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# Introduction: Fluorine Chemistry

Scientific and commercial interests in fluorine chemistry burgeoned after 1980, largely fueled by the need to replace industrial chlorofluorocarbons and the rapidly growing practical opportunities for organofluorine compounds in crop protection, medicine, and diverse materials applications. (See *Organofluorine Chemistry, Principles and Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994.) Although fluorine chemistry is much less abstruse now than when I entered the field a generation ago, it remains a specialized topic and most chemists are unfamiliar, or at least uncomfortable, with the synthesis and behavior of organofluorine compounds. This thematic issue comprising nine articles is aimed at both increasing the nonspecialist's comfort level with fluorine chemistry and updating the specialist on the structure and properties of reactive intermediates and modern fluorinating reagents.

The chemical behavior of fluorocarbons becomes much more understandable and predictable when the underlying effects of fluorination on reactive intermediates are understood. The first set of articles addresses these effects. Dolbier comprehensively reviews the literature of the past 20 years on the structure, reactivity, and chemistry of fluoroalkyl radicals in solution. Brahms and Dailey next survey fluorocarbenes and fluoroalkylcarbenes, including numerous methods for their generation. Farnham then covers developments in the chemistry of perfluorinated carbanions, principally since the discovery of long-lived species. The final article on fluorinated carbocations by Krespan and Petrov unfortunately did not materialize in time for this issue, but it will appear separately in a future issue of *Chemical Reviews*.

Traditional fluorinating methods based on HF exchange or addition, for example, still dominate the synthesis of fluorinated compounds but there has been an upsurge in the development of more specialized selective reagents for the synthesis of high-value fluorinated materials. Six general classes of modern reagents with diverse applications are discussed in the articles that follow. Burton, Yang, and Qiu give the first comprehensive review of fluorinated N, P, As, Sb, and S ylides plus related fluorophosphonate, sulfoxide, sulfone, and sulfoximine anion salts. Rozen surveys the various available electrophilic hypofluorite fluorinating agents, most of which are produced in situ from $F_2$. Lal, Pez, and Syvret give a complementary review of electrophilic NF reagents that have a wide range of reactivities—and somewhat controversial fluorination mechanisms. Umemoto reviews electrophilic perfluoroalkylating reagents, including his well-known perfluoroalkylphenyliodonium triflates (FITS reagents) and his more recent (trifluoromethyl)dibenzoheterocyclic salts for electrophilic trifluoromethylations. Sawada surveys the use of various fluorinated peroxides for free-radical, or single-electron-transfer, fluoroalkylations. The final article by Petrov and Resnati is the first comprehensive survey of the synthesis, properties, and reactions of fluorinated oxaziridines. Their utility is not as fluorinating agents but rather as versatile oxygen-transfer agents that are much more powerful oxidants than their hydrocarbon counterparts.

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