1-octyne (**1b**) reacted with triethylsilane (**2a**) at 100°C for 36 h to give (hexylethynyl)triethylsilane (**3ba**) in 93% yield. Cyclohexylacetylene (**1c**) and

3,3-dimethyl-1-butyne (**1d**) afforded the desired alkynylsilanes **3ca** and **3da** in high yields with good selectivities, respectively.



1 **2** **3** **4** **5** **6**

a: R^1=Ph
b: R^1=C_6H_{13}
c: R^1=cyclohexyl
d: R^1=^{t}Bu

a: SiR^2_3=$SiEt_3$
b: SiR^2_3=$SiMe_2Ph$
c: SiR^2_3=$SiMe_2Bu^t$
d: SiR^2_3=$SiMe_2OSiMe_3$
e: SiR^2_3=$SiMe_2(OEt)$

ab: R^1=Ph, SiR^2_3=$SiMe_2Ph$
ac: R^1=Ph, SiR^2_3=$SiMe_2Bu^t$
ad: R^1=Ph, SiR^2_3=$SiMe_2OSiMe_3$
ae: R^1=Ph, SiR^2_3=$SiMe_2(OEt)$
ba: R^1=C_6H_{13}, SiR^2_3=$SiEt_3$
ca: R^1=cyclohexyl, SiR^2_3=$SiEt_3$
da: R^1=^{t}Bu, SiR^2_3=$SiEt_3$

(3)

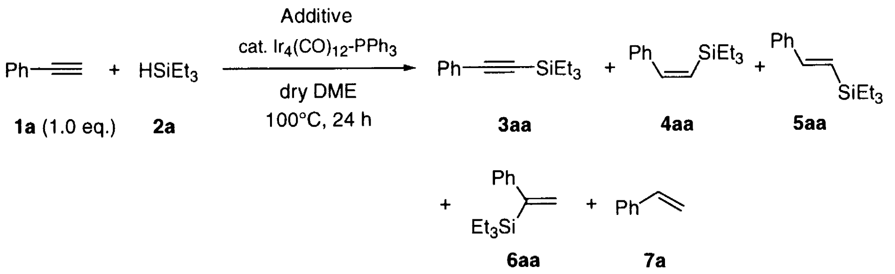
Table 2
Dehydrogenative silylation of acetylenes with hydrosilanes[a]

Run	R^1	SiR^2_3	cat. (mol%) $Ir_4(CO)_{12}$	cat. (mol%) PPh_3	Conditions	Yields[b] (%)	Ratio[c]
1	Ph	$SiMe_2Ph$	2	24	100°C, 24 h	**3ab** (80), **4ab** (4), **5ab** (11), **6ab** (1)	83/17
2	Ph	$SiMe_2Bu^t$	2	24	120°C, 40 h	**3ac** (95), **4ac** (2), **5ac** (2), **6ac** (0)	96/4
3	Ph	$SiMe_2OSiMe_3$	2	24	100°C, 24 h	**3ad** (73), **4ad** (4), **5ad** (13), **6ad** (3)	78/22
4	Ph	$SiMe_2(OEt)$	2	48	100°C, 24 h	**3ae** (79), **4ae** (5), **5ae** (10), **6ae** (3)	81/19
5	C_6H_{13}	$SiEt_3$	1	12	100°C, 36 h	**3ba** (93), **4ba** (1), **5ba** (2), **6ba** (2)	95/5
6	cyclohexyl	$SiEt_3$	2	24	100°C, 40 h	**3ca** (93), **4ca** (0), **5ca** (5), **6ca** (2)	93/7
7	^{t}Bu	$SiEt_3$	2	24	120°C, 36 h	**3da** (83), **4da** (0), **5da** (15), **6da** (0)	85/15

[a] All reactions were carried out with acetylene (**1**; 2.30 mmol), hydrolsilane (**2**; 1.00 mmol), iridium carbonyl, and triphenylphosphine in dry DME (1.0 ml) unless otherwise noted. [b] Yields were determined by GLC based on employed hydrolsilane (**2**). [c] Ratio= **3**/ (**4** + **5** + **6**).

Our method may be accompanied with the generation of molecular hydrogen in situ. Thus, we examined the reaction in the presence of unsaturated compounds which were expected to act as a hydrogen-scavenger (Eq. (4) and Table 3). An equimolar reaction of phenylacetylene (**1a**) and triethylsilane (**2a**) in the absence of any hydrogen-scavenger afforded (phenylethynyl)triethylsilane (**3aa**) and styrene in 55% and 38% yields, respectively, in addition to 39% of unchanged **2a**. When the reaction was carried out in the presence of 1.1 equiv. of diethyl maleate, the desired product **3aa** was obtained in 79% yield with 57% yield of diethyl succinate. Diphenylacetylene and diethyl fumarate are also effective for trapping molecular hydrogen which is generated in situ, preventing phenylacetylene (**1a**) from hydrogenation.

In conclusion, the dehydrogenative silylation of terminal alkynes with hydrosilanes was effectively catalyzed by $Ir_4(CO)_{12}$–PPh_3 to give the corresponding silylacetylenes in good yields with high selectivities.



(4)

Table 3

Reaction of phenylacetylene (**1a**) with triethylsilane (**2a**) in the presence of H_2-scavengers[a]

Run	Additive (eq.)	Yields[b] (%)					
		2a (recovered)	**3aa**	**4aa**	**5aa**	**6aa**	**7a**
1	none	39	55	trace	trace	0	38
2[c]	diethyl fumarate (1.1)	9	75	trace	trace	trace	24
3[d,e]	diethyl maleate (1.1)	trace	79	2	trace	trace	21
4[f]	diphenylacetylene (5.0)	15	83	trace	trace	trace	19

[a] All reactions were run with phenylacetylene (**1a**; 1.00 mmol), triethylsilane (**2a**; 1.00 mmol), iridium carbonyl (0.5 mol%), triphenylphosphine (6 mol%), and additive in dry DME (1.0 ml) at 100°C for 24 h unless otherwise noted. [b] Yields were determined by GLC based on employed **2a**. [c] Diethyl succinate (46%[b]) was obtained. [d] Phenylacetylene (**1a**; 6%[b]) was recovered. [e] Diethyl succinate (57%[b]) was obtained. [f] Stilbene (53%[b]; cis/trans= 41/12) was formed.

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7. General procedure. A mixture of phenylacetylene (**1a**, 2.3 mmol), triethylsilane (**2a**, 1.0 mmol), $Ir_4(CO)_{12}$ (0.01 mmol), PPh_3 (0.12 mmol), and dry DME (1.0 ml) was stirred at 100°C for 24 h under Ar in a Pyrex tube. GLC analysis of the reaction mixture revealed that (phenylethynyl)triethylsilane (**3aa**) was formed in 96% yield. The mixture was evaporated to be freed of solvent in vacuo. **3aa** was isolated by column chromatography on silica gel eluted with hexane, and had spectroscopic data identical with reported data.