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Rhodium-Catalyzed Intermolecular Silylcarbamoylation of Acetylenic Bonds

Isamu Matsuda*, Kiyoshi Takeuchi, and Kenji Itoh

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, JAPAN

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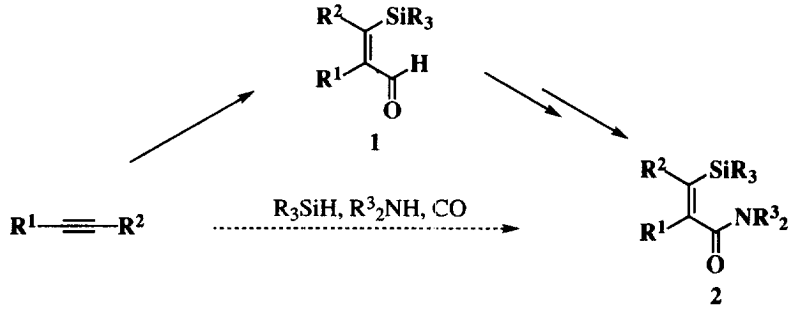
Abstract: α,β-Unsaturated amides are readily formed by silylcarbamoylation of an acetylenic bond which is accomplished intermolecularly by a one-pot reaction of four components, an alkyne, a hydrosilane, an amine, and CO in the presence of a catalytic amount of $Rh_4(CO)_{12}$.

Keywords: α,β-Unsaturated amides; carbonylation of alkynes; hydrosilanes; rhodium catalyst

Triorganosilylalkenes containing the carbonyl function at the other sp^2 carbon, **1** and **2**, are quite interesting from the aspects of both organosilicon chemistry and organic synthesis.[1] These compounds may be formed by a virtual *syn* addition of R_3Si–C(=O)X (X = H or NR^3_2) to an acetylenic triple bond; however, such an intuitive pathway has not yet been realized. Recently we found a practical protocol for the synthesis of **1**, "silylformylation" of alkynes,[2] in the course of our research for new reactions related to incorporation of CO into unsaturated bonds. As a result, an amide **2** can be formally constructed on the basis of the route utilizing CO as a skeletal component, since **1** would be readily transformed to **2** according to conventional procedures. If the formation of **2** is accomplished by a single operation to an alkyne under CO pressure, the protocol is far more advantageous than the indirect one (Scheme 1). The presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) completely changes the pattern from silylformylation to the formation of β-lactone and β-lactam skeletons, respectively, in the reaction of propargyl alcohols and propargyl amines with ^{t}BuMe$_2$SiH under CO pressure.[3] This finding prompts us to direct our concern to a one-pot procedure for the formation of **2**. We report herein a successful rhodium-catalyzed "silylcarbamoylation" of alkynes which is achieved directly by the assembly of four components, an alkyne, a hydrosilane, an amine, and CO.

Scheme 1



Although the major product was **1** (R_3Si = Me_2PhSi, R^1 = Ph, R^2 = H, R^3 = Et, 67 %) in the $Rh_4(CO)_{12}$-catalyzed reaction of phenylacetylene with a mixture of Me_2PhSiH and two equivalent moles of Et_2NH under CO

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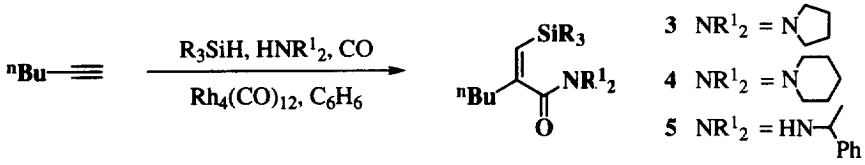
pressure (20 kg/cm^2), we were encouraged to find that the amino group was incorporated to form an amide **2** (R_3Si = Me_2PhSi, R^1 = Ph, R^2 = H, R^3 = Et, 19 %) even in the reaction containing Et_2NH not as a solvent, but as a reagent.[4]

Thus, an intermolecular silylcarbamoylation was scrutinized by using 1-hexyne as a model alkyne. The results are summarized in Table 1. The choice of a hydrosilane is crucial for the selective formation of **3**. Silylcarbamoylation to give **3a** became the major course despite the low yield; however, silylformylation was still remarkable in the reaction with Me_2PhSiH (entry 1 in Table 1). In contrast to Me_2PhSiH, Et_2MeSiH increased the yield of **3b** to 46% and suppressed the silylformylation to less than 5%. Silylformylation products were not detected in the reaction of either $^iPr_3SiH$ or $^tBuMe_2SiH$ despite the moderate yield of **3** (entries 3 and 4 in Table 1). A longer reaction time increases the yield of **3**, whereas it results in lowering the ratio of the *Z*-form (entries 5 and 6 in Table 1). Reaction temperature is also an important factor to accelerate the reaction rate (entry 7 in Table 1). When acetonitrile was used as a solvent instead of C_6H_6, the ratio of stereoisomers was not affected even after prolonged time (48 h, entry 8 in Table 1). Though the addition of 5 mol % of DBU slightly improved the yield of **3**, the presence of an extra mole of pyrrolidine resulted in remarkable acceleration of silylcarbamoylation (entries

Table 1. Silylcarbamoylation of 1-hexyne.[a]



Entry	Hydrosilane	Amine	Conditions (°C/h)	Amide	Yield (%) [b]	*Z*:*E*
1	Me_2PhSiH	Pyrrolidine	95/12	**3a**	19 [c]	85:15
2	Et_2MeSiH	Pyrrolidine	95/12	**3b**	46 [d]	96:4
3	$^iPr_3SiH$	Pyrrolidine	95/12	**3c**	57	100:0
4	$^tBuMe_2SiH$	Pyrrolidine	95/12	**3d**	59	97:3
5	$^tBuMe_2SiH$	Pyrrolidine	95/2	**3d**	36	100:0
6	$^tBuMe_2SiH$	Pyrrolidine	95/40	**3d**	67	87:13
7	$^tBuMe_2SiH$	Pyrrolidine	50/48	**3d**	21	100:0
8	$^tBuMe_2SiH$	Pyrrolidine	95/48	**3d**	70 [e]	98:2
9	$^tBuMe_2SiH$	Pyrrolidine	95/40	**3d**	78 [f]	86:14
10	$^tBuMe_2SiH$	Pyrrolidine	95/12	**3d**	90 [g]	97:3
11	$^tBuMe_2SiH$	Piperidine	95/48	**4d**	30	100:0
12	$^tBuMe_2SiH$	1-Phenylethylamine	95/12	**5d**	14 [h]	—

[a] Reactions were conducted in C_6H_6 (10 ml) solution containing 3 mmoles each of 1-hexyne and a hydrosilane, an amine, and 0.0067 mmoles of $Rh_4(CO)_{12}$ under CO pressure (20 kg/cm^2). [b] Isolated yield. [c] Silylformylation product (10 %) was formed concomitantly. [d] Silylformylation product (< 5%) was formed concomitantly. [e] Acetonitrile was used as a solvent. [f] The reaction was carried out in the presence of DBU (5 mol %). [g] Two moles of pyrrolidine was added. [h] Silylformylation product (68 %) was formed concomitantly.

9 and 10 in Table 1). The presence of two equivalent moles of pyrrolidine is not critical for high conversion of 1-hexyne; the presence of a slight excess (1.3 equivalent moles) is sufficient for the practical operation. Piperidine and 1-phenylethylamine decreased the yields of **3** (entries 11 and 12 in Table 1).

The present reaction is quite feasible for the introduction of a silyl group and a carbamoyl group into an acetylenic bond simultaneously in which the carbamoyl part is constructed from gaseous CO and an amine. Thus, several types of alkynes were subjected to the reaction under similar conditions. The results are summarized in Table 2. The behavior of 1-hexyne, 1-octyne, and phenylacetylene did not change intrinsically. They gave amide **2a**, **2b**, and **2e**, respectively, in good yields under similar conditions (entries 1, 2, and 5 in Table 2). Bulky substituents on the *sp* carbon resulted in low yields of **2** (entries 3 and 4 in Table 2). The hydroxy group of propargyl alcohols remained intact to give **2** although it is known that α-silylmethylene-β-lactones [3a] are formed in the absence of pyrrolidine under similar conditions (entries 6, 7, 9, and 10 in Table 2). Concomitant formation of β-lactones was completely suppressed by the protection of the hydroxy group as the corresponding trimethylsilyl ether (entry 8 in Table 2). An internal acetylenic bond was also susceptible to silylcarbamoylation (entry 10 in Table 2).

Table 2 Silylcarbamoylation composed of alkynes, $^{t}BuMe_2SiH$, pyrrolidine, and CO.[a)]

Entry	Alkyne		Equivalent moles of pyrrolidine	Amide **2**		
	R^1	R^2			Yield (%) [b)]	*Z*:*E*
1	n-Pentyl	H	1.3	**2a**	82	96:4
2	n-Hexyl	H	1.3	**2b**	89	94:6
3	Trimethylsilylmethyl	H	1.0	**2c**	52	28:72
4	Cyclohexyl	H	1.3	**2d**	44	100:0
5	Phenyl	H	1.3	**2e**	73	96:4
6	1-Hydroxyethyl	H	1.0	**2f**	26 [c)]	100:0
7	1-Hydroxyethyl	H	2.0	**2f**	22	100:0
8	1-Trimethylsiloxyethyl	H	1.2	**2f**	48 [d)]	100:0
9	1-Hydroxy-1-methylethyl	H	1.0	**2g**	35 [e)]	100:0
10	1-Hydroxycyclohexyl	H	1.0	**2h**	50 [f)]	100:0
11	Phenyl	Methyl	1.1	**2i**	53 [g)]	92:8

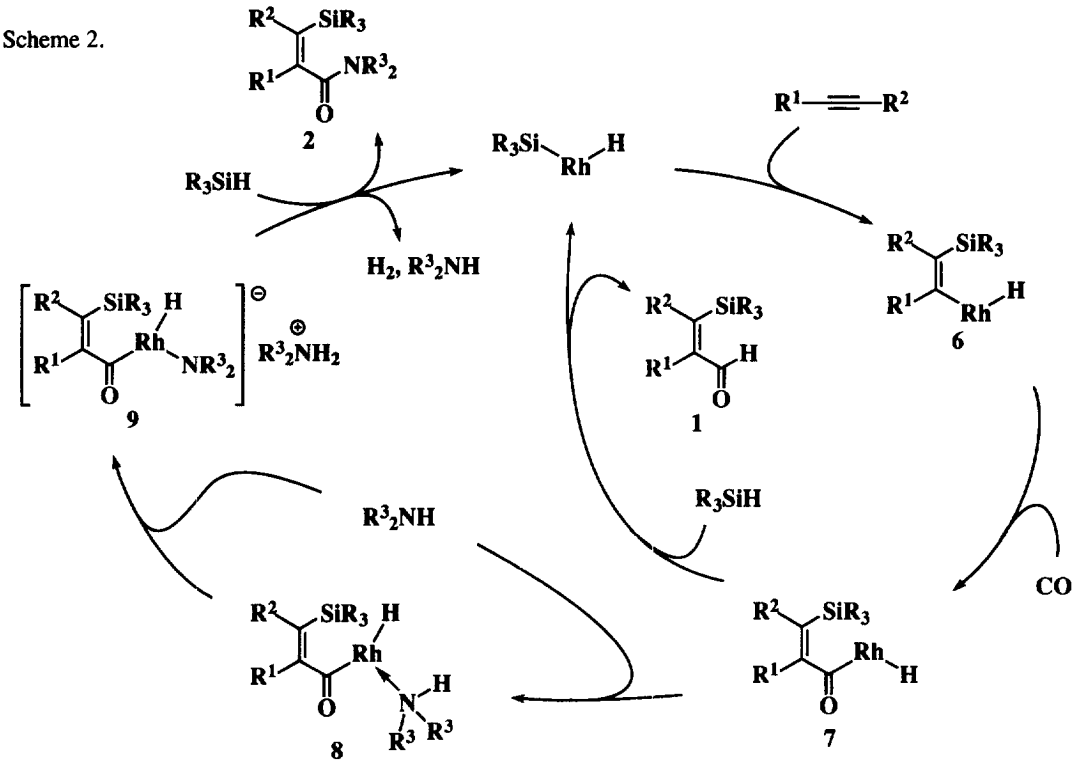
[a)] Reactions were conducted in C_6H_6 (10 ml) solution containing 1-hexyne (3 mmoles), $^{t}BuMe_2SiH$ (3 mmoles), pyrrolidine, and $Rh_4(CO)_{12}$ (0.0067 mmoles) under CO pressure (20 kg/cm^2). [b)] Isolated yield. [c)] The corresponding β-lactone (10 %) was formed concomitantly. [d)] Isolated as the protodesilylated form **2f**. [e)] The corresponding β-lactone (24 %) was formed concomitantly. [f)] The corresponding β-lactone (2 %) was formed concomitantly. [g)] The regio-isomer was detected in the ^{1}H nmr spectrum; however, it was not isolated.

It is quite interesting that silylformylation can be altered to silylcarbamoylation by the addition of reagent quantity of a primary or secondary amine into the identical starting materials. This fact suggests a common intermediate participates in both reactions although no information is available regarding the reaction mechanism. Thus, the following scheme shown in Scheme 2 can be proposed as a plausible rationale for the formation of **2**.

The first stage of the reaction is an oxidative addition of a hydrosilane to give a Rh–Si species which serves to trigger the subsequent insertion of an alkyne and CO to form the pivotal intermediate **7**. The amine in the mixture interacts with **7** to form **8** and the subsequent rhodate complex **9** which liberates **2**.

This type of CO incorporation achieves a formal *syn* addition of a triorganosilyl group and a carbamoyl group into an acetylenic bond. Since various types of diverse starting substrates are available in this reaction, the present method provides a powerful tool for the designation of amides.

Scheme 2.



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