

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

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D. I. Davies, M. J. Parrott



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Free Radicals in Organic Synthesis D. I. Davies, M. J. Parrott, 2012-12-06 *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 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

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 Samir Z. Zard, 2003 Introduction and some general concepts General principles chain reactions based on stannane chemistry Further chain reactions of stannanes Organo silicon germanium and mercury hydrides The Barton decarboxylation and related reactions Atom and group transfer reactions The persistent radical effect non chain processes Redox processes Some concluding remarks

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 to carbon 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 to carbon 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

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

Radical Reactions in Organic Synthesis Guerino Sacripante, 1986 alpha Bromo and alpha alpha dibromoazetidinones were converted stereoselectively to the alpha alkylazetidinones 149 and 153 or to beta alkylazetidinones 151 154 and 159 by a free radical addition onto olefins 148 or allyltributyltin

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 an approach for an efficient economically beneficial and ecological 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.

The Enigmatic Realm of **Radical Reactions In Organic Synthesis**: Unleashing the Language is Inner Magic

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