



## Digest paper

## Advances in chemoselective and/or stereoselective semihydrogenation of alkynes



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## ABSTRACT

The chemoselective semihydrogenation of alkynes is one of the most important reactions in synthetic organic chemistry. During the last decade or so, a multitude of innovative catalytic methods have been developed to address the selective hydrogenation of alkynes. This digest focuses on the recent developments in chemoselective semihydrogenation of alkynes to alkenes.

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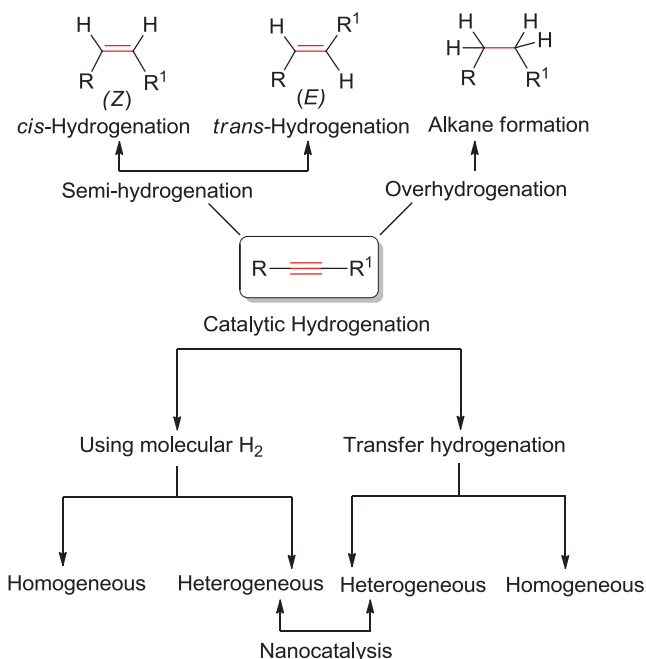
## Introduction

Chemo- and stereo-selective hydrogenation of alkynes leading to the preferential formation of *cis*- or *trans*-alkenes, by avoiding over-hydrogenation or reduction of other functional groups, is an important reaction that can be achieved by using either a homogeneous or a heterogeneous catalyst.<sup>1</sup> Stereoselective semihydrogenation of internal alkynes to valuable (*Z*)-alkenes is a key step

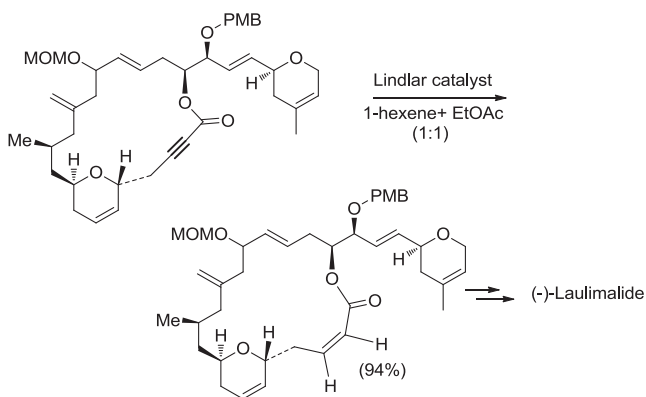
in the synthesis of vitamins and natural products and is also a relevant industrial reaction with applications in fields like polymerization.<sup>2</sup> This reduction can be accomplished *via* catalytic approaches either by using H<sub>2</sub> gas or *via* transfer hydrogenating agents.<sup>3</sup> The best known or 'benchmark' Lindlar catalyst, which is 5–10 wt% Pd deposited on BaSO<sub>4</sub> or CaCO<sub>3</sub> and "poisoned" with a lead co-catalyst (lead acetate or lead oxide) and quinoline in order to decrease its catalytic activity so that the reaction can be intercepted at the alkene stage, is extensively utilized for the selective hydrogenation of alkynes to (*Z*)-alkenes.<sup>3,4</sup> Despite the widespread use, it has several limitations (*vide infra*) and hence new

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**Scheme 1.** Major facets of alkyne hydrogenation.



**Scheme 2.** Synthesis of the natural product (-)-laulimalide using Lindlar catalyst.

catalytic routes are being explored extensively. The transfer hydrogenation also has become popular during the last few years due to better chemo- and stereo-selectivities of the desired products. Over-hydrogenation to alkanes is undesirable in most cases and hence proper catalytic modifications are required to alleviate this problem. In multifunctional molecules, functional group tolerance may also become a major issue. This digest delves on the recent advances in the chemoselective hydrogenation of alkynes to alkenes. The essential topics are highlighted in [Scheme 1](#). We focus primarily on the developments during the last decade, although reference to other articles prior to this are mentioned where

deemed appropriate. We shall first consider hydrogenation using molecular  $H_2$  and then look into transfer hydrogenation.

## Hydrogenation using molecular hydrogen ( $H_2$ )

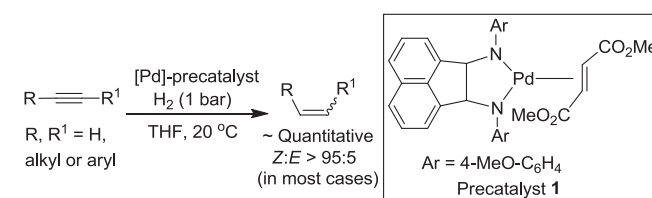
### (Z)-Selective semihydrogenation of alkynes using molecular $H_2$

As mentioned above, hydrogenation by Lindlar catalyst is probably the most facile procedure for obtaining (Z)-alkenes under reasonably mild conditions. It is also commercially available and does not require inert atmosphere. The general reactivity order is diynes > enynes > alkynes > alkenes. An example of its use in the synthesis of natural product (-)-laulimalide is given in [Scheme 2](#).<sup>5</sup> The two hydrogens are most likely delivered suprafacially to the  $\pi$ -system of the alkyne by a sequence of hydrometallation/reductive elimination steps. The perceived disadvantages of this catalyst include (i) isomerization of (Z)-alkene to (E)-alkene, (ii) poor reproducibility from batch to batch ('batch variability'), (iii) safe handling ( $H_2$ ) requirement, (iv) possible over-reduction to alkanes particularly in cases where terminal alkynes are involved, (v) double bond migration and (vi) toxicity of Pb/quinoline waste products.

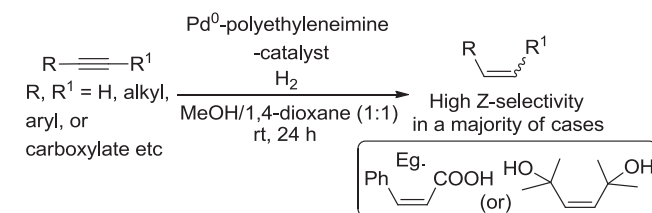
Another useful example using Lindlar catalyst is the Z-selective semi-hydrogenation of ynamides that leads to the formation of enamides. Dichloromethane was used as the solvent ([Scheme 3](#)).<sup>6</sup> In some cases, the authors have also used ethyl acetate as the solvent. In one instance, they succeeded in getting the E-isomer preferentially by using Dibal-H in dichloromethane medium; while Lindlar catalyst in EtOAc afforded the Z-isomer.

Elsevier and co-workers demonstrated the chemo- and stereo-selective hydrogenation of alkynes to (Z)-alkenes in the presence of the homogeneous [Pd]-precatalyst **1** ([Scheme 4](#)).<sup>7</sup> Functional groups such as ester, carboxylic acid and nitro were well-tolerated and in many cases, authors reported that the system worked better than the Lindlar catalyst. In the reaction pathway, it was assumed that the alkyne would first displace fumarate in the pre-catalyst which then would undergo suprafacial hydrogenation. A second alkyne would then release this *cis*-alkene and the cycle is repeated.

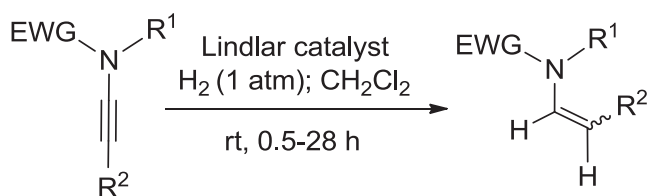
Sajiki et al. utilized a novel 5% Pd<sup>0</sup>-polyethyleneimine catalyst, prepared earlier by Meyers and Royer,<sup>8</sup> for the partial hydrogenation of alkynes to obtain *cis*-alkenes ([Scheme 5](#)).<sup>9</sup> This Pd<sup>0</sup>-PEI-catalyst offered a variety of functionalized alkenes without affecting the other reducible functionalities like COOH, N-Cbz, O-TBS and



**Scheme 4.** *cis*-Hydrogenation using a [Pd]-precatalyst **1**.



**Scheme 5.** (Z)-selective hydrogenation using a Pd<sup>0</sup>-polyethyleneimine catalyst.



**Scheme 3.** Formation of (Z)-enamides from ynamides using Lindlar catalyst.

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