

Communications

Palladium Catalyzed Hydrogenation of α,β -Unsaturated Sulfones and Phosphonates

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Summary: The binuclear palladium complex, [(Bu₂PH)PdPBU₂]₂, when treated with oxygen, catalyzes the hydrogenation of the double bond of α,β -unsaturated sulfones and phosphonates in THF at room temperature and 1 atm of hydrogen pressure. Saturated sulfones and phosphonates were isolated in 49–93% yields.

The selective hydrogenation of the carbon–carbon double bond of α,β -unsaturated carbonyl compounds under mild conditions is an important reaction in organic synthesis.¹ The use of homogeneous catalysis to effect this transformation has attracted considerable attention. For example, we recently described a mild and selective method for the reduction of α,β -unsaturated ketones and aldehydes catalyzed by the binuclear palladium complex [(Bu₂PH)PdPBU₂]₂ (1) in good to excellent yields.²

Only a few methods exist in the literature for effecting the reduction of the carbon–carbon double bond in α,β -unsaturated sulfones and phosphonates. The most commonly used reactions in the case of sulfones involve metal

Table 1. Hydrogenation of α,β -Unsaturated Sulfones Catalyzed by [(Bu₂PH)PdPBU₂]₂ Pretreated with Oxygen

entry	substrate ^a	mol reactn % of time cat. (h)	product ^b	iso- lated ^c yield (%)
1		2 5		83
2		2 1		83
3		2 2		60
4		2 24		49
5		4 24		65 ^d
6		4 4		93

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(1) (a) Keinan, E.; Greenspoon, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 8, Chapter 3.5, pp 523–578. (b) Siegel, S. *Ibid.* Chapter 3.1, pp 449–463.

(2) Sommovigo, M.; Alper, H. *Tetrahedron Lett.* **1993**, *34*, 59.

(3) (a) Simpkins, N. S. In *Tetrahedron Organic Chemistry Series Volume 10; Sulphones in Organic Synthesis*; Pergamon Press: New York, 1993; p 118. (b) Musicki, B.; Widlanski, T. S. *Tetrahedron Lett.* **1991**, *32*, 1267. (c) Sakakibara, T.; Takai, I.; Yamamoto, A.; Iizuka, H.; Hirasawa, K.; Ishido, Y. *Tetrahedron Lett.* **1990**, *31*, 3749. (d) Ley, S. V.; Simpkins, N. S.; Whittle, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 503.

(4) (a) Bigge, C. F.; Johnson, G.; Ortwine, D. F.; Drummond, J. T.; Retz, D. M.; Brahce, L. J.; Coughnour, L. L.; Marcoux, F. W.; Probert, A. W., Jr. *J. Med. Chem.* **1992**, *35*, 1371. (b) Francis, J. E.; Webb, R. L.; Ghai, G. R.; Hutchison, A. J.; Moskal, M. A.; deJusius, R.; Yokoyama, R.; Rovinski, S. L.; Contrado, N.; Dotson, R.; Barclay, B.; Stone, G. A.; Jarvis, M. F.; *J. Med. Chem.* **1991**, *34*, 2570. (c) Bigge, C. F.; Drummond, J. T.; Johnson, G.; Malone, T.; Probert, A. W., Jr.; Marcoux, F. W.; Coughnour, L. L.; Brahce, L. J. *J. Med. Chem.* **1989**, *32*, 1580.

^a The unsaturated sulfones were prepared as described in ref 8. ^b Products were identified by comparison of spectral results [IR, NMR (¹H, ¹³C), MS] with literature data. The following sulfone is new. 2-Methyl-1-phenylethyl *p*-tolyl sulfone: ¹H NMR (CDCl₃) δ 1.42 (d, 3H, *J* = 5.3 Hz, CH₃), 2.39 (s, 3H, *p*-CH₃), 3.26–3.40 (m, 3H, -CH, -CH₂), 7.03–7.27 (m, 7H, ArH), 7.64–7.69 (m, 2H, ArH); ¹³C NMR (CDCl₃) δ 144.4, 144.1, 136.9, 129.7, 128.7, 127.8, 126.7, 126.6 (aromatics), 63.4 (CH₂), 35.0 (CH), 22.1 (*p*-CH₃), 21.6 (CH₃); MS *m/e* 274 [M]⁺. Anal. Calcd for C₁₆H₁₈O₂S: C, 70.04; H, 6.61. Found: C, 70.34; H, 6.61. ^c Isolated by column chromatography. ^d Isolated by preparative HPLC.

hydrides such as NaBH₄, [(PPh₃)CuH]₆, etc.,³ while palladium on activated carbon at 50 psi of H₂ was used

Table 2. Hydrogenation of α,β -Unsaturated Phosphonates Catalyzed by $[(\text{Bu}^t\text{PH})\text{PdPBu}^t_2]_2$ Pretreated with Oxygen

entry	substrate ^a	mol % of cat.	reactn time (h)	product ^b	isolated ^c yield (%)
1		2	24		75
2		5	21		85
3		2	0.5		88
4		2	18		57 ^d
5		2	2.5		80 ^d

^a The unsaturated phosphonates were prepared by the method described in ref 9. ^b Products were identified by comparison of spectral results [IR, NMR (¹H, ¹³C), MS] with literature data. The following phosphonate is new. 1-Phenylethylphosphonic acid diphenyl ester: ¹H NMR (CDCl₃) δ 1.78 (dd, 3H, $J = 7.5, 9.9$ Hz), 3.56 (qq, 1H, $J = 7.5$ Hz), 6.81–7.46 (m, 15H); ¹³C NMR (CDCl₃) δ 150.6, 136.8, 129.6, 129.5, 128.9, 128.6, 127.5, 124.9, 120.5, 120.4 (aromatics), 38.3, 39.4 (CH), 15.6 (CH₃); MS m/e 338 [M]⁺. Anal. Calcd for C₂₀H₁₉O₃P: C, 71.00; H, 5.66. Found: C, 71.28; H, 5.61. ^c Isolated by Kugelrohr distillation. ^d Isolated by column chromatography.

for the hydrogenation of α,β -unsaturated phosphonates.⁴ To our knowledge there are no publications on the use of homogeneous transition metal catalysts for these transformations.⁵ We report that the binuclear palladium complex on exposure to oxygen generates an excellent catalyst for the chemoselective reduction of the double bond of unsaturated sulfones and phosphonates. A recent paper showed that the catalytic species formed by reaction of **1** with O₂ is the mononuclear complex [Pd(O₂PBu^t₂)(OPBu^t₂)(OHPBu^t₂)], which contains a novel η^2 -phosphinate ligand.⁶

(5) The anionic hydride complex Et₄N⁺[HCr₂(CO)₁₀]⁻, catalyzes the hydrogenation of the vinyl phosphine oxide, CH₂=CHP(O)Ph₂ (Fuchikami, T.; Ubukata, Y.; Tanaka, Y. *Tetrahedron Lett.* **1991**, 32, 1199). We are indebted to a reviewer for bringing this relevant work to our attention.

(6) Leoni, P.; Marchetti, F.; Pasquali, M. *J. Organomet. Chem.* **1993**, 451, C25.

(7) Leoni, P.; Sommovigo, M.; Pasquali, M.; Sabatino, P.; Braga, D. *J. Organomet. Chem.* **1992**, 423, 263.

Reaction of an α,β -unsaturated sulfone or phosphonate with hydrogen in the presence of **1**,⁷ pretreated with oxygen in THF at room temperature under 1 atm of hydrogen pressure, proceeded smoothly affording the corresponding saturated sulfone or phosphonate in good to high yields. The ratio of substrate/**1** ranged from 20 to 50/1 depending on the reactivity of the starting material. Results are summarized in Tables 1 and 2.

The carbon–carbon double bond of monosubstituted α,β -unsaturated sulfones (Table 1, entries 1–4) was easily hydrogenated using 2 mol % of catalyst pretreated with oxygen. These reactions proceed under 1 atm of hydrogen and are complete in 1–24 h. In the case of β -substituted sulfones the reactivity of the β,β -disubstituted sulfone (entry 6) was higher than that of the β -monosubstituted analog (entry 5). A sulfone having a tetrasubstituted double bond did not undergo hydrogenation under the same conditions. The results in Table 2 show that the carbon–carbon double bond in α,β -unsaturated phosphonates can be easily hydrogenated under the same reaction conditions as those found for sulfones. α -Phenyl-substituted vinyl phosphates are more reactive than their β -phenyl substituted isomers.

The following procedure is typical: Oxygen was bubbled for 10 min through a solution of THF (5 mL) containing **1** (24.0 mg, 0.03 mmol). The solution was stirred overnight at room temperature and slowly turned to yellow. Methyl vinyl sulfone (0.158 g, 1.5 mmol) was added, and hydrogen was bubbled through the reaction at ambient conditions with stirring. The reaction was monitored by gas chromatography, and after 1 h the reaction was filtered through neutral alumina and the solvent was removed by rotary evaporation. Pure ethyl methyl sulfone (0.135 g, 83%) was isolated by column chromatography and characterized by IR, ¹H-NMR, and mass spectrometry.

In conclusion, the palladium complex generated in situ from **1** and oxygen is an excellent catalyst for the exceptionally mild hydrogenation of the carbon–carbon double bond in α,β -unsaturated sulfones and phosphonates in fine isolated yield.

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(8) Kamigata, N.; Sawada, H.; Kobayashi, M. *Chem. Lett.* **1979**, 159.

(9) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1980**, 21, 3595.