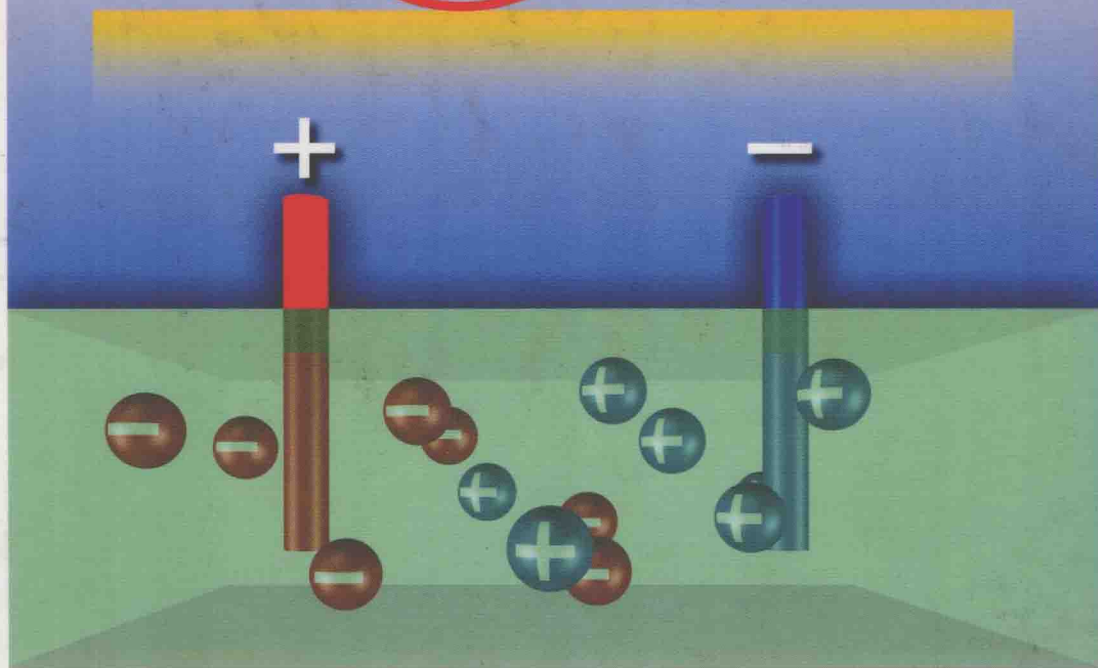
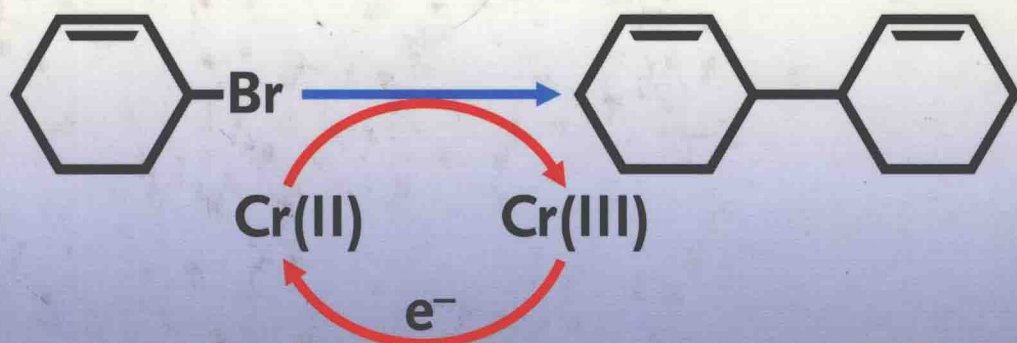


Electroorganic Reduction Synthesis

Volume 2



Sigeru Torii

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KODANSHA

WILEY-VCH Verlag GmbH & Co. KGaA

Sigeru Torii

Professor Emeritus, Okayama University, Japan

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Preface

Awareness of the versatility and uniqueness of electrolytic procedures in organic synthesis is increasing in recent years as a result of various applications being spread gradually to cover many areas of academic and industrial organic chemistry. Such advances in methodology brought about a general interest among organic chemists with versatile synthetic devices of great promise, and basic concepts for the design of conditions for electrolysis are now becoming familiar to them by considering the complex interaction between components and reactive species in electrolysis media as the reaction site.

Electroorganic synthesis and its applications have been developed largely over the past two decades with a clear structure and its focus on synthetic methods. Most efforts of electroorganic synthetic chemists have been devoted especially to the investigation of electrolysis conditions for obtaining the desired products. Consequently, product-selectivity has been found to be derived from the most appropriate choice of a combination of influential factors such as solvents, electrolytes, electrode materials, additives, electrolysis methods (direct or indirect) together with electrolysis equipment and applied voltages (electrode potential).

This is a companion volume to *ELECTROORGANIC SYNTHESSES Methods and Applications Part I: Oxidations* published by VCH Weinheim and Kodansha Tokyo in 1985. The present two-volume monograph consists of 13 chapters on electrochemical reduction and its product selectivity and covers all important organic substance classes such as aldehydes, ketones, acids, esters, acids anhydride, olefins, aromatics, and nitrogen-, sulfur-, selenium- and tellurium-containing compounds, together with halogenated compounds, alcohol and related derivatives, organic compounds involving group IIIA, IVA, VA, IB and IIB elements, organometallic compounds as well as the methodology on indirect reduction redox mediators, electrogenerated base-assisted reactions, and electropolymerization. The last chapter (13) deals with electroreduction together with electrooxidation in the course of polymerization reactions.

Like the preceding volume on oxidation, this work also provides a survey of synthetically interesting references on electroreduction reactions of organic compounds in terms of conditions for electrolysis and product selectivity, and aims to present the results in a form useful for synthetic applications. Although over 3400 references are cited, the author has not attempted to provide an exhaustive review, and articles which appeared before 1965 have generally not been included. The results presented here can be readily understood on the basis of organic chemical considerations, and detailed discussion of electrode reactions and reaction mechanisms is not included, since the major aim of this book is to aid electrosynthetic studies. Appendix 1, which indicates the relation between partial structures before and after electrolysis together with typical conditions for electrolysis, should assist

readers in gaining easy access to the appropriate conditions for electrolysis for a desired functionalization.

The author is particularly indebted to Professor Dr. Hideo Tanaka for his invaluable assistance in checking the references, discussing the contents and commenting on the manuscript. I acknowledge the careful secretarial work of Ms. Yuuko Fukushima, Ms. Noriko Sera, Ms. Hiroko Nakanishi and Ms. Naomi Miyake, who arranged the data concisely and typed the manuscript. The author sincerely thanks Ms. Fukushima for her devoted assistance in arranging the manuscript in a most careful manner over a long period of time. Mr. Ippei Ohta of Kodansha were always helpful and cooperative, and I am grateful to Ms. Cecilia M. Hamagami for assistance in finalizing the English manuscript. Finally, special thanks to my wife, Hiroko, for her constant support and encouragement.

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Abbreviations and Symbols

Electrodes

DME	Dropping mercury electrode
GC	Glassy carbon
HMDE	Hanging mercury drop electrode
NHE	Normal hydrogen electrode
OTE	Optically transparent electrode
RDE	Rotating disc electrode
PRDE	Rotating ring-disc electrode
SCE	Saturated calomel electrode
SHE	Standard hydrogen electrode
SUS	Stainless steel electrode

Techniques

CP	Constant potential
CV	Cyclic voltammetry
DPSC	Double potential step chronoamperometry
LSV	Linear sweep voltammetry
dc pol, ac pol	dc, ac polarography

Solvents

AcOH	Acetic acid
Ac ₂ O	Acetic anhydride
aq.	aqueous
BN	Benzonitrile
CH ₂ Cl ₂	Dichloromethane
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EtOH	Ethanol
Glyme	1,2-Dimethoxyethane
HMPA(HMPT)	Hexamethylphosphoramide
MeCN(AN)	Acetonitrile
Me ₂ CO	Acetone
MeOH	Methanol
NMP	<i>N</i> -Methylpyrrolidone
PC	Propylene carbonate
Py	Pyridine
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMP	Trimethyl phosphate

Chemicals, Ligands, Radicals

Ac	Acetyl
acac	Acetylacetone
aib	Tripeptide of α -aminoisobutyric acid
Ant	Anthracene
Ar	Aryl
bipy(bpy)	2,2'-Bipyridine
Boc	<i>t</i> -Butoxycarbonyl
Bu	Butyl
Bn	Benzyl
Bu ₄ NBF ₄	Tetrabutylammonium tetrafluoroborate
Bu ₄ NBr	Tetrabutylammonium bromide
Bu ₄ NClO ₄	Tetrabutylammonium perchlorate
Bu ₄ NI	Tetrabutylammonium iodide
Bu ₄ NOTs	Tetrabutylammonium tosylate
Bu ₄ NPF ₆	Tetrabutylammonium hexafluorophosphate
CbZ	Benzoyloxycarbonyl
COT	Cyclooctatetraene
Cp	Cyclopentadiene
Cyclam	1,4,8,11-tetraazacyclotetradecane
Dim	Diimine
DMPBF ₄	Dimethylpyrrolidinium tetrafluoroborate
dppe	1,2-bis(diphenylphosphino)ethane, (Ph ₂ PCH ₂) ₂ dppe 1,2-bis(diphenylphosphino)propane, (Ph ₂ PCH ₂) ₂ CH ₂
E ⁺	Electrophile
Et	Ethyl
Et ₄ NClO ₄	Tetraethylammonium perchlorate
Et ₄ NI	Tetraethylammonium iodide
Et ₄ NOTs	Tetraethylammonium tosylate
EWG	Electron withdrawing group
Fc	Ferrocenyl
H ₂ P	Porphyrin
H ₂ OP	Octaethylporphyrin
KCl	Potassium Chloride
KI	Potassium iodide
KClO ₄	Potassium perchlorate
LiBr	Lithium bromide
LiCl	Lithium chloride
LiClO ₄	Lithium perchlorate
Me	Methyl
Me ₄ NBF ₄	Tetramethylammonium tetrafluoroborate
Me ₄ NClO ₄	Tetramethylammonium perchlorate
Me ₃ SiCl(TMSCl)	Trimethylchlorosilane
MP	Metalloporphyrin
MsOH	Methanesulfonic acid

MTPP	Tetraphenylmetalloporphyrine
NaClO ₄	Sodium perchlorate
Naph	Naphthalene
Nu	Nucleophile
Pa	Polyacetylene
Pc	Phthalocyanine
Ph	Phenyl
phen	1,10-Phenanthroline
PPh ₃	Triphenylphosphine
Pr	Propyl
Pr ₄ NClO ₄	Tetrapropylammonium perchlorate
R	Alkyl
Sal	Salicylaldehyde
salen	<i>N,N</i> -ethylenebis(salicylideneamine)
Bu ₄ NClO ₄	Tetrabutylammonium perchlorate
Et ₄ NClO ₄	Tetrabutylammonium perchlorate
THP	Tetrahydropyran
TMA	Tetramethylammonium
TPA	Tetrapropylammonium
<i>sec(s)</i>	Secondary
<i>tert(t)</i>	Tertiary

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