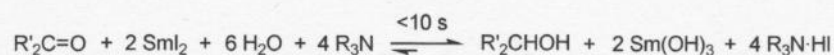


Abstract

This thesis describes the use of various lanthanide(II) based single-electron transfer reagents in organic synthesis. The preparation of some of these lanthanide(II) halides (LnX_2) necessitate extended reaction times, therefore a new general method was developed based on heating in a microwave reactor. This method facilitates rapid preparation of samarium(II) iodide (SmI_2), samarium(II) bromide (SmBr_2), ytterbium(II) iodide (YbI_2) and europium(II) iodide (EuI_2) in tetrahydrofuran (THF).

Several couplings and reduction reactions employing LnX_2 require addition of hexamethylphosphoramide (HMPA) in order to shorten the reaction times and to enhance the coupling efficiency. Due to the carcinogenic nature of HMPA new LnX_2 mixtures were developed that exclude its use in several reactions. Addition of coordinating alcohols to SmI_2 was shown to enhance the rate of reduction of a simple aliphatic ketone (3-heptanone) up to 255 times the rate of SmI_2 in THF.

Addition of water and a simple aliphatic amine to SmI_2 in THF gave rate enhancements of more than 100 000 times that of SmI_2/MeOH in this reduction, which corresponds to full conversion of the ketone to the alcohol in less than ten seconds.



The powerful mixtures of $\text{SmI}_2/\text{H}_2\text{O}/\text{amine}$ have also been shown to give instantaneous reduction of several other functional groups, e.g. imines, halides and α,β -unsaturated esters. In addition, the $\text{SmI}_2/\text{H}_2\text{O}/\text{amine}$ mixtures have been used in several new applications, e.g. reduction of conjugated carbon-carbon double bonds, cleavage of allyl protected alcohols and coupling of ketimines.

In order to explain the course of these reactions and the origin of the extreme rate enhancements, thorough mechanistic studies are also presented.

Keywords: alkyl halide, allyl deprotection, cleavage, coupling, imine, ketone, lanthanide, mechanism, microwave, rate enhancement, reduction, samarium, single-electron transfer, titration

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