

Urushibara Nickel¹



[7440-02-0]

Ni

(MW 58.69)

InChI = 1/Ni

InChIKey = PXHVJJICTQNCMI-UHFFFAOYAH

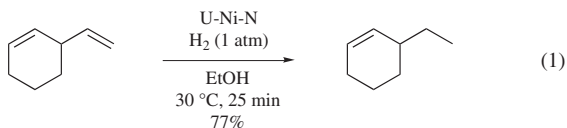
(precipitated metal hydrogenation catalyst; useful principally in reduction of alkynes and alkenes to alkanes,² reduction of carbonyls to alcohols,³ dehydrogenations,¹ and reductive desulfurizations¹)

Preparative Methods: Urushibara catalysts are prepared by acid (U-Ni-A), base (U-Ni-B), or neutral (U-Ni-N) digestion of precipitated nickel. Similar catalysts can be prepared using either iron or cobalt.¹

Handling, Storage, and Precautions: Urushibara catalysts do not appear to degrade upon short exposure to air.⁴ Protection from moisture is required for long-term storage.

Urushibara Catalysts. The Urushibara catalysts are a family of precipitated metal catalysts that have been compared to the more common **Raney Nickel** catalysts. Although the two can catalyze many of the same reactions, Urushibara metals offer several advantages: they are nonpyrophoric, are easily generated, have a long shelf life, and can catalyze highly regio- and stereoselective reductions.

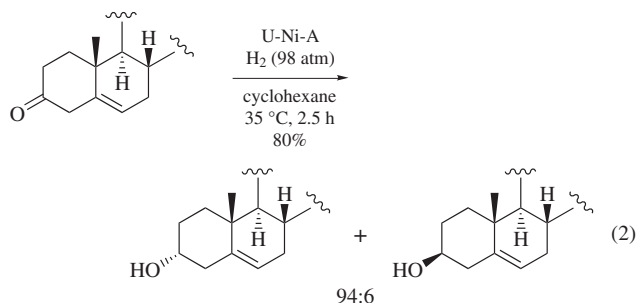
Catalytic Hydrogenation of Alkynes and Alkenes. Alkenes and alkynes can be reduced to the corresponding alkanes using moderate to high pressures of H₂ and temperatures. In eq 1, the exocyclic alkene is hydrogenated selectively with the use of U-Ni-N. Longer hydrogenation times and use of other Urushibara catalysts result in complete reduction of this substrate. The use of Raney nickel in this example results in nonspecific reduction.² Aromatic rings can also be saturated; however, these reactions only proceed at high temperature or under pressure.¹



Catalytic Hydrogenation of Carbonyl Compounds. Ketones and aldehydes can be reduced to their respective alcohols using Urushibara catalysts with hydrogen at atmospheric pressure and room temperature. eq 2 demonstrates the regio- and stereoselectivity that can be obtained using Urushibara catalysts.³

Use of Raney nickel results in an equimolar mixture of the two stereoisomers. Hydrogenolysis of the resulting C–O bond can occur with aryl-substituted compounds, giving the corresponding hydrocarbons.¹

Dehydrogenations. Urushibara catalysts have been used as dehydrogenation catalysts. Numerous examples exist with steroidal compounds using cyclohexanone as the hydrogen acceptor. In general, dehydrogenations using Urushibara catalysts are comparable to those of Raney nickel.¹



Reductive Desulfurizations. Urushibara catalysts, specifically U-Ni-A, have been used in desulfurizations of sulfur-containing compounds such as thiols, sulfides, disulfides, and thioacetals without competing reduction of alkenes. Reductive desulfurizations can be performed using Raney nickel with comparable yields.¹

Miscellaneous Reductions. Urushibara catalysts have been employed to reduce oximes, nitriles, hydroxylamines, nitro, and nitroso compounds. These reductions can be very dependent on reaction conditions. Yields of products are generally high and steric biasing can lead to high levels of stereocontrol.¹

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