

SELENIUM-MEDIATED REDOX INTERCONVERSIONS OF NITROGEN-CONTAINING FUNCTIONAL GROUPS

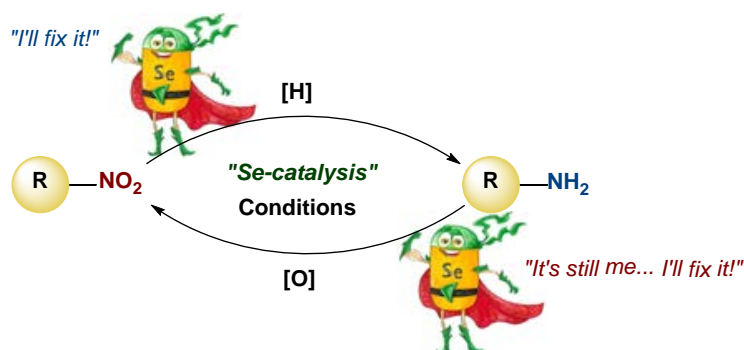
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Oxidative and reductive functional group interconversion reactions occupy a central position in organic chemistry, often representing a key step in a wide array of synthetic sequences. In this context, selenium-catalysed oxidations are of fundamental importance in organic synthesis and in biology. Selenium(IV) oxide, diselenides, and seleninic acids are commonly employed to catalyse oxidation reactions, generally occurring with hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) as oxidants.^[1] A number of selenium catalysed reactions including, amongst others, epoxidation and dihydroxylation of alkenes, conversion of aldehydes to carboxylic acids or esters (*i.e.* Baeyer–Villiger oxidation), and sulfides into sulfones are well established.^[1] Additionally, selenium-mediated thiol-disulfide interconversion reactions, playing a key role in biology and being involved in the maintenance of the essential redox balance in cells, have been deeply investigated.^[1,2]

In this scenario, selenium-mediated oxidations of nitrogen-containing functional groups are far less explored and only few methodologies dealing with the synthesis of nitroso derivatives or azoxyarenes have been described.^[3] Furthermore, in spite of their significant utility, the development of selenium-mediated reduction protocols has received yet very limited attention.

In this communication, our recent studies on selenium-mediated oxidative and reductive interconversions of nitrogen-containing functional groups will be discussed. Particularly, selenium-mediated protocols for the oxidation of anilines to nitroarenes and for the reduction of nitroarenes to anilines will be considered.^[4] Attention will be devoted to the investigation of the reaction mechanism, with particular emphasis to the identification of active selenium-containing species involved. The use of ⁷⁷Se NMR spectroscopy as a versatile tool to elucidate the mechanism of Se-mediated transformations will also be showed.^[4,5]



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