

## SELECTIVE HETEROGENEOUS PALLADIUM-CATALYZED HYDROGENATIONS OF WATER-SOLUBLE ALKENES AND ALKYNES

James M. Tour\*<sup>1</sup> and Shekhar L. Pandalwar  
Department of Chemistry, University of South Carolina  
Columbia, South Carolina 29208

**Abstract.** Treatment of water-soluble alkenes or alkynes with palladium(II) acetate and triethoxysilane at room temperature afforded the corresponding hydrogenated products in high yields. Simple introduction of a stoichiometric amount of hydrogen is accomplished by using triethoxysilane as the hydrogen source.

Catalytic hydrogenations are extremely important reactions in the laboratory and for bulk industrial conversions. Although heterogeneous catalysts are often the simplest reagents to use in catalytic processes,<sup>2</sup> they usually lack the selectivity of their homogeneous counterparts.<sup>3</sup> Here we describe the preparation of finely divided palladium metal dispersed in a siloxane polymer matrix which serves as a selective heterogeneous hydrogenation catalyst at room temperature for the reduction of unsaturated sodium carboxylates in aqueous solvent.<sup>4</sup>

We recently reported the chemo- and stereoselective reduction of alkenes and alkynes using palladium(II) acetate and triethoxysilane in a mixture of THF and water (5:1).<sup>5</sup> Evidence strongly supported that the process was a palladium(0)-catalyzed H<sub>2</sub>-based reduction process involving the formation of palladium metal finely dispersed in a siloxane polymer matrix. The molecular hydrogen (determined by mass spectrometry) was generated by the hydrolysis the silane Si-H moiety with the water to form Si-OH and H<sub>2</sub>.<sup>5,6</sup> Though the previously described procedure worked excellently for the selective conversion of unactivated internal alkynes to the corresponding alkenes, it was not appropriate for the reduction of  $\alpha,\beta$ -unsaturated alkynyl esters to the alkenyl esters nor for the high yield conversion of terminal alkynes to alkenes. The procedure described here provides a general method for the reduction of alkenyl and alkynyl acids to the corresponding fully saturated acids as well as a method for the selective reduction of  $\alpha,\beta$ -unsaturated alkynyl acids to the *Z*-alkenyl acids, and the facile conversion of terminal alkynyl acids to the corresponding terminal alkenes. This provides a simple alternative to the Lindlar reduction process. In the Lindlar process, however, one must carefully monitor the amount of hydrogen gas introduced into the reaction system or else over reduction can occur resulting in alkane formation.<sup>7</sup> In the procedure described herein, selective introduction of one molar equivalent of hydrogen is possible by the simple addition of one equivalent of triethoxysilane.

The standard procedure (method A) is as follows. To a solution of sodium hydroxide (66 mg, 1.65 mmol) in water<sup>8</sup> (5 mL) was added *E*-cinnamic acid (148 mg, 1.0 mmol). To the homogeneous solution was added palladium(II) acetate<sup>9,10</sup> (11 mg, 0.05 mmol) and the solution was stirred for 5 min. Triethoxysilane<sup>9,11</sup> (0.47 mL, 2.5 mmol) was slowly added over 10 min at room temperature.

Table I: Reductions using 5 mole % of Pd(OAc)<sub>2</sub> and triethoxysilane in water.

Entry	Substrate	Method <sup>a</sup>	Time (h)	Products	Yield (%) <sup>b</sup>
1		A	4		93
2		A	4	No Reaction	---
		B	5	H <sub>11</sub> C <sub>5</sub> -CO <sub>2</sub> H	69 <sup>c</sup>
3		B <sup>d</sup>	5	H <sub>11</sub> C <sub>5</sub> -CO <sub>2</sub> H	78
4		A	4	ref. f	---
		B	5.5	C <sub>4</sub> H <sub>9</sub> -CO <sub>2</sub> H	96
5		B <sup>e</sup>	5		95
					1 : 12 : 2
6		A	4	H <sub>15</sub> C <sub>7</sub> -CO <sub>2</sub> H	92
		A <sup>e</sup>	4		70
					16 : 1
7		A <sup>e</sup>	4		83
					12 : 1
8		A <sup>e</sup>	0.25		86
					(>20:1 Z/E)

a. The reaction was carried out at room temperature according to the procedure described in the text. b. Isolated yields. c. The yield was depressed due to the volatility of the product. d. A second portion of triethoxysilane (2.5 equiv.) was added after 1 h. e. Only 1 equiv. of triethoxysilane was used. f. Several isomeric products were obtained.

Hydrogen evolution started immediately and the solution became black. Stirring was continued for 4 h at room temperature before filtering the solution through celite. The alkaline aqueous filtrate was extracted once with chloroform (3 mL) and acidified with 3 N hydrochloric acid. The acidified aqueous solution was extracted with chloroform (4 x 5 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford 140 mg (93%) of an oily product that solidified on standing (mp 48-49°C) which was hydrocinnamic acid.<sup>12</sup> The reactions do not proceed in the absence of palladium(II) acetate and in no case was hydrosilylated material observed.

The scope of the reduction process is shown in Table I and several points are noteworthy. Though *E*-cinnamic acid is readily reduced under the standard conditions (entry 1, method A), *E*-2-hexenoic acid (entry 2, method A) is completely unreactive. However, by the introduction of 5-10 mol % of propargyl alcohol prior to the addition of triethoxysilane (method B), the reduction proceeds to completion. Though the propargyl alcohol has a profound influence on the course of the reaction, we are presently not able to rationalize its exact mechanistic action. It has been shown that soluble Pd-complexes can be formed by the reaction of Pd-black with acetylenes, hence, the propargyl alcohol may form a soluble and more reactive palladium species.<sup>13</sup> The selective reduction of alkynes to alkenes is shown in entries 6-8. In these cases, only one equivalent of triethoxysilane was added and the reaction vessel was immediately closed (stop cock) in order to maintain the hydrogen atmosphere within the system.

Additionally, the siloxane supported palladium metal catalyst could also be isolated and reused with an external hydrogen source. For example, we added triethoxysilane to palladium(II) acetate in water as described above but without an organic substrate. The bubbling was visually complete in less than 1 h, however, stirring was continued for 4 h and the catalyst was separated by filtration. After the volatile material had been removed *in vacuo* for 2 days, a gray powder remained. The powder was added to water and the slurry was stirred for 10 min. Addition of aqueous sodium cinnamate afforded only a small amount of reduced material, presumably due to Si-H residues remaining on the polymer which were confirmed by the FTIR analysis (2263  $\text{cm}^{-1}$ ) of the initial gray powder. When the reaction was then placed under an atmosphere of hydrogen (1 atm), the reduction of the remaining olefin proceeded smoothly. Hence, though we can not presently rule out a hydrosilylation mechanism, evidence suggests that palladium-catalyzed  $\text{H}_2$ -based hydrogenation may be a major mechanistic pathway in the reduction reactions described.

**Acknowledgements.** We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Department of Health and Human Services, Biomedical Research Support Grant for their generous support of this work.

### References and Notes

1. Recipient of an Office of Naval Research Young Investigator Award (1989-1992).
2. For some heterogeneous hydrogenation methods, see: Rylander, P. N. "Hydrogenation Methods", Academic Press: Orlando, Florida, 1985. Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem Rev.* 1985, 85, 129.

- Ram, S.; Ehrenkauffer, R. E. *Synthesis*, **1988**, 91. Weir, J. R.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 4926. Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3985. Brown, C. A. *J. Org. Chem.* **1970**, *35*, 1900.
3. For some homogeneous hydrogenation methods, see: Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657. James, B. R. "Homogeneous Hydrogenation", Wiley: New York, 1973. James, B. R. *Adv. Organometal. Chem.* **1979**, *17*, 319. Birch, A. D.; Williamson, D. H. *Org. React.* **1976**, *24*, 1. Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63. Faller, J. W. in "Homogeneous Catalysis with Metal Phosphine Complexes", Pignolet, L. H., Ed.; Plenum: New York, 1983, Chapter 2. James, B. R. in "Comprehensive Organometallic Chemistry", Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: New York, 1982; Vol 8, p 285. Halpern, J. *Inorg. Chim. Acta.* **1981**, *50*, 11. Sanchez-Delgado, R. A.; DeOchoa, D. L.; *J. Mol. Cat.* **1979**, *6*, 303. Greenspoon, N.; Keinan, E. *J. Org. Chem.* **1988**, *53*, 3723. Tsuji, J.; Suguira, T.; Minami, I. *Synthesis* **1987**, 603. Grigg, R. Mitchell, T. R. B.; Suthivaiyakit, S. *Tetrahedron Lett.* **1979**, 1067.
  4. Use of finely dispersed metal particles or colloids in a polymer matrix for selective catalysis is an area which has recently attracted much interest. See: Wang, Y.; Liu, H.; Jiang, Y. *J. Chem. Soc. Chem. Commun.* **1989**, 1878. Hirai, H.; Ohtaki, M.; Komiyama, M. *Chem. Lett.* **1986**, 269; **1987**, 149. Li, X.; Liu, H.; Jiang, Y. *J. Mol. Cat.* **1987**, *39*, 55. Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. Tamagawa, H.; Oyama, K.; Yamaguchi, T.; Tanaka, H.; Tsuiki, H.; Ueno, A. *J. Chem. Soc. Faraday Trans. 1* **1987**, *83*, 3189. Ueno, A.; Suzuki, H.; Kotera, Y. *J. Chem. Soc. Faraday Trans. 1* **1983**, *79*, 127. Sinfelt, J. H.; Via, G. H. *J. Catal.* **1979**, *56*, 1. de Jongste, H. C.; Ponec, V.; Gault, F. G. *J. Catal.* **1980**, *64*, 389. Jiang, X.-Z.; Stevenson, S. A.; Dumesic, J. A. *J. Catal.* **1985**, *91*, 11. Tauster, S. J.; Fung, S. C.; Carten, R. L. *J. Am. Chem. Soc.* **1980**, *100*, 180. Tauster, S. J.; Fung, S. C. *J. Catal.* **1978**, *55*, 29. Kunimorr, K.; Matsui, S.; Uchijima, T. *J. Catal.* **1984**, *85*, 253. Boudart, M. *J. Catal.* **1965**, *4*, 704. Otero-Scripper, P. H.; Wachter, W. A.; Butt, J. B.; Burwell, R. L., Jr.; Cohen, J. B. *J. Catal.* **1978**, *53*, 414. Anderson, J. R. *Structure of Metallic Catalysts*; Academic Press: New York, 1975.
  5. Tour, J. M.; Cooper, J. P.; Pandalwar, S. L. *J. Org. Chem.* **1990**, *55*, 3452.
  6. Sommer, L. H.; Barie, W. P., Jr.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1959**, *81*, 251. Sommer, L. H.; Korte, W. D.; Frye, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 3463.
  7. Lindlar, H.; Dubois, R. *Org. Synth.* **1973**, *V*, 880. McEwen, A. B.; Guttieri, M. S.; Maier, W. F.; Laine, R. M.; Shvo, Y. *J. Org. Chem.* **1983**, *48*, 4436.
  8. Deionized water was degassed with a stream of argon prior to use.
  9. Purchased from Aldrich Chemical Company, Inc.
  10. Though the initial studies on these hydrogenation methods were carried out using commercial palladium(II) acetate, later lots obtained from the same distributor proved to be ineffective for the same efficient transformation. We could only obtain reproducible results by the preparation of palladium(II) acetate from palladium sponge (Aldrich) using nitric and acetic acid according to standard procedures. See: Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.
  11. The triethoxysilane *must* be freshly distilled before use or else the reductions do not proceed to completion.
  12. All compounds were characterized spectroscopically and compared to previously reported spectra.
  13. Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161.

(Received in USA 2 May 1990)