

Sigeru Torii

Electroorganic Reduction Synthesis

Volume 2



KODANSHA



WILEY-
VCH

WILEY-VCH Verlag GmbH & Co. KGaA

Sigeru Torii

Professor Emeritus, Okayama University, Japan

This book was carefully produced. Nevertheless, authors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Published jointly by

Kodansha Ltd., Tokyo (Japan),

WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (Federal Republic of Germany)

Library of Congress Card No. : applied for.

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by

Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>.

ISBN 4-06-213081-5 (KODANSHA)

ISBN 3-527-31539-X (WILEY-VCH)

ISBN 978-3-527-31539-0 (WILEY-VCH)

Copyright © Kodansha Ltd., Tokyo, 2006

All rights reserved. No part of this book may be reproduced in any form, by photostat, microfilm, retrieval system, or any other means, without the written permission of Kodansha Ltd. (except in the case of brief quotation for criticism or review)

Printed in Japan

Contents

Preface.....	v
8. Electroreduction of Alcohols, Ethers and Esters	433
8.1 Reduction of Alcohols	433
8.2 Reductive Removal of Alcohols and Phenols	434
8.2.1 Reduction of Methanesulfonates, Triflates and Other Esters.....	434
8.2.2 Electroreductive Etherification and Transesterification.....	437
8.3 Reductive Cleavages of Carbon-Oxygen Bonds	439
8.3.1 Reductive Cleavage of Oxiranes (Epoxides)	439
8.3.2 Reductive Cleavage of Carbon-Oxygen Bonds Other than Epoxides	441
8.3.3 Reductive Cleavage of Peroxides.....	447
8.4 Miscellaneous	447
References.....	448
9. Electroreduction of Organic Compounds Involving Group IIIA, IVA, VA, IB and IIB Elements	451
9.1 Reduction of Organic Compounds Containing Group IIIA, IVA and VA Elements.....	451
9.1.1 Reduction of Organosilicon Compounds.....	451
9.1.2 Reduction of Organotin Compounds	465
9.1.3 Reduction of Organolead Compounds	470
9.1.4 Reduction of Organogermane Compounds.....	472
9.1.5 Reduction of Organic Compounds Containing Group VB	474
9.1.6 Reduction of Organic Compounds Containing Group IIIB Elements	483
9.2 Reduction of Organic Compounds Containing Group IB and IIB Elements	484
9.2.1 Reduction of Organomercury Compounds	484
9.2.2 Reduction of Organic Compounds Containing Zn and Cd.....	488
9.2.3 Reduction of Organic Compounds Containing Group IB Elements.....	491
9.2.3.1 Reduction of Organocopper Compounds.....	491
9.2.3.2 Reduction of Organosilver and Organogold Compounds.....	494
References.....	495
10. Electroreduction of Organometallic Compounds.....	501
10.1 Electroreduction of Organo-Metal Complexes Involving Group VIII Elements (Ni, Co and Fe)	501
10.1.1 Reactions of Organo-Nickel Complexes.....	501

10.1.2	Reactions of Organo-Cobalt Complexes.....	506
10.1.3	Reactions of Organo-Iron Complexes.....	514
10.1.4	Precious Metal Complexes (Pd, Pt, Rh and Ir)	521
10.1.4.1	Reactions of Organo-Palladium Complexes	521
10.1.4.2	Reactions of Organo-Platinum Complexes.....	524
10.1.4.3	Reactions of Organo-Rhodium and Organo-Iridium Complexes	526
10.1.5	Reactions of Ruthenium and Osmium Compounds (Ru, Os)	529
10.1.5.1	Reactions of Organo-Ruthenium Complexes.....	529
10.1.5.2	Reactions of Organo-Osmium Complexes.....	531
10.2	Electroreduction of Organo-Metal Complexes Involving Group VIB, VB and VIIB Elements (Cr, Mo, IV, Mn, Re, Ti)	532
10.2.1	Reactions of Organo-Metal Complexes (Cr, Mo and W)	532
10.2.1.1	Reactions of Organo-Chromium Complexes	532
10.2.1.2	Reactions of Organo-Molybdenum Complexes.....	535
10.2.1.3	Reactions of Organo-Tungsten Complexes	540
10.2.2	Organo-Metal Complexes Containing (Mn and Re).....	542
10.2.2.1	Reactions of Organo-Manganese Complexes	542
10.2.2.2	Reactions of Organo-Rhenium Complexes.....	543
10.2.3	Organo-Metal Complexes Containing Group IVB and VB Elements Ti, Hf, V, Nb, Ta.....	544
10.2.3.1	Organo-Metal Complexes Containing Ti and Zr	544
10.2.3.2	Organo-Metal Complexes Containing V and Nb.....	544
10.3	Organo-Metal Complexes Involving Lanthanides.....	545
	References.....	546

11. Indirect Electroreduction Using Metal Complex Redox and Organic Redox

	Mediators	553
11.1	Indirect Electroreduction with Mediators Having Group VIII Elements	554
11.1.1	Mediators Containing Nickel, Cobalt and Iron	554
11.1.1.1	Nickel Complex Mediators	554
11.1.1.2	Cobalt Complex Mediators	568
11.1.1.3	Iron Complex Mediators	575
11.1.2	Mediators Containing Palladium, Rhodium, Iridium and Platinum	581
11.1.2.1	Palladium Complex Mediators.....	581
11.1.2.2	Rhodium and Iridium Complex Mediators	586
11.1.2.3	Platinum Complex Mediators	589
11.1.3	Mediators Containing Ruthenium and Osmium	589
11.1.3.1	Ruthenium Complex Mediators	589
11.1.3.2	Osmium Complex Mediators	592
11.2	Indirect Electroreduction with Mediators Having Group VIB and VIIB Elements	593
11.2.1	Mediators Containing Chromium, Molybdenum and Tungsten	593
11.2.1.1	Chromium Complex Mediators.....	593
11.2.1.2	Molybdenum Complex Mediators	596
11.2.1.3	Tungsten Complex Mediators	597
11.2.2	Mediators Containing Manganese and Rhenium	599

11.2.2.1 Manganese Complex Mediators.....	599
11.2.2.2 Rhenium Complex Mediators.....	600
11.3 Indirect Electroreduction with Mediators Having Group IV, IIB and VIA Elements.....	601
11.3.1 Mediators Containing Titanium, Tin and Lead.....	601
11.3.1.1 Titanium Complex Mediators.....	601
11.3.1.2 Tin Complex Mediators.....	603
11.3.1.3 Lead Complex Mediators.....	603
11.3.2 Mediators Containing Zinc, Mercury and Cadmium.....	605
11.3.2.1 Zinc Complex Mediators.....	605
11.3.2.2 Mercury and Cadmium Complex Mediators.....	607
11.3.3 Mediators Containing Selenides or Tellurides.....	609
11.4 Miscellaneous Metal Complex Mediators.....	611
11.4.1 Samarium-catalyzed Reactions.....	611
11.4.2 Use of Mediators Containing Antimony (Stibium) and Bismuth.....	612
11.4.3 Copper-catalyzed Reactions.....	613
11.5 Indirect Electroreduction with Organic Redox Mediators.....	614
11.5.1 Enzymatic Organic Redox Mediators.....	614
11.5.1.1 NAD and NADP Coenzymes and Methylviologen as Organic Redox Mediators.....	614
11.5.1.2 NAD^+/NADH , $\text{MV}^{2+}/\text{MV}^+$ Double Mediator Organic Redox Systems.....	616
11.5.1.3 Miscellaneous Bioorganic Mediators.....	621
11.5.2 Nonbiological Organic Redox Mediators.....	622
References.....	628
12. Electrogenerated Base-assisted Conversion.....	635
12.1 Role of Electrogenerated (EG) Bases in Electrosynthetic Reactions.....	635
12.2 Electrogenerated Anion-radicals and Carbanions as EG Bases.....	635
12.2.1 EG Bases from Carbonyl Compounds.....	635
12.2.1.1 Reaction of EG Bases (Anion Radicals and Carbanions) from Carbonyl Compounds.....	635
12.2.1.2 Reaction of Carbanions Stabilized by Carbonyl Groups.....	641
12.2.2 Reaction of Carbanions Stabilized by Cyano Groups.....	653
12.2.3 Reaction of Carbanions Adjacent to Halogen Atoms.....	659
12.2.4 Reaction of Carbanions Adjacent to Aromatic Systems.....	663
12.2.5 Reaction of Carbanions Adjacent to Hetero Atoms.....	666
12.2.6 Reaction of EG Bases from Alkyl and Aryl Halides.....	668
12.3 Electrogenerated Amide Ions as EG Bases.....	671
12.3.1 Reaction of EG Bases Derived from Azo Compounds.....	671
12.3.2 Reaction of EG Bases Derived from Carbonylated Nitrogen Compounds.....	676
12.3.3 Reaction of EG Bases from Miscellaneous Nitrogen Compounds.....	683
12.4 Miscellaneous EG Bases.....	687
12.4.1 Reaction of EG Bases from Miscellaneous Systems.....	687
12.4.2 Reaction of Superoxides as EG Bases.....	691
12.4.2.1 Generation and Characteristic Features of Superoxide.....	691
12.4.2.2 Reaction of Superoxides as EG Bases.....	692

12.4.2.3 Reaction of Superoxide as a Nucleophile and an Oxidant.....	693
References.....	698
13. Electropolymerization	703
13.1 Electronic Conducting Polymers	703
13.1.1 Polypyrrole Conducting Polymers	703
13.1.1.1 Electropolymerization of Pyrroles and Doping of Polypyrroles.....	705
13.1.1.2 Polypyrroles as Modified Electrodes, Membranes, Batteries and Others...	710
13.1.1.3 Miscellaneous Pyrrole Conducting Polymers	713
13.1.2 Polythiophene Conducting Polymers.....	715
13.1.2.1 Electropolymerization of Thiophene and Doping of Polythiophenes.....	716
13.1.2.2 Polythiophene Films in Rechargeable Storage Batteries	723
13.1.3 Aromatic Conjugated Polymers	724
13.1.3.1 Electropolymerization of Aromatic Hydrocarbons and Doping of Aromatic Conjugated Polymers	724
13.1.3.2 Polyphenylenes as Rechargeable Battery Electrode Materials	729
13.1.4 Polyacetylene Conducting Polymers.....	730
13.1.4.1 <i>n</i> - and <i>p</i> -Type Doped Polyacetylenes	731
13.1.4.2 Polyacetylene Films in Rechargeable Storage Batteries	733
13.1.4.3 Miscellaneous Conducting Polymers	734
13.1.5 Polyaniline Conducting Polymers.....	735
13.1.5.1 Electropolymerization of Anilines and Doping of Polyanilines	735
13.1.5.2 Conducting Polymers from Other Aromatic Amines.....	738
13.1.6 Miscellaneous Conducting Polymers.....	739
13.1.6.1 Electropolymerization of Miscellaneous Compounds	739
13.1.6.2 Electrodes Modified with Conducting Polymers	741
13.2 Electrochemically Associated Polymers.....	743
13.2.1 Electroinitiated Polymerization.....	743
13.2.1.1 Electroinitiated Polymerization of Aliphatic Olefins.....	743
13.2.1.2 Electroinitiated Polymerization of Aromatic Olefins	748
13.2.1.3 Small Ring-Opening Electropolymerization.....	751
13.2.1.4 Electroinitiated Polymerization of Phenols.....	751
13.2.1.5 Electroinitiated Polymerization of Miscellaneous Compounds.....	753
13.2.2 Electrochemical Behaviors of Polymers	754
13.2.2.1 Fluorine Atom-containing Polymers.....	754
13.2.2.2 Polymers Bearing Quinone Moieties	755
13.2.2.3 Polymers Bearing Pyridyl Moieties	756
13.2.2.4 Polymers Bearing Porphyrinic and Phthalocyanyl Moieties	758
References.....	759
Appendix.....	767

Abbreviations and Symbols	xiii
Index	xvii

Contents for Volume 1

1. Electrochemical Reduction and Product Selectivity	1
2. Electroreduction of Aldehydes, Ketones, Acids, Esters and Acids Anhydride	39
3. Electroreductive Reaction of Olefins	127
4. Electroreductive Reaction of Aromatic Compounds	161
5. Electroreduction of Nitrogen Compounds	185
6. Electroreduction of Sulfur, Selenium and Tellurium Compounds	277
7. Electroreduction of Halogenated Compounds	331
