SHORT COMMUNICATION

Reduction of Carbonyl Compounds with Various Hydrosilane-Rhodium(I) Complex Combinations

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It has been known that the hydrosilation of carbonyl compounds can be effected by various catalytic systems such as metal halides *e.g.* $ZnCl_2$[1] and H_2PtCl_6,[2] and UV light.[3] Among them, metal or metal halide catalyst systems have been used within the limit of monohydrosilanes, mainly due to the fact that the disproportionation of polyhydrosilane is also catalyzed by these substances.[4] Gilman and Wittenberg[5] found that diphenylsilane adds to benzophenone at temperature of 220—270°C, but the reaction conditions are too drastic to allow the use of a wide variety of carbonyl compounds in solution. We found that tris(triphenylphosphine)chlororhodium (**1**) is an extremely effective catalyst for the hydrosilation of carbonyl compounds in comparison with other knwon catalysts. Now we wish to report the effective hydrosilation of carbonyl compounds, which is equivalent to hydrogenation after hydrolysis, using a variety of hydrosilane-rhodium(I) complex **1** combinations. The hydrosilation with monohydrosilanes was found to take place under very mild conditions to give the expected products. Further, the rate of the reaction was found to increase when dihydro- and trihydrosilanes were employed, and the disproportionation of these hydrosilanes were virturally negligible.

A typical procedure is described for the hydrosilation of cyclohexanone by diphenylsilane: To a mixture of 0.98 g (10 mmol) of cyclohexanone and 1.84 g (10 mmol) of diphenylsilane, 9.5 mg (0.1 mol%) of $(Ph_3P)_3RhCl$ (**1**) was added, and the mixture was stirred at ice-cold temperature, and the hydrosilation was completed within 10 min. *n*-Hexane (50 m*l*) was added to the reaction mixture, the resulting precipitate filtered off, the solvent was evaporated, and the residual solution was distilled under reduced pressure, and 2.78 g (98%) of cyclohexyloxydiphenylsilane (**2 g**) was obtained. The silylether **2 g** thus obtained was smoothly hydrolyzed by $MeOH-KOH-H_2O$ solution to afford cyclohexanol quantitatively. Results of the hydrosilation using various hydrosilanes, ketones and aldehydes are summarised in Table 1.

Table 1. Silylethers (**2**) obtained by the hydrosilation of ketones and aldehydes using hydrosilane-rhodium (I) complex combinations[a)]
$[(R^1R^2CHO)_nSiR_{4-n}]$

	R^1	R^2	*n*	Silyl group	Conditions	Yield (%)
a	Ph	H	1	$PhMe_2Si-$	r. t., 5 min	94
b	Me	Me	1	Ph_3Si-	reflux, 120min	98
c	Ph	Me	1	Et_2HSi-	r. t., 5 min	95
d	Ph	Ph	1	Et_2HSi-	r. t., 5 min	95
e	*n*-Pr	H	1	$PhMeHSi-$	r. t., 5 min	98
f	Ph	Ph	1	Ph_2HSi-	80°, 30 min	93
g	$-(CH_2)_5-$		1	Ph_2HSi-	0°, 10 min	98
h	$-(CH_2)_5-$		2	$PhHSi=$	0°, 10 min	98
i	$-(CH_2)_5-$		3	$PhSi\equiv$	70°, 6 hr	98

a) Amount of **1** used was 0.1—1.0 mol%.

Table 2. Silylenolethers (**3**) obtained by the hydrosilation of α,β-unsaturated ketones and aldehydes[a)]
$[(R^1R^2CHCH=CR^3\text{-}O)_nSiR_{4-n}]$

	R^1	R^2	R^3	*n*	Silyl gronp	Conditions	Yield (%)
a	Ph	H	H	1	Et_3Si-	60°, 15 min	96
b	Me	Me	Me	1	$PhMe_2Si-$	50°, 30 min	98
c	Me	H	H	1	Ph_3Si-	60°, 30 min	97
d	Ph	H	Me	1	Et_2HSi-	50°, 10 min	85
e	Ph	H	H	2	$PhHSi=$	10°, 5 min	99

a) Amount of **1** used was 0.1—0.5 mol%.

The hydrosilation of α,β-unsaturated ketones and aldehydes also proceeded smoothly under mild conditions to give the adducts in fairly high yield. In these cases, the reaction proceeded in a manner of 1,4-addition, and afforded silylenolethers **3**, which were easily hydrolyzed to saturated ketones or aldehydes by $acetone-MeOH-H_2O-K_2CO_3$ quantitatively. These findings clearly indicate that the reaction using hydrosilane-rhodium(I) complex combinations with α,β-unsaturated carbonyl compounds may open a new route to selective hydrogenation of the carbon-carbon double bond in α,β-unsaturated carbonyl compounds, and also open an important route to the preparation of silylenolethers, which are much interested as a synthetic intermediate. Results are listed in Table 2.

Though a hydrosilane has been known as a reducing agent for certain ketones, the scope of those reactions is limited to a very narrow area as quoted before. However, many carbonyl systems became able to be reduced by hydrosilane-rhodium(I) complex combinations taking advantage of easily hydrolyzable character of silylethers. Application of this reducing method to other systems and the mechanism of the reaction are now under active investigation. We believe that this reducing method has a wide potential utility as hydroboration.

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