Rhodium-Catalyzed Acylation of Vinylsilanes with Acid Anhydrides: Application to the Transformation of α-Acyloxy Vinylsilanes to Unsymmetrical 1,2-Diketones

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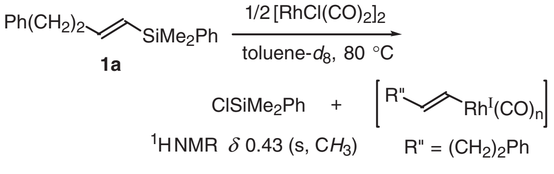
Acylation of vinylsilanes with acid anhydrides is catalyzed by $[RhCl(CO)_2]_2$ to give α,β-unsaturated ketones. The application of this catalytic system to the acylation of α-acyloxy vinylsilanes affords α-acyloxy enones in good yields, which are converted to unsymmetrical 1,2-diketones or their mono acetals.

Acylation of vinylsilanes has provided a regioselective preparation of α,β-unsaturated ketones, and is generally performed by the treatment with acid halides or anhydrides in the presence of Lewis acid such as $AlCl_3$.[1] However, the use of more than a stoichiometric amount of Lewis acid is required in this transformation and the development of the catalytic processes is strongly desired in the synthetic point of view.

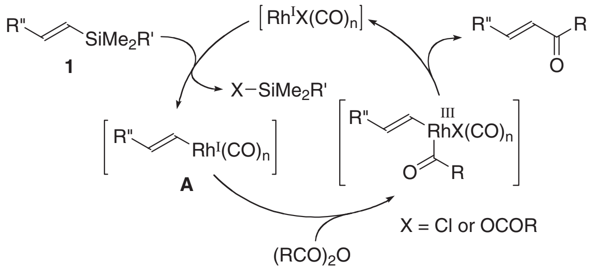
We have found that the rhodium(I) carbonyl complex, $[RhCl(CO)_2]_2$, is available for the transmetalation of acylsilanes to generate acylrhodium intermediates in the intramolecular cyclization reaction of δ-alkynoylsilanes.[2] Because vinylsilane also bears an sp^2 carbon–silicon bond like acylsilane, it was expected that transmetalation between the Rh(I) complex and vinylsilane would occur to afford vinylrhodium intermediate. Accordingly, β-alkyl vinylsilane **1a** was allowed to react with an equimolar amount of $[RhCl(CO)_2]_2$ in toluene-d_8 at 80 °C and the reaction was monitored by ^1H NMR. The formation of chlorodimethylphenylsilylane was observed as the result of metal exchange (Eq 1). For the transmetalation between transition metal complexes and vinylsilanes, the use of fluoride ion or the introduction of alkoxy or hydroxy group on the silyl group is essential to activate vinylsilanes, as being reported in the transition metal-catalyzed arylation of vinylsilanes with aryl halides to prepare vinyl arenes.[3–5] It is noteworthy that the transmetalation proceeded without any activating reagents in the present metal exchange between $[RhCl(CO)_2]_2$ and vinylsilane **1a**.



(1)

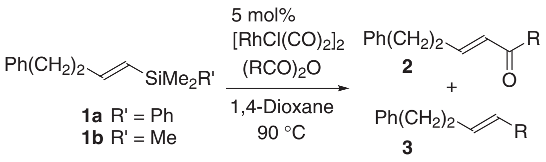
The catalytic acylation of vinylsilane with acid anhydride was supposed to proceed by applying this transmetalation. That is, the generation of vinylrhodium intermediate **A** would be followed by sequential oxidative addition of acid anhydride and reductive elimination of α,β-unsaturated ketone along with the regeneration of Rh(I) catalyst (Scheme 1).

In fact, β-alkyl vinylsilanes **1a** and **1b** reacted with various acid anhydrides in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ to give enones, as being summarized in Table 1.[6]



Scheme 1. Rh(I)-catalyzed acylation of vinylsilane **1**.

Table 1. Rh(I)-catalyzed acylation of β-alkyl vinylsilane **1**.[a]



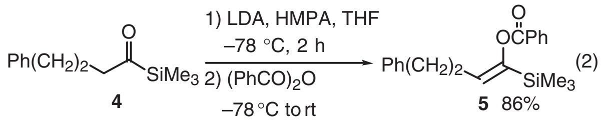
Entry	1	$(RCO)_2O$ R	Time / h	Products / %[b]			
1	**1a**	Me	7	**2a**	84	**3a**	–
2	**1a**	Et	18	**2b**	67	**3b**	–
3	**1a**	*i*-Pr	18	**2c**	72	**3c**	–
4	**1a**	Ph	18	**2d**	74	**3d**	5
5	**1b**	Me	18	**2a**	82	**3a**	–
6	**1b**	Ph	24	**2d**	76	**3d**	6

[a]Vinylsilane **1** : $[RhCl(CO)_2]_2$: $(RCO)_2O$ = 1.0 : 0.05 : 3.0.
[b]Isolated yield based on vinylsilane **1**.

The acylation of dimethylphenylvinylsilane **1a** with acetic anhydride proceeded at 90 °C, and α,β-unsaturated ketone **2a** was obtained in 84% yield (Entry 1). Propionic anhydride and isobutyric anhydride also reacted smoothly with **1a** (Entries 2 and 3). In the reaction with benzoic anhydride, the desired phenyl vinyl ketone **2d** was obtained in 74% yield with 5% yield of phenylated product **3d** (Entry 4). Even trimethylvinylsilane **1b** reacted with acid anhydrides under the same reaction conditions to give the corresponding enones **2** in good yields (Entries 5 and 6).

It was not confirmed whether this acylation reaction initiated by the transmetalation or by the oxidative addition of acid anhydride to the Rh(I) complex. To have insight into the initial step, a stoichiometric amount of $[RhCl(CO)_2]_2$ was allowed to react with acetic anhydride at 80 °C, but no reaction occurred. This result supports the hypothesis of the reaction mechanism shown in Scheme 1.[7]

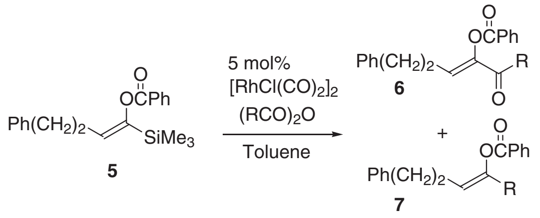
The rhodium catalyzed acylation was applied to the synthesis of 1,2-diketones and their derivatives from α-acyloxy vinylsilanes **5**, which were easily prepared stereoselectively in *E*-form by the *O*-acylation of lithium enolate of the corresponding acylsilane **4** (Eq 2).[8]



(2)

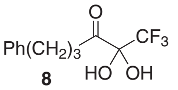
As summarized in Table 2, α-acyloxy vinylsilane **5** exhibited an sufficient reactivity in the acylation reaction.[6] Both of primary and secondary carboxylic acid anhydrides gave acylation products **6a–c** in excellent yields (Entries 1–4),[9] whereas the acylation with pivaric anhydride gave only 7% yield of product **6d** (Entry 5). In the reaction with benzoic anhydride, the benzoylation product **6e** was obtained in 66% yield with 24% yield of decarbonylative coupling product **7e** (Entry 6). Trifluoroacetylation proceeded as well and the corresponding diketone **8** was obtained as a hydrate form in 79% yield, after purification by silica gel column chromatography (Entry 7).

Table 2. Rh(I)-catalyzed acylation of α-benzoyloxy vinylsilane **5**.[a]



Entry	(RCO)$_2$O R	Temp. / °C	Time / h	Products / %[b]			
1	Me	80	4	**6a**	98	**7a**	–
2[c]	Me	80	12	**6a**	87	**7a**	–
3	Et	80	2	**6b**	99	**7b**	–
4	*i*-Pr	80	3	**6c**	97	**7c**	–
5[d]	*t*-Bu	80	24	**6d**	7	**7d**	–
6	Ph	80	5	**6e**	66	**7e**	24
7	CF$_3$	50	4	**6f**	(79)[e]	**7f**	–

[a] Vinylsilane **5** : [RhCl(CO)$_2$]$_2$:(RCO)$_2$O = 1.0:0.05:3.0.
[b] Isolated yield based on vinylsilane **5**.
[c] 1.2 molar amounts of Ac$_2$O was used.
[d] Vinylsilane **5** was recovered in 8% yield.
[e] Hydrate **8** was obtained in 79% yield.



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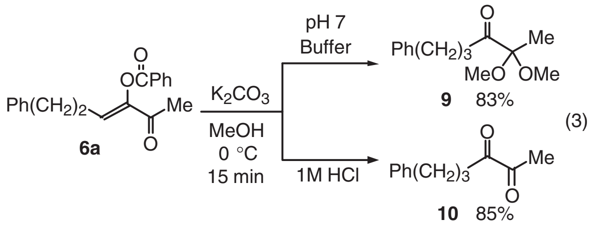
Thus obtained α-benzoyloxy ketone **6a** could be converted to α-dimethoxy ketone **9** in 83% yield by the treatment with K_2CO_3 in methanol and neutral work up. While, acidic work up gave 1,2-diketone **10** in 85% yield (Eq 3). On the whole, the present rhodium-catalyzed reaction of α-acyloxy vinylsilanes **5** provided a novel method for the preparation of unsymmetrical 1,2-diketones **10** and their derivatives **6a** and **9**, which are regarded as regioselectively masked forms at each of carbonyl group of 1,2-diketone **10**.



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References and Notes

1 For Lewis acid mediated electerophilic acylation of vinylsilanes, see: AlCl$_3$; I. Fleming and A. Pearce, *Chem. Commun.*, **1975**, 633; W. E. Fristad, D. S. Dime, T. R. Bailey, L. A. Paquette, *Tetrahedron Lett.*, **1979**, 1999; TiCl$_4$; A. Tubul and M. Santelli, *Tetrahedron*, **44**, 3975 (1988); SnCl$_4$; F. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, *J. Org. Chem.*, **45**, 1046 (1980); ZnCl$_2$; T. Sasaki, A. Nakanishi, and M. Ohno, *J. Org. Chem.*, **47**, 3219 (1982).

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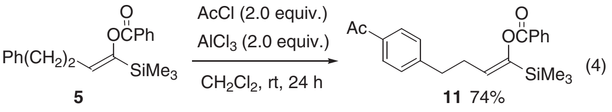
6 General procedure is as follows. A mixture of vinylsilane (0.2 mmol), [RhCl(CO)$_2$]$_2$ (0.01 mmol), and acid anhydride (0.6 mmol) in 1,4-dioxane or toluene (2 mL) was heated at a temperature for a period given in the Tables.

7 For oxidative addition of acid anhydride to rhodium(I) species, see: C. G. Frost and K. J. Wadsworth, *Chem. Commun.*, **2001**, 2316; K. Oguma, M. Miura, T. Satoh, and M. Nomura, *J. Organomet. Chem.*, **648**, 297 (2002).

8 For stereoselective generation of enolate of acylsilane by using HMPA, see: M. Honda, W. Oguchi, M. Segi, and T. Nakajima, *Tetarahedron*, **58**, 6815 (2002).

9 Lewis acid mediated electerophilic acylation of α-oxygenated vinylsilane has never been reported. In fact, in the reaction of α-benzoyloxy vinylsilane **5** with acetyl chloride in the presence of AlCl$_3$, the desired α-benzoyloxy α,β-unsaturated ketone was not obtained but the Friedel–Crafts acylation of phenyl group proceeded to give **11** in 74% yield (Eq 4).



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