

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

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