Extremely Chemoselective Silylformylation and Silylcarbocyclization of Alkynals

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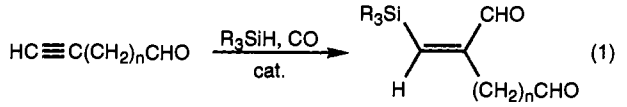
The silylformylation of alkynes catalyzed by Rh or Co–Rh complexes, which gives the corresponding β-formylvinylsilanes in high yields, has been extensively studied in recent years.[1-3] Novel silylcarbocyclizations (SiCACs) of alkenynes and diynes have also been investigated.[4] Quite recently, Wright and coworkers reported a Rh(I)-catalyzed silylformylation of aldehydes, forming α-(silyloxy)aldehydes.[5] In the course of our study on the reactions of hydrosilanes with alkynes, alkenynes, diynes in the presence or absence of carbon monoxide, we looked at the chemoselectivity in the reactions of hydrosilanes with alkynals catalyzed by Rh and Rh–Co complexes in the presence of carbon monoxide. Our primary interests were to determine which functionality would be more reactive under the standard silylformylation conditions, acetylene or aldehyde, and to investigate a new carbocyclization process involving both functionalities. We describe here our finding that an acetylene moiety reacts exclusively in the presence of an aldehyde functionality and also the discovery of a new SiCAC reaction of 5-hexyn-1-al giving 2-(*exo*-silylmethylene)-1-cyclopentanol.

Three alkynals, 5-hexyn-1-al (**1**), 6-heptyn-1-al (**2**), and 7-octyn-1-al (**3**), were chosen as the substrates, and the reactions of **1-3** (1.00 mmol) with different hydrosilanes were carried out in the presence of Rh or Rh–Co catalysts (0.5 mol%) at 25 °C and 10 atm of carbon monoxide in toluene (3.0 mL). Results are summarized in Table 1.

As Table 1 shows, the reactions of **1-3** give the corresponding (*Z*)-2-(silylmethylene)-1,ω-dialdehydes **4-6** in high isolated yields after purification by column chromatography on silica gel. These dialdehydes are the sole products of the reactions, and the yields determined by NMR are ≥95% in all cases (eq 1). The electronic



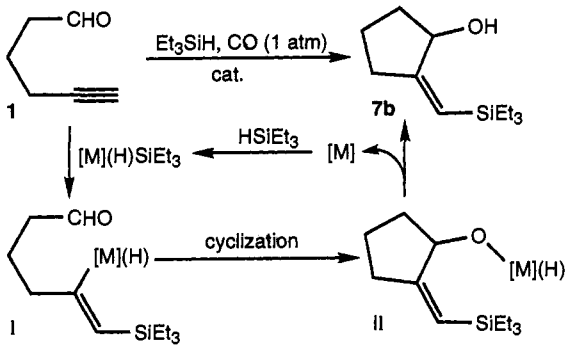
(1)

1-3: n=3-5 **4-6**: n=3-5

a: R_3Si = $PhMe_2Si$, **b**: R_3Si = Et_3Si, **c**: R_3Si = $^tBuMe_2Si$, **d**: R_3Si = Ph_2MeSi, **e**: R_3Si = Ph_3Si

nature of hydrosilanes does not appear to have any influence on the chemoselectivity,[6] but trialkylsilanes such as $EtMe_2SiH$, Et_3SiH, and $^tBuMe_2SiH$ substantially slow down the reaction so that excess hydrosilane (5 equiv) is necessary for the reaction to proceedsmoothly and to complete within 20 h. Among the hydrosilanes examined, $PhMe_2SiH$ provides the fastest reaction. It should be noted that the formyl moiety remains intact even when excess hydrosilane is used. When the reaction of **3** with $PhMe_2SiH$ is run using $[Rh(CO)_2Cl]_2$, $[Rh(NBD)Cl]_2$, or $[Rh(COD)Cl]_2$ as the catalyst, the formation of a small amount of (*E*)-isomer ((*E*)-**3a**) is observed. This isomerization is not observed at all when $Rh(acac)(CO)_2$, $Rh_2Co_2(CO)_{12}$,[7] $(^tBuNC)_4RhCo(CO)_4$,[8] and $[Rh(NBD)_2]BF_4$ are employed.

Scheme 1



The results unambiguously demonstrate that an acetylene functionality reacts exclusively with a hydrosilane in the presence of an aldehyde functionality under the standard silylformylation conditions. To the best of our knowledge, these are the first examples which clearly determine the relative reactivity of acetylene vs aldehyde functionality, showing unexpectedly high reactivity of the acetylene functionality. It has been shown that 1,4-, 1,5-, and 1,6-dialdehydes are versatile and useful intermediates in organic syntheses.[9] The silylformylation of alkynals serves as a new and efficient method for the synthesis of dialdehydes bearing vinylsilane moieties for further functionalization.

When 5-hexyn-1-al (**1**) (1.00 mmol) was reacted with Et_3SiH (5.00 mmol) using $Rh_2Co_2(CO)_{12}$ (1.0 mol%) as the catalyst at 25 °C and 1 atm of carbon monoxide for 72 h in toluene (2.0 mL), a new SiCAC took place to give (*Z*)-2-(*exo*-TESmethylene)-1-cyclopentanol (**7b**) as the major product (80%) accompanied by small amounts of a hydrosilylation product, (*E*)-1-TES-1-hexen-6-al (**8b**) (11%) and (*Z*)-**4b** (9%) (≥95% total yield by NMR; 77% total isolated yield after column chromatography on silica gel). A small amount of the SiCAC product **7b** was formed when other rhodium complexes, e.g., Rh(acac)-$(CO)_2$ and $[Rh(NBD)_2]BF_4$ were employed as catalysts, but $Rh_2Co_2(CO)_{12}$ and $(^tBuNC)_4RhCo(CO)_4$ have given by far the best results so far. A possible mechanism for the new SiCAC reaction is proposed in Scheme 1. The proposed mechanism includes a carbocyclization process through the intramolecular trapping of a β-(silylethenyl)metal intermediate (**I**) by the aldehyde moiety. It is noteworthy that the new SiCAC reaction took place only with **1**, which gives 5-membered ring product **7b**, and no SiCAC reactions were observed for **2** and **3**, which should form 6- and 7-membered rings, respectively.

(1) (a) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (b) Ojima, I.; Donovan, R. J.; Eguchi, M.; Shay, W. R.; Ingallina, P.; Korda, A.; Zeng, Q. *Tetrahedron* **1993**, *49*, 5431. (c) Ojima, I.; Donovan, R. J.; Ingalina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423–438. (d) Ojima, I.; Zhang, Z.; Korda, A.; Ingallina, P.; Clos, N. In *New Science in Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Ed.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1992; Chapter 19, pp 277–296.

(2) (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. (c) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431.

(3) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11.

(4) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580.

(5) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059.

(6) When $(MeO)_3SiH$ was used for the reaction of **3**, the hydrosilylation product, (*E*)-1-(trimethoxysilyl)-1-octen-8-al ((*E*)-**9f**), was formed exclusively (≥95% yield by NMR). In this case, the reaction took place exclusively on the alkyne moiety, leaving the formyl group intact, i.e., the chemoselectivity is the same as that of silylformylation.

(7) (a) Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F. *J. Organomet. Chem.* **1973**, *59*, 379. (b) Horvath, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* **1986**, *5*, 1441.

(8) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1991**, *10*, 3211.

(9) (a) McMurry, J. E.; Rico, J. G. *Tetrahedron Lett.* **1989**, *30*, 1169. (b) Chiara, J. L.; Cabri, W.; Hanessian, S. *Tetrahedron Lett.* **1991**, *32*, 1125. (c) Takano, S.; Yamane, T.; Takahashi, M.; Ogasawara, K. *Tetrahedron: Asymmetry* **1992**, *3*, 837. (d) González, F. S.; Díaz, R. R.; Calvo-Flores, F. A. G.; Berenguel, A. V.; Martínez, J. J. G. *Synthesis* **1992**, 631. (e) Fatiadi, A. J. *Synthesis* **1974**, 229.

0002-7863/94/1516-3643$04.50/0

Table 1. Reactions of Hydrosilanes with Alkynal Catalyzed by Rh and Rh–Co Complexes in the Presence of Carbon Monoxide[a]

entry	alkynal	catalyst (mol %)	hydrosilane (equiv)	time (h)	solvent	product (isolated yield)[b,c]
1	**1**	$Rh(acac)(CO)_2$ (0.5)	$PhMe_2SiH$ (1)	7.5	toluene	**4a** (74%)
2	**1**	$Rh_2Co_2(CO)_{12}$ (0.5)	$PhMe_2SiH$ (1)	7	toluene	**4a** (73%)
3	**1**	$[Rh(NBD)_2]BF_4$ (0.5)	$^tBuMe_2SiH$ (5)	16	THF	**4c** (85%)[d]
4	**2**	$Rh(acac)(CO)_2$ (0.5)	$PhMe_2SiH$ (1)	18	toluene	**5a** (81%)
5	**2**	$[Rh(NBD)_2]BF_4$ (0.5)	$^tBuMe_2SiH$ (5)	18	THF	**5c** (75%)
6	**3**	$Rh(acac)(CO)_2$ (0.5)	$PhMe_2SiH$ (1)	17	toluene	**6a** (89%)
7	**3**	$Rh_2Co_2(CO)_{12}$ (0.5)	$PhMe_2SiH$ (1)	16	toluene	**6a** (78%)
8	**3**	$(^tBuNC)_4RhCo(CO)_4$ (0.5)	$PhMe_2SiH$ (1)	17	toluene	**6a** (70%)
9	**3**	$[Rh(NBD)_2]BF_4$ (0.5)	$PhMe_2SiH$ (1)	16	toluene	**6a** (80%)
10	**3**	$[Rh(CO)_2Cl]_2$ (0.5)	$PhMe_2SiH$ (1)	18	toluene	**6a** (75%)[e]
11	**3**	$[Rh(NBD)Cl]_2$ (0.5)	$PhMe_2SiH$ (1)	18	toluene	**6a** (74%)[f]
12	**3**	$[Rh(COD)Cl]_2$ (0.5)	$PhMe_2SiH$ (1)	24	toluene	**6a** (76%)[g]
13	**3**	$Rh(acac)(CO)_2$ (0.5)	Et_3SiH (5)	16	toluene	**6b** (62%)
14	**3**	$Rh(acac)(CO)_2$ (0.5)	$^tBuMe_2SiH$ (5)	17	toluene	**6c** (71%)
15	**3**	$Rh(acac)(CO)_2$ (0.5)	Ph_2MeSiH (1)	24	toluene	**6d** (93%)
16	**3**	$Rh(acac)(CO)_2$ (0.5)	Ph_3SiH (1)	40	toluene	**6e** (89%)

[a] All reactions were run with 1.00 mmol of alkynal in toluene (3.0 mL) at 25 °C and 10 atm of CO unless otherwise noted. [b] 100% conversion for all reactions. Yields determined by ^1H NMR analyses were ≥95% in all cases. [c] All silylformylation products were (*Z*)-isomers unless otherwise noted. [d] Including 8% of **7c**. [e] (*Z*):(*E*) = 87:13. [f] (*Z*):(*E*) = 83:17. [g] (*Z*):(*E*) = 76:24.

Further studies on the scope and limitations as well as applications of extremely chemoselective silylcarbonylations and the SiCAC reaction are actively underway.

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Supplementary Material Available: General experimental procedures for the chemoselective silylformylation and SiCAC reaction and characterization data for new compounds **4-6** (**a–e**), **7b**, **8b**, and **9f** (5 pages). This material is contained in many libraries on microfiche, immediately follow this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.