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[Lab. of Medicinal Chemistry]

**Easy and Partial Hydrogenation of Aromatic Carbonyls to Benzyl Alcohols
Using Pd/C(en)-Catalyst.**

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The preparation of the alcohol from the corresponding carbonyl compound is normally accomplished by stoichiometric metal hydride reagents or catalytic homogenous hydrogenations using Rh or Ru complexes. However, few widely acceptable heterogeneous hydrogenation methods for aromatic aldehydes or ketones to corresponding alcohols have been developed. Although the heterogeneous hydrogenation of aliphatic carbonyls does not occur easily as a rule, aromatic carbonyls hydrogenolyze to methylene compounds smoothly *via* formation of the intermediary benzyl alcohol. Therefore, it is extremely difficult to isolate the intermediary benzyl alcohol selectively when hydrogenating aromatic carbonyl compounds using a palladium catalyst. The present study describes a mild and neutral technique using an easily handled, and heterogeneous Pd/C-ethylenediamine complex [Pd/C(en)] catalyst has been developed for the efficient chemoselective hydrogenation method of aromatic carbonyl groups to benzyl alcohols.

[*Tetrahedron Lett.*, **39**, 7127-7130 (1998)]

[Lab. of Medicinal Chemistry]

**Suppression Effect of the Pd/C-Catalyzed Hydrogenolysis of a Phenolic
Benzyl Protective Group by the Addition of Nitrogen-containing Bases.**

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A mild and chemoselective hydrogenation method using 5% Pd/C for olefin, *N*-Cbz, benzyl ester and nitro functionalities distinguishing from the benzyl protective group for the phenolic hydroxyl group has been developed by the employment of 2,2'-dipyridyl as an additive. The suppressive effect on the benzyl ether hydrogenolysis was strongly influenced by the sorts of nitrogen-containing bases employed as an additive.

[*J. Org. Chem.*, **63**, 7990-7992 (1998)]

[Lab. of Medicinal Chemistry]

**The Formation of a Novel Pd/C-Ethylenediamine Complex Catalyst:
Chemoselective Hydrogenation without Deprotection of the *O*-Benzyl
and *N*-Cbz Groups.**

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A Pd/C catalyst formed an isolable complex with ethylenediamine employed as the catalytic poison *via* one-to-one interaction between Pd metal and ethylenediamine and its complex catalyst [Pd/C(en)] chemoselectively hydrogenated a variety of reducible functionalities such as olefin, acetylene, nitro, benzyl ester, and azido distinguishing *O*-benzyl or *N*-Cbz protective group. These findings reinforce the potential of an *O*-benzyl and *N*-Cbz groups as a protective group in the organic synthesis and the Pd/C(en) catalyst has been identified as a novel and chemoselective catalyst for the hydrogenation.

[*Tetrahedron.*, **54**, 13981-13996 (1998)]

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**Novel Type of Pd/C-Catalyzed Hydrogenation Using a Catalyst Poison:
Chemoselective Inhibition of the Hydrogenolysis for *O*-Benzyl
Protective Group by the Addition of a Nitrogen-containing Base.**

Hironao SAJIKI and Kosaku HIROTA*

A mild and chemoselective hydrogenation method for a variety of reducible functional groups distinguishing from aliphatic and aromatic benzyl ethers was accomplished by the addition of an appropriate nitrogen-containing base to the Pd/C-catalyzed hydrogenation system. Especially, by using of Pd/C-2,2'-dipyridyl combination as a catalyst for the hydrogenation, the aliphatic and the phenolic *O*-benzyl protective groups can be retained without any hydrogenolysis. These methods would increase the utility of the *O*-benzyl protective group in organic synthesis. Moreover, the simplicity of this method makes it an attractive new tool to organic chemist.