TRANSFORMATIONS OF HALOGENATED AND CHALCOGENATED ORGANIC COMPOUNDS FOLLOWING THE PRINCIPLES OF GREEN CHEMISTRY

Abstract

Herein we present some novel synthetic methods, compounds and reagents in the context of halogen and chalcogen organic chemistry with emphasis on green chemistry principles and sustainable development. Due to unsustainable exploitation of natural resources and environmental pollution, green chemistry was established on environmentally friendly principles. Halogenated and chalcogenated organic compounds are important materials, solvents, reagents, synthons and natural compounds, that are used in medicine, industry, and agrochemistry. Despite quick development of this field, there is still a great need for preparation of existing and novel motifs under alternative conditions that follow sustainable development. Organic sulfoxides were deoxygenated to sulfides using 37% aqueous HCl and affordable reagent NaSH, that produce environmentally benign waste. Product of scaled-up reaction was isolated by direct distillation. New, rapid, and convenient method for oxidation of organic sulfides that selectively proceeds with *t*-BuOCl under green reaction conditions. Reaction was temperature- and solvent-dependent and product sulfoxides and sulfones were isolated by removal of solvent. The method was easily scalable and tested on polymeric substrate. The mechanism was explored. Previously unknown *N*-iodo sulfoximines were prepared from sulfides via one-pot approach in green solvent methanol. The method was scaled-up and further transformations were explored. We developed new sustainable method for oxidation of organic selenides using 30% aqueous H_2O_2 solution. Two reagents for electrophilic selenocyanation were prepared and -SeCN motif was introduced under sustainable conditions. 2-Amino-4*H*-pyrans were regioselectively chloro-functionalised with *t*-BuOCl under neat reaction conditions to afford α,*N*-dichloroimines that were isolated by removal of volatiles. Gold was dissolved in ethanol with catalytic amount of iodine, 33% aqueous H_2O_2 and inexpensive and non-toxic ligand. Doctoral thesis presents an important contribution to green chemistry topics of sulfur and selenium organic compound redox reactions, halogen and chalcogen functional group electrophilic transfer and synthesis, reactivity of haloimine structural motif and noble metal recycling.

Key words: green chemistry, organic chemistry, halogen, chalcogen, oxidation, reduction, sulfide, sulfoxide, sulfone, sulfoximine, selenide, selenoxide, haloimine, chlorofunctionalisation, selenocyanate, electrophilic transfer, sulphur, selenium, iodine, chlorine, gold, recycling, catalysis