

## ABSTRACT

New, simple, safe, full metal-free synthetic methodologies and protocols for efficient and selective oxidative transformations of organic compounds, emphasizing principles of green and sustainable chemistry, were developed. The developed and optimized new reaction systems were further on successfully used for aerobic oxidation of various primary and secondary alcohols and chloro-, bromo-, iodo- transformations of organic compounds. The synthetic values of the newly developed reaction systems were illustrated on larger scale (> 20 mmol) experiments with improved green chemical profiles.

A four-component full metal-free reaction system  $\text{air}/\text{NH}_4\text{NO}_3(\text{cat.})/\text{TEMPO}(\text{cat.})/\text{HCl}(\text{cat.})$ , using air oxygen as terminal oxidant, which is catalytically activated by redox cycles of nitrogen oxides released from catalytic amounts of  $\text{NH}_4\text{NO}_3$  and catalyzed by nitroxyl radical (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO) under acidic conditions, was found to be able to oxidize various primary and secondary benzyl, aromatic, heteroaromatic, allyl and alkyl alcohols to the corresponding carbonyl compounds efficiently and selectively. The synthetic value of such reaction system and its green chemical profile was illustrated on a 100 mmol scale-up experiment in an open-air system using a renewable and reusable polymer-supported form of TEMPO (OXYNITROX<sup>®</sup>S100), while benzaldehyde was isolated in high yield without using organic solvents.

New, efficient and selective full metal-free reaction system  $\text{air}/\text{NH}_4\text{NO}_3(\text{cat.})/\text{H}_2\text{SO}_4(\text{cat.})/\text{I}_2$  was discovered and developed, using iodine as a source of iodine atoms, air as the terminal oxidant,  $\text{NH}_4\text{NO}_3$  as catalyst and  $\text{H}_2\text{SO}_4$  as the activator of the overall process. It was shown that the efficiency and selectivity of reaction systems depends on various factors: solvent, reaction temperature, strength and molar ratio of added acid and molar ratio of added  $\text{NH}_4\text{NO}_3$ . The above described and optimized reaction system was further on used for electrophilic iodination of activated aromatic molecules and aromatic, heteroaromatic and alkyl methyl ketones at alpha to carbonyl position. Lastly iodination of 1-(4-methoxyphenyl)ethanone on a 20 mmol scale under an open-air system was performed and quantitative conversion achieved.

Catalytic amount of molecular iodine in reaction system  $\text{air}/\text{NH}_4\text{NO}_3(\text{cat.})/\text{HCl}$  was shown as an efficient and effective catalyst for quantitative and regioselective chlorination of various methyl ketones on alpha to carbonyl position. A reaction mechanism was proposed, predicting aerobic oxidative iodination of methyl ketone on alpha position, catalyzed by nitrogen oxides in the first step followed by nucleophilic displacement of iodine atom with chlorine under  $\text{S}_{\text{N}}2$  nucleophilic substitution. The synthetic value of such reaction system and its potential further use on industrial scale was evaluated by efficient and selective  $\alpha$ -chlorination of 1-(4-methoxyphenyl)ethanone under atmospheric pressure (open-air system) on a 20 mmol scale. Additionally the recovery of reaction solvent and ammonium cations was performed.

Novel multifunctional ionic liquids  $[\text{RNH}_3^+][\text{NO}_3^-]/\text{HX}$  and  $[\text{BMIM}(\text{SO}_3\text{H})][(\text{NO}_3)_x(\text{X})_y]$  ( $\text{X} = \text{Br}, \text{Cl}$ ) were generated and used as an efficient solvent and promoter for selective aerobic oxidative bromination and chlorination of arenes under mild reaction conditions in high yields.

**Key words:** green chemistry, air, ammonium nitrate, oxidation, halogenation.