PREFACE TO VOLUME 91

Fluorine has to be the most schizophrenic element in the Periodic Table. In its nascent form it is the most reactive element, combining indiscriminately and exothermically with anything it contacts. However, once bound into organic compounds, it renders them extremely inert, thus imbuing them with highly valued properties in products that permeate our everyday lives. Mario Markus sums it up beautifully in his *Chemical Poems: One for Each Element,* in which he juxtaposes the dichotomy of hyperreactivity and civility; "The homicidal maniac blinds or kills whoever comes near . . . ..Why? Because he wants an electron, that's all. Let us give him the pittance that he wants. Now we see how calm he becomes . . . " The inertness of organofluorine compounds leads to myriad applications from non-stick frying pans to refrigerants to medical implants.

However, for the synthetic organic chemist, the extraordinary chemical stability of carbon-fluorine bonds has found widespread application in fine-tuning the physico-chemical properties of pharmaceutical, agrochemical, and liquid crystalline substances. In particular the trifluoromethyl group has become a highly prized substituent by dint of its high electronegativity, lipophilicity, steric size, and resistance to chemical degradation by oxidative, reductive, hydrolytic, photolytic, and thermal insults. Given the broad utility of the trifluoromethyl group, it is not surprising that the number of methods for selective and efficient introduction of this group into many different organic substrates has been a major focus of research for the past decades. This field has grown so rapidly with so many important advances that it would be impossible to comprehensively cover all such methods even in a single volume of *Organic Reactions.* Accordingly, Volume 91 contains a single chapter dedicated to one of the most useful methods for introducing a perfluoroalkyl group, namely nucleophilic perfluoroalkylation.

We are extremely fortunate that three of the worlds' leading experts on nucleophilic perfluoroalkylation have teamed up to produce the first, comprehensive treatment of this extremely important transformation. Prof. Petr Beier, Dr. Mikhail Zibinsky, and Prof. G. K. Surya Prakash have combined their many years of first-hand research experience and encyclopedic knowledge of the field in a massive, but yet highly accessible and authoritative treatise covering all of the methods for delivering perfluoroalkyl groups from dozens of different sources to scores of different substrates. The resulting matrix of possibilities for combinations of perfluoroalkyl donor and organic acceptor would inevitably paralyze the practitioner with a bewildering abundance of options. In view of this challenge, the authors have provided tabular listings of the recommended reagents for perfluoroalkylation of the most common substrates. Even if one is not immediately interested in performing a perfluoroalkylation, reading this chapter provides a fascinating overview of the extraordinary diversity of donors ranging from the ubiquitous Rupert-Prakash

reagent (trifluoromethyltrimethylsilane) to perfluoroalkyltellurium reagents to perfluoroalkyllithium, −indium, −copper, −silver, and -zinc reagents. A still greater congregation of electrophiles is covered ranging from organohalides to carbonyl groups to azomethines to carboxyl derivatives all the way to Main Group and Transition Metal electrophiles and even xenon! Finally, the most recent advances for introducing perfluoroalkyl groups with control of newly created stereogenic centers are also covered.

The Tabular Survey contains over 540 pages of all examples of nucleophilic perfluoroalkylation contained in the literature through the first quarter of 2014. The tables are organized by electrophilic substrate, thus allowing the reader to quickly locate the class of compounds of specific interest. Moreover, extensive subtables have been compiled that allow direct comparison of different methods that have been applied to a given substrate, thus facilitating an immediate evaluation of the appropriate choice for that specific target.

Volume 91 represents the thirteenth single chapter volume to be produced in our 75-year history (the fourth in a row and sixth in the past twelve volumes!). Such single-chapter volumes represent definitive treatises on extremely important chemical transformations. The organic chemistry community owes an enormous debt of gratitude to the authors of such chapters for the generous contribution of their time, effort, and insights on reactions that we clearly value.

It is appropriate here to acknowledge the expert assistance of the entire editorial board, in particular Michael Martinelli who oversaw the early development of this chapter. The contributions of the authors, editors, and the publisher were expertly coordinated by the board secretary, Robert M. Coates. In addition, the *Organic Reactions* enterprise could not maintain the quality of production without the dedicated efforts of its editorial staff, Dr. Danielle Soenen, Dr. Linda S. Press, Ms. Dena Lindsey, and Dr. Landy Blasdel. Insofar as the essence of *Organic Reactions* chapters resides in the massive tables of examples, the authors' and editorial coordinators' painstaking efforts are highly prized.

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