SYNLETT Spotlight 155

Selectfluor (F-TEDA-BF₄)

C₇H₁₄B₂ClF₉N₂

Compiled by Laxmi Manral

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Selectfluor¹ is one of the most reactive electrophilic fluorinating reagents. It is a white, free-flowing, virtually non-hygroscopic, high-melting solid (mp 170 °C)² and is soluble in few polar solvents, e.g. MeCN, DMF, H₂O, MeNO₂, ionic liquids. It is a safe, stable, non-toxic, easy-to-handle reagent that is amenable to industrial production. It provides an alternative to molecular fluorine which is a hazardous, highly toxic, strong oxidant, with little or no specificity.¹ Selectfluor helps in the fluorination of steroidal enol acetates,³ monofluoro ketomethylene dipeptide isomerase,⁴ carbanions, and Grignard reagents, and in the α -fluorination of sulfides,² aldehydes and ketones.⁵ Besides these properties (in two-electron processes), it also shows oxidative characteristics, and forms potent indium sources with molecular iodine, although it decomposes in the presence of iodide ion. It is also useful in the conversion of common anions into electrophiles.⁶

Preparation

Selectfluor is commercially available. It can be prepared by the alkylation of DABCO (TEDA) with dichloromethane. After counter-anion exchange with NaBF₄ and precipitation of NaCl from MeCN solution, fluorination with F₂ provides F-TEDA-BF₄.¹

Abstracts

(A) Selectfluor is a versatile reagent for fluoroalkylation of alkenes and acetylenes under mild conditions. This reaction follows Markovnikov-type regioselectivity.^{7,8}

(B) Selectfluor also helps in the deprotection of PMP, THP, and 1,3-dithiones. Acetonitrile and nitromethane (5% H₂O content) can be used as solvent. In the presence of 1.2 equivalents of Selectfluor, deprotection is complete in five hours.⁹

(C) Selectfluor acts as a mediator for the introduction of a perfluoroalkyl moiety containing a functional group at the benzylic position in hexamethylbenzene, in the presence of polyfluoroalcohol or potassium salts of perfluoroalkane carboxylic acid.¹⁰

(D) Selectfluor provides one-pot fluorination and anomeric functionalisation of a carbohydrate. In the presence of a nucleophile, it reacts with glycols to give 2-deoxy-2-fluoro derivatives with concurrent introduction of a nucleophile to the anomeric position.¹¹

(E) Selectfluor can be used as an excellent promoter for allylation of aldehydes and amines with allyltributyltin in one step, to form homoallylic alcohols or amines.¹²

(F) Selectfluor allows the green electrophilic fluorination of indole compounds in high chemoselectivity and yield. In the presence of thiols, intermediate sulfides are formed.¹³

(G) Selectfluor provides a straightforward route for the synthesis of difluorinated carbonyl compounds upon reaction with enamines under mild conditions.¹⁴

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