## **Rhodium Catalyzed Transformation of Propargylamines to** 2-Silylmethyl-2-alkenals: Formal Silylformylation of Allenes

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**Summary**: Propargylamines are effectively transformed to 2-dimethylphenylsilylmethyl-2-alkenals by the interaction of two equivalents of  $Me_2PhSiH$  under silylformylation conditions catalyzed by  $Rh_4(CO)_{12}$ . The products are not obtained directly by silylformylation of the corresponding allenes.

We have reported rhodium-catalyzed silylformylation of an acetylenic bond in a one-pot reaction of alkyne, triorganosilane, and carbon monoxide.<sup>1</sup> During the search for scope and limitation of this reaction, we found a novel procedure to form  $\alpha$ -silylmethylene- $\beta$ -lactones<sup>2</sup> and  $\alpha$ -silylmethylene- $\beta$ -lactams<sup>3</sup> from substituted propargyl alcohols and substituted propargyl amides, respectively, by a simple modification of the reaction conditions (Scheme 1). In contrast with these clear patterns, we were confronted with an intractable result in the reaction of 3-dialkylamino-1-propyne (4) under similar conditions. A small amount of 2-silylmethyl-2-propenal (5) was the sole identified product. This type of compound is susceptible to both species, electrophiles and nucleophiles because of the presence of a formyl part and an allylsilyl part in the same molecule. In fact, one of these is utilized as a useful building block in organic synthesis<sup>4</sup>, however, the only known approach<sup>4</sup> to such a compound is oxidation of the corresponding alcohol derived from 2-methyl-2-propen-1-ol or other sources<sup>5, 6</sup> by a multi-step operation. This makes it attractive to explore an economical operation for the preparation of **5**. We report herein a novel one-pot transformation of propargylamine derivative (4) to **5** under silylformylation conditions.



When 3-dibenzylamino-1-propyne (4c) and an equivalent of Me<sub>2</sub>PhSiH were subjected to typical silylformylation conditions {1 mol % of Rh<sub>4</sub>(CO)<sub>12</sub>, CO (20 kg/cm<sup>2</sup>), C<sub>6</sub>H<sub>6</sub>, 100 °C, 2h}, 2-(dimethyl-phenyl)silylmethyl-2-propenal (5a)<sup>7</sup> was isolated in a low yield as the sole formyl compound regardless of the presence or absence of Et<sub>3</sub>N. The identical product was obtained in a similar yield at lower temperature. In these reactions an appreciable amount of 4c was recovered intact. The yield of 5a under similar conditions was dramatically improved by an additional equivalent mole of Me<sub>2</sub>PhSiH. Compound 7c (R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=R<sup>4</sup>=CH<sub>2</sub>Ph) expected from usual silylformylation of 4c was isolated as a minor product in a limited reaction at lower temperature (entry 9 in Table 1). These results are summarized in Table 1. Comparison of the <sup>1</sup>H NMR spectrum of the reaction mixture with those of separated products reveals that the isolated products, 5a, Me<sub>2</sub>PhSiOH, (Me<sub>2</sub>PhSi)<sub>2</sub>O, and (PhCH<sub>2</sub>)<sub>2</sub>NH are formed during the carbonylation reaction (entry 7 in Table 1). On the other hand, authentically prepared N,N-dibenzylaminodimethylphenylsilane (6c) readily decomposes to (Me<sub>2</sub>PhSi)<sub>2</sub>O and (PhCH<sub>2</sub>)<sub>2</sub>NH under CO pressure in the presence of a catalytic amount of Rh<sub>4</sub>(CO)<sub>12</sub>. Therefore, it is deduced that the above three compounds accompanying the formation of 5a are formed by the consecutive steps. The profile for the formation of 5a is shown as equation 1.



Entry	Ratio of	Temperature	Reaction time	Amine	Yield of	
	Me <sub>2</sub> PhSiH:4c	(°C)	(h)		5a (%)	
1	1:1	100	2		23	
2	1:1	100	2	Et <sub>3</sub> N	38	
3	1:1	50	5		32	
4	1:1	50	5	Et <sub>3</sub> N	37	
5	1:1	20	12		34	
6	1:1	20	12	Et <sub>3</sub> N	38	
7	2:1	100	2		94	
8	2:1	100	2	Et <sub>3</sub> N	74	
9	2:1	50	13		72 i)	
10	1:2	100	2		24	
11	1:2	100	2	Et <sub>3</sub> N	14	

Table 1. Reactions of 4c with Me<sub>2</sub>PhSiH under CO.

i) In addition to 5a, 20 % of 7c was isolated.

The present silylformylation was applied to various types of 4 under similar conditions.<sup>8</sup> Alkyl substituents on the nitrogen atom of 4 appreciably affect the formation of 5. Compared with the smooth and complete conversion of 4c, reactivity of 4a ( $R^1=R^2=H$ ,  $R^3=R^4=Me$ ) was very low and hydrosilylation of 4a was observed as a side reaction. A usual silylformylation product 7b<sup>7</sup> ( $R^1=R^2=H$ ,  $R^3=Me$ ,  $R^4=CH_2Ph$ ) was exceptionally isolated as a minor product in the reaction of 4b, even at 100 °C. The effect of substituents is critical and remarkable in the bulkier 4 (entries 9, 10, and 11 in Table 2). The yield of 5 is also greatly affected by the presence of substituents on the propargyl carbon of 4 (entries 3, 5, and 10 in Table 2). These results imply that the reaction of 4 is affected mainly by a steric factor originating from substituents on the nitrogen and the propargyl carbon of 4. The results are summarized in Table 2.



Although the catalytic behavior of rhodium is ambiguous at present, the fact that 7b was accompanied by the formation of 5a under standard conditions gives a clue to the catalytic cycle. When the isolated 7b was subsequently treated with an equivalent amount of Me<sub>2</sub>PhSiH under silylformylation conditions, only a minor portion of 7b changed to 5a, while the rest remained intact. These results suggest that 7 is not a precursor to

Entry	Propargylamines						Product	
	4	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	<b>5</b> i)	Yield (%)	
1	<b>4</b> a	Н	Н	Me	Me	5a	40 <sup>ii)</sup>	
2	4b	Н	н	Me	CH <sub>2</sub> Ph	5a	83 iii)	
3	4c	н	н	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	5a	94	
4	4d	Me	Н	<sup>n</sup> Bu	<sup>n</sup> Bu	5 d	72 ii), iv)	
5	4e	Me	н	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	5 d	90 iv)	
6	4 f	<sup>n</sup> C <sub>5</sub> H <sub>11</sub>	н	-(CH <sub>2</sub> )5-		5f	93 iv)	
7	4g	Me	Me	-(CH <sub>2</sub> )5-		5 g	65	
8	4 h	-(CH <sub>2</sub> ) <sub>4</sub> -		<sup>n</sup> Bu	<sup>n</sup> Bu	5 h	44 ii)	
9	<b>4</b> i	-(CH <sub>2</sub> )5-		-(CH <sub>2</sub> )5-		5 i	80	
10	4j	-(CH <sub>2</sub> )5-		CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	5 i	20 <sup>ii)</sup>	
11	4k	-(CH <sub>2</sub> )5-		Н	CH <sub>2</sub> Ph	5i	88	

Table 2. Reactions of 4 with two equivalents of  $Me_2PhSiH$  under  $CO^8$ .

i) See reference 7.

ii) Contaminated by small amount of a mixture of hydrosilylated products.

iii) In addition to 5a, 10 % of 7b was isolated. iv) Almost single geometry (Z>98 %).9

form 5, but that both 7 and 5 could be derived competitively from the common intermediate 8. Apart from the mechanistic point of view, the present transformation is very interesting as a novel and general method for the synthesis of 5. The identical products could be formally constructed from silylformylation of allenes, however, hydrosilylation to give a mixture of products is the sole coupling pattern in the Rh<sub>4</sub>(CO)<sub>12</sub> catalyzed reaction of allenes with Me<sub>2</sub>PhSiH, even under CO pressure. Thus, the present approach provides an equivalent route to the silvlformylation of allenes.

Acknowledgments: This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. We thank Professor Kenji Itoh (T.U.T.) for helpful discussion.

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- 7. All these compounds were identified by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz), and IR (CCl<sub>4</sub>) spectra. For example, 5a:colorless liquid b.p. 82 °C/0.5 torr (Kuegel-rohr distillation), <sup>1</sup>H-NMR 0.25 (s, 6H, SiCH<sub>3</sub>), 1.98 (d, 2H, J=1.0 Hz, SiCH<sub>2</sub>), 5.80 (d, 1H, J=0.8 Hz, =CH), 5.95 (q, 1H, J=1.0 Hz, =CH), 7.35 (m, 3H, Ph), 7.50 (m, 2H, Ph), 9.45 (s, 1H, CHO), <sup>13</sup>C-NMR -3.56 (SiCH<sub>3</sub>), 16.84 (SiCH<sub>2</sub>), 127.88 (Ph metha), 129.31 (Ph para), 132.24 (=CH<sub>2</sub>), 133.77 (Ph ortho), 138.00 (Ph q), 147.84 (=C q), 194.70 (CHO), IR v<sub>C=O</sub> 1690 cm<sup>-1</sup>. 5d:colorless liquid b.p. 80 °C/0.4 torr (Kuegel-rohr distillation), <sup>1</sup>H-NMR 0.26 (s, 6H, SiCH<sub>3</sub>), 1.66 (t of d, 3H, J=7.0 and 0.7 Hz, CCH<sub>3</sub>), 1.95 (s, 2H, SiCH<sub>2</sub>), 6.41 (t of q, 1H, J=7.0 and 0.8 Hz, =CH), 7.35 (m, 3H, Ph), 7.52 (m, 2H, Ph), 9.32 (s, 1H, CHO), <sup>13</sup>C-NMR -3.02 (SiCH<sub>3</sub>), 13.77 (SiCH<sub>2</sub>), 14.88 (CCH<sub>3</sub>), 127.89 (Ph metha), 129.26 (Ph para), 133.72 (Ph ortho), 138.67 (Ph q), 142.64 (=C q), 147.13 (=CH), 195.14 (CHO), IR v<sub>C=0</sub> 1690 cm<sup>-1</sup>. **5**i:colorless liquid b.p. 105 °C/0.5 torr (Kuegel-rohr distillation), <sup>1</sup>H-NMR 0.23 (s, 6H, SiCH<sub>3</sub>), 1.4 - 1.7 (m, 6H, 3xCH<sub>2</sub>), 2.00 (s, 2H, SiCH<sub>2</sub>), 2.10 (t, 2H, J=6.0 Hz, CH<sub>2</sub>), 2,69 (t, 2H, J=5.5 Hz, CH<sub>2</sub>), 7.35 (m, 3H, Ph), 7.50 (m, 2H, Ph), 10.16 (s, 1H, CHO), <sup>13</sup>C-NMR -2.58 (SiCH<sub>3</sub>), 14.64 (SiCH<sub>2</sub>), 26.36 (CH<sub>2</sub>), 27.56 (CH<sub>2</sub>), 28.69 (CH<sub>2</sub>), 29.09 (CH<sub>2</sub>), 33.61 (CH<sub>2</sub>), 127.59 (Ph metha), 128.86 (Ph para), 131.68(=C q), 133.63 (ph ortho), 138.96 (Ph q), 159.40 (=C q), 189.95 (CHO), IR  $v_{C=0}$  1660 cm<sup>-1</sup>. All new compounds gave satisfactory combustion analyses.
- 8. The typical procedure is as follows: Into a glass tube containing  $Rh_4(CO)_{12}$  (0.005 g, 0.007 mmol) and benzene (6 ml) saturated by CO were successively added, at room temperature under CO atmosphere by syringe, Me<sub>2</sub>PhSiH (0.407 g, 2.99 mmol) in C<sub>6</sub>H<sub>6</sub> (1.5 ml) and 4c (0.319 g, 1.36 mmol) in C<sub>6</sub>H<sub>6</sub> (1 ml). The tube was put in a 100 ml stainless steel autoclave and then the reactor was pressurized by CO to 20 kg/cm<sup>2</sup>. The contents were stirred for 3 h at 100 °C and cooled to ambient temperature. After excess CO was purged in a hood, the reaction mixture was treated by the ordinary procedure to give 5a (94 %).
- 9. Z-Geometry of 5d and 5f was deduced by the observation of a remarkable NOE effect between the vinyl proton and the formyl proton (Varian VXR 500).

(Received in Japan 2 July 1992)