Electrochemically-enabled methods for aryl radicals generation and their synthetic utility

Dr Bartłomiej Sadowski

Centre of New Technologies, University of Warsaw

INTRODUCTION

Radicals are atoms or particles bearing unpaired electrons. Free radicals are present in our daily life, *e.g.* reactive oxygen species (ROS) emerge during breathing. It is believed that exactly these species are the main cause of DNA damage and hence the process of aging. Nevertheless radials, especially the more stable ones, are useful tools in modern biology or materials chemistry.

Radicals take part in many chemical reactions. Their high reactivity, caused by the presence of an unpaired electron, often result in many side processes, thus reactions do not proceed with satisfactory efficiency. Benzene rings bearing unpaired electrons, so-called aryl radicals, are highly useful intermediates in many chemical transformations. Their major disadvantage is low stability, and hence high reactivity. The development of highly efficient transformations involving aryl radicals constitutes a big challenging for modern organic chemists. Aryl radicals are mainly produced via an oxidation or reduction reaction (so-called redox reactions), therefore it is necessary to use a chemical oxidant or reductant, often in large excess. It eventually results in production of a large amount of waste, which is highly undesirable from the perspective of environmental protection. **Therefore, it is necessary to develop new methods of producing aryl radicals that would reduce the amount of post-reaction waste, ensure the most efficient use of resources and energy, as well as exhibit higher selectivity.**

Due to the deepening of climate crisis, more and more emphasis is placed on producing electricity from renewable sources, such as wind power and solar energy. Therefore, electric energy has come to be seen by synthetic chemists as a green oxidizing or reducing agent. Accordingly, the field called electrochemical synthesis is developing more and more dynamically nowadays. Although the first examples of transformations of organic compounds induced by electricity come from the nineteenth century, an increase in interest in this synthetic methodology has only recently been observed, mainly due to the availability of commercially available, dedicated devices for carrying out this type of reaction. Recently, there is also a significant increase in interest in a new synthetic method, based on a combination of photochemistry and electrochemistry, the so-called synthetic photoelectrochemistry.

AIM OF THE PROJECT AND APPROACH

The aim of this project is to use simple and readily available aryl boronic acid derivatives as radical precursors, employing modern (photo)electrochemical methods. In the initial stage of the project, we will perform a comprehensive optimization of the envisioned transformation, in order to minimize power consumption as well as maximize overall efficiency. Aryl radicals produced in such a way will be converted into more complex chemicals, mainly in one-pot, two-step procedures. Consequently, we will gain an access to completely new synthetic toolbox, that allows us to synthesize new compounds in a simple way from readily available reagents.

SIGNIFICANCE OF THE PROJECT RESULTS

It is expected that the developed methodology will allow to perform fully controlled transformations of aryl boronic acid derivatives into more complex molecules, minimizing the power consumption and the production of waste at the same time, what may contribute to its application in other fields of science, *e.g.* synthesis of new, biologically-active compounds and modifications of already known pharmaceuticals, environmentally-friendly and energy-saving production of chemicals, or modification of materials.