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CHEMOSELECTIVE CATALYTIC HYDROGENATION OF ALKENES BY LINDLAR CATALYST

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

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-Al_2O_3.[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-Al_2O_3 catalyst was unsuccessful. However, catalytic hydrogenation of dihydropyranone **1** was carried out smoothly using Lindlar catalyst ($Pd/CaCO_3$, 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 alkenes,[4] 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.

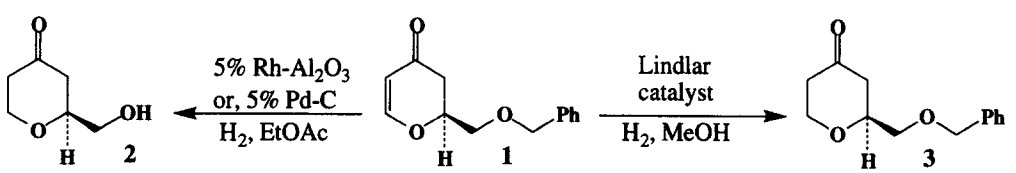

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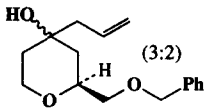
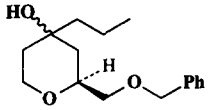
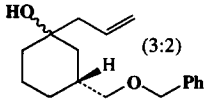
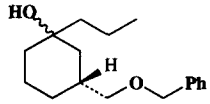
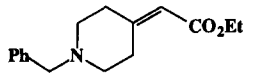
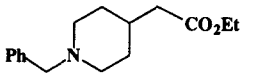
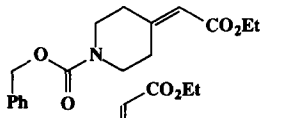
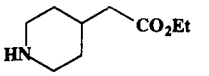
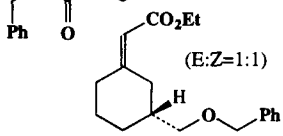
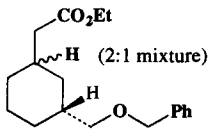
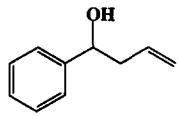
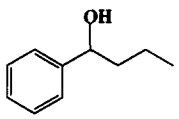
Table I. Chemoselective reduction of various olefins with Lindlar catalyst

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

[a]Method A: using a Parr hydrogenation apparatus; Method B: using a hydrogen filled balloon

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.

References and Notes:

1. For monographs on reductions, see; (a) Hudlicky, T. *Reductions in Organic Chemistry*, Wiley Interscience, New York, **1984**; (b) Augustine, L. R.; Ed. *Reduction*, Marcel Dekkar, New York, **1968**.
2. (a) Bindra, J. S.; Grodski, A. *J. Org. Chem.* **1978**, *16*, 3240; (b) Caine, D.; Smith, Jr. T. L. *J. Am. Chem. Soc.*, **1980**, *102*, 7570.
3. (a) Czech, B. P.; Bartsch, A. R. *J. Org. Chem.* **1984**, *49*, 4076; (b) Saiki, H. *Tetrahedron 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, L. F.; 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.

7. Financial support of this work by the National Institute of Health (GM53386) is gratefully acknowledged.