

Tetrahedron Letters 40 (1999) 6963-6966

TETRAHEDRON LETTERS

Rhodium-Catalyzed Reduction of Esters to Alcohols Using Diphenylsilane

Tetsuo Ohta,* Masahiro Kamiya, Keisuke Kusui, Tsugumi Michibata, Mami Nobutomo, and Isao Furukawa

Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0394, Japan

Received 15 March 1999; revised 19 July 1999; accepted 21 July 1999

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 / 4PPh₃ 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. © 1999 Elsevier Science Ltd. All rights reserved.

Reduction of carbonyl compounds giving alcohols is useful for organic synthesis, and numerous catalytic¹ 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} Reduction⁷⁻¹⁰ 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.

 $\begin{array}{cccc} O & Ph_2SiH_2 (2) \\ R^1 & OR^2 & \hline THF, rt & \\ 1 & & & & & \\ \end{array} \begin{array}{cccc} NaOH & R^1CH_2OH & + & R^2OH \\ \hline THF, rt & & & & & & \\ \end{array}$

Typically, in a 80-mL Schlenk tube were placed RhCl(PPh₃)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 Ph₂SiH₂ (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

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°	1.0	3	6	51
8c,e	1.0	3	24	56

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

a Reaction conditions: substrate **1a** (2.0 mmol), Ph₂SiH₂, [RhCl(cod)]₂, PPh₃ (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(PPh₃)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)]₂¹² was effective for this reduction as well, while employing 1,10-phenanthroline as a ligand¹³ 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)(PPh₃)₃. Our experiment using RhCl(CO)(PPh₃)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.

		Substrate			Reaction	Yield (%) ^c of
Entry		<u>R1</u>	R ²	Catalystb	time (h)	alcohol 3
1	1a	C9H19	C ₂ H ₅	Α	72	98
2 ^d	1 b	C9H19	i-C4H9	Α	72	92
3	1 b			В	6	95
4d	1 c	$C_{11}H_{23}$	i-C ₃ H ₇	Α	72	66
5	1 c			В	6	80
6 ^d	1 d	CH ₃	$C_{10}H_{21}$	А	72	94°
7d	1 e	C ₆ H ₅ CH ₂	C ₂ H ₅	А	72	92
8d,f	1 f	C ₆ H ₅	C ₂ H ₅	Α	144	70
9d	1f			В	24	56
10	1 g	Br(CH ₂) ₆	C_2H_5	А	72	92
11d	1 g			В	24	92
12d	1 h	Undecanoic y-lactone		А	72	63g

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

a Reaction conditions: substrate 1 (2.0 mmol), Ph₂SiH₂ (6.0 mmol), catalyst, THF (2 mL), room temperature. Work up: 1M NaOH aq. b A: [RhCl(cod)]₂ (0.025 mmol), PPh₃ (0.10 mmol), B: RhCl(PPh₃)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), PPh₃ (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 ethers¹⁰ or of amides to amines⁹ 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. Furthermore Wilkinson's complex and silane are stable in air and to moisture. Consequently, 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.

We are grateful to Dr. Takayuki Yamashita for helpful discussions during the course of this work. This work was partially supported by Doshisha University's Research Promotion Fund and a grant to RCAST at Doshisha University from the Ministry of Education, Japan.

REFERENCES AND NOTES

- Reviews, see: (a) Ojima, I.; Iguchi, M.; Tzamarioudaki, M. In Comprehensive Organometallic Chemistry II; Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Hegedous, L. S. Eds.; Pergamon; 1995, Vol 12, pp. 9-39. (b) Birch, A. J.; Williamson, D. H. Org. React., 1976, 24, 1. (c) Takaya, H.; Noyori, R. In Comprehensive Organic Synthesis; Trost, B. M.; Fleming, I. Eds.; Pergamon Press:Oxford, 1991; Vol. 8, chapter 3.2.
- (a) Schrock, R. R.; Osborn, J. A. J. Chem. Soc., Chem. Commun. 1970, 567. (b) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. J. Am. Chem. Soc. 1998, 120, 13529.
- (a) Brieger, G.; Nestrick, T. J. Chem. Rev. 1974, 74, 567. (b) Johnstone, R. A. W.; Wilby, A. H. Chem Rev. 1985, 85, 129. (c) Zassinovich, G.; Mestroni, G.; Gladiali, S. Chem. Rev. 1992, 92, 1051. (d) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. J. Am. Chem. Soc. 1995, 117, 7562.
- 4. Ojima, I. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1479-1526.
- Homogeneous hydrogenation of carboxylic esters, see: (a) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. J. Chem. Soc., Chem. Commun. 1980, 783. (b) Grey, R. A.; Pez, G. P.; Wallo, A. J. Am. Chem. Soc. 1981, 103, 7536.
- 6. Heterogeneous hydrogenation, see: Adkins, H. Org. React. 1954, 8, 1.
- (a) Calas, R. Pure Appl. Chem. 1966, 13, 61. (b) Boyer, J.; Corriu, R. J. P.; Perz, R.; Poirier, M.; Reye, C. Synthesis 1981, 558. (c) Chuit, C.; Corriu, R. J. P.; Perz, R.; Reye, C. Synthesis 1982, 981.
- (a) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. J. Am. Chem. Soc. 1991, 113, 5093. (b) Berk, S. C.; Buchwald, S. L. J. Org. Chem. 1992, 57, 3751. (c) Verdaguer, X.; Berk, S. C.; Buchwald, S. L. J. Am. Chem. Soc. 1995, 117, 12641. (d) Verdaguer, X.; Hansen, M. C.; Berk, S. C.; Buchwald, S. L. J. Org. Chem. 1997, 62, 8522, and references cited therein.
- 9. Rh-catalyzed reduction of amides to amines by hydrosilylation, see: Kuwano, R.; Takahashi, M.; Ito, Y. *Tetrahedron Lett.* **1998**, *39*, 1017.
- Mn-mediated reduction of esters to ethers by hydrosilylation, see: Mao, Z.: Gregg, B. T.; Cutler, A. R. J. Am. Chem. Soc. 1995, 117, 10139.
- 11. After the reaction, additions of bibenzyl (0.365 g, 2.0 mmol, as an internal standard), additional THF (10 mL), and 1M NaOH aq. (10 mL), stirring the resulting mixture for 3 hours, extraction with diethyl ether, concentration, and then analysis of the crude mixture by ¹H NMR revealed the yield of the product.
- 12. Ohta, T.; Ito, M.; Tuneto, A.; Takaya, H. J. Chem. Soc., Chem. Commun., 1994, 2525.
- 13. 1,10-Phenanthroline and its derivatives were reported as a good ligand for the hydrogenation of ketones. see; (a) Mestroni, G.; Zassinovich, G.; Camus, A. J. Organomet. Chem. 1977, 140, 63. (b) Mestroni, G.; Spogliarich, R.; Camus, A.; Martinelli, F.; Zassinovich, J. Organomet. Chem. 1978, 157, 345.
- 14. (a) Tsurugi, J.; Nakao, R.; Fukumoto, T. J. Am. Chem. Soc., 1969, 91, 4587. (b) Nakao, R.; Fukumoto, T.; Tsurugi, J. J. Org. Chem. 1972, 37, 76. (c) Nagata, Y.; Dohmaru, T.; Tsurugi, J. J. Org. Chem. 1973, 38, 795. (d) Nakao, R.; Fukumoto, T.; Tsurugi, J. Bull. Chem. Soc. Jpn. 1974, 47, 932.