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LETTERS

Efficient Semihydrogenation of the C-C Triple Bond Using Palladium on Pumice as Catalyst

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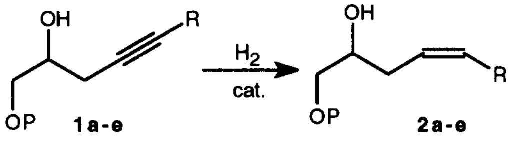
***Abstract*:** An efficient semihydrogenation of C-C triple bonds was achieved using palladium on pumice as the catalyst with a metal loading of 3% wt. The results obtained showed better selectivity when compared with Pd/C and better activity when compared with Lindlar's catalyst. Hydrogenation of sterically hindered alkynes is slow on Pd/pumice. The selectivity with respect to alkenes is probably due to the presence of sodium ions in the pumice structure that increases the electron density on the supported metal. © 1999 Elsevier Science Ltd. All rights reserved.

The semihydrogenation of carbon-carbon triple bonds is a particularly valuable and frequently used application of heterogeneous catalysis in synthetic chemistry.[1] The hydrogenation of an alkyne can be virtually stopped at the semihydrogenation stage because the alkyne is more strongly bound than the alkene, and competes effectively for the catalytic sites, blocking re-adsorption of the alkene, or displacing it. Moreover, high selectivity can be achieved by adding to the reaction mixture a nitrogen base, such as quinoline, pyridine or ethylenediamine, that is reversibly adsorbed onto the catalyst in competition with the alkyne and the product alkene.[1,2]

Because the semihydrogenation reaction is a powerful tool in synthetic organic chemistry, we considered it worth developing a new catalyst for such reactions. As a part of an ongoing investigation into the preparation of *cis*-homoallylic alcohols as starting materials for the stereoselective synthesis of tetrahydrofurans,[3] we studied the selective synthesis of *cis*-alkenes by hydrogenation of an alkyne using palladium on pumice with a metal loading of 3% wt as catalyst,[4] avoiding the use of a nitrogen base.



1a : P = TBDMS, R = CH_2CH_2OBn
1b : P = TBDMS, R = CH_2OBn
1c : P = 4-Me-C_6H_4-SO_2, R = C_5H_{11}
1d : P = 4-Me-C_6H_4-SO_2, R = $C(CH_3)_3$
1e : P = 4-Me-C_6H_4-SO_2, R = $Si(CH_3)_3$

The substrates **1a-e** were prepared by reaction of the protected glycidol with the appropriate alkyne in the presence of BuLi/ $BF_3{\cdot}Et_2O$. Stirring a suspension in absolute ethanol of the hydroxyalkyne **1a-e** (typically 0.023 M) and palladium on pumice (molar ratio alkyne/Pd = 55) at 25 °C with a flow of hydrogen of 1.0 or 0.2 nL/min (pressure 1 atm) provided the *cis*-homoallylic alcohols **2a-e** after filtration through Celite, concentration and flash column chromatography.[5] All the reactions were monitored by HPLC *via* recording the disappearance of the alkyne and the formation of the *cis*-homoallylic alcohols[6] and the saturated alcohols. The results were compared with hydrogenation reactions performed using Pd/C (10%) or the Lindlar's catalyst (5%) as catalyst.

The data obtained are shown in table together with the reaction times and selectivities at 99% conversion of the alkyne.

These data show that the Pd/C and Pd/pumice catalysts effect similar rates except for compounds **1d,e** where R is a bulky group. However the Pd/pumice provides better selectivities as compared to Pd/C in all cases examined. Although Lindlar's catalyst shows good selectivities, the reactions proceed at much slower rates.

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Table - Reaction times and selectivities for the hydrogenation of **1a-e** with Pd/pumice, Lindlar's catalyst and Pd/C.

		Pd/pumice 3%		Lindlar 5%		Pd/C 10%	
entry	Compd.	t(min)	selectivity	t(min)	selectivity	t(min)	selectivity
1	**1a**	7	90%	240	94%^{a}	5	72%
2	**1a**	30	93%^{b}			7	80%
3	**1b**	30	93%^{b}				
4	**1c**	30	94%	400	41%^{c}	20	66%
5	**1d**	400	91%	300	48%^{d}	20	87%
6	**1e**	150	60%	400	68%^{e}	20	13%

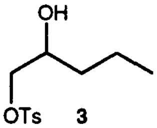
a: conv. 94 %; b: flow 0.2 nL/min; c: conv. 45 %; d: conv. 51 %; e: conv. 86 %

Furthermore with Pd/C, the hydrogenation is not easy to control because the hydrogenation of the initially formed *cis*-homoallylic alcohol soon starts. In fact, after 15 minutes, compound **2a** disappeared giving the corresponding saturated alcohol (75%) and its debenzylated derivative (25%). Similar behavior was found with Pd/pumice for compound **1a** (entry 1), but after 15 minutes compound **2a** was still present (85%) with only 15% of the saturated alcohol. The complete disappearance of the *cis*-homoallylic alcohols **2a** was observed after 160 minutes giving a lower amount of the debenzylated alcohol (10%). Compound **1b** gave an identical result.

The Pd/pumice catalyst may be useful in hydrogenation of benzylated *cis*-homoallylic alcohols to the corresponding saturated alcohols causing, in comparison with the Pd/C, less debenzylation.

With Pd/pumice, using a lower flow of H_2 (entries 2, 3), the hydrogenation of the initially formed alkene became very slow, allowing efficient control of the semihydrogenation reaction and better selectivity. In fact, after 110 minutes, we still found a very high amount of *cis*-homoallylic alcohols **2a,b** (91%). For compounds **1c** (entry 4) the hydrogenation of the C-C double bond was slow also with a higher flow of H_2 (1.0 nL/min). With Pd/C, using a lower flow of H_2 (entry 2) an improvement of the selectivity was found, but the reaction still showed poor control because the initially formed alkene was quickly hydrogenated.

For compound **1e** (entry 6) low selectivity was found with the three catalysts; this is mainly due to the formation of a side product that was identified as the desilylated alcohol **3**, in addition to the corresponding alcohol.



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The performance of the Pd/pumice catalyst in alkyne hydrogenation and the selectivity with respect to alkenes is probably due to the presence of sodium ions in the pumice structure that increase the electron density on the supported metal.[7] Indeed, the adsorption of the alkene onto the metal becomes progressively lower as the electron density on the metal increases. Moreover, the low specific surface area (5 m^2/g)[8] of pumice determines the growth of large metal particles, producing few neighbouring catalytic sites. This could be the reason of the slow hydrogenation process of a bulky substrate on a Pd/pumice catalyst.

In conclusion we believe that Pd/pumice is an interesting catalyst and efforts to develop other synthetic applications are in progress.

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5. *Typical procedure* : Compounds 1 (0.46 mmol) in absolute ethanol (20 mL) were stirred with Pd/pumice (30 mg) or Pd/C (9 mg) or Lindlar's catalyst (18 mg) for the time indicated in the table. The reactions were performed in a three necked glass reactor with jacket. The reactor was connected to a line operating at a constant atmospheric pressure of H_2 by using the first two necks. The last neck, closed by a silicone septum, allowed withdrawing of samples for HPLC analysis. The suspension was magnetically stirred.The constant temperature (25.0±0.1°C) was ensured by a thermostat.
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