Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Selective Alkene Hydrogenation with Atomic Hydrogen Permeating Through a Pd Sheet Electrode

Shojiro Maki [a], Yasuhiro Harada [a], Takashi Hirano [a], Haruki Niwa [a], Yasuki Yoshida [b], Setsuro Ogata [b], Shuji Nakamatsu [b], Hiroshi Inoue [c] & Chiaki Iwakura [c]

[a] Department of Applied Physics and Chemistry, The University of Electro-communications, Chofu, Tokyo, 182-8585, Japan

[b] Permelec Electrode LTD, Endo, Fujisawa, Kanagawa, 252-0816

[c] Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Sakai, Osaka, 599-8531

To cite this article: Shojiro Maki, Yasuhiro Harada, Takashi Hirano, Haruki Niwa, Yasuki Yoshida, Setsuro Ogata, Shuji Nakamatsu, Hiroshi Inoue & Chiaki Iwakura (2000) Selective Alkene Hydrogenation with Atomic Hydrogen Permeating Through a Pd Sheet Electrode, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:19, 3575-3583, DOI: 10.1080/00397910008087273

To link to this article: http://dx.doi.org/10.1080/00397910008087273

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [Texas A & M International University] at 20:16 07 October 2014

SYNTHETIC COMMUNICATIONS, 30(19), 3575–3583 (2000)

SELECTIVE ALKENE HYDROGENATION WITH ATOMIC HYDROGEN PERMEATING THROUGH A Pd SHEET ELECTRODE

Shojiro Maki,[1)]* Yasuhiro Harada,[1)] Takashi Hirano,[1)] Haruki Niwa,[1)] Yasuki Yoshida,[2)] Setsuro Ogata[2)], Shuji Nakamatsu[2)], Hiroshi Inoue,[3)] Chiaki Iwakura[3)]

1) Department of Applied Physics and Chemistry, The University of Electro-communications, Chofu, Tokyo 182-8585, Japan
2) Permelec Electrode LTD. Endo, Fujisawa, Kanagawa 252-0816
3) Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531.

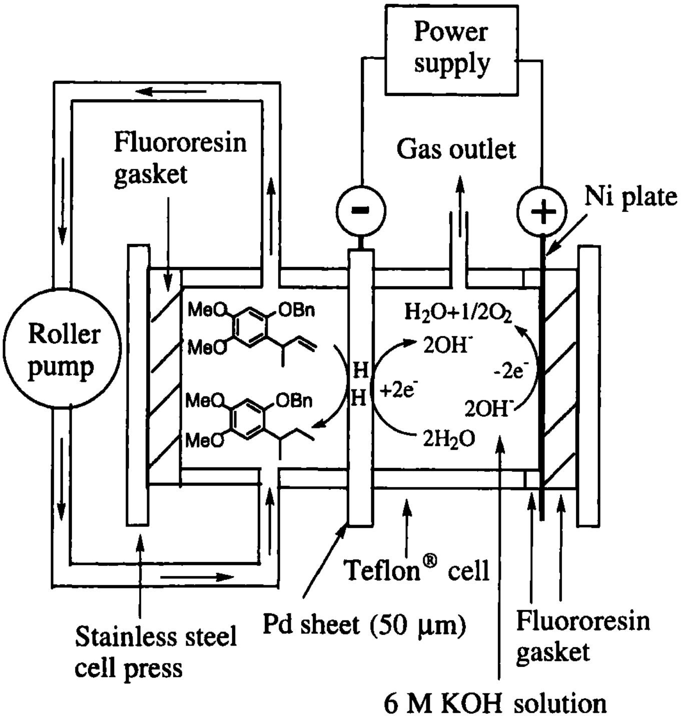
Abstract: Chemoselective hydrogenation of olefinic double bonds without concomitant hydrogenolysis of allylic and benzylic C-O linkages was performed successfully by the aid of active hydrogen permeated through a Pd sheet electrode.

Hydrogenation of an alkene is quite important for organic syntheses employing a catalyst (Pd, Ni, Pt) which chemisorbes active hydrogen[1]. However, hydrogenolysis[2] of allylic C-O bonds and benzyloxy groups (Bn-O-) also takes place under the same conditions. Therefore, it is difficult for alkenes having an allyloxy and/or benzyloxy group to be hydrogenated by active hydrogen without the hydrogenolysis. A new hydrogenation system utilizing

www.dekker.com

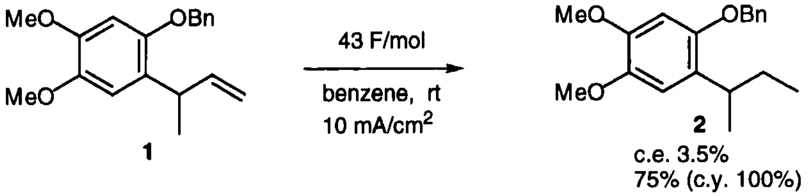
electrochemically produced active hydrogen has been successful in the saturation of several unsaturated organic compounds such as styrene and its derivates[3]. The reaction cell is made up of two compartments separated by a Pd sheet as a cathode, where galvanostatic electrolysis of water is carried out to produce the active hydrogen at one side of the Pd sheet, and a substrate is hydrogenated at the opposite side surface by active hydrogen permeating through the Pd sheet (Fig. 1).

Fig. 1



A typical reaction of an alkene bearing a benzyloxy group is shown in Scheme 1. The compound **1** was subjected to hydrogenation in benzene with a reaction concentration of 7.0 mM to give a selective reduction compound **2** in 75% yield (c.y. 100%) and a current efficiency (c.e.) of 3.5%.

Scheme 1

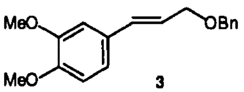
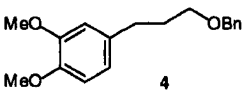
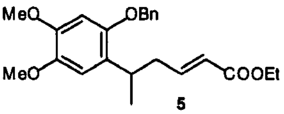
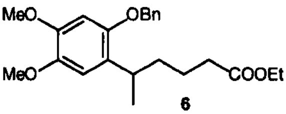
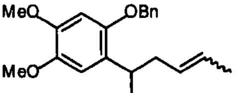
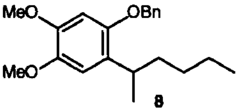
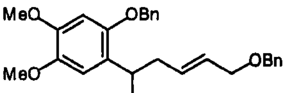
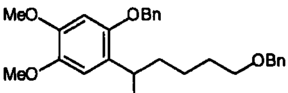
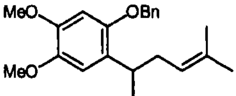
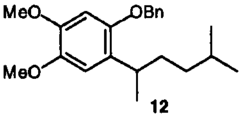
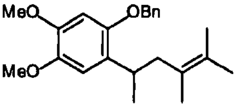
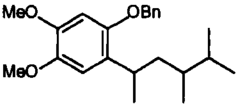
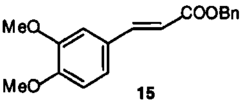
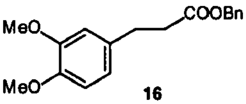
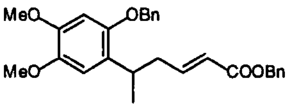
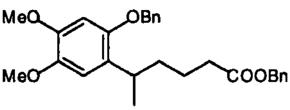
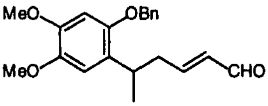
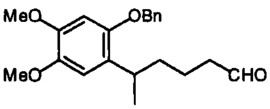


Some alkenes were subjected to hydrogenation in the same way to give corresponding hydrogenated products without hydrogenolysis in 100% conversion yields as summarized in Table 1.

The compound **3** bearing a styrylic olefin and an allylic benzyloxy group was selectively hydrogenated to give **4** in 20% yield (c.e. 3.6%). The α,β-unsaturated ester **5** was also converted into the saturated ester **6** in 46% yield (c.e. 3.4%). The disubstituted alkenes **7** and **9** were hydrogenated without hydrogenolysis in this condition to give **8** and **10** in 64% and 20% yields (c.e. 1.8% and 0.50%), respectively. The compound **11** including a trisubstituted olefin was subjected to hydrogenation, though it acquired a long reaction time, to give the corresponding product **12** in 70% yield (c.e. 0.46%). In the case of the tetrasubstituted alkene **13**, the reaction took place quite slowly to afford **14** in 8% yield (c.e. 0.02%) recovering the starting material (92%) passing through even 1600 F/mol. The benzyl esters[4] **15** and **17** were also converted into **16** and **18** in 46% and 12% yields (c.e. 4.4% and 0.89%), respectively. As a superior point, the aldehyde **19** was subjected to hydrogenation to give **20** in 13% yield (c.e. 0.48%). It is well known that Wilkinson's complex[5] is effective for hydrogenation[6] without hydrogenolysis, however, because of the accompanying deformylation[7], this method is difficult to apply to aldehydes. As shown in Scheme 2, although **19** was hydrogenated, deformylation took place, as well, to give **20** and **21** in 32% (c.y. 52%) and 28% (c.y. 38%) yields, respectively. In the cases of using EtOAc or benzene as the solvent, compound **19** was recovered.

Control reactions employing Pd-C as a catalyst are shown in Scheme 3. **1** was immediately reduced to the phenol **22** in 93% yield using MeOH as the solvent, however, in the case of using benzene, compound **1** was recovered in

Table 1. Hydrogenation of alkenes[a].

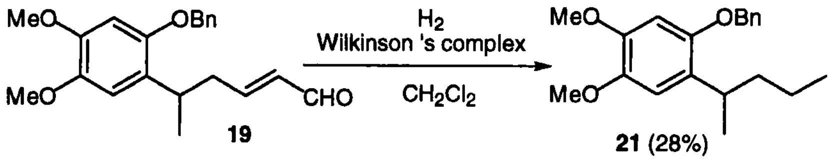
Entry	Substrate	F/mol	Products	Yields[b] (c.e.)(%)
1	 **3**	11	 **4**	20 (3.6)
2	 **5**	27	 **6**	46 (3.4)
3	 **7** Z/E=7/1	69	 **8**	64[c] (1.8)
4	 **9**	80	 **10**	20 (0.50)
5	 **11**	1600	 **12**	70 (0.46)
6	 **13**	1600	 **14**	8 (0.02)
7	 **15**	21	 **16**	46 (4.4)
8	 **17**	27	 **18**	12 (0.89)
9	 **19**	27	 **20**	13 (0.48)

a) The reaction concentration was standardized in 7.0 mM.

b) These conversion yields were 100% in all cases.

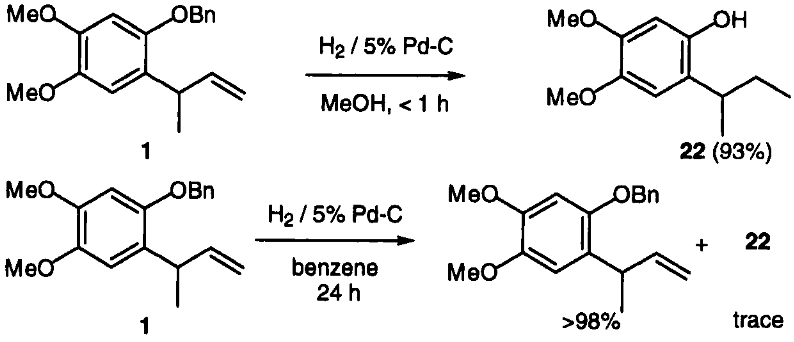
c) The geometrical isomer ratio of the recovered starting material was Z/E=3/1.

Scheme 2

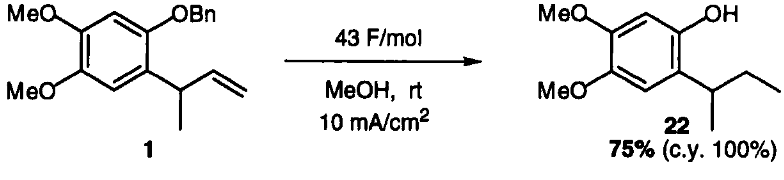


more than 98% yield. Even using the new hydrogenation system, when the MeOH was employed, **1** was converted into **22** in 75% yield (Scheme 4).

Scheme 3

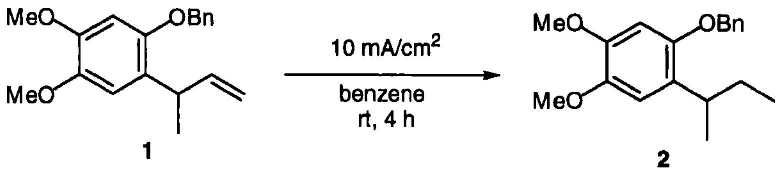


Scheme 4



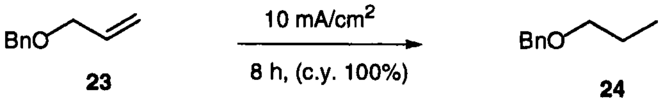
Where as this hydrogenation system achieves hydrogenation of an alkene without hydrogenolysis, the current efficiency is low. Accordingly, we investigated the effect of reaction concentration for current efficiency employing **1** and allyl benzyl ether (**23**) as substrates. The results were summarized in Table 2 and 3. The current efficiencies were increased depending on the reaction concentration rising. As shown an entry 6 in the Table 2, the reaction was almost completed at 6.3 F/mol which is calculated from the current efficiency of entry 5 in Table 2.

Table 2. Effect of reactant concentration for current efficiency.



entry	mol/l	**1** (%)	**2** (%)	F/mol	c.e. (%)
1	0.007	50	50	21	4.8
2	0.014	40	60	11	11
3	0.035	60	40	4.4	18
4	0.070	47	53	2.2	24
5	0.350	93	7	0.44	32
6	0.350	0	100	21	9.5
7	0.350	<2	>98	6.3	32

Table 3. Effect of reactant concentration for current efficiency.



entry	mol/l	**23** (%)	**24** (%)	F/mol	c.e. (%)
1	0.007	42	58	43	2.7
2	0.035	17	83	8.5	20
3	0.35	72	28	0.85	33
4	3.5	95	5	0.085	100
5	7.0 (neat)	95	5	0.085	100

In the case of the simple compound **23**, when the reaction concentration was 3.5 M, the current efficiency was achieved 100% (entry 4 in Table 3). It was remarkable that the selective reduction was carried out even under neat conditions to give **24** (entry 5). This indicated that the new hydrogenation system has applications for large scale synthesis. In addition, the Pd sheet has with stood long practical experiments using more than 1000 hours already. The endurance test of the Pd sheet applying practical hydrogenation is in progress.

Experimental Section

Pretreatment of a Pd Sheet Electrode: For the purpose of arrangement Pd atoms, removing residual internal stress in the Pd sheet and removing surface oxides, the Pd sheet was heated by a gas burner until red. For the palladization, an aqueous solution of 6 M KOH was put in the compartment having a Ni sheet anode and then, an aqueous solution of 1 M HCl 2.8×10^{-2} M $PdCl_2$ was filled into the other compartment for the deposition of Pd black. The palladization was carried out using atomic hydrogen, which was produced with galvanostatic electrolysis at various current densities for different periods. During the palladization, a $PdCl_2$ solution was circulated with a roller pump or a magnetic stirrer. The amount of the deposit, determined from the weight gain after each deposition, was 4.5 mg cm^{-2}. The prepared Pd/Pd black electrode was rinsed with distilled water and then dried with Ar gas.

Conditions of Hydrogenation: Alkenes including a benzyloxy group were hydrogenated as shown in Fig. 1. During the reaction, the substrates were circulated at a rate of 2.4 cm^3 min^{-1} with a roller pump (Furue Science, RP-NE). The hydrogenation reactions were conducted using galvanostatic electrolysis at 10 mA cm^{-2} at room temperature. IR spectra were taken on a JASCO IR-810 spectrometer. ^1H NMR spectra were recorded on the JEOL Lambda-270 (270 MHz) spectrometer: Chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane in $CDCl_3$, and coupling constants are reported in Hz. ^{13}C NMR spectra were recorded on a JEOL Lambda-270 (67.5 MHz) spectrometer. Low-resolution mass spectra (EIMS) were measured on a JEOL JMS-600H instrument with an ionization potential of 70 eV. High-resolution mass spectra (HREIMS) were measured on a HITACHI M80-B instrument.

1: IR (neat) 1510, 1610 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.30 (3 H, d, *J* = 7.0 Hz), 3.82 (6 H, s), 4.09 (1 H, dq, *J* = 7.0, 11.0 Hz), 4.91-5.15 (2 H, complex), 5.03 (2 H, s), 6.57 (1 H, s), 6.71 (1 H, s), 7.29-7.45 (5H, complex); HREIMS: found *m/z* 298.1560 (M$^+$); calcd for $C_{19}H_{22}O_3$ 298.1569.

2: IR (neat) 1510, 1615 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (3 H, t, *J* = 7.6 Hz), 1.18 (3 H, d, *J* = 6.9 Hz), 1.51-1.63 (2 H, complex), 3.13 (1 H, tq, *J* = 7.2, 6.9 Hz), 3.83 (3H, s), 3.85 (3 H, s), 5.02 (2 H, s), 6.51 (1 H, s), 6.72 (1H, s), 7.31-7.44 (5 H, complex); ^{13}C NMR (68.7 MHz, $CDCl_3$) δ 12.18 (q), 20.87 (q), 30.14 (t), 33.21 (d), 55.98 (q), 56.53 (q), 71.74 (t), 98.81 (d), 110.94 (d), 127.18 (d), 127.65 (d), 128.30 (s), 128.38 (d), 137.55 (s), 143.47 (s), 147.08 (s), 150.12 (s); HREIMS: found *m/z* 300.1728 (M$^+$); calcd for $C_{19}H_{24}O_3$ 300.1725.

21: IR (neat) 1500, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3 H, t, *J* = 7.3 Hz), 1.21 (3 H, d, *J* = 7.0 Hz), 1.21-1.38 (2 H, complex), 1.47-1.73 (2 H, complex), 3.26 (1 H, tq, *J* = 7.2, 7.0 Hz) 3.86 (3 H, s), 3.89 (3 H, s), 5.01 (2 H, s), 6.60 (1 H, s), 6.76 (1 H, s), 7.33-7.48 (5 H, complex); HREIMS: found *m/z* 314.1888 (M$^+$); calcd for $C_{20}H_{26}O_3$ 314.1882.

22: IR (neat) 1520, 1610, 3380 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (3 H, t, *J* = 7.5 Hz), 1.22 (3 H, d, *J* = 6.6 Hz), 1.60 (2 H, quin, *J* = 7.5 Hz), 2.84 (1 H, tq, *J* = 6.6, 7.5 Hz), 3.81 (3 H, s), 3.83 (3 H, s), 4.52 (1 H, br. s, OH), 6.41 (1 H, s), 6.66 (1 H, s); HREIMS: found *m/z* 210.1254 (M$^+$); calcd for $C_{12}H_{18}O_3$ 210.1256.

References

[1] Newham, J.; *Chem. Rev.*, **1963**, *63*, 123.

[2] (a) Fletcher, H. G.; *Methods Carbohydr. Chem.*, **1963**, *II*, 166. (b)

Bindra, J. S.; Grodski, A.; *J. Org. Chem.*, **1978**, *43*, 3240. (c) House, H. O.; "Modern Synthetic Reactions", W. A. Benjamin, Inc., **1972**, 23-26.

[3] (a) C. Iwakura, T. Abe and H. Inoue, *J. Electrochem. Soc.*, **1996**, *143*, L71. (b) H. Inoue, T. Abe and C. Iwakura, *J. Chem. Soc., Chem. Commun.*, **1996**, 55. (c) Yoshida, Y.; Ogata, S.; Nakamatsu, S.; Shimamune, T.; Inoue, H.; Iwakura, C.; *J. Electroanal. Chem.*, **1998**, *444*, 203-207. (d) Inoue, H.; Yoshida, Y.; Ogata, S.; Shimamune, T.; Inoue, H.; Iwakura, C.; *J. Electrochem. Soc.*, **1998**, *145*, 138-141.

[4] Nicolau, K. C.; Yue, E. W.; La Greca, S.; Nadin, .; Yang, Z.; Leresche, J. E.; Tsuri, T.; Naniwa, Y.; De Riccardis, F.; *Chem. Eur. J.*, **1995**, *1, No. 7*, 467-494.

[5] (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G.; *J. Chem. Soc.*, **1966**, 1711. (b) Birch, A. J.; Williamson, D. H.; *Org. React.*, **1976**, *24*, 1.

[6] Ireland, R. E.; Bey, P.; *Org. Synth., Coll.*, **1988**, *Vol. 6*, 459.

[7] (a) Tsuji, J.; Ohno, K.; *Synthesis*, **1969**, 157. (b) Ohno, K.; Tsuji, J.; *J. Am. Chem. Soc.*, **1968**, *90*, 99. (c) Walborsky, H. M.; Allen, L. E.; *J. Am. Chem. Soc.*, **1971**, *93*, 5465. (d) Iley, D. E.; Fraser-Raeid, B.; *J. Am. Chem. Soc.*, **1975**, *97*, 2563.

Received in Japan 10/4/99