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TECHNIQUES OF CHEMISTRY

VOLUME V, PART I

TECHNIQUE OF
ELECTROORGANIC SYNTHESIS

Edited by
NORMAN L. WEINBERG



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Supervisor, Research Center
Hooker Chemical and Plastics Corporation
Grand Island, New York

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TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

VOLUME I

PHYSICAL METHODS OF CHEMISTRY, in Five Parts
(INCORPORATING FOURTH COMPLETELY REVISED AND AUGMENTED
EDITION OF PHYSICAL METHODS OF ORGANIC CHEMISTRY)
Edited by Arnold Weissberger and Bryant W. Rossiter

VOLUME II

ORGANIC SOLVENTS, Third Edition
John A. Riddick and William S. Bunger

VOLUME III

PHOTOCHROMISM
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VOLUME IV

**ELUCIDATION OF ORGANIC STRUCTURES BY PHYSICAL
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Edited by K. W. Bentley and G. W. Kirby

VOLUME V

TECHNIQUE OF ELECTROORGANIC SYNTHESIS, in Two Parts
Edited by Norman L. Weinberg

VOLUME VI

**INVESTIGATION OF RATES AND MECHANISMS OF
REACTIONS**, Third Edition, in Two Parts
Part I: *Edited by Edward S. Lewis*
Part II: *Edited by Gordon G. Hammes*

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can easily be recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

*Research Laboratories
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ARNOLD WEISSBERGER

PREFACE

For too long the field of electroorganic synthesis has been considered "more of an art than a science." This attitude was appropriate until quite recently. However, the progress made in electroanalytical methods, especially in polarography and cyclic voltammetry of organic compounds, coupled with product isolation studies has given us new insight into the electrochemical reaction variables (potential, current density, adsorption, electrode material, etc.) and their interdependency. The result is that the organic chemist has at his disposal a highly useful synthetic tool, with great potentialities inherent in the technique for developing *electrode specific syntheses* including products that are not easily attainable by other methods.

For many years, the excellent chapter of Professor Sherlock Swann, Jr., in *Technique of Organic Chemistry* (Vol. II, 1956) has served as a primary source and incentive for those entering the field; but the technique of electroorganic synthesis has undergone much change since the appearance of that work. It has now become customary to carry out electrosyntheses under controlled potential conditions using three electrodes, the third one being a reference electrode. This contrasts with earlier synthetic studies in which constant current conditions were usually employed. This does not negate the value of the earlier literature. It is still important to know the products and which electrode material, added catalytic substances, pH, temperature, and so on were found necessary in a particular synthesis. Much can be learned from this older work which is directly applicable today. The new techniques using potentiostatic methods, however, are found superior mainly because they lead to fewer side products.

An approach for a particular synthesis that the organic chemist with a minimum of electrochemical background can easily follow involves, as a start, examination of the literature for suitable starting materials and conditions that fulfill the requirements of both the chemical and electrochemical reaction variables. This is followed by

1. setting up an electrochemical cell, usually with three compartments separating anode, cathode, and reference electrodes.

2. selection of a suitable controlled potential by determining current-potential curves on the background solution (solvent plus supporting

electrolyte) and with added substrate. The curves should be obtained on solutions with the concentrations of materials intended for use. Such curves are readily derived using a constant current power supply and a vacuum tube voltmeter, although a potentiostat is a great convenience (Chapter II). Knowledge of oxidation and reduction potentials (Chapter XII) can greatly aid in making a judicious choice of the operating electrode potential.

The electrolysis is carried out, products are isolated, and, if need be, the reaction variables are revised (these are often the electrode material and the solvent/supporting electrolyte) if necessary with repetition of steps 1 and 2.

The above is only one possible approach. Another approach involves the complementary use of electroanalytical methods to help sort out the possible reaction pathways and establish appropriate mechanisms (Chapters III and V).

The two volumes include the following:

1. An introduction to the field, valuable to the organic chemist in the laboratory as well as to the engineer considering scale-up (Chapter II).
2. A brief review of electrochemistry and the electroanalytical approach presenting some fundamental principles as well as an understanding of current problems (Chapters II, III, and V).
3. A critical review of the various electrochemical reactions of organic compounds, containing extensive tables of data (Chapters IV–XI).
4. Discussions of important electrosyntheses, including the scope, limitations, technical problems, comparisons with chemical methods, and mechanistic considerations.
5. Actual examples in recipe style.
6. Oxidation and reduction potential data in a form useful to the organic chemist (Chapter XII).

I sincerely thank the contributing authors for their painstaking efforts, conscientiousness of purpose, and patience. These works were envisioned by Dr. A. Weissberger to whom especial thanks are due. I am greatly indebted to Dr. Gerhard Popp of the Eastman Kodak Research Laboratories for his considerable help in reviewing the manuscripts. Thanks are due also to Professor Jack Stocker of Louisiana State University in New Orleans, Professor Albert J. Fry of Wesleyan University, and other reviewers acknowledged by the authors of this work. Their primary reward as well as mine will be to see the technique of electroorganic synthesis adopted into the arsenal of methods of organic chemists everywhere.

NORMAN L. WEINBERG

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Chapter I

INTRODUCTION

N. L. Weinberg

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The development of electroorganic chemistry can be considered from the following related standpoints: electroorganic synthesis, technological advances, and mechanistic electroorganic chemistry.

Electroorganic Synthesis

Historically, synthetic electroorganic chemistry made its debut in 1801 with the electrochemical oxidation of alcohol[1]. Several works have been compiled[2-7] detailing the many electroorganic reactions that have been discovered over the years. Perhaps the majority of these reactions have their chemical analogies; however, there exists a growing body of reactions which remain unique because of the nature of the product formed and/or the mode of formation. These special reactions are emphasized in the chapters relating to synthetic aspects. Undoubtedly, these unique reactions are in part the result of the electrochemical reaction variables operating in the heterogeneous system. A number of these unique reactions have been identified as proceeding from ion-radical intermediates. It is increasingly apparent that the electrochemical method offers the most convenient general technique for generating ion radicals. The study of these interesting species is fast becoming a new frontier for organic chemists[8].

In the same article[9] defining his new terms: *electrode, anode, cathode, electrolyze, ion, anion, cation*, Faraday wrote of his work on the electrolysis of alkali metal acetates:

"When a very strong solution (of potassium acetate) was used more gas was evolved at the anode than at the cathode in the proportion of 4 to 3 nearly; that from the anode was a mixture of carbonic oxide and carbonic acid; that from the cathode pure hydrogen. When a much weaker solution was used, less gas was evolved at the anode than at the cathode, and it now contained carburetted hydrogen* as well as carbonic oxide and carbonic acid."

Hermann Kolbe[10] reexamined the electrochemical oxidation of salts of carboxylic acid with the intention of proving the existence of radicals. Today

*Now known to be chiefly ethane.

the "Kolbe electrosynthesis" is the most widely known organic electrode process and its mechanistic subtleties [11] still command a sizeable portion of the literature of the field. The anodic reactions of carboxylate salts is brought up to date in this work by J. H. P. Utley (Chapter VI).

The concept of controlled potential electrolysis has had a great impact on modern electroorganic synthesis. Its first proponent, Fritz Haber [12], as early as 1898, noted the importance of the electrode potential. Thus in the reduction of nitrobenzene he found phenylhydroxylamine at low negative potentials, and aniline at more negative potentials. He wrote:

"The electric current up to this time has been regarded in electroorganic chemistry as a means of reaction whose results are determined through current density, current duration and occasionally, through the material of the electrode. This view is incomplete, for oxidation and reduction processes depend mainly on the potential of the electrode at which they take place. The current density, current duration and electrode material are important only in so far as they determine the electrode potential and its changes in the process of electrochemistry."*

Haber's important concept was rather difficult to apply in the laboratory for many years following the publication of his pioneering work. Almost all research was carried out by controlling current density and duration for the simple reason that manual control of the electrode potential requires continuous attendance of the experimenter. It was in this period (1910 to 1940) that F. Fichter and his co-workers in Switzerland carried out an enormous number of electroorganic reactions (mostly in aqueous media) and painstakingly separated and characterized what was often a complex mixture of products. Fichter's textbook [3] *Organische Elektrochemie* is a compilation of interesting and potentially useful reactions, many of which are worthy of reinvestigation, using modern methods.

In 1942 A. Hickling [13] solved the difficulty of manual potential control by constructing a device to automatically control the potential of the working electrode. The "potentiostat" has revolutionized synthetic electroorganic chemistry—the method of controlled potential electrolysis generally leads to fewer side-products, and mechanistic studies are facilitated and made considerably more meaningful. In addition, with this device it is possible to carry out a specific oxidation or reduction of a particular functional group in a complex molecule without affecting other sensitive functions in the molecule [14-16].

Technological Advances

In view of the apparent success in converting organic compounds through

*It is now well recognized that electrode material and current density are important variables in many electrochemical reactions.

electrochemistry, the question arises as to why so few industrial processes are based on electroorganic chemistry. Indeed since the inception of industrial electroorganic processes in Germany near the turn of this century, the number of processes "on stream" at any time could be counted on the fingers of one hand. One reason for the lack of technological achievement is that often a catalytic process using gaseous hydrogen or oxygen forces the electrochemical method into obsolescence. It is for this reason, for example, that the electrochemical processes for conversion of anthracene to anthraquinone [17,18] or for glucose to sorbitol [19] were terminated. However, a more important reason for lack of technological success is that commercial-size scaleup of an electrochemical process is difficult, more difficult generally than a chemical process. The reaction variables in electrochemical processes are complex and, in spite of recent progress, still poorly understood. Thus, whereas a set of the usual reaction variables may be listed as temperature, pressure, time, pH, concentration of reactants, and so on, an electrochemical process requires, *in addition*, an understanding of the role of current density (current per unit area of electrode surface), working electrode potential (potential of the anode or cathode measured against a reference electrode), nature of the electrode material, nature of the solvent/supporting electrolyte system, electric field at the electrode-solution interface (i.e., at the double layer), adsorption on the electrode of one or more components of the solution (especially the organic substrate), membrane or separator material, and the cell design.

Cell design is of crucial importance in view of the fact that commercial cells demand thousands of amperes to be practical [20-24]. For example, to convert one mole of an organic compound to a product in a two-electron process with 100% current efficiency* requires passage of a current of 53.6 A for a period of one hour.

Goodridge in a recent article [20] summarizes:

"Probably one of the most important features (of an industrial cell) is the requirement of a large electrode area per unit volume of reactor. Since capital costs are a direct function of the volume of the reactor, scale-up of area is always expensive. This is the case when dealing with organic electrode reactions where current densities are usually small. Ideally, one would like to be able to scale up volumetrically"

As we shall see in Chapter II by F. Goodridge and C. J. H. King, novel approaches to electrochemical cell design are now being studied and piloted. Preliminary results are indeed promising.

Mechanistic Electroorganic Chemistry

Mechanistic electroorganic chemistry has seen its greatest developments

*Current efficiency may be defined as the percentage of the total electrons transferred which are utilized in the formation of the desired product.

within the last two decades. Already much is known about the electrogeneration of reactive intermediates and subsequent followup chemical and electrochemical reactions. Cation radicals, carbonium ions, or uncharged radicals are formed at the anode, and, at the cathode, anion radicals, carbanions, or uncharged radicals. Much has been learned about the reaction pathways of these species through product isolation, polarography[25], cyclic voltammetry[26], coupled electro-analytical and spectroscopic techniques[27], and a host of other methods. It is still, nevertheless, obvious to the electroorganic chemist that mechanistic electroorganic chemistry has a long way to go in adequately explaining the roles of the chemical and electrochemical reaction variables as well as, as is often the case, their interdependence. Chapter III, by B. E. Conway and E. J. Rudd, presents the principles involved in our present understanding of these variables. R. F. Nelson, Chapter V, explores our current understanding of the mechanistic pathways for the comparatively well-developed area of electrochemical oxidation of nitrogen functions. With increased knowledge of mechanistic aspects, it is anticipated that many new and useful "electrode-specific" reactions will be discovered.

Industrial Applications

In terms of industrial processes, electrochemical processes are not likely to replace catalytic processes on economic grounds; but there are many areas where electrochemical processing should be of interest. For example, many present chemical processes suffer from pollution problems which may be traced to a spent (and often uneconomically recoverable) oxidizing or reducing agent. Electroorganic synthesis can be inherently pollution free at the process site (the electricity generating plant may not be). Correspondingly, electrochemistry offers [28] the possibility of modifying noxious effluent liquors without addition of any further potentially polluting reagents. Electrochemistry should be seriously considered when the stoichiometric use of an oxidizing or reducing agent is required—often electrochemical regeneration of a catalytic amount of the chemical reagent is very practical. Electrochemistry should be examined as an alternative when the existent process is of the multistage type or proceeds in poor yields. Certainly electrochemistry should be considered when there is no known chemical procedure; thus there are many products which have only been synthesized electrochemically. Electrochemical routes may be found more economical as well, if a cheaper raw material can be utilized or if, by using electrochemistry, a continuous operation is facilitated.

Developing Areas in Electroorganic Synthesis

Trends within recent years would indicate that the following areas will command increasing attention by workers in the field:

1. *Cell design and scaleup*, including the use of new stable anode materials

(so-called dimensionally stable anodes or DSA's^R) for electrosynthesis.

2. *Electroanalytical studies* to elucidate the mechanisms of electroorganic reactions.

3. *The role of adsorption* of the substrate on the electrode or alignment in the double layer (see Chapter III by B. E. Conway and E. J. Rudd) in determining the nature of the products (stereochemistry, isomer ratios, etc.).

4. *Functionalization* of hydrocarbons, olefins, aromatics (often the analogous chemical route requires a multistep scheme).

5. *Electrochemical halogenation*, especially electrofluorination.

6. *Electrogeneration of unusual valence states of inorganic reagents* to provide redox couples for accomplishing unusual syntheses.

7. *Electroinitiated polymerizations* (see Chapter XI by B. L. Funt and J. Tanner) including electrochemical deposition of monomers as coatings on metal surfaces.

8. *Electrochemical-biochemical processes*.

9. *Environmental control* of organic pollutants through electrochemical destruction.

Electroorganic chemistry is now a rapidly growing field compared to the relative dormancy prior to the last decade. The "black magic" associated with the field is disappearing and being replaced by a sound mechanistic basis. It is believed by this author that the near future will see adoption of the techniques of electroorganic chemistry by many organic chemists interested in synthesis, that organic laboratories will have potentiostats and associated equipment, and that instructors of organic chemistry will devote some time to this oldest-now-newest branch of organic chemistry.

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Chapter II

EXPERIMENTAL METHODS AND EQUIPMENT

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