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A NOVEL METHOD FOR THE REDUCTION OF SCHIFF BASES USING CATALYTIC HYDROSILYLATION

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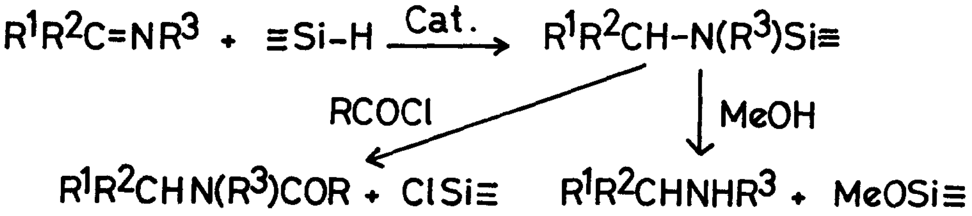
The reduction of Schiff bases to form secondary amines has been accomplished by catalytic hydrogenation[1] and by various reagents such as magnesium in methanol[2], $LiAlH_4$[3], and $NaBH_4$[4]. More recently, $[Fe_3(CO)_{12}]$ was reported to effective for the reaction[5]. We found that the reduction of various carbonyl compounds was successfully accomplished via hydrosilylation catalysed by rhodium (I) catalyst under mild conditions[6]. Now, we wish to report a novel and powerful method for the reduction of Schiff bases under neutral and mild conditions as an application of transition metal or metal complex catalysed hydrosilylation.



According to our method, silyl-protected amines can be obtained in the first step, which are known to be a versatile reagent in organic syntheses[7]. Corresponding amines are readily obtained by methanolysis of the silyl-amines at room temperature. For the purpose of obtaining amines, it is not necessary to isolate the silylamines. Results are summarized in Table 1.

As for the hydrosilylation of Schiff bases, only one example was reported[8], which was performed by the use of triethylsilane and benzylideneaniline with $ZnCl_2$ as a catalyst under rather drastic conditions. It was found that the reaction proceeded under much milder conditions in exceedingly high yield when certain transition metal complexes or transition metal salts such as $(Ph_3P)_3RhCl$ or $PdCl_2$ are employed as a catalyst. The reaction seems to be affected also by the hydrosilane used. Thus, dihydrosilanes were found to react more smoothly than monohydrosilanes and trihydrosilanes. When dihydrosilanes such as Et_2SiH_2, $PhMeSiH_2$ and Ph_2SiH_2 were used, the activity sequence of the catalysts[9] was found to fall in the order $(Ph_3P)_3RhCl \gg (Ph_3P)_2Rh(CO)Cl > Py_2RhCl(dmf)BH_4 > [(1,5\text{-hexadiene})RhCl]_2 > [(1,5\text{-cyclooctadiene})RhCl]_2 > PdCl_2 > (Ph_3P)_2PdCl_2$. Chloroplatinic acid cannot be practically used because of the occurrence of many side reactions, and $ZnCl_2$ did not display any catalytic activity under the conditions employed[9]. It was found that $PdCl_2$ was the most effective when monohydrosilanes such as Et_3SiH and $PhMe_2SiH$ were used. In a practical sense, it can be said that dihydrosilane-$(Ph_3P)_3RhCl$ combination is the most effective for the reaction.

The reduction of benzilidenemethylamine using diethylsilane is typically described: To a mixture of benzylidenemethylamine (2.38 g, 20 mmol) and diethylsilane (1.94 g, 22 mmol) in 10 ml of benzene was added 90 mg of $(Ph_3P)_3RhCl$ (0.5 mol%) and the mixture was stirred at room temperature for 1 hr. Then, 10 ml of methanol was added to the reaction mixture and stirred for 10 min. Benzylmethylamine (2.28 g, 95%) was obtained by distillation under reduced pressure The diethylsilyl derivative, $PhCH_2N(Me)SiHEt_2$ (bp 65°/0.25 mm), was obtained by distillation of the reaction mixture under reduced pressure before methanol was added[11].

The silylamine could be converted to an amide by treatment with acyl chlorides, e.g., benzylmethyltriethylsilylamine was converted to the benzoyl derivative of benzylmethylamine, $PhCON(Me)CH_2Ph$[10] or the acetyl derivative, $MeCON(Me)CH_2Ph$[10] in almost quantitative yield by the reaction with equimolar benzoyl chloride or acetyl chloride in n-hexane at room temperature

In conclusion, this new method may be equal or superior to $LiAlH_4$[3] or $NaBH_4$[4] in effecting the reduction of Schiff bases, which is performed in non-aqueous, neutral and mild conditions. Moreover, it should be noted that intermediate hydrosilylated products can be used directly for many reactions as silyl-protected amines.

Table 1. Reduction of Schiff Bases via Hydrosilylation

Schiff Base	Hydrosilane	Cat. (Mol%)	Conditions	Product after methanolysis	Yield (%)
$PhCH{=}NMe$	Et_2SiH_2	0.5^a	30°, 0.5 hr	$PhCH_2NHMe$	95
	Ph_2SiH_2	0.5^a	0°, 3 hr		92
	Et_3SiH	0.5^a	100°, 20 hr		65
	Et_3SiH	0.5^b	55°, 24 hr		90
$PhCH{=}NBu^n$	Et_2SiH_2	0.5^a	55°, 1.5 hr	$PhCH_2NHBu^n$	96
	$PhMeSiH_2$	0.5^a	55°, 0.5 hr		93
$PhCH{=}NPh$	Et_2SiH_2	0.2^a	50°, 2 hr	$PhCH_2NHPh$	96
	Et_3SiH	0.5^a	100°, 15 hr		91
$PhMeC{=}NPh$	Et_2SiH_2	0.5^a	55°, 72 hr	$PhMeCHNHPh$	85

[a] $(Ph_3P)_3RhCl$ [b] $PdCl_2$

Table 2. New Silylamines Obtained by Hydrosilylation of Schiff Bases

Silylamine	bp (°C/mmHg)	Chemical Shift of Si-H (τ)	νSi-H (cm^{-1})
$PhCH_2N(Me)SiHEt_2$	65/0.25	5.60 (quintet)	2100
$PhCH_2N(Me)SiHPh_2$	145/0.03	4.59 (s)	2110
$PhCH_2N(Me)SiEt_3$	88/0.20	---	---
$PhCH_2N(Bu^n)SiHEt_2$	78/2.5	5.76 (quintet)	2100
$PhCH_2N(Bu^n)SiHMePh$	141/0.5	4.96 (quartet)	2110
$PhCH_2N(Ph)SiHEt_2$	126/0.2	4.60 (quintet)	2105
$PhMeCHN(Ph)SiHEt_2$	107/0.15	5.57 (quintet)	2120

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