

Stereochemistry of Radical Reactions

Concepts, Guidelines and Synthetic Applications

by Dennis P. Curran, Ned A. Porter & Bernd Giese

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Chapter 1

Radical Reactions in Organic Synthesis

1.1 Introduction

As recently as a decade ago, organic radicals were regarded as interesting reactive intermediates with limited synthetic potential. As a rule, radical reactions were thought to be “messy”, and the few “clean” radical reactions, like allylic and benzylic brominations with *N*-bromosuccinimide (NBS), were viewed as the exceptions that proved the rule. This view of radicals probably arose because of the notion that highly reactive intermediates could not be selective. The concept of selectivity pervades organic synthesis, and with good reason—selectivity is the key to high yields.

The logic that reactive intermediates such as radicals cannot participate in selective reactions with controlled, predictable outcomes is faulty. Research on the structures and reactions of organic radicals conducted largely by physical organic chemists in the 60s and 70s¹ laid the foundation for the synthetic explosion that followed in the 80s and is still ongoing.² Synthetic chemists gradually came to realize that it is only relative rates that are important for selectivity; the simple fact that radicals often react with high absolute rates is actually desirable, not undesirable. They began to realize the difference between radical/radical reactions, which often occur at the diffusion-controlled limit and are hence unselective, and radical/molecule reactions, which occur with a huge range of rate constants. They learned that the rates of radical/radical reactions are easily minimized by choosing reaction conditions in which radical concentrations are low, and that the rates of radical/molecule reactions—that is, the selectivities—can be adjusted by the experimenter over a wide range by choice of reaction partners, concentrations, temperature, and other variables.

Radical-molecule reactions are now recognized to frequently be both chemo- and regioselective. It is ironic that radical reactions, once thought to be capricious and unpredictable, have a higher level of predictability in

Radical Reactions In Organic Synthesis

Guerino Sacripante



Radical Reactions In Organic Synthesis:

Radical Reactions in Organic Synthesis Samir Z. Zard, 2003 Samir Zard provides a description of radical reactions and their applications in organic synthesis This book shows that an with an elementary knowledge of kinetic and some common sense it is possible to harness radicals into a tremendously powerful tool for solving synthetic problems *Free Radicals in Organic Synthesis* D. I. Davies, M. J. Parrott, 2012-12-06 **Free Radical Chain Reactions in Organic Synthesis** William B. Motherwell, David Crich, 1992 Written for both the experienced practitioner and the newcomer this book provides essential guidance to the practical aspects of free radical chain reactions The book presents tried and tested synthetic schemes as well as a selection of recently developed methods describing rationally designed highly efficient syntheses giving high yield interconversions of functional groups and carbon b1carbon bond formation under mild neutral conditions Written by two experienced practitioners in the field this volume explodes the myth that free radicals are highly reactive non selective intermediates Contains an extensive introduction discussing principles advantages and disadvantages of radical chain reactions Demonstrates functional group interconversions by radical chain reactions Lists carbon b1carbon bond formations Presents inter and intramolecular radical chain reactions Includes many examples and experimental details selected by experienced practitioners in this field **Advanced Free Radical Reactions for Organic Synthesis**, 2004-01-14 Free radical reactions have become increasingly important and a very attractive tool in organic synthesis in the last two decades due to their powerful selective specific and mild reaction abilities Advanced Free Radical Reactions for Organic Synthesis reviews information on all types of practical radical reactions e g cyclizations additions hydrogen atom abstractions decarboxylation reactions The book usefully provides experimental details for the most important reactions as well as numerous references to the original literature By covering both the fundamentals and synthetic applications it is therefore suitable for both new and experienced researchers chemists biochemists natural product chemists and graduate students This title is the definitive guide to radical chemistry for all scientists Introduces and reviews the use of radicals to perform synthetic transformations Practical details are provided for the most important methods Numerous references to the original literature **Reagents for Radical and Radical Ion Chemistry** David Crich, 2013-05-30 Radicals and radical ions are important intermediates with wide use in organic synthesis The first book to concentrate on reagents for the creation and use of radicals and radical ions this new volume in the Handbooks of Reagents for Organic Synthesis series compiles articles taken from the e eros database on reagents for use in radical and radical chemistry to help the chemist in the lab choose the right reagents Reflecting the enormous growth of radical chemistry over the past ten years this is an essential guide for all synthetic chemists Radical Reactions in Organic Synthesis Guerino Sacripante, 1986 alpha Bromo and alpha alpha dibromoazetidiones were converted stereoselectively to the alpha alkylazetidiones 149 and 153 or to beta alkylazetidiones 151 154 and 159 by a free radical addition onto olefins 148 or allyltributyltin *Radical Reactions in*

Aqueous Media Tamara Perchyonok, 2009-11-10 Chemists are now moving away from volatile environmentally harmful and biologically incompatible organic solvents. With its low cost, ready availability and capacity to remove environmentally unfriendly by-products, water is an obvious replacement. Recent advances in free radical chemistry in water have expanded the versatility and flexibility of homolytic carbon-hydrogen, carbon-carbon, carbon-halogen, carbon-nitrogen bond formations in aqueous media. This textbook highlights the substantial progress which has been made in the last decade to tame the reactive free radical species in aqueous phase reactions. It describes carbon-hydrogen bond formations in aqueous media via radical reactions with a specific focus on HAT (Hydrogen Atom Transfer). Suitable for students of chemistry, industrial chemists and academic researchers, it combines extensive knowledge of free radical chemistry with the latest innovations and creative applications. Divided into five main areas, it covers the generation of carbon-centred free radicals, radical initiators, solubility of substrate, suitability of free radical hydrogen donors and HAT reactions in aqueous media. The book describes radical reactions in organic and aqueous media and their applications in total synthesis, DNA structural probing, isotope labelling, living polymerization and various other applications. It shows that armed with an elementary knowledge of kinetics and some common sense, it is possible to harness radicals into tremendously powerful tools for solving synthetic problems. Written with the needs of students in mind, it offers just the right level of detail for undergraduate study. All the basic principles and facts on each topic area are presented in a concise yet comprehensive style that is appropriate for both core and specialist courses. It provides a step-wise introduction, taking students from the basic principles of radical reactions through to their applications in industry and their role in biological and environmental processes. Case studies are used to illustrate reactions in landmark synthesis and problems with outlined answers test the reader's understanding. There are also suggestions for further reading.

Domino Reactions in Organic Synthesis Lutz F. Tietze, Gordon Brasche, Kersten Gericke, 2006-12-13 Domino reactions enable you to build complex structures in one-pot reactions without the need to isolate intermediates; a dream comes true. In this book, the well-respected expert Professor Lutz Tietze summarizes the possibilities of this reaction type and provides an approach for an efficient, economically beneficial and ecologically benign synthesis. A definite must for every organic chemist.

Modern Methods of Organic Synthesis W. Carruthers, Iain Coldham, 2004-10-14 The fourth edition of this well-known textbook discusses the key methods used in organic synthesis, showing the value and scope of these methods and how they are used in the synthesis of complex molecules. All the text from the third edition has been revised to produce a modern account of traditional methods and an up-to-date description of recent advancements in synthetic chemistry since the previous edition. A new chapter on the functionalisation of alkenes has been included and greater emphasis on highly stereoselective reactions and radical chemistry has been placed. Reference style has been improved to include footnotes on each page, allowing easy and rapid access to the primary literature. The book will be of significant interest to chemistry and biochemistry students at advanced undergraduate and graduate level as well as researchers in academia and industry who

wish to familiarise themselves with modern synthetic methods

Comprehensive Organic Synthesis, 2014-02-14 The second edition of Comprehensive Organic Synthesis winner of the 2015 PROSE Award for Multivolume Reference Science from the Association of American Publishers builds upon the highly respected first edition in drawing together the new common themes that underlie the many disparate areas of organic chemistry These themes support effective and efficient synthetic strategies thus providing a comprehensive overview of this important discipline Fully revised and updated this new set forms an essential reference work for all those seeking information on the solution of synthetic problems whether they are experienced practitioners or chemists whose major interests lie outside organic synthesis In addition synthetic chemists requiring the essential facts in new areas as well as students completely new to the field will find Comprehensive Organic Synthesis Second Edition Nine Volume Set an invaluable source providing an authoritative overview of core concepts Winner of the 2015 PROSE Award for Multivolume Reference Science from the Association of American Publishers Contains more than 170 articles across nine volumes including detailed analysis of core topics such as bonds oxidation and reduction Includes more than 10 000 schemes and images Fully revised and updated important growth areas including combinatorial chemistry new technological industrial and green chemistry developments are covered extensively

In-Depth Advanced Organic Chemistry Rajeev Khatri, 2025-02-20 In Depth Advanced Organic Chemistry is a comprehensive guide to the study of carbon containing compounds often referred to as the chemistry of life We cover a wide range of topics from the synthesis of complex molecules to the study of reaction mechanisms and catalysis making this book an authoritative resource for students researchers and professionals We begin with an introduction to organic chemistry principles including molecular structure chirality and spectroscopic techniques The book progresses to discuss the synthesis of complex organic molecules using techniques such as retrosynthetic analysis asymmetric synthesis and transition metal catalysis We also explore reactions of organic molecules covering traditional organic reactions and modern synthetic methods like click chemistry and metathesis reactions Our study of reaction mechanisms includes chemical kinetics and computational chemistry to understand reaction pathways Additionally we discuss principles of catalysis including homogeneous and heterogeneous catalysis and the use of enzymes as biocatalysts The final section delves into the context of biology and medicine covering topics such as the synthesis of pharmaceutical compounds enzyme mechanisms and the use of organic molecules in chemical biology In Depth Advanced Organic Chemistry is an essential reference offering theoretical knowledge and practical insights for mastering organic chemistry

Click Reactions in Organic Synthesis Srinivasan Chandrasekaran, 2016-09-13 Endlich ein Buch zu Click Reaktionen mit Schwerpunkt auf der organischen Synthese Beschrieben werden das Click Konzept die zugrunde liegenden Mechanismen und Hauptanwendungsgebiete N TZLICH Die Click Chemie ist ein wirkungsvoller Ansatz um auf einfache Weise komplexe organische Molek le aus verf gbaren Ausgangsmaterialien zu erzeugen der Traum jedes Organikers EINZIGARTIGER SCHWERPUNKT Aufgrund des besonderen Schwerpunkts auf der organischen Synthese ist

dieses Buch für jeden Synthesechemiker von hohem Interesse HILFREICH Click Reaktionen sind stereospezifisch einfach durchzuführen hoch ergiebig und lassen sich in einfach zu entfernenden oder nicht schädlichen Lösungsmitteln durchführen INTERDISZIPLINÄR Das Click Konzept ist bei der Herstellung natürlicher Produkte bioaktiver Verbindungen von Kohlenhydraten Arzneimitteln Polymeren supramolekularer Strukturen und Materialien weit verbreitet

Organic Synthesis Michael Smith, 2024-08-13 Organic Synthesis 5e provides a reaction based approach to this important branch of organic chemistry Updated and accessible this eagerly awaited revision offers a comprehensive foundation for graduate students coming from disparate backgrounds and knowledge levels to provide them with critical working knowledge of basic reactions stereochemistry and conformational principles This reliable resource uniquely incorporates molecular modeling content problems and visualizations and includes reaction examples and homework problems drawn from the latest in the current literature There have been advancements in organic reactions particularly organometallic reactions and there is a need to show how these advancements have influenced current organic synthesis The goal is to revise and update the examples of reaction examples taken from the synthesis literature from about 2017 2023 The reactions illustrate those that are used most often in modern organic synthesis but recent examples will show their current relevance Where new approaches and new reactions have been developed for organic synthesis examples will be added as new material Provides new content reaction examples and study problems from recent research Features improved organization new art and new chapter content on process chemistry and green organic chemistry Includes revised homework for each chapter with new examples and questions

Strategic Applications of Named Reactions in Organic Synthesis Laszlo Kurti, Barbara Czako, 2005-04-29 Kurti and Czako have produced an indispensable tool for specialists and non specialists in organic chemistry This innovative reference work includes 250 organic reactions and their strategic use in the synthesis of complex natural and unnatural products Reactions are thoroughly discussed in a convenient two page layout using full color Its comprehensive coverage superb organization quality of presentation and wealth of references make this a necessity for every organic chemist The first reference work on named reactions to present colored schemes for easier understanding 250 frequently used named reactions are presented in a convenient two page layout with numerous examples An opening list of abbreviations includes both structures and chemical names Contains more than 10 000 references grouped by seminal papers reviews modifications and theoretical works Appendices list reactions in order of discovery group by contemporary usage and provide additional study tools Extensive index quickly locates information using words found in text and drawings

Stereochemistry of Radical Reactions Dennis P. Curran, Ned A. Porter, Bernd Giese, 2008-09-26 As little as a decade ago radicals were regarded as interesting reactive intermediates with little synthetic use However recent results show that radicals have an enormous potential for applications in stereoselective reactions it's all a matter of knowing what method to use and how to apply it Three world experts in the field have combined their expertise and present the concepts to

understand and even to predict the course of stereoselective radical reactions In addition guidelines are established which will enable the readers to plan and carry out their own stereoselective syntheses with radicals A comprehensive list of references provides an easy access to the primary literature The Stereochemistry of Radical Reactions is a highly topical introduction to this burgeoning field of research Both advanced students and researchers active in the field will welcome this book as a source of concepts and ideas *Comprehensive Organic Synthesis: Additions to and substitutions at C-C[pi]-Bonds* Barry M. Trost, 1991 Volume 4 focuses on additions and the resulting substitutions at carbon carbon bonds Part 1 includes processes generally considered as simple polar reactions reactive electrophiles and nucleophiles adding to alkenes and alkynes A major topic is Michael type addition to electron deficient bonds featured in the first six chapters In part 2 are collected the four general processes leading to nucleophilic aromatic substitution including radical chain processes and transition metal activation through to complexation Metal activated addition generally by nucleophiles to alkenes and polyenes is presented in part 3 including allylic alkylation catalyzed by palladium The coverage of nonpolar additions in part 4 includes radical additions organometal addition Heck reaction carbene addition and 1,3 dipolar cycloadditions *Silver Catalysis in Organic Synthesis, 2 Volume Set* Chao-Jun Li, Xihe Bi, 2019-04-29 Dieses Fachbuch untersucht systematisch die Leistungsfähigkeit der Silberkatalyse behandelt neu entwickelte organische Reaktionen und den Reaktionsmechanismus Der Schwerpunkt liegt auf den Eigenschaften und dem Vergleich der Vorteile dieser Katalyse in der organischen Synthese

Advances in Organic Synthesis Atta-ur-Rahman, 2013-01-10 *Advances in Organic Synthesis* is a book series devoted to the latest advances in synthetic approaches towards challenging structures It presents comprehensive articles written by eminent authorities on different synthetic approaches to selected target molecules and new methods developed to achieve specific synthetic transformations Contributions are written by eminent scientists and each volume is edited by an authority in the field *Advances in Organic Synthesis* is essential for all organic chemists in the academia and industry who wish to keep abreast of rapid and important developments in the field *Advanced Organic Chemistry* Reinhard Brückner, 2002 A best selling mechanistic organic chemistry text in Germany this text's translation into English fills a long existing need for a modern thorough and accessible treatment of reaction mechanisms for students of organic chemistry at the advanced undergraduate and graduate level Knowledge of reaction mechanisms is essential to all applied areas of organic chemistry this text fulfills that need by presenting the right material at the right level *A Foundation Course for College Organic Chemistry* B. S. Balaji, 2024-08-22 To understand and improve the underlying principles that govern how organic reactions occur *A Foundation Course for College Organic Chemistry* follows a brick by brick building approach Emphasis is given to interrelating experimental facts and findings with predictions mechanism and inferences results Discussions focus on clarifying how complex organic reactions occur which is based on electronegativity differences movement of electrons through framework or bonds and addition or removal of atoms hydrogen halogens or groups hydroxy amino The book begins

with simple rules governing the deconstruction of reactions and applies them to explain how esterification amide and cyanide hydrolysis reactions proceed The importance of stereochemistry used in drug development biology and medicine aromatic electrophilic and nucleophilic substitutions reaction kinetics and dynamics is explained with suitable examples Features A systematic and structured approach is used to study all aspects of reactive intermediates generation structure geometry and reactions of carbocations carbanions and carbon free radicals This book incorporates scientific methods to deduce reaction mechanisms with simple and relevant explanations and limitations A proper explanation is given to understand the influence of functional groups on the stability and reactivity of intermediates pKa HSAB principles structure activity relations and how these can be exploited in organic chemistry Information is presented in an accessible way for students teachers researchers and scientists

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