Wilkinson's Catalyst Catalyzed Selective Hydrogenation of Olefin in the Presence of an Aromatic Nitro Function: A Remarkable Solvent Effect

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Abstract: Optimal conditions for chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) catalyzed selective saturation of a double bond in the presence of a nitro function are developed. Aryl iodide and benzyl ether are also tolerated under these hydrogenation conditions.

The nitro group is certainly one of the most reducible functions in transition metal catalyzed hydrogenation process.[1] Therefore, selective saturation of an olefin in the presence of an aromatic nitro group is a demanding task and, indeed, very few general methods have been described in the literature. While selective reduction of a double bond in the presence of a nitro function with Baker's yeast[2] and metal hydride[3] have been reported,[4] their application seems to be limited to Michael acceptors. For the reduction of an isolated double bond without touching the nitro group, the diimide protocol[5] and hydrogenation catalyzed by homogeneous catalysts such as chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst)[6] have been reported by a number of groups and are well-recognized. However, to the best of our knowledge, no systematic studies have been carried out to determine the optimal conditions even with Wilkinson's catalyst and, indeed, reduction of aromatic nitro compounds to aniline derivatives under hydrogenation conditions has been documented.[7] In connection with our ongoing project, a process allowing selective saturation of an olefin in the presence of an aromatic nitro group was required (Scheme 1). Being unable to realize this transformation with various in situ generated diimide species,[8] we turned our attention to the Wilkinson's catalyst and observed a remarkable solvent effect, which constitutes the subject of the present note.

Scheme 1

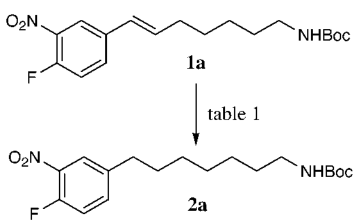

Table 1. Hydrogenation of Olefin (1a) Catalyzed by Wilkinson's Catalyst: A Survey of Reaction Conditions

entry	solvent	pressure/time	yield of **2a** (%)[a]
1	MeOH	1 atm/48 h	80
2	C_6H_6[b]	1 atm/48 h	0
3	C_6H_5Me[c]	1 atm/48 h	<20
4	C_6H_5Me	3 bar/48 h	<50
5	$MeOH/C_6H_6$[d]	1 atm/48 h	0
6	$MeOH/C_6H_5Me$[d]	1 atm/48 h	trace
7	$MeOH/C_6H_5Me$	3 bar/48 h	<50
8	THF	1 atm/7 h	91
9	^{t}BuOH−THF[e]	1 atm/5 h	95
10	MeOH−THF[e]	1 atm/48 h	93

[a] Isolated yield. [b] Benzene. [c] Toluene. [d] v/v = 2/1. [e] v/v = 1/1.

In the hydrogenation of olefins catalyzed by Wilkinson's catalyst, benzene, methanol, and a benzene−methanol mixture were the most frequently used reaction media.[9] To our surprise, however, the hydrogenation of **1a** in benzene at 1 atm led only to the recovered starting material after 48 h of stirring. Although selective saturation of olefin did occur in methanol, the long reaction time required (48 h) prompted us to investigate in detail the solvent effect on this transformation. As shown in Table 1, tetrahydrofuran (THF) turned out to be the solvent of choice (entry 8).[10] The addition of a protic cosolvent, notably the *tert*-butyl alcohol, accelerated further the reaction course (entry 9). Overall, under optimized conditions (4% Wilkinson's catalyst, 1/1 *tert*-BuOH−THF at rt, 1 atm), olefin **1a** was reduced within 5 h to provide

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(1) Rylander, P. N. *Catalytic Hydrogenation in Organic Syntheses*; Academic Press: New York, 1979; pp 114−137.

(2) Takeshita, M.; Yoshida, S.; Kohno, Y. *Heterocycles* **1994**, *37*, 553−562.

(3) (a) Aizpurua, J. M.; Oiarbide, M.; Palomo, C. *Tetrahedron Lett.* **1987**, *28*, 5365−5366. (b) Gupta, A.; Haque, A.; Vankar, Y. D. *J. Chem. Soc., Chem. Commun.* **1996**, 1653−1654.

(4) Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751−762.

(5) Pasto, D. J.; Taylor, R. T. In *Org. React.*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1991; Vol. 40, pp 91−155.

(6) (a) Birch, A. J.; Williamson, D. H. In *Org. React*; Dauben, W. G., Ed.; John Wiley & Sons: New York, 1976; Vol. 24, pp 1−186. (b) Burgess, K.; Van der Donk, W. A. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 2, pp 1253−1261.

(7) For examples, see: (a) Love, C. J.; McQuillin, F. J. *J. Chem. Soc., Perkin Trans. I* **1973**, 2509−2512. (b) Amer, I.; Bravdo, T.; Blum, J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1987**, *28*, 1321−1322.

(8) Following conditions allowing the in situ generation of diimide were examined: (a) $NH_2OH{\cdot}HCl$, KOH; (b) $PhIO(Ac)_2$, $NH_2NH_2{\cdot}H_2O$; (c) potassium azo dicarboxylate, AcOH.

(9) (a) Birch, A. J.; Walker, K. A. M. *J. Chem. Soc. C* **1966**, 1894−1896. (b) Harmon, R. E.; Parsons, J. L.; Cooke, D. W.; Gupta, S. K.; Schoolenberg, J. *J. Org. Chem.* **1969**, *34*, 3684−3685.

(10) Both THF and *tert*-butyl alcohol have been examined as hydrogen-donating solvents in transfer hydrogenation of olefins catalyzed by Wilkinson's catalyst (at high temperature in a sealed tube); see: Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Org. Chem.* **1975**, *40*, 237−240.

(11) (a) Biellmann, J. F.; Jung, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 1673−1674. (b) Augustine, R. L.; Van Peppen, J. F. *J. Chem. Soc., Chem. Commun.* **1970**, 495−496.

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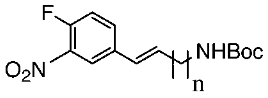
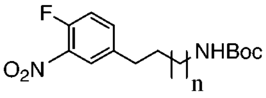
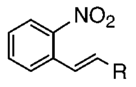
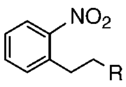
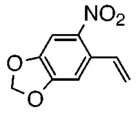
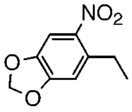
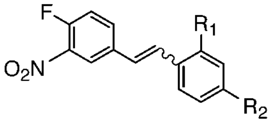
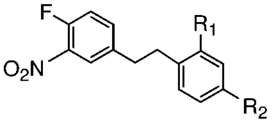
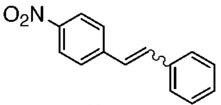
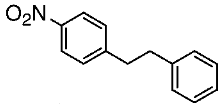
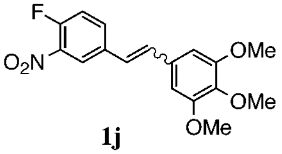
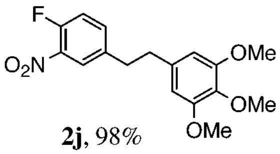
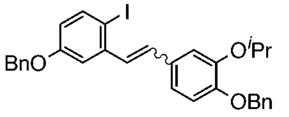
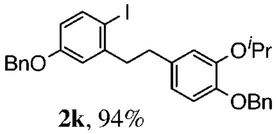
the desired saturated nitro aromatic alkane **2a** in 95% yield.

Table 2. Selective Hydrogenation: a Substrate Survey

Substrate	product/yield[a]
 **1a** n = 5 **1b** n = 7	 **2a** n = 5, 95% **2b** n = 7, 95%
 **1c** R = COOMe **1d** R = CH_2OH **1e** R = CH_2N_3	 **2c** R = COOMe, 82% **2d** R = CH_2OH, 80% **2e** R = CH_2N_3, 12%[b]
 **1f**	 **2f**, 80%
 **1g** $R_1 = NO_2$, R_2 = H **1h** R_1 = H, $R_2 = NO_2$	 **2g** $R_1 = NO_2$, R_2 = H, 89% **2h** R_1 = H, $R_2 = NO_2$, 84%
 **1i**	 **2i**, 82%
 **1j**	 **2j**, 98%
 **1k**	 **2k**, 94%

[a] Isolated yield. [b] Recovered starting material accounted for the mass balance.

The reaction conditions thus developed were found to be quite general and have been applied to the selective reduction of various substrates such as nitro-substituted cinnamates, allylic alcohols, styrenes, and stilbenes (Table 2). The benzyl ether and even aryl iodide (**1k**) were tolerated under these mild hydrogenation conditions. The yield was generally excellent except for the allyl azide (**1e**). In this case, the conversion is low due to probably the increased stability of the rhodium−olefin complex via the participation of the azide function.[6] As expected, it was observed that the reduction of *cis*-olefin is faster than the trans counterpart. Indeed, during the reduction of geometrically pure *cis*-**1k**, partial isomerization of *cis*-**1k** to *trans*-**1k** was observed when the reaction medium was not carefully degassed.[11]

In conclusion, we developed general conditions allowing selective hydrogenation of olefins in the presence of an aromatic nitro function. In view of the widespread use of the nitro group as an activating group and as a surrogate of other functional groups, such a selective reduction process should find applications in complex organic synthesis.

Experimental Section

General Procedure. To a solution of substrate **1** in degassed solvent (1/1 THF/*tert*-butyl alcohol, 0.14 M) and saturated by hydrogen was added 4% Wilkinson's catalyst. The solution was stirred under a hydrogen atmosphere at room temperature. When the hydrogenation was deemed complete by TLC, the reaction mixture was filtered through a short pad of alumina and washed thoroughly with diethyl ether. Purification by flash chromatography on silica gel provided the saturated nitro aromatic alkane **2** in excellent yield (Table 2).

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Supporting Information Available: Full characterization data for compounds **2a**−**k.** This material is available free of charge via the Internet at http://pubs.acs.org.

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