



BASICS OF ELECTROORGANIC  
SYNTHESIS

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# BASICS OF ELECTROORGANIC SYNTHESIS

Demetrios K. Kyriacou

*The Dow Chemical Company*

*Western Division*

*Research and Development Department*

*Pittsburg, California*



Y078166



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York · Chichester · Brisbane · Toronto

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***Library of Congress Cataloging in Publication Data:***

Kyriacou, Demetrios K

Basics of electroorganic synthesis.

"A Wiley Interscience publication."

Bibliography: p.

Includes index.

1. Electrochemistry. 2. Chemistry, Organic—  
Synthesis. I. Title.

QD273.K97 1981

547.2

80-25326

ISBN 0-471-07975-8

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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*To the memory of my Father*

# PREFACE

It is almost a standard requirement that the author of a new textbook prepare an apologia for writing the book. The plethora of such books apparently demands this formality. There is, however, no compelling reason to write one for this book. No other field of chemistry is represented by fewer books than electroorganic synthesis. Only a few such books have recently made their appearances. One can easily discern, in the prefaces of these books, the authors' passionate hopes that this neglected field of organic synthesis can be popularized. It is absurd that even advanced organic chemistry books find it unnecessary to spare a paragraph's space for electroorganic synthesis.

There is, therefore, a need for textbooks about electroorganic chemistry at all levels, and for books written especially for organic practitioners in industrial laboratories.

This textbook is written for the industrial organic chemist who would like to use the electrolytic method of synthesis but who lacks the background knowledge to do so. No attempt is made to document the status of electroorganic synthesis by quoting exhaustively from research papers in the vast international literature. That is unnecessary and entirely beyond my ability and the scope of this book. Rather I portray the *idiosyncrasy* of the electroorganic phenomenon and its practical synthetic value. Selected examples from the literature and from my own work are described at a *beginner's level*.

The book consists of four short chapters and an appendix. Chapter 1 describes the general electroorganic reaction and illustrates the general mode of *thinking* and *doing* in the area of electrosynthesis. Chapter 2 is a brief survey of electroorganic reactions. Chapter 3 is concerned with some special topics, and Chapter 4 with the praxis of electroorganic synthesis. The Appendix contains some basic electrochemical concepts and principles, as well as various items

and comments useful to the neophyte in the field. I have also included, in the General Bibliography, references to other introductory and advanced books on electrochemistry and electroorganic synthesis.

I would like to thank my wife, Eléni, who patiently typed the manuscript.

DEMETRIOS K. KYRIACOU

*Pittsburg, California*  
*March 1981*

**BASICS OF  
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# INTRODUCTION

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In their distant origins all chemical phenomena reveal themselves as fundamentally electrical. All chemical reactions, therefore, might be called electrochemical reactions. From a practical perspective, however, an electrochemical reaction is one that can be performed in an *electrolytic cell*. The method of carrying out organic syntheses in electrolytic cells is the *electroorganic* method of synthesis.

All cells must contain at least two electrodes in contact with an electrically conducting liquid medium in order for the *electrodeic*, or electrochemical, reactions to be possible. The term electrodeic is very descriptive in that it implies the necessary presence of electrodes. Electrodes are conductors of electricity. They constitute one phase of the electrolytic system, while the liquid medium, or the solution to be electrolyzed, constitutes the other phase. The presence of these two phases clearly defines all electrodeic reactions as heterogeneous reactions. The heterogeneous nature of the reactions is in the elementary event, namely, the *electron exchange act* at the electrified interface between electrode and solution. This electron transfer phenomenon is, of course, omnipresent in nature. Electrochemistry, therefore, is an interdisciplinary science. As such it could be rigorous in its demands on its student and practitioner. However, the knowledge of electrochemistry needed for most practical organic syntheses in the laboratory is very modest, while the benefits can be disproportionately great.

Electroorganic synthesis is an old method. Despite that, it has been practiced by only a small number of industrial chemists since the time of Faraday. One of the main reasons, most observers agree, for the virtual absence of electroorganic research laboratories in industry and for the very slow progress of industrial electroorganic processes has been the difficulty of scaling up such processes. Another reason might be that only a few organic chemists in industrial laboratories have had the opportunity to become knowledgeable in this chemicophysical, as it were, method of synthesis. In addition, only in the last two decades has an understanding of the fundamental mechanisms of electroorganic reactions become possible. The current scarcity of raw materials and energy has generated a vigorous interest in electroorganic synthesis. New and improved cells and electrode materials, and a better understanding of the underlying principles are bound to mitigate many of the scale-up problems.

In certain specialty areas, such as the pharmaceutical and agrochemical areas, where chemical and stereochemical selectivities are needed, and where the electricity cost might be a relatively minor factor for large-scale production, the electrolytic method of synthesis could be especially desirable. Most importantly, electroorganic chemistry can be called upon to contribute in the efforts to abate pollution. The bench organic chemist, for whom this book is written, will find the technique of electrosynthesis to be a very convenient alternative, as well as one with very high intellectual appeal.

# 1

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# ELECTROORGANIC SYNTHESIS AND TECHNIQUE IN GENERAL

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The underlying primary physical process for all chemical and electrochemical reactions must involve the *motion of electrons*. In purely chemical reactions this motion creates the kind of activated complex that leads to products. In electrochemical reactions the motion of electrons is different. This chapter is an exposition of the nature of the electroorganic reaction insofar as it pertains to organic synthesis.

## 1.1a The Generalized Electroorganic Reaction

All electrochemical reactions are referred to as either *anodic* or *cathodic* reactions. The former occur at the *anode*, that is, the positive electrode, while the latter take place at the *cathode*, the negative electrode. Such reactions are carried out in a suitable *electrolysis cell*, or *electrolyzer*, as depicted in Fig. 1.1.

Anodic reactions are fundamentally *deelectronations*, or oxidations in the usual sense, whereby the substance gives up electrons to the anode, as it would to an oxidizing agent. Cathodic reactions are *electronations*, or reductions, whereby the substance accepts electrons from the cathode, as it would from a reducing agent.



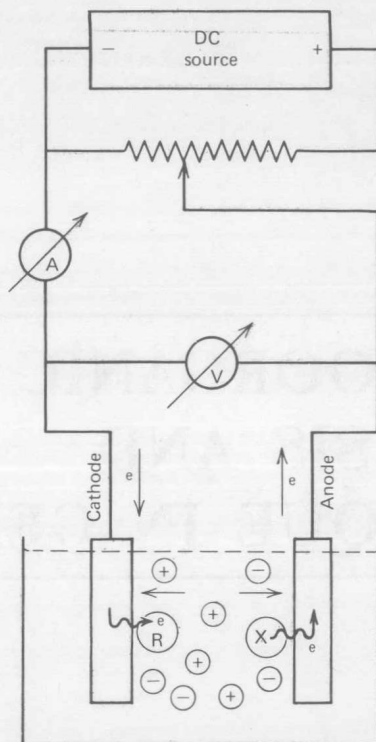


Figure 1.1 Schematic Representation of Electrolysis Cell.

As a result of these primary electron transfer reactions, chemical bonds break and new bonds are formed, as with all types of organic reactions. Almost all types of organic reactions are possible by the electrochemical method: additions, substitutions, cleavages, eliminations, couplings, cyclizations, oxidations, and reductions of functional groups. Our concepts of *polar* and *free-radical* mechanisms can be applied to electroorganic reactions in the same way as to conventional organic reactions.

The generalized electroorganic reaction is symbolized in Fig. 1.2. Note here that the electrode, the anode (Fig. 1.2a) is shown to be deficient in electrons near its surface. The organic species, R, *reduces* the electrode by donating electrons to it. These donated electrons are removed from the reduced surface via the external circuit, the wire, so that the reduction reaction may continue. Were it not for this electron removal, the electrodic reaction would stop as soon as electrostatic forces arose that opposed further *net* electron transfer at the interface between electrode and solution. For cathodic reactions (Fig. 1.2b) the events are similar but, in the physical sense, exactly oppo-