

Rhodium(II) Acetate Catalysed Hydrosilylation of Enamides and *N*-Vinylureas leading to 1-(Trialkylsilyl)alkylamine Derivatives

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The $[\text{Rh}_2(\text{OAc})_4]$ catalysed hydrosilylation of enamides and *N*-vinylureas with dimethylphenylsilane proceeds smoothly in a regio- and site-selective manner to give 1-(trialkylsilyl)alkylamine derivatives in good to high yields.

Transition metal-catalysed hydrosilylation of carbon-carbon double bonds has been one of the most important methods for the introduction of trialkylsilyl groups into organic molecules.¹ Since the regio- and stereo-selectivity of the reactions are highly affected by the substitution patterns of the substrates, much effort has been devoted to find appropriate catalysts in order to attain highly selective transformations. In spite of extensive studies in this area, hydrosilylation of functionalized olefins has been less examined. In particular, transition metal-catalysed hydrosilylation of enamines and enamides has to our knowledge not been reported, although addition of trichlorosilane to enamines derived from ketones in the absence of a catalyst has been reported.^{2,3} Herein we report that hydrosilylation of enamides and *N*-vinylureas proceeds regio- and site-selectively in the presence of a catalytic amount of $[\text{Rh}_2(\text{OAc})_4]$ to give 1-(trialkylsilyl)alkylamine derivatives in good to high yields.

A mixture of *N*-benzyl enamide **1a** and dimethylphenylsilane was stirred with 2 mol % of $[\text{Rh}_2(\text{OAc})_4]$ under reflux in toluene for 3 h (Scheme 1). After silica gel column chromatography of the reaction mixture 1-(dimethylphenylsilyl)propylamide **2** was obtained in 50% yield.[†] It is of note that the silyl group is selectively introduced at the carbon adjacent to nitrogen. $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$, $[\text{RhH}(\text{PPh}_3)_3]$, $[\text{Rh}(\text{acac})_3]$, $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $[\text{RhCl}(\text{PPh}_3)_3]$ ⁴ were also examined as catalysts but the reactions proceeded less effectively giving **2** in at most 30% yield along with unreacted starting materials.

Hydrosilylation of enamides and *N*-vinylureas **1b-d** was carried out with dimethylphenylsilane in the presence of a catalytic amount of $[\text{Rh}_2(\text{OAc})_4]$. The results are summarized in Table 1.[†] The reaction was complete within 5 h. The nature of the substituents on the nitrogen did not affect the regioselectivity of the reaction. The 1-silylalkylamine derivatives, which are not easily accessible by known methods,⁵ but which are important as synthetic precursors,⁶ were obtained as products in all cases. The proton attached to nitrogen in **1b** and **1c** remained intact under the reaction conditions. For **1b** even 0.02 mol% of the catalyst was sufficient to afford the product in good yields.

The hydrosilylation of *N,N*-divinylureas **3-6**⁷ was also examined. As listed in Table 2,[†] the reaction using dimethyl-

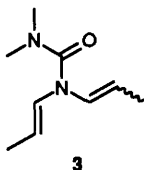
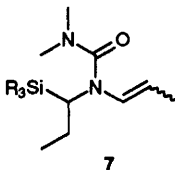
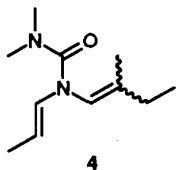
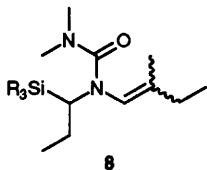
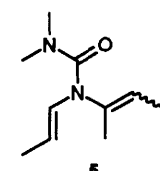
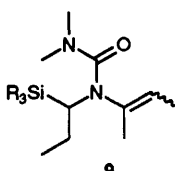
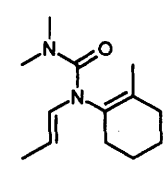
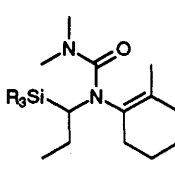
phenylsilane proceeded in a highly regio- and site-selective manner. The use of HSiCl_3 or $\text{HSi}(\text{OEt})_3$ resulted only in the recovery of starting material or a complex mixture. With dimethylphenylsilane the less substituted alkenyl group was hydrosilylated, and only one of the four possible regioisomers

Table 1 Results of the rhodium(II) acetate catalysed hydrosilylation of enamides and *N*-vinylureas **1a-1d**^a

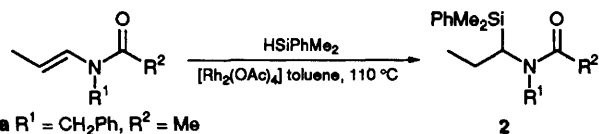
Substrate	Catalyst % [Rh ₂ (OAc) ₄]	t/h	Yield (%) ^b
1a	1	3	50
1b	0.2	4	87
1c	0.1	2	74
	0.02	5	60
1d	2	5	47

^a Reaction conditions: enamide or *N*-vinylurea (1 mmol), HSiPhMe_2 (1.3 mmol), $[\text{Rh}_2(\text{OAc})_4]$ (as given in Table), degassed toluene (5 ml), 110 °C. ^b Isolated yields.

Table 2 Results of the rhodium(II) acetate catalysed hydrosilylation of *N,N*-divinylureas **3-6**^a

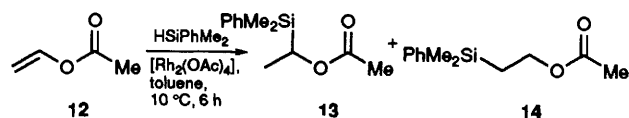
Substrate	Catalyst % [Rh ₂ (OAc) ₄]	Yield (%) ^b	Product ^c	Ratio ^d E : Z
	2	93		82:18
	0.1	72		80:20
	2	74		78:22
	2	75		67:33
	2	38(94) ^e		-

^a Reaction conditions: *N,N*-divinylurea (1 mmol), HSiPhMe_2 (1.3 mmol), $[\text{Rh}_2(\text{OAc})_4]$ (as given in Table), degassed toluene (5 ml), for 3 h, at 110 °C. ^b Isolated yields. ^c $\text{R}_3 = \text{PhMe}_2$. ^d Ratio of the stereoisomeric mixture of the product. ^e GLC yields in parentheses determined by the internal standard method.

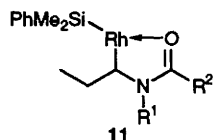


1a $\text{R}^1 = \text{CH}_2\text{Ph}$, $\text{R}^2 = \text{Me}$
b $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$
c $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{NMe}_2$
d $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{NMe}_2$

Scheme 1



Scheme 2



was obtained. No hydrosilylation products were obtained with 7–10 even in the presence of an excess amount of hydrosilane.

Although the mechanistic detail of the present reaction is not clear at the present stage,[‡] the carbonyl group of enamides and *N*-vinylureas appears to play an important role in controlling the regioselectivity. The five-membered cyclic intermediate **11** may be formed in preference to a six-membered one by coordination of the carbonyl oxygen to Rh.⁸ The directing effect of the carbonyl group was further demonstrated by the reaction of vinyl acetate **12** to give products **13** and **14** in 61% yields (**13** : **14** = 72 : 28), Scheme 2. The silyl group was predominantly introduced at the internal carbon of the terminal alkenyl group probably *via* an intermediate similar to **11**.

In summary, [Rh₂(OAc)₄] was successful in the hydrosilylation of enamides and *N*-vinylureas. The reaction exhibited high regio- and site-selectivity. The introduction of a silyl group to the carbon adjacent to nitrogen has been attained in a catalytic way. Further application of the present reaction and synthetically important 1-silylalkylamine derivatives will be reported in due course.

Received, 13th June 1994; Com. 4/03561E

Footnotes

† All new compounds described herein gave spectral data and analytical results consistent with the assigned structures.

‡ After the reaction the green [Rh₂(OAc)₄] disappeared and a black solid was recovered.

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