# Rhodium(I)-Catalyzed Acylation of Alkyne with Acylsilane: Transformation of 5- or 6-Alkynoylsilane to $\alpha$-Alkylidenecycloalkanone

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Rhodium(I)-catalyzed intramolecular acylation of alkynyl group proceeds by the use of acylsilanes having an alkynyl moiety. 5- and 6-Alkynoylsilanes are converted to $\alpha$-alkylidenecycloalkanones by treatment with $[RhCl(CO)_2]_2$ in the presence of acetic acid via transmetallation between the acylsilane moiety and a rhodium(I) complex.

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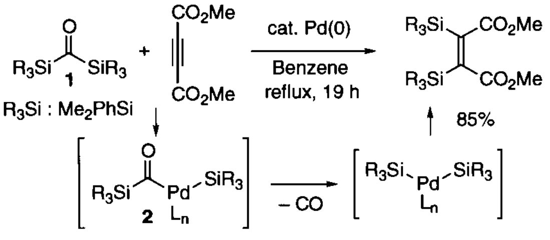
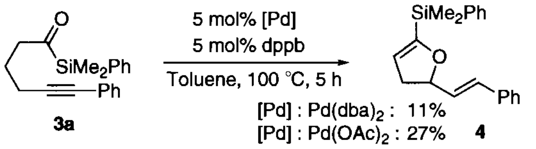
We previously reported palladium(0)-catalyzed disilylation of alkyne with disilyl ketone **1**, in which the oxidative addition of the carbonyl carbon–silicon bond of **1** toward a low valent palladium complex was proposed as the key step of the catalytic cycle (Scheme 1).[1]



**Scheme 1**. Pd(0)-catalyzed reaction of disilyl ketone with alkyne.

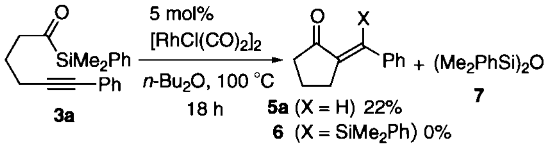
In the above catalytic reaction, carbonyl group of disilyl ketone **1** was not introduced to alkyne because of the rapid elimination of carbon monoxide from unstable silylcarbonylpalladium(II) species **2**. Although it was expected that catalytic acylation might be achieved by employing acylsilane in stead of disilyl ketone, simple acylsilanes such as acetylsilane could not be used for the metal-catalyzed acylation because of its low reactivity toward the metal catalyst. The neighboring effect of coordination groups is widely known in the activation of carbon–hydrogen bonds[2] and carbon–carbon bonds[3] with transition-metal complexes. We, therefore, examined intramolecular acylation of alkynoylsilane, expecting that the coordination of the alkynyl moiety might accelerate the activation of carbonyl carbon–silicon bond.[4,5]

5-Alkynoylsilane **3a** was synthesized by Katritzky's method with a slight modification of the last hydrolysis step.[6] Treatment of acylsilane **3a** with $Pd(PPh_3)_4$, however, resulted in the recovery of the starting material. Only when bis(diphenylphosphino)-butane (dppb) was added as the ligand of palladium catalysts (eq 1), the isomerization product, cyclic vinyl ether **4**, was obtained, whereas acylation of the alkynyl moiety could not be detected.[7]



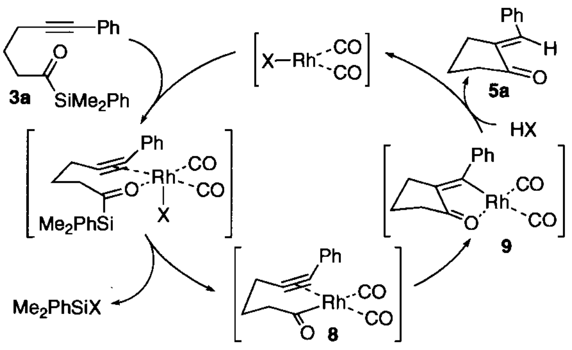
(1)

Group 9 metals are frequently employed in the reactions of alkynes such as the Pauson–Khand type reaction.[8] Accordingly, we tried the reaction of acylsilane **3a** with a rhodium(I) catalyst, $[RhCl(CO)_2]_2$. That is, when acylsilane **3a** was treated with 5 mol% of $[RhCl(CO)_2]_2$, the desired product, 2-benzylidenecyclopentanone **5a**, was obtained in 22% yield along with recovery of the starting material (eq 2).



(2)

The product **5a** seemed to be generated via cleavage of the carbonyl carbon–silicon bond by the rhodium catalyst. In this reaction, none of the acyl-silylation product **6** was detected, and dimethylphenylsilyl group of the consumed acylsilane **3a** was recovered as disiloxane **7** after work up. These facts indicated a mechanism depicted in Scheme 2. After the coordination of the alkynyl moiety to the rhodium center, transmetallation takes place to give acyl rhodium(I) species **8**.[9] Then intramolecular acyl-rhodation of alkynyl group proceeds to generate vinylrhodium(I) intermediate **9**. The cyclized product **5a** seems to be formed by protonation of vinyl rhodium(I) species **9** at the last step of the catalytic cycle with a small amount of water contaminant in the solvent.

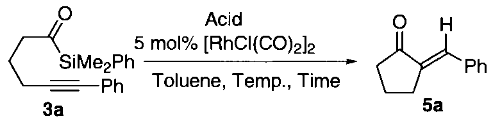


**Scheme 2**. Proposed mechanism of the Rh(I)-catalyzed cyclization of **3a**.

Because it was considered that the last protonation step might be accelerated by the addition of protic acids, the reactions were investigated in the presence of some protic acids (Table 1).

The strong acid such as *p*-toluenesulfonic acid gave only cation cyclization[10] product **10** in 40% yield (Entry 1). The yield of 2-benzylidenecyclopentanone (**5a**) was increased in the presence of carboxylic acids such as trifluoroacetic acid and acetic acid (Entries 2–5). Particularly, when the acylation was carried out at 70 °C in the presence of 10 molar amounts of acetic acid, **5a** was obtained in 77% yield after complete consumption of

**Table 1**. $[RhCl(CO)_2]_2$-catalyzed reaction of 5-alkynoylsilane **3a** in the presence of protic acids



| Entry | Acid[c] | Temp. / °C | Time | Yield of **5a** | (Recovery of **3a**) |
|---|---|---|---|---|---|
| 1[a] | p-TsOH(2) | 70 | 5 h | 0% | ( 0%) |
| 2 | $CF_3CO_2H$ (2) | 70 | 5 h | 45% | (<14%) |
| 3[b] | AcOH (2) | 100 | 5 h | 40% | ( 0%) |
| 4 | AcOH(10) | 70 | 5 h | 56% | (36%) |
| 5 | AcOH(10) | 70 | 12 h | 77% | ( 0%) |
| 6 | $H_2O$(10) | 100 | 5 h | 10% | (64%) |

[a] Cyclopentenyl ketone **10** was obtained as a side product in 40% yield. [b] 2-Diphenylmethylidenecyclopentanone (**11**) was obtained in 8% yield. [c] The number in each parentheses shows the molar amounts of added acid.

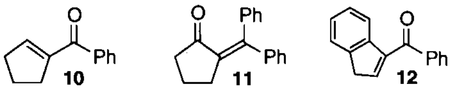
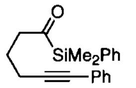
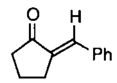
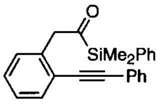
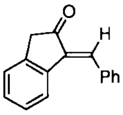
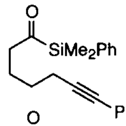
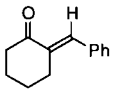
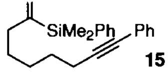


**Figure 1**. Side products.

acylsilane **3a** (Entry 5). The use of smaller amounts of acetic acid (2 molar amounts) at higher temperature (100 °C), however, decreased the yield of 2-benzylidenecyclopentanone (**5a**) to 40% and 2-diphenylmethylidenecyclopentanone (**11**) was formed in 8% yield.

**Table 2**. $[RhCl(CO)_2]_2$-catalyzed cyclization of acylsilane[a]

| Entry | Acylsilane | | Temp. Time | Product / Yield | | (Recovery of Acylsilane) |
|---|---|---|---|---|---|---|
| 1 |  | **3a** | 70 °C<br>12 h |  | **6a**<br>77% | ( 0%) |
| 2[b] |  | **3b** | 70 °C<br>12 h |  | **6b**<br>52% | ( 0%) |
| 3 |  | **13** | 100 °C<br>24 h |  | **14**<br>22% | (37%) |
| 4 |  | **15** | 100 °C<br>50 h | – | | (95%) |

[a] The reactions were carried out in the presence of 5 mol% of $[RhCl(CO)_2]_2$ and 10 molar amounts of acetic acid in toluene. [b] Indenyl ketone **12** was obtained as a side product in 6% yield.

This rhodium(I)-catalyzed cyclization was applied to the intramolecular acylation of some other alkynoylsilanes (Table 2). The cyclization of acylsilane **3b**, which involves *o*-phenylene tether, was converted to 1-benzylidene-2-indanone (**6b**) in 52% yield with 6% of indenyl phenyl ketone **12** as a side product. Thus, in the formation of cyclopentanone derivatives, the starting materials **3a** and **3b** were consumed completely and the cyclized products were obtained in moderate yield (Entries 1 and 2).[11] The cyclization of alkynoylsilane **13** having a tetramethylene tether required higher temperature (100 °C) and longer reaction time (24 h), and α-benzylidenecyclohexanone (**14**) was obtained in 22% yield (Entry 3). The acylation was not observed in the reaction of acylsilane **15** with a pentamethylene tether, and **15** was recovered completely even after a long reaction time (Entry 4).

As mentioned above, it was found that the transmetallation between acylsilane and rhodium(I) complex proceeds, in the case that the acylsilanes have a coordination site at appropriate position. This finding would provide the possibility to utilize acylsilanes for transition metal-catalyzed acylation reaction.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

## References and Notes

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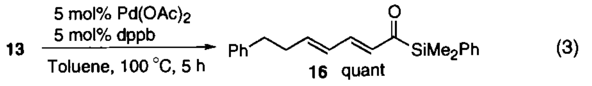

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8 For the Rh(I)-catalyzed Pauson–Khand type reaction, see: T. Kobayashi, Y. Koga, and K. Narasaka, *J. Organomet. Chem.*, **624**, 73 (2001); N. Jeong, B. K. Sung, and Y. K. Choi, *J. Am. Chem. Soc.*, **122**, 6771 (2000). For the cobalt-catalyzed reactions, see: B. Y. Lee, Y. K. Chung, N. Jeong, Y. Lee, and S. H. Hwang, *J. Am. Chem. Soc.*, **116**, 8793 (1994); J. W. Kim and Y. K. Chung, *Synthesis*, **1998**, 142; T. Sugihara and M. Yamaguchi, *J. Am. Chem. Soc.*, **120**, 10782 (1998); D. B. Belanger and T. Livinghouse, *Tetrahedron Lett.*, **39**, 7641 (1998); M. Hayashi Y. Hashimoto, Y. Yamamoto, J. Usuki, and K. Saigo, *Angew. Chem. Int. Ed.*, **39**, 631 (2000); K. Hiroi, T. Watanabe, R. Kawagishi, and I. Abe, *Tetrahedron Asymm.*, **11**, 797 (2000); K. Hiroi, T. Watanabe, R. Kawagishi, and I. Abe, *Tetrahedron Lett.*, **41**, 891 (2000). For the iridium-catalyzed reactions, see: T. Shibata and K. Takagi, *J. Am. Chem. Soc.*, **122**, 9852 (2000).
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