

Review

Chemically oxidative fluorination with fluoride ions



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ABSTRACT

Although the chemical oxidation of fluoride ions is generally challenging due to the high electronegativity of fluorine, in the past four years, a number of oxidative fluorination reactions via the reactivity umpolung of substrates or fluorides have been developed. These reactions can introduce fluorine into nucleophilic or electron-neutral systems. This short review provides a summary on the recent developments of oxidative fluorination of arenes, alkanes, and alkenes with fluorides promoted by various oxidants. These newly developed reactions are of high selectivity and efficiency, and provide a pathway for the more efficient use of the abundant, yet less nucleophilic fluorides.

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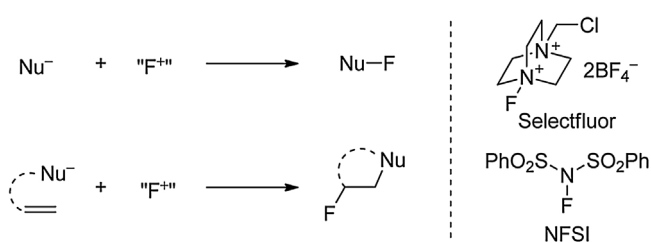
1. Introduction

Fluorine, as an element with a small van der Waals radius (147 pm) and the highest electronegativity (3.98) in the periodic table, is usually considered as “a small atom with big ego” due to its important application in life sciences- and materials-related researches [1]. Introduction of fluorine atom or fluorinated moiety often imparts beneficial properties, such as metabolic

stability, binding affinity, unique biological properties, and corrosion resistance to the target molecule, and a variety of fluorine-containing pharmaceuticals, agrochemicals, and materials have been developed [2]. Recently, increasing attention has been paid to the development of practical and selective fluorination reagents and exploitation of conceptually new methods for the formation of carbon–fluorine bonds [3].

Conventionally, fluorine atoms can be introduced in several manners: (1) electrochemical fluorination of C–H bonds with HF (the Simons process) or a fluoride salt; (2) radical fluorination of hydrocarbons with fluorine gas or CoF_3 ; (3) nucleophilic fluorination of pre-functionalized substrates bearing a leaving group; (4)

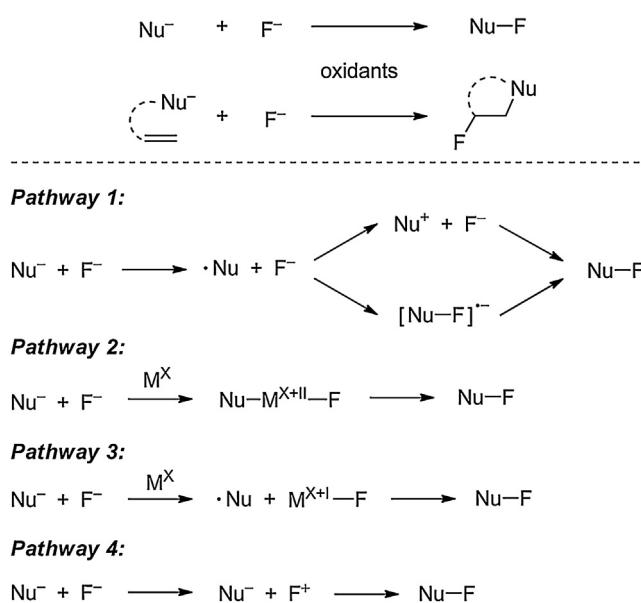
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Scheme 1. Electrophilic fluorination with Selectfluor and NFSI.

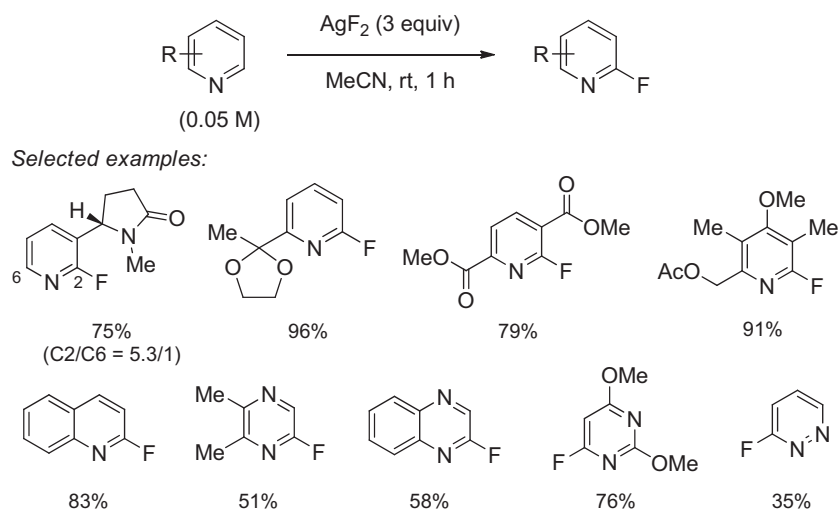
fluoride-addition across a double or triple carbon–carbon bond [2]. Recently, electrophilic fluorination of anionic carbon centers, C–H bonds, and unsaturated compounds such as alkenes has become a common method for selective introduction of fluorine atoms due to the mildness of the reaction conditions (Scheme 1) [3a–c]. However, the electrophilic fluorination reagents represented by Selectfluor and NFSI are obtained from elemental fluorine [4], a very strong oxidant usually prepared by electrolysis of anhydrous HF. Considering that the fluoride ion is stable and abundant in nature [5], the direct oxidative fluorination of substrates with a fluoride ion is an ideal alternative method for the current electrophilic fluorination reactions (Scheme 2). Particularly, in recent years, the development of ^{18}F radiolabeling for positron emission tomography (PET) imaging also calls for the development of oxidative fluorination with ^{18}F fluorides, not only because ^{18}F fluorides are much easier to access and handle than ^{18}F fluorine gas, but also because the fluorination with ^{18}F fluorides can be conducted without added ^{19}F carrier, which produces the ^{18}F labeled probes in higher specific radioactivity [3d–e].

Mechanistically, the oxidative fluorination with fluoride ion can proceed in four ways (Scheme 2): (1) oxidation of the substrate to form an electrophilic carbon center (carbocation, radical cation, or high-valency metal fluorides) followed by nucleophilic fluorination (Pathway 1); (2) oxidation of the substrate to form a

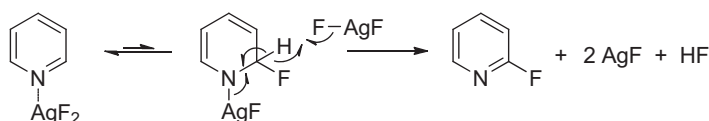


Scheme 2. Oxidative fluorination with fluoride ion.

high-valent metal fluorides followed by reductive elimination (Pathway 2); (3) oxidation of the substrate to form a carbon-centered radical or radical cation species followed by fluorination with the fluorine radical or its equivalents (high-valency metal fluorides) (Pathway 3); (4) oxidation of fluoride to fluoronium ion followed by electrophilic fluorination (Pathway 4). The fourth pathway is less possible to occur because even the oxidation of fluoride to fluorine radical is not a trivial transformation due to the high electronegativity of fluorine [6]. Historically, the elemental fluorine was prepared via electrolysis of anhydrous HF [7]. It was not until 1986 that Christie reported the first truly chemical



Scheme 3. AgF_2 -mediated C–H fluorination of pyridines and diazines.



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