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Preface

"I didn't think that radical chemistry could be so mild and selective," is the nicer version of comments one often hears after seminars. What is the underlying reason for the misconception? Probably that radical transformations often seem counterintuitive to those brought up with classical retrosynthetic schemes. As a result, the use of radicals is considered by many synthetic chemists as a last resort only to be used when other more traditional methods have failed. Additionally, radical reactions are usually regarded as being unselective and involving toxic reagents.

This is, of course, false; such a conservative approach neglects the mild, selective, and original solutions available through using radical chemistry for demanding synthetic problems. Moreover, a solid physical organic understanding of the mechanism behind most radical reactions has now been established. This basis serves us well in predicting many results as well as in developing novel reactions. In short, radical chemistry has developed with amazing speed from a laboratory curiosity into an integral, predictable, and highly productive part of organic chemistry. This account is meant to further spread this point of view.

The first volume (*Methods and Mechanisms*) concentrates on the mechanistic aspects of radical chemistry and the development of novel methods, while the second volume (*Complex Molecules*) focuses on the use of radicals in synthetic applications. While such traditional separation (novel methods are increasingly aimed at preparing complex molecules and the synthesis of complex molecules requires careful planning) may seem a little outdated at the beginning of the 21st century, it is nevertheless employed for the sake of convenience.

The chapters, written by leading experts, provide state-of-the-art reviews of exciting and pertinent topics of current research in radical chemistry. These include a discussion of computed data concerning radical stabilities and their evaluation, the surprising chemistry of radical cations, modern concepts and reagents for enantioselective radical chemistry, the mechanistic aspects of epoxide opening via electron transfer, the evolution of ecologically benign and efficient tin-free radical reactions, the attractive novel reagents and radical traps for unusual cyclizations, the exciting possibilities of xanthate derived radical processes, the emerging field of radical chemistry on solid supports,

the recent development of highly versatile radical tandem reactions, the mild and selective derivatization of amino acids and sugars through the use of radicals, and the increasing use of Cp_2TiCl-catalyzed and -mediated radical reactions in natural product synthesis.

Of course not all of the exciting recent developments in radical chemistry can be covered in depth in just two books. It is therefore planned to expand this series in the near future. I offer my apologies to the authors left out this time and ask them to contribute next time!

Hopefully this book will meet the challenge of convincing a large number of scientists of the benefits of radical chemistry and spark novel developments in the fields of new radical methodology and the application of radical reactions in the synthesis of complex molecules.

Bonn, February 2006 Andreas Gansäuer

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Radicals in Synthesis I

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