Pergamon

Tetrahedron Letters 40 (1999) 4703–4706

TETRAHEDRON
LETTERS

Rhodium-Catalyzed Domino Silylformylation of Enynes Involving Carbocyclization

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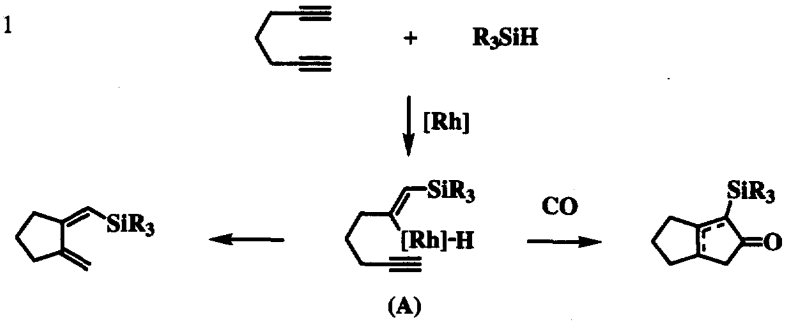
Received 23 March 1999; revised 22 April 1999; accepted 23 April 1999

Abstract: 1,6-Enyne derivatives readily react with a hydrosilane and carbon monoxide in the presence of a catalytic amount of a rhodium complex to give 5-membered ring products containing a silylmethylene group and a formylmethyl group on the adjacent carbon atoms. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: carbonylation; carbocyclization; rhodium catalyst; silylrhodation

Transition metal-catalyzed carbocyclization has recently become a popular and fascinating method for the construction of fused ring systems. There are cumulative examples of domino carbocyclization in palladium chemistry where several patterns to generate a metal-carbon species have been known.[1] The catalytic Pauson-Khand reaction is a representative example of such cyclization methodology.[2] During our research in rhodium-catalyzed silylformylation of alkynes,[3] we revealed that insertion of an alkyne into a Rh–Si bond (in other words, "silylrhodation" of an acetylenic bond) is an elementary step to obtain a (vinyl)rhodium species. If the generated (vinyl)rhodium species has sufficient reactivity toward another carbon-carbon unsaturated bond in the same molecule, silylrhodation would provide a trigger for the sequential carbocyclization. In fact, 1-methylene-2-silylmethylene cyclopentane[4] and bicyclo[3.3.0]octenone[5] frameworks are independently constructed depending on the absence or the presence of CO in the rhodium-catalyzed one-pot reaction as shown in Scheme 1. The formation of these products can be rationalized by assuming the common (vinyl)rhodium intermediate (A), which implies the possibility of the rhodium-catalyzed novel silylformylation of enynes. We report here rhodium-catalyzed domino silylformylation of enynes involving carbocyclization.

Scheme 1



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PII: S0040-4039(99)00849-7

When a benzene solution (10 ml) of **1a** (1.0 mmol), Me_2PhSiH (1.2 mmol), and a catalytic amount (0.5 mol%) of $Rh_4(CO)_{12}$ was heated for 14 h at 90 °C under CO pressure (20 kg/cm^2) in a glass tube kept in a stainless steel autoclave, the starting **1a** was consumed completely. After chromatographic separation of the reaction mixture, two cyclic products, **2a**[6] and **3a**,[6] were isolated in 74% and 11% yield, respectively (eq. 1). The formation of the silylcarbocyclization product, **3a**,[7] was completely suppressed under higher CO pressure (entry 2 in Table 1), and the yield of **3a** increased slightly with lowering CO pressure (entry 3 in Table 1). On the other hand, formylation was completely suppressed under CO or N_2 atmosphere, and **3a** was obtained as a main product together with a small amount of **5a** (entries 4 and 5 in Table 1). In contrast to the results of the previous reports,[2d, 2e] the presence of Me_2PhSiH completely suppressed the formation of the Pauson-Khand

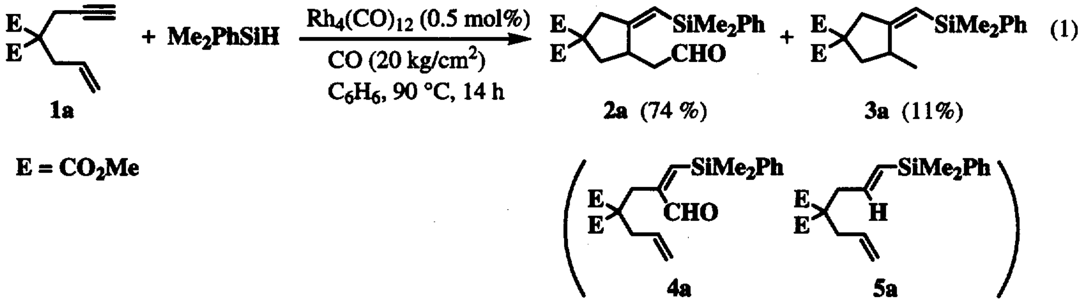


Table 1. Rhodium-catalyzed domino silylformylation of **1a** involving carbocyclization[a]

Entry	Hydrosilane	Catalyst precursor	CO pressure (kg/cm^2)	Yield (%)[b] **2a**	**3a**
1	Me_2PhSiH	$Rh_4(CO)_{12}$	20	74	11
2	Me_2PhSiH	$Rh_4(CO)_{12}$	36	85	-
3	Me_2PhSiH	$Rh_4(CO)_{12}$	5	60	19
4	Me_2PhSiH	$Rh_4(CO)_{12}$	1	-	30 [c]
5	Me_2PhSiH	$Rh_4(CO)_{12}$	- [d]	-	39 [e]
6	Me_2EtSiH	$Rh_4(CO)_{12}$	20	76 (**2a'**)	4 (**3a'**)
7	Et_2MeSiH	$Rh_4(CO)_{12}$	20	52 (**2a''**)	30 (**3a''**) [f]
8	$^tBuMe_2SiH$	$Rh_4(CO)_{12}$	20	34 (**2a'''**)	-
9	Me_2PhSiH	$Rh(CO)_2(acac)$	20	89	-
10	Me_2PhSiH	$[Rh(COD)(DPPB)]^+ClO_4^-$	20	76	5
11	Me_2PhSiH	$[Rh(CO)_2Cl]_2$	20	72	-

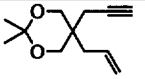
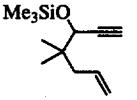
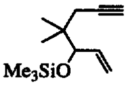
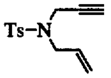
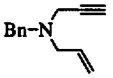
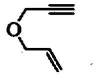
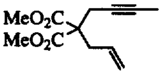
[a] Reactions were carried out on a 1.0 mmol scale of **1a** and 1.2 mmol scale of hydrosilane in C_6H_6 solution at 90 °C using a rhodium catalyst (0.005 mmol). [b] Isolated yields. [c] Compound **5a** was concomitantly obtained in an isolated yield of 25%. [d] The reaction was carried out under N_2 atmosphere. [e] Compound **5a** was concomitantly obtained in an isolated yield of 34%. [f] Compound **4a''** was concomitantly obtained in an isolated yield of 5%.

products under low pressure of CO. Noteworthy is that product **4a** of which olefinic part remains intact was not detected at all. This point is quite different from the result of silylformylation of 1-penten-4-yne[3b, 3d] under similar conditions.

Other hydrosilanes, Me_2EtSiH, Et_2MeSiH, and $^tBuMe_2SiH$, reacted under the present reaction conditions with **1a** to give **2a'**,[6] **2a''**,[6] and **2a'''**,[6] respectively, though the yield of **2** was markedly affected by the hydrosilane used (entries 6, 7, and 8 in Table 1). Various rhodium complexes such as $Rh(CO)_2(acac)$, $[Rh(COD)(DPPB)]^+ClO_4^-$, and $[Rh(CO)_2Cl]_2$ as well as $Rh_4(CO)_{12}$ can be used in the present reaction (entries 9, 10, and 11 in Table 1). $Rh_4(CO)_{12}$ and $Rh(CO)_2(acac)$ were employed in the following experiments as a representative cluster and mononuclear catalyst precursor, respectively.

The scope and limitation of the present domino silylformylation are demonstrated in Table 2. 1,6-Enynes, **1b**, **1c**, and **1e**, reacted smoothly to give exclusively the corresponding 5-membered ring compounds **2** in good yields. In the case of **1d**, a small amount of **4d** was accompanied with **2d** (entries 5 and 6 in Table 2). Surprisingly, **2f** was not formed in the reaction of **1f**, but the normal silylcarbocyclization product **3f** was obtained as the sole product under similar conditions (entries 9 and 10 in Table 2). This is contrary to the

Table 2. Reaction of various 1,6-enyne derivatives with Me_2PhSiH [a]

Entry	1,6-Enyne (**1**)		Catalyst precursor	Yield (%) of products [b]		
				2 [6]	**3** [6]	**4**
1		**1b**	$Rh_4(CO)_{12}$	76	-	-
2			$Rh(CO)_2(acac)$	89	-	-
3		**1c**	$Rh_4(CO)_{12}$	69 [c]	-	-
4			$Rh(CO)_2(acac)$	79 [c]	-	-
5		**1d**	$Rh_4(CO)_{12}$	66 [c]	-	9
6			$Rh(CO)_2(acac)$	65 [c]	-	12
7		**1e**	$Rh_4(CO)_{12}$	59	-	-
8			$Rh(CO)_2(acac)$	74	-	-
9		**1f**	$Rh_4(CO)_{12}$	-	88	-
10			$Rh(CO)_2(acac)$[7]	-	78	-
11		**1g**	$Rh_4(CO)_{12}$	37	-	-
12			$Rh(CO)_2(acac)$[7]	37	-	-
13		**1h**	$Rh_4(CO)_{12}$	85	-	< 3 [d]
14			$Rh(CO)_2(acac)$	67	9	22 [d]

[a] Reactions were carried out on a 1.0 mmol scale of **1** and 1.2 mmol scale of Me_2PhSiH in C_6H_6 solution at 90 °C for 14 h under 20 kg/cm^2 of CO using a rhodium catalyst (0.005 mmol). [b] Isolated Yields. [c] Isolated as a mixture of diastereoisomers. The ratio was estimated as approximately 1 to 1 by the ^1H NMR spectra. [d] Isolated as a mixture of regioisomers.

result of **1e**. The role of the substituent on the nitrogen atom in **1e** and **1f** is not clear yet. Surprisingly, the desired aldehyde **2h** was obtained as a major product by the reaction of **1h** with Me$_2$PhSiH under CO pressure (entries 13 and 14 in Table 2), which indicates that the regiochemistry of silylrhodation toward an acetylenic bond is well controlled even in an internal alkyne.

In conclusion, we have developed a novel and practical method for preparation of (2-silylmethylenecyclopentyl)acetaldehydes by rhodium-catalyzed domino silylformylation of enynes involving carbocyclization. This process may proceed via silylrhodation of an acetylenic bond, the subsequent intramolecular insertion of an olefinic part into the vinyl-rhodium bond, followed by the successive insertion of CO, and reductive elimination of the product. The products obtained here would be useful as a building block to construct several fused ring systems.

Acknowledgment. This work was supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. We thank the Shin-etsu Chemical Co. Ltd. for a gift of ^{t}BuMe$_2$SiH.

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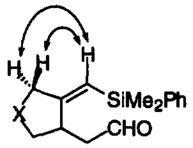
6. These compounds were fully characterized by IR, ^{1}H, and ^{13}C NMR spectra, and gave satisfactory results of combustion analyses. It is confirmed by the observation of an appreciable NOE enhancement (≈ 6%) between two couples of the protons as shown in the figure that the stereochemistry resulted from *syn* addition in the silylrhodation step remains intact in **2**.



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