

T. Shono

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# Electroorganic Chemistry as a New Tool in Organic Synthesis



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With 7 Figures and 49 Tables



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Professor Tatsuya Shono  
Kyoto University  
Department of Synthetic Chemistry  
Faculty of Engineering  
Yoshida, Sakyo  
Kyoto 606/Japan

### List of Editors

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## Preface

Although the first electroorganic reaction used in organic synthesis is probably the famous Kolbe electrolysis published in 1849, no other remarkable reactions have been found until the reductive dimerization of acrylonitrile to adiponitrile was developed by Dr. M. M. Baizer of Monsanto Co. in 1964. Since then, the electroorganic chemistry has been studied extensively with the expectation that it is a new useful tool for finding novel reactions in organic synthesis.

The purpose of this book is not to give a comprehensive survey of studies on electrochemical reactions of organic compounds but to show that the electroorganic chemistry is indeed useful in organic synthesis.

Thus, this book has been written under the following policies.

- (1) Since this monograph is mainly concerned with organic synthesis, only few studies carried out from the viewpoint of electrochemical, theoretical, or analytical chemistry are mentioned.
- (2) Since electroorganic chemistry covers a great variety of reactions, the types of reactions described in this book are selected mainly with regard to their application in organic synthesis. Simple transformations of functional groups are only described in particular cases, and also some well established processes such as the Kolbe electrolysis, pinacolic coupling, and hydrodimerization are only briefly mentioned.
- (3) Since many reports have already been published for each type of these reactions, only a limited number of the relevant papers are cited in this book.
- (4) In this book, electroorganic reactions are divided into two major types, namely oxidation and reduction. Oxidations are further classified according to the structure of the substrate, whereas reductions are classified by the type of reaction.
- (5) Since many review articles <sup>1-22)</sup> and monographs <sup>23-36)</sup> describing electroorganic chemistry from a variety of standpoints have already been published, the author

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attempted to present the material under an aspect which is different from these publications.

The author is deeply grateful to Drs. Yoshihiro Matsu-mura, Shigenori Kashimura, and Kenji Tsubata for their kind assistance in collecting data, and also to Mrs. Yohko Ohmizu for her great efforts in typing the manuscript.

Kyoto, February 1984

Tatsuya Shono

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# 1. Introduction

The term electroorganic chemistry is often used in the same meaning as organic electrochemistry. Although the difference between these two terms is not always clear, the latter seems to emphasize electrochemistry rather than organic chemistry and to involve electrochemical, electrotheoretical, and electroanalytical studies of organic compounds. On the other hand, the former is basically organic chemistry and offers variety of potentials which are beneficial to organic synthesis as briefly surveyed below.

## 1.1 Inversion of Polarity of Substrates

In electroorganic reactions, the active species is generated on the electrode surface through electron transfer between a substrate molecule and the electrode as shown in Eq. (1),<sup>1</sup> in which the substrate molecule is transformed to a cation radical or an anion radical, depending on the direction of electron transfer. When the substrate molecule is a radical or ionic species, the transformation of the substrate is such as shown in Eq. (2).



As is well known, an organic reaction between two substrate molecules is not achievable when the polarity of the reaction site is the same in both substrates. Thus, the reaction usually takes place between a nucleophilic site (Nu) and an electrophilic site (E). In organic synthesis, however, it is not uncommon that reaction between two groups of the same polarity is required to synthesize the target compound. Then, inversion of the polarity of one of the groups is the necessary means of achieving such a type of reaction, though this inversion (Umpolung) is not always facile in organic chemistry. As Eqs. (1) and (2) clearly show, in an electroorganic reaction, the generation

<sup>1</sup>  $-e$ , removal of one electron;  $-2e$ , removal of two electrons;  $-[e]$ , removal of electrons

## 1. Introduction

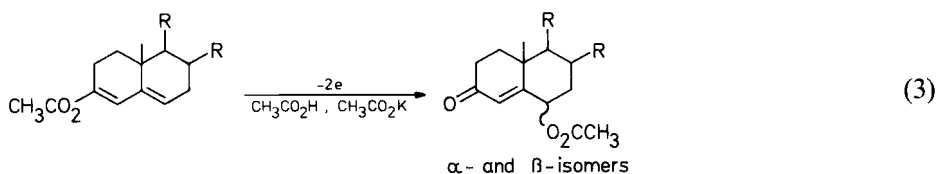
of active species through electron transfer between a substrate and electrode always involves inversion of polarity of the substrate. Thus, this facile inversion of polarity makes electroorganic chemistry a unique tool in organic synthesis.

## 1.2 Interface Reactions

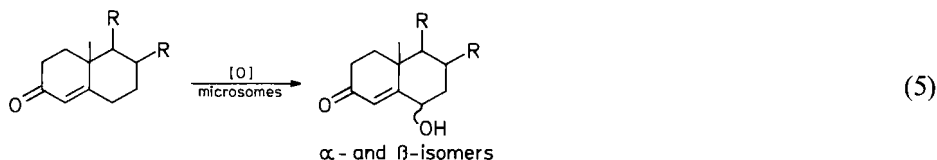
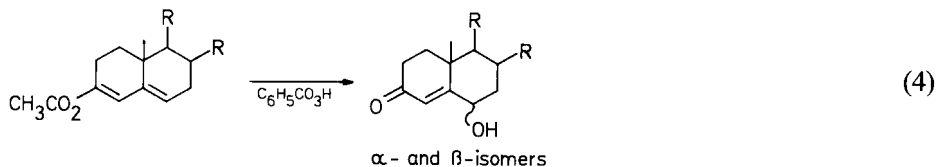
As described above the active species is formed on the electrode surface which is an interface between solid and solution. The active species formed under such special circumstances shows unique characteristics in reactivity.

### 1.2.1 Stereochemistry

One of these characteristics is stereospecificity. The stereospecificities observed in the acetoxylation of methylcyclohexenes (Section 2.2.2.) and in the intramolecular cyclization of non-conjugated olefinic ketones (Section 3.1.1.) are typical examples of stereospecific reactions taking place at the interface. Another interesting example of the stereospecificity has been observed in the anodic acetoxylation of some cyclic dienol acetates carried out in acetic acid containing potassium acetate as the supporting electrolyte (3).

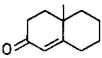
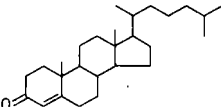
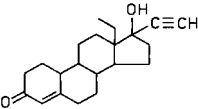
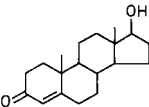


The same products are also obtained by oxidation of the dienol acetates with perbenzoic acid or by oxidation of the corresponding enones with the liver microsomal oxidation system (4, 5).



The stereoconfiguration of the products obtained by the anodic method shows a remarkable similarity with the microsomal oxidation products whereas perbenzoic acid oxidation in a homogeneous solution exhibits poor stereospecificity (Table 1) [1].

**Table 1.** Stereospecificity in Anodic, Chemical, and Microsomal Oxidations

Substrate	Product ratio ( $\beta$ -isomer/ $\alpha$ -isomer)		
	Anodic method	Microsomal method	Chemical method
	13.9	14.1	3.0
	12.3	11.8	2.8
	10.3	8.4	2.9
	13.3	12.1	3.8

The similarity of anodic and microsomal oxidations may be explained by the fact that both types of oxidations take place at the interface.

### 1.2.2 Distribution of Active Species

The active species generated on the electrode surface generally reacts with other reagents before it is diffused uniformly into the solution, whereas in the usual organic homogeneous reaction the distribution of active species is uniform in solution. Due to this difference the electrogenerated active species displays unique characteristics. For example, as shown in Section 3.1.2., the carbanion formed by the reduction of an iminium cation is alkylated with alkyl halides in high yields under highly acidic reaction conditions (6).



## 1. Introduction

Since it is not possible to alkylate the carbanion in acidic homogeneous solution before it is protonated, reaction (6) is assumed to involve alkylation of the carbanion in the vicinity of the electrode before it is diffused into the acidic solution.

The famous Kolbe electrolysis seems to be a typical example showing the uniqueness of the distribution of the electrogenerated active species. Thus, the free-radical species formed at rather high concentration on the anode surface through anodic oxidation of a carboxylate anion dimerizes before it is diffused into solution, whereas the same radical species generated in a homogeneous solution by the usual chemical method forms a dimer as a minor product but mainly abstracts hydrogen from hydrogen donors, e.g. from the solvent.

## Reference

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## 2. Anodic Oxidations

### 2.1 Anodic Cleavage of Aliphatic Carbon—Hydrogen Bonds and Carbon—Carbon Single Bonds

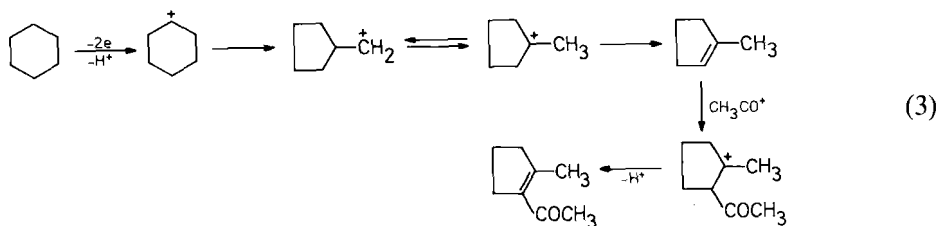
Direct anodic oxidation of alkanes may be performed if they have ionization potentials lower than about 10 eV [1]<sup>1</sup>. Such oxidations can be classified into two types of reactions, cleavage of C—H bonds (1) and C—C bonds (2).



The extremely high oxidation potentials of alkanes, however, make it difficult to carry out the oxidation in commonly used solvents like acetonitrile. Since the first intermediates generated in these oxidations are carbonium ions as illustrated by Eqs. (1) and (2), their stabilization with strongly acidic solvents like anhydrous fluorosulfonic acid lowers the oxidation potentials of the hydrocarbons [2]<sup>2</sup>.

#### 2.1.1 Cleavage of Carbon—Hydrogen Bonds

The controlled potential electrolysis of cyclohexane carried out at 1.85 V in fluorosulfonic acid containing 1.15 M acetic acid yields an  $\alpha,\beta$ -unsaturated ketone as a single product in 30% current yield (3).

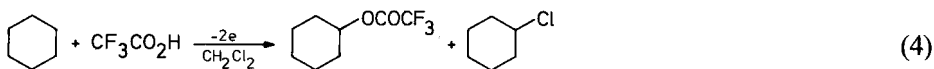


<sup>1</sup> The ionization potential and half-wave oxidation potential ( $E_{1/2}$ , 0.14 M  $(\text{C}_2\text{H}_5)_4\text{-NBF}_4/\text{CH}_3\text{CN}$ ) of some alkanes are as follows: isopentane, 10.10 eV (3.00 V); 2-methylpentane, 10.00 (3.01 V); 2,2-dimethylbutane, 10.19 (3.28 V); octane, 10.24 (> 3.4 V).

<sup>2</sup> The oxidation potentials of some alkanes in fluorosulfonic acid containing 1.15 M acetic acid are as follows: isopentane, 1.8 V *vs.* Pd/H<sub>2</sub>; 2-methylpentane, 1.68 V; octane, 1.64 V.

## 2. Anodic Oxidations

The acetyl cation is formed from acetic acid. Although  $\alpha,\beta$ -unsaturated ketones are always formed in the anodic oxidation of alkanes in fluorosulfonic acid containing acetic acid, the products are mixtures of isomers. This anodic oxidation is therefore not widely utilized in organic synthesis. In more weakly acidic solution, different products are obtained [3]. Thus, the anodic oxidation of cyclohexane in  $\text{CH}_2\text{Cl}_2$  containing 2.5 M  $\text{CF}_3\text{CO}_2\text{H}$  yields cyclohexyl trifluoroacetate ( $Y = 91\%$ ) and cyclohexyl chloride ( $Y = 4\%$ ).



The oxidation of alkanes like decane gives, however, mixtures of products.




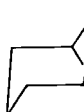
In the anodic oxidation, adamantane is a unique compound among alkanes. It has a rather low oxidation potential, and its anodic oxidation in acetonitrile affords acetoamidoadamantane in 90% yield [4]<sup>3</sup>.



This reaction involves direct oxidation of adamantane to adamantyl cation as the active intermediate. A variety of substituted adamantanes can be oxidized forming similar products in satisfactory yields.

### 2.1.2 Cleavage of Carbon—Carbon Single Bonds

The direct anodic cleavage of saturated aliphatic carbon-carbon bonds is only possible if an electron is removed from the highest occupied molecular orbital (HOMO) of the C—C bond e.g. due to the presence of strain in the bond [5]. The oxidation potentials ( $E_{1/2}$  V *vs.* SCE) of some strained hydrocarbons are shown below together with the ionization potentials (IP eV) [5–6].

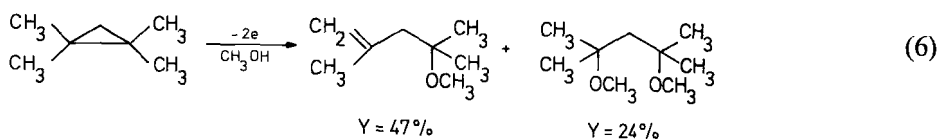
	$E_{1/2}$ 0.91 IP 7.40		$E_{1/2}$ 1.73 IP 8.46
	$E_{1/2}$ 1.91 IP 8.60		$E_{1/2}$ 1.50 IP 8.15

<sup>3</sup> Oxidation potential of adamantane:  $E_p/2$ , 2.36 V, sweep rate 0.1 V/s,  $10^{-2}$  M substrate,  $10^{-1}$  M  $(\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$ ,  $10^{-1}$  M  $\text{Ag}/\text{Ag}^+$  reference.



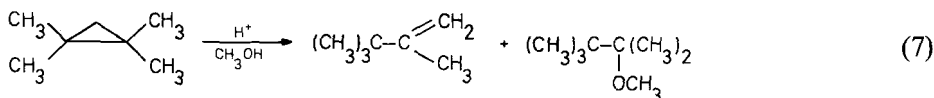
## 2.1 Aliphatic Carbon—Hydrogen Bonds and Carbon—Carbon Single Bonds

Tetramethylcyclopropane is the simplest strained hydrocarbon which is easily oxidized by the anodic method in methanol to give two products with a total yield of 71% [6]:



The cleavage of the C—C bond shows a remarkable selectivity since the most substituted bond is split, and products resulting from cleavage of the other bonds are not formed.

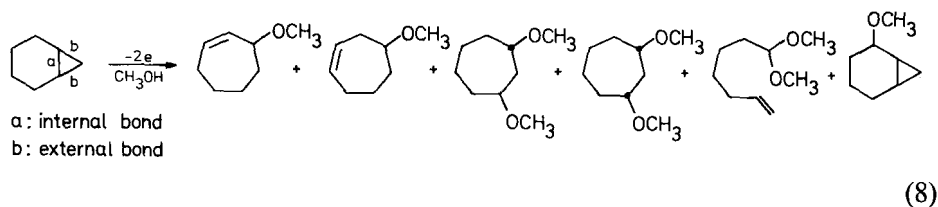
Furthermore, the anodic cleavage is in sharp contrast to the selectivity of C—C bond cleavage observed in the reaction of tetramethylcyclopropane with acidic methanol in which the less substituted bond is cleaved.



This difference of selectivity may be explained as follows: In the anodic oxidation, the electron is transferred to the anode from the most strained C—C bond where the ionization potential is lowest whereas in the acidic solvolysis, the proton attacks the less hindered site.

The marked difference between the reaction pattern of the anodic oxidation and that of the common chemical oxidation is also demonstrated by the following reactions [7].

The anodic C—C bond cleavage of bicyclo[4.1.0]heptane in methanol takes place exclusively at the internal bond which is the most strained (8).



On the other hand, the selectivities (external/internal) observed in the bond cleavage of the same compound by acidic solvolysis and by oxidation with metallic oxidizing agents are lower, and the cleavage mainly occurs at the external bond (Table 1).

Similar exclusive external bond cleavage is observed in the acidic solvolysis of *cis*- and *trans*-bicyclo[6.1.0]nonanes and *cis*-bicyclo[5.1.0]octane [8]. In