J. Org. Chem. 1990, 55, 3452-3453

Highly Selective Heterogeneous Palladium-Catalyzed Hydrogenations Using Triethoxysilane and Water

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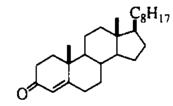
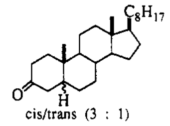
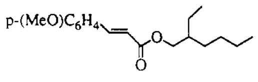
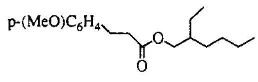
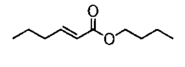
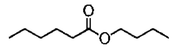
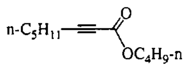
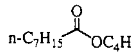
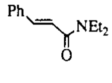
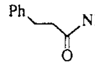
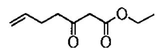
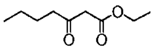
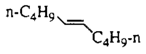
Received April 9, 1990

Summary: Treatment of alkenes or alkynes at ambient temperature with triethoxysilane and 5 mol % of palladium(II) acetate in a mixture of tetrahydrofuran and water affords the corresponding hydrogenated products. Excellent chemoselectivities and stereoselectivities can be obtained using this process.

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,[2] they usually lack the selectivity of their homogeneous counterparts.[3] Herein we describe the preparation of finely divided palladium metal dispersed in a siloxane polymer matrix which serves as a highly chemoselective and stereoselective heterogeneous hydrogenation catalyst at room temperature.[4] Upon the introduction of methyl propynoate, however, the reactivity of the system increases and a more potent catalyst is obtained at the expense of the selectivity. Interestingly, water must be present in the reaction medium and the hydrogen gas is generated in situ; hence, no external source of hydrogen is necessary. Conversely, one can use the preformed heterogeneous catalyst as a reductant with an external hydrogen source which makes it particularly attractive for an industrial process.

During the course of a palladium(II) acetate catalyzed polymerization of triethoxysilane in water, we noticed the formation of a black solution with concomitant hydrogen evolution (determined by mass spectrometry). The black suspended material is finely divided palladium metal dispersed on a polysiloxane matrix. This is based on elemental analysis and transmission and scanning electron micrographs using energy dispersive analysis with X-rays (EDX) of the recovered polymer. Though water is essential for this process, the addition of THF to the mixture allows us to use this reaction system for the selective reduction of organic compounds.[5]

Table I. Hydrogenations Using Triethoxysilane and Catalytic Palladium(II) Acetate

entry	substrate	conditions[a]	product	% yield[b]
1		A	 cis/trans (3 : 1)	96
2		A		92
3		A	No reaction	...
		B		99
4		A		81
5		A	Starting material/reduced (1:3)	...
		C		90
6		A[c]		81
7		A	No reaction	...
		B	$n\text{-}C_{10}H_{22}$	10[d]
8	$n\text{-}C_4H_9C\equiv CC_4H_9\text{-}n$	A		100[d,e]
		C[f]	$n\text{-}C_{10}H_{22}$	90[d]

[a] For methods A, B, and C, see text. In each case, the reactions were allowed to stir for 0.5–5 h before filtration through a plug of silica gel. [b] Isolated yields (unless otherwise noted) of homogeneous material obtained after filtration from the catalyst. No other products were observed. [c] The rate of the reduction can be increased dramatically using methods B or C. [d] Capillary gas chromatograph yield relative to a dodecane internal standard. The volatility of the product prohibited high isolation yields. [e] >20:1 Z/E isomeric ratio determined by NMR. [f] Under these conditions, the complete reaction required 24 h.

The reduction process involves the addition of triethoxysilane[6,7] (2.5 equiv) to a solution of the alkene or alkyne (1 equiv) and palladium(II) acetate[6,8] (0.05 equiv) in a

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(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, FL, 1985. Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129. Ram, S.; Ehrenkaufer, 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: James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. James, B. R. *Adv. Organomet. 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.; Sutthivaiyakit, 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) We have observed the reductions of unsaturated sodium carboxylates in exclusively water solvent under similar conditions.

(6) Purchased from Aldrich Chemical Co., Inc.

(7) The triethoxysilane *must* be freshly distilled before use or else the reductions do not proceed to completion.

0022-3263/90/1955-3452$02.50/0

mixture of THF[9] and water[10] (5:1) at room temperature (method A). The reactions are exceedingly clean, affording only the hydrogenated products. The products were isolated simply by filtration[11] from the siloxane-supported palladium followed by drying and removal of the solvent in vacuo. No further purification was necessary to afford pure material. Note that in the absence of water, only traces of hydrogenated product were formed while 95% of the starting alkene remained unchanged. Hence, water is essential for this reaction. Likewise, the reaction does not proceed in the absence of palladium(II) acetate.

The scope of this hydrogenation process is presented in Table I, and several points are noteworthy. The standard reduction process (method A) proceeds readily on α,β-unsaturated ketones and esters (entries 1, 2, and 4). On the contrary, (*E*)-butyl 2-hexenoate (entry 3) was totally unreactive under the standard conditions while *N*,*N*-diethyl cinnamamide (entry 5) was slow to reduce. We noticed, however, by adding methyl propynoate [1 equiv (method B) and 10 mol % (method C), respectively] *prior* to the introduction of triethoxysilane, the hydrogenation reactions proceeded rapidly to completion. Excellent chemoselectivity is observed in that while terminal olefins hydrogenated cleanly (entry 6), internal unactivated olefins remained unreduced (entry 7, method A). Likewise, when the terminal olefin keto ester (1 mmol) in entry 6 and (*E*)-5-decene (1 mmol) were added to the same flask and treated with palladium(II) acetate (0.05 mmol) and triethoxysilane (2.5 mmol), after 0.5 h, the terminal olefin was completely reduced (98% yield) while the (*E*)-5-decene was totally unreacted. The superb stereoselectivity of this process is demonstrated by entry 8 (method A) in the reduction of 5-decyne to (*Z*)-5-decene (>20:1 *Z*:*E*) in 100% yield and *this now represents a simple alternative to the Lindlar reduction process.*[12,13] In the Lindlar reduction, one must carefully monitor the quantity of hydrogen gas introduced into the reaction system or else overreduction can occur resulting in the formation of the alkane.[13] In the process described herein, such an over reduction was not observed. However, if one desires complete reduction to the alkane, introduction of methyl propynoate (10 mol %) allows for the conversion of the internal alkyne to the alkane (entry 8, method C). Similarly, though (*E*)-5-decene (entry 7) was totally unreactive under the standard conditions (method A), addition of 1 equiv of methyl propynoate (method B) allowed for complete hydrogenation of the olefinic moiety. Though the methyl propynoate addition has a profound influence on the course of the reaction, we are presently not able to rationalize its exact mechanistic action. We do observe that a more vigorous evolution of hydrogen ensues in the presence of the methyl propynoate. It has been shown that soluble Pd complexes can be formed by the reaction of Pd-black with acetylenes; hence, the methyl propynoate may form a soluble and more reactive palladium species.[14]

If the reaction (method C) was carried out on 1-decene in D_2O instead of H_2O, a mixture of d_0, d_1, d_2, d_3, and d_4 compounds were obtained in the ratio of 4:4:2:1:0.1, respectively, as determined by mass spectrometry. The higher *d*-containing compounds can arise via a deuteropalladation, dehydropalladation, deuteropalladation mechanism, which can occur when an alkylpalladium species is formed.[2] In related systems, we observed that the deuterium was equally distributed between C1 and C2 by ^1H and ^2H NMR spectroscopy.

Additionally, we could isolate the palladium-deposited polymer and manipulate it in the air over a period of several weeks. The solid was then resuspended in THF/water, and 5-decyne was introduced. Hydrogenation did not ensue until the reaction was exposed to a hydrogen atmosphere (1 atm, balloon). After 45 min, 5-decene was obtained in 100% yield.[15] Hence, this system responds as an excellent heterogeneous catalyst using an external hydrogen source.

From a mechanistic standpoint, several pathways must be considered. One could envision a palladium-catalyzed hydrosilylation followed by protodesilylation.[3] However, throughout the course of this hydrogenation study, there was no evidence for the formation of hydrosilylated material, and subjection of $RSi(OEt)_3$ compounds (R = carbon group) to the identical reaction conditions did not cleave the carbon–silicon bond. Another possible mechanistic scheme may involve a hydropalladation followed by Si transmetalation and reductive elimination of a hydrido alkenylpalladium species.[16] Additionally, the observations are consistent with a mechanistic pathway involving the palladium-catalyzed H_2-based hydrogenation. The molecular hydrogen can readily come from the hydrolysis of the Si–H linkage in the silane since it is known that R_3Si–H compounds react with HOR′ species in the presence of metal salts to form R_3Si–OR′ and H_2.[17] This latter mechanism is also consistent with the deuterium studies, and the results from the direct reaction of the isolated palladium-deposited polymer with molecular hydrogen. It should be noted, however, that further mechanistic studies are necessary since even heterogeneous metal systems can afford homogeneous metal complexes as the active catalysts.[14]

A detailed elemental, thermal, and microscopic analysis of the palladium-deposited siloxane material will be described shortly. Additionally, the utilization of this methodology for the deposition of transition metal(0) species on polysiloxanes is being explored as a powerful method for the encapsulation of finely divided metals into ceramic materials by the sol-gel process.

Acknowledgment. We thank the Department of Health and Human Services, Biomedical Research Support Grant, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support. We also thank Dr. N. Watabe and Dana Dunkelberger of the University of South Carolina Electron Microscopy Center for their assistance. The scanning electron microscope was purchased with a grant from the National Science Foundation (BIR-8805143).

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(8) Though the results in this communication were obtained by using commercial palladium(II) acetate, when subsequent lots purchased from the same distributor were used, we obtained widely varied results. In some cases, the reactions showed poor stereoselectivity or, in other cases, they did not proceed to more than 5% conversion. Recrystallization of the commercial material aided to some degree; however, consistent and reliable results have required the preparation of palladium(II) acetate from palladium sponge according to the following procedure: Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(9) Distilled over sodium and benzophenone prior to use.

(10) Deionized water was degassed with a stream of argon prior to use.

(11) Filtrations were done through a 1-in. plug of silica gel.

(12) McEwen, A. B.; Guttieri, M. S.; Maier, W. F.; Laine, R. M.; Shvo, Y. *J. Org. Chem.* **1983**, *48*, 4436.

(13) Lindlar, H.; Dubois, R. *Org. Synth.* **1973**, *V*, 880.

(14) Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161.

(15) Capillary gas chromatograph yield relative to a dodecane internal standard. The volatility of the product prohibited a high isolation yield.

(16) Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657.

(17) 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.