

Zinc/Nickel Couple¹



[7440-66-6]

Zn

(MW 65.39)

InChI = 1/Zn

InChIKey = HCHKCACWOHOZIP-UHFFFAOYAS

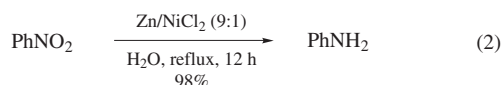
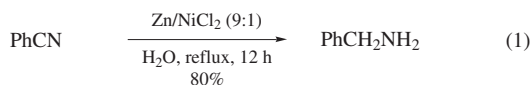
(reducing reagent for a variety of organic functional groups;² coupling agent for alkenyl and aryl halides;³ induces addition of organic halides to alkenes;⁴ reagent for Simmons–Smith cyclopropanation⁵)

Physical Data: dark gray powder, of variable composition.

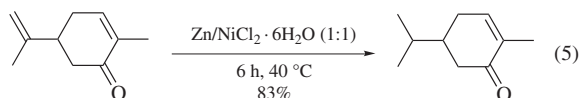
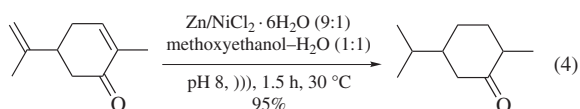
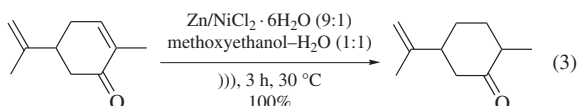
Preparative Methods: the zinc/nickel couple is usually prepared from zinc dust and **Nickel(II) Chloride** or **Nickel(II) Bromide** (dry or hydrate). Zinc dust (10 g) suspended in water (3 mL) and 4.04 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were added to 10 mL of water at 60 °C. After disappearance of Ni^{II} coloration, the solid is filtered, washed, and dried under reduced pressure. The couple is frequently prepared immediately before use. It can be prepared in the presence of the organic substrates in alcohols or DMF, etc., and in the presence of **Triphenylphosphine**, **Potassium Iodide**, or **Pyridine**. Sonication at room temperature improves both the preparation and the reaction step.

Handling, Storage, and Precaution: the Zn/Ni couple seems to have good stability in air.

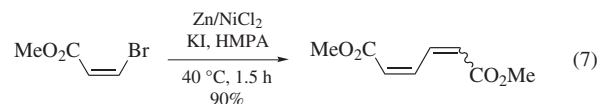
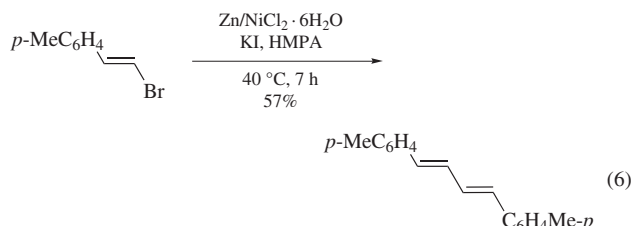
Hydrogenation Reagent. Many organic functionalities can be reduced by the zinc/nickel couple in water or aqueous organic solvents.^{1,6} It has been reported that nitriles are reduced to primary amines with almost no secondary amine (eq 1),² but this result has not been confirmed. Nitro groups are reduced to amines in high yields (eq 2).



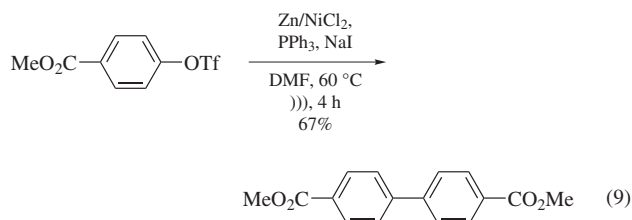
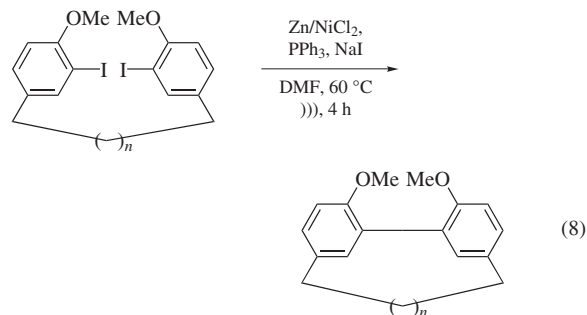
Halides, alkenes, saturated aldehydes, and ketones react readily with the Zn/Ni couple.^{1,2} Water is essential as the source of hydrogen. Hydrogenation of alkenes proceeds rapidly, but that of carbonyl groups more slowly. Although original reaction conditions involved heating, improved yields were obtained by sonication (eq 3).^{7,8} Adjusting the pH (eq 4) and the nickel to zinc ratio (eq 5) change the selectivity. Use of D_2O instead of water as the hydrogen source yields 1,2-dideuterated alkanes.⁹



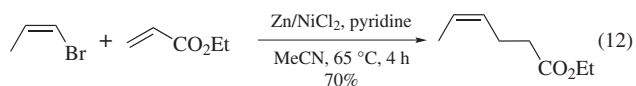
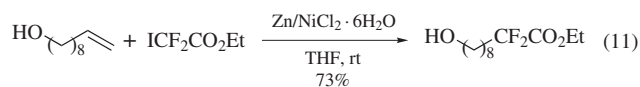
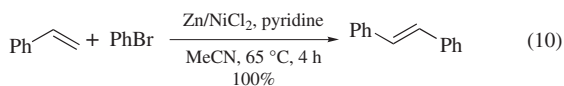
Coupling of Alkenyl and Aryl Halides. Alkenyl halides couple to provide dienes in the presence of Zn, NiCl_2 , and **Potassium Iodide** (eqs 6 and 7). The KI helps the formation of the Zn/Ni couple and exchanges the substrate halogen atom for iodine.³ Reaction with Ni^0 occurs in the next step, followed by the coupling itself. Chlorides do not react. Generally, one alkenic unit retains its configuration, but the second one is frequently isomerized (eq 7).



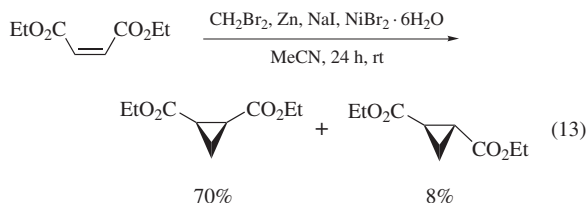
Aryl and heteroaryl halides undergo the Ullmann coupling in high yields under mild conditions.¹⁰ The method was used in cyclophane synthesis (eq 8).¹¹ Aryl trifluoromethanesulfonates are equally successfully coupled under sonication (eq 9).¹²



Additions of Alkyl, Alkenyl, or Aryl Groups to Alkenes. The Zn/Ni couple is an example of the new class of reagents that permit organometallic-like reactions under nonanhydrous conditions (see also **Zinc/Copper Couple**). With styrene, a Heck-type addition–elimination sequence is observed (eq 10).⁴ A Reformatsky-like reaction occurs between ethyl difluoroiodoacetate and nonactivated alkenes (eq 11).¹³ Conjugate additions take place with activated alkenes (eq 12), even when alkenyl or aryl halides are used which are inert with the Zn/Cu couple.¹⁴



Cyclopropanation. Electron-deficient alkenes undergo the Simmons–Smith cyclopropanation in the presence of NaI and *Dibromomethane* (eq 13). With fumarate and maleate esters, the reaction proves to be nonstereoselective, in contrast to the zinc/cobalt couple.⁵



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