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PREFACE

The last years have seen a rapid development in the use of radicals for the synthesis of organic molecules. This is primarily due to the fact that:

because of the mechanistic studies in the last three decades the main features of radical reactions are now known;
radicals in chain reactions have been generated from nearly every important organic functional group;
radical chains can be constructed in which reactions between radicals and non-radicals occur with high selectivities.

In the past, the mild reaction conditions and high selectivities of radical reactions have been often overlooked. Actually, as the articles in this symposium demonstrate, radicals exhibit high chemoselectivities; that is, they react with different functional groups with very different rates, furthermore OH and NH_2 groups are attacked so slowly that they are tolerated without protection. Radicals also show high regioselectivities, for example α,β-unsaturated ketones and esters are attacked exclusively at the olefinic carbon atom and intramolecular radical reactions give different products than their ionic counterparts. Radical rearrangements are less common than rearrangements of cations and the cleavage of a β-C—X bond is less pronounced than in anions. This means that during radical reactions, adjacent chiral centres easily survive. Intramolecular cyclization and intermolecular reactions of cyclic radicals impressively demonstrate that even the stereoselectivity of radical reactions can be high. However, for noncyclic radicals, much work has yet to be done to improve the stereoselectivity. Most of the papers in this symposium describe the synthetic applications of chain reactions, but it is also possible to form products by radical-radical reactions. These reactions occur in most cases with a diffusion-controlled rate and it is often difficult to influence their selectivities.

I hope that this symposium will show that radical chemistry offers new and useful methods for the synthesis of target molecules and I would like to thank the contributors to the symposium for their excellent manuscripts.

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