Published in final edited form as:

Tetrahedron Lett. 1998 February 26; 39(9): 947–948. doi:10.1016/S0040-4039(97)10666-9.

CHEMOSELECTIVE CATALYTIC HYDROGENATION OF ALKENES BY LINDLAR CATALYST

Arun K. Ghosh and K. Krishnan

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607.

Abstract

Commercially available Lindlar catalyst (10% by weight) in methanol, selectively hydrogenates various alkenes in the presence of benzyl ether and benzyl amine functionalities.

Graphical Abstract

While numerous methods are available in the literature for the reduction of alkynes and alkenes using a variety of catalysts, selective reduction of an alkene in the presence of benzyl ether and benzylamine functionalities has not been fully addressed.¹ Selective reduction of an alkene was previously accomplished in the presence of a benzyl ether by a catalytic hydrogenation over 5% Rh-Al₂O₃^{2a}. Also, selective cleavage of benzyl ether in the presence of an olefin was carried out using hydrogenation over 5% Pd-C.^{2b} There are few known reports in the literature where reduction of a double bond or the cleavage a Cbz-group was achieved selectively in the presence of a benzyl ether by hydrogenation over 5% Pd-C and 5% butyl amine or ammonia.³ During the course of our studies towards synthesis of high affinity nonpeptidal ligands for the HIV-protease substrate binding site, we required a selective method for the conversion of dihydropyranone 1 to tetrahydropyranone 3. Attempted selective hydrogenation of 1 using 5% Pd-C or 5% Rh-Al₂O₃ catalyst was unsuccessful. However, catalytic hydrogenation of dihydropyranone 1 was carried out smoothly using Lindlar catalyst (Pd/CaCO₃, PbO) in the absence of quinoline for 12 h to provide tetrahydropyranone 3 in 96% isolated yield. While Lindlar catalyst has been widely used for selective reduction of alkynes to alkenes⁴, its potential for selective olefin hydrogenation has not found precedent until recently.⁵ Herein, we report the chemoselective hydrogenation of a variety of olefins by commercially available (Aldrich) Lindlar catalyst in methanol.

To ascertain the generality of this selective reduction procedure, we applied it in several olefinic systems and found that this transformation is general to mono or di- or tri-substituted olefins. As shown in Table I, the reaction conditions are compatible to the presence of a benzyl ether (entries 1, 2 and 5), the benzyl amine (entries 3 and 4) functionality or substituted benzyl alcohol (entry 6).⁶ However, a Cbz-protecting group does

not survive under these conditions. In conclusion, this method should find broad application in organic synthesis.

Acknowledgments

Financial support of this work by the National Institute of Health (GM-53386) is gratefully acknowledged.

References and Notes:

1. (a) For monographs on reductions, see; Hudlicky T. Reductions in Organic Chemistry, Wiley Interscience, New York, 1984; (b) Augustine L Ed. Reduction, Marcel Dekkar, New York, 1968.
2. (a) Bindra J Grodski A J. org. Chem 1978, 16, 3240; (b) Caine D; Smith TL, Jr. J. Am. Chem. soc, 1980, 102, 7570,
3. (a) Czech B Bartsch AR. J. org. Chem 1984, 49, 4076; (b) Saiki HTetrahedron Lett. 1995, 36, 3465.
4. March J Advanced Organic Chemistry, Fourth edition, Wiley Interscience 1992.
5. For a recent method for hydrogenation of an ene-ester in the presence of a benzyl groups and a sterically hindered N-Bn group, see, Shi Y; Peng LF; Kishi Y. J. Org. Chem 1997, 62, 5666.
6. In a typical procedure, a mixture of olefin (1 mmol) and Lindlar catalyst (10% by wt) in methanol (10 mL) was stirred under a hydrogen filled balloon or on a Parr apparatus under 20 psig for few hours. After this period, the mixture was filtered through a pad of celite, the solvent was evaporated and the residue was passed through a short silica gel column (50% ethyl acetate/hexane) to give the title hydrogenation product.

Table I.

Chemoselective reduction of various olefins with Lindlar catalyst

Entry	Substrate	Time (method) ^a	Product	Yield%
1.		2 h (A)		96
2.		2h(A)		98
3.		50 min (B)		97
4.		45 min (B)		95
5.		40 min (B)		98
6.		2.5 h(A)		96

^aMethod A: using a Parr hydrogenation apparatus; Method B: using a hydrogen filled balloon