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Preface

The Kolbe oxidation of carboxylic acids was reported in 1834 and could be regarded as the beginning of electroorganic synthesis. Further studies followed, but anodic oxidation through the intervening years was not applied extensively to organic synthesis. Beginning in the late 1960's use of anodic oxidation increased for the preparation of intermediates for further synthetic transformations. Organic electrochemistry is still regarded by some chemists as an exotic method for preparing compounds involving a judicious choice of electrode and supporting electrolyte and requiring an expensive potentiostat to supply the current. However, an increasing number of useful synthetic transformations can be effected by anodic oxidations under constant current conditions using equipment available in most research laboratories.

The papers in this symposium deal with both direct and indirect anodic oxidation. In the former case the electrochemical route sometimes affords products unavailable by conventional organic chemistry, e.g., the formation of quinone bisketals from anodic oxidation of 1,4-dimethoxyaromatic compounds. It also serves as a reagentless method for effecting a chemical transformation which can be conducted using a conventional oxidant. For both situations the electrochemical reaction is performed without a stoichiometric amount of expensive and/or toxic oxidant. Anodic oxidation of organic substrates is one of the most environmentally acceptable ways to effect chemical transformations: it is not necessary to dispose of spent oxidant and both the solvent and in principle the supporting electrolyte can be recycled.

Some synthetic applications electrochemically generate an oxidant and then reoxidize spent oxidant during the course of the reaction, allowing the initial oxidant to be employed in less than stoichiometric quantities. This general method is referred to as an indirect oxidation since the chemical transformation is performed by a reagent electrochemically generated at the anode. Indirect anodic oxidation is very convenient when handling large (or small) amounts of oxidant and when an expensive and/or toxic oxidant is being used in a reaction.

The articles in this symposium issue include both direct and indirect synthetic anodic oxidations and illustrate the broad scope of this chemistry. Topics range from the use of electrochemical oxidation as a key step in natural products synthesis to industrial applications of anodic oxidation chemistry. For convenience the articles have been grouped into two major categories: direct and indirect electrochemical processes. The first articles deal with reactions derived from the oldest of electrochemical reactions, the Kolbe electrolysis. This is followed by articles having as a primary focus synthetic processes arising from: anodic methoxylations; phenol oxidations; oxidations of amides, phosphines, alcohols, and ethers; and reactions leading to formation of heterocyclic compounds. The second section concerns indirect oxidations effected by a number of different mediators.

The broad coverage of anodic oxidation represented by these articles hopefully will encourage further consideration of these reactions as key steps in synthetic procedures. Although synthetic anodic oxidation chemistry traces its origin to the early 1800's, it is an area which has shown much growth in the past twenty years and promises to be of increasing use in synthesis.

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