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LETTERS

Rhodium-Catalyzed Reduction of Esters to Alcohols Using Diphenylsilane

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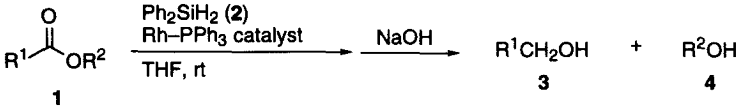
Abstract: Carboxylic esters were reduced to alcohols by diphenylsilane catalyzed by a Rh complex at room temperature. For example, ethyl decanoate and ethyl phenylacetate were converted to decanol and 2-phenylethanol by $[RhCl(cod)]_2$ / $4PPh_3$ for 72 hours in 98 and 92% yields, respectively. Wilkinson's catalyst is also usable, and the reduction of ethyl decanoate finished in 6 hours at room temperature. The bromo-substituent on ethyl 7-bromoheptanoate remained intact through this reduction.

Reduction of carbonyl compounds giving alcohols is useful for organic synthesis, and numerous catalytic[1] or stoichiometric reagents have been developed. Aldehydes and ketones are catalytically reduced to the corresponding alcohols by hydrogenation,[2] transfer hydrogenation,[3] and reduction using silane in the presence of transition metal catalysts.[4] On the other hand, catalytic reduction of carboxylic esters to alcohols is difficult, and only few examples of hydrogenation have been reported so far.[5,6] Reduction[7–10] using silane catalyzed by metal halides has been applied for the reduction of esters to alcohols,[7] but the reaction conditions are severe or a stoichiometric amount of metal halides is used. Recently, Buchwald *et al.* reported the reduction of carboxylic esters to alcohols using silane in the presence of a titanium complex,[8] but a reducing reagent or heating is needed for producing an active catalyst. We found that carboxylic esters were reduced to alcohols in excellent yields using silane in the presence of a rhodium complex.



Typically, in a 80-mL Schlenk tube were placed $RhCl(PPh_3)_3$ (46.3 mg, 0.05 mmol) and THF (2 mL). To this were added ethyl decanoate (**1a**) (0.47 mL, 2.0 mmol) and Ph_2SiH_2 (**2**) (1.1 mL, 6.0 mmol), and the solution was stirred at room temperature for 6 hours. To the mixture were added THF (10 mL) and 1M NaOH aq. (10 mL), and after stirring for 3 hours the product was extracted with diethyl ether. Purification by column chromatography after concentration of the organic layer gave 0.288 g of decanol (**3a**, 91% yield). The reduction of **1a** under various conditions is shown in Table 1. The yields in Table 1 were determined by ^1H NMR spectroscopic analysis using an internal standard method.[11]

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Table 1. Reduction of ethyl decanoate (**1a**) by diphenylsilane (**2**) in the presence of a Rh complex[a]

Entry	Rh, mol%	Ratio of **2** / **1a** (eq.)	Reaction time (h)	Yield (%)[b] of **3a**
1	5.0	4	72	96
2	2.5	4	72	92
3	1.0	4	72	40
4	2.5	3	72	98
5	2.5	2	72	72
6[c]	2.5	3	6	96 (91)[d]
7[c]	1.0	3	6	51
8[c,e]	1.0	3	24	56

a Reaction conditions: substrate **1a** (2.0 mmol), Ph_2SiH_2 , $[RhCl(cod)]_2$, PPh_3 (2 eq. to Rh atom), THF (2 mL), room temperature. Work up: 1M NaOH aq. b Determined by ^1H NMR spectroscopic analysis by an internal standard (bibenzyl) method. c $RhCl(PPh_3)_3$ was used as catalyst. d Isolated yield. e at 50 °C.

Using other silanes (phenylsilane, triphenylsilane, triethylsilane, trichlorosilane, *etc.*) decreased the yields of the alcohol **3a**. Silane **2** was needed in more than 3 equiv. to the ester for obtaining a high yield of **3a** (entries 1, 4 and 5). The amount of catalyst was critical for this reaction. That is, the ratio of rhodium atom vs substrate **1a** needs more than 2.5 mol% (entries 1,2,and 3). Other catalyst systems were also investigated. BINAP–$[RhCl(cod)]_2$[12] was effective for this reduction as well, while employing 1,10-phenanthroline as a ligand[13] resulted in low yield of the alcohol **3a**. Recently, Ito *et al.* reported the reduction of amides to amines by a diphenylsilane–Rh system. Their reduction system is similar to our system, but they demonstrated that the ester group in the substrates remained unreacted by use of $RhCl(CO)(PPh_3)_3$. Our experiment using $RhCl(CO)(PPh_3)_3$ as a catalyst also showed that this complex has a low catalytic activity for the reduction of **1a** (12% yield of **3a**). Interestingly, Wilkinson's catalyst is very effective for this reduction, and **1a** was converted to **3a** within 6 hours (entry 6). Even though this complex showed good catalytic activity, the yields of **3a** was not improved using 1.0 mol% of this complex at higher reaction temperature for longer reaction time (entries 7 and 8).

This reduction was applied to a variety of esters **1b-h** and representative results are listed in Table 2. Linear and aliphatic esters **1a**, **1b**, and **1d** were reduced smoothly to the corresponding alcohols in good yields (entries 1, 2, 3 and 6). Sometimes standard work up using 1M NaOH aq. resulted in moderate yields, while work up using 6M NaOH aq. gave better yields. For example, the yield of the product from the reaction of **1f** increased from 47 by work up with 1M NaOH aq. to 70% by work up with 6M NaOH aq. This apparently is to due to the hydrolysis of the silicon–oxygen bond in alkoxysilane, in which the sterically bulky alkoxy group prevents smooth hydrolysis. Esters of secondary alcohols were reduced slowly (**1c** and **1h**, entries 4,5 and 12). The bromo-substituent on the substrate did not suffer in the course of this reaction (**1g**, entries 10 and 11), but olefinic esters were converted to a complex mixture, in which a ester moiety was reduced to the hydroxymethylene group accompanied with hydrosilylation or dehydrosilylation of C=C bond.

Table 2. Reduction of esters **1** by diphenylsilane (**2**) in the presence of a rhodium complex[a]

Entry	Substrate			Catalyst[b]	Reaction time (h)	Yield (%)[c] of alcohol **3**
		R^1	R^2			
1	**1a**	C_9H_{19}	C_2H_5	A	72	98
2[d]	**1b**	C_9H_{19}	i-C_4H_9	A	72	92
3	**1b**			B	6	95
4[d]	**1c**	$C_{11}H_{23}$	i-C_3H_7	A	72	66
5	**1c**			B	6	80
6[d]	**1d**	CH_3	$C_{10}H_{21}$	A	72	94[e]
7[d]	**1e**	$C_6H_5CH_2$	C_2H_5	A	72	92
8[d,f]	**1f**	C_6H_5	C_2H_5	A	144	70
9[d]	**1f**			B	24	56
10	**1g**	$Br(CH_2)_6$	C_2H_5	A	72	92
11[d]	**1g**			B	24	92
12[d]	**1h**	Undecanoic γ-lactone		A	72	63[g]

[a] Reaction conditions: substrate 1 (2.0 mmol), Ph_2SiH_2 (6.0 mmol), catalyst, THF (2 mL), room temperature. Work up: 1M NaOH aq. [b] A: $[RhCl(cod)]_2$ (0.025 mmol), PPh_3 (0.10 mmol), B: $RhCl(PPh_3)_3$ (0.05 mmol). [c] Determined by ^1H NMR spectroscopic analysis by an internal standard method. [d] Work up: 6M NaOH aq. [e] Yield of octanol **4e**. [f] $[RhCl(cod)]_2$ (0.05 mmol), PPh_3 (0.20 mmol). [g] 1,4-Undecanediol was obtained.

The reaction mechanism is not clear yet. Trichlorosilane was known to reduce esters to the corresponding ethers via a radical mechanism.[14] Even though the formation of a trace amount of ethers was observed in our catalysis, high alcohol selectivities (more than 95% selectivities of alcohols in each case) and no reaction without a rhodium complex suggested that some interaction between the silane and a rhodium complex. In recent reduction of esters to ethers[10] or of amides to amines[9] by hydrosilylation using Mn or Rh complexes, oxidative addition of silane to a metal complex was suggested. So, it is considered that our reaction also proceeds through oxidative addition of silane to a Rh complex producing hydrido(silyl)rhodium, followed by reduction of the ester with this rhodium hydride species.

Finally, Rh-catalyzed reduction of esters using diphenylsilane proceeded smoothly. This is the first example of the reduction of esters to alcohols using silanes in the presence of a late-transition metal catalyst. This catalysis needs no heating, no pressurization, and no activation by reduing reagent. Futhermore Wilkinson's complex and silane are stable in air and to moisture. Conseqently, the method in this letter is thought to be a simple and easy for the reduction of esters to alcohols. Applicability of this reduction system to other functionalities and the mechanistic study are now underway.

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