P52.- SELECTIVE HYDRIDE-FREE COPPER CATALYZED REDUCTION OF AROMATIC NITRO COMPOUNDS

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The use of environmentally benign enabling technologies such as microwave and ultrasound irradiation either alone or combined (CMUI), represents an important improvement in chemical processes. Besides energy and time saving, more efficient and selective chemical transformations have been observed.

In synthetic organic chemistry, one of the most direct way to pursue Green Chemistry principles is the use of truly efficient catalytic reactions. The application of non-conventional techniques has been successfully applied in copper heterogeneous catalysis. In the last decade this approach gained more and more attention due to important advantages: (1) compared to other transition-metal, copper catalysts are inexpensive, readily available, insensitive to air, and can be easily handled. (2) are extremely versatile and effective in different reaction types.

Catalytic reduction of aromatic nitro compounds for the preparation of the corresponding aryl amines is among the most important and widely used reactions in organic chemical synthesis and many synthetic routes have been reported, including the use of NiRaney/$NaBH_4$, Zn/NH_4Cl, Fe/NH_4Cl,...

However, all these systems involve strong and hazardous reducing agents such as H_2, $NaBH_4$, formic acid, and hydrazine hydrate. Thus, a simple- and inexpensive alternative reducing agent that offers more-environmentally friendly reaction conditions and higher efficiency is desirable.

We reported an efficient and hydride free method for the chemo selective reduction of aromatic nitro compounds catalyzed by Cu nanoparticles under combined microwave and ultrasound irradiation (CMUI). The reaction protocol can be performed with the aim to selectively obtain the azo derivative as well the fully reduced amino. In this way, while using high temperature a fast hydrogenation of the nitro compounds leads to the corresponding anilines, the use of softer conditions allow a lower hydrogenation and a higher coupling rate, resulting in high selectivity to azobenzene. A wide range of anilines with different substituents was achieved with excellent yields and in a very short reaction time. Symmetric azocompounds can be selectively obtained from nitro compounds in a single reduction step, reaching high conversion and selectivity. Bio-glycerol as a source of hydrogen for transfer hydrogenation reactions makes the process attractive due to ease of handling, non-toxic nature and environmental perspectives.

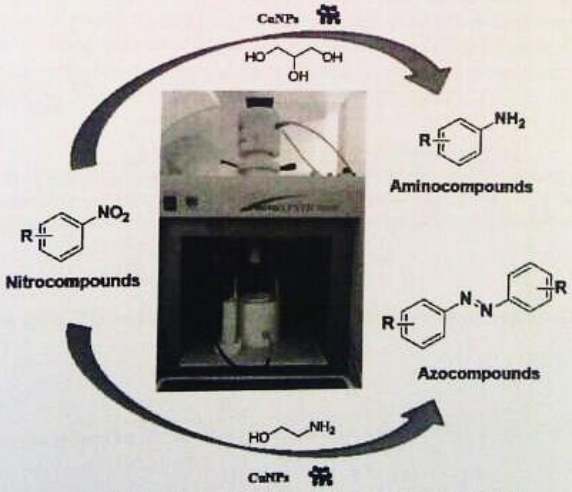

Figura 1. Selective hydride free copper catalyzed reduction.

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