Electrochemical generation of aryl and vinyl radicals and their radical cyclization followed by fixation of carbon dioxide

Hisanori Senboku, a,b,c Jun-ya Michinishi, a Asahi Katayama, a and Shoji Hara a,b,c

a Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
b Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
c Chemical Sciences and Engineering Division, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

Electroreductive generation of carbon radicals from organic halides is one of the useful and eco-friendly alternatives to conventional radical generation using toxic organotin reagents such as tributyltin hydride. Successful electroreductive generation of carbon-centered radicals without BuSnH has been carried out by direct, metal complex-catalyzed, or mediated (indirect) electrochemical reduction of organic halides and diazonium salts, and its application to radical cyclization reactions has also been performed to synthesize carbon- and heterocycles. However, most of the termination steps in electroreductive radical reactions are merely protonation of the resulting anion, yielding protonated cyclic compounds, and little attention has been given to the use of the resulting radical for further reactions, especially carbon-carbon bond-forming reactions. To the best of our knowledge, Ni-catalyzed tandem cyclization-carboxylation of unsaturated haloaryl ethers is the only example in electroreductive “radical-type” cyclization followed by C-C bond formation with carbon dioxide.

During the course of our studies in electro-organic chemistry, we recently succeeded in selective generation of aryl radicals from 2-allyloxybromobenzenes by direct, metal complex-catalyzed, or mediated (indirect) electrochemical reduction of organic halides and diazonium salts, and its application to radical cyclization reactions has also been performed to synthesize carbon- and heterocycles. Moreover, this protocol was successfully applied to vinyl radical generated from 1d followed by carboxylation.

We also found that the present ERCC reaction was applicable to vinyl bromides.

References


