

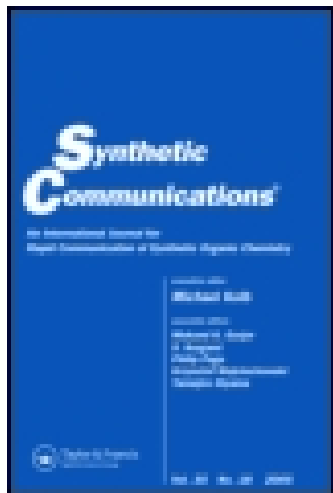
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Facile Conversion of Arenediazonium Salts to the Corresponding Fluoroarenes Using Boron Trifluoride Diethyl Ether Complex

Kojichi Shinhama^a, Shinji Aki^a, Takuya Furuta^a & Jun-ichi Minamikawa^a

^a Process Research Div., Second Tokushima Factory, Otsuka Pharmaceutical Co., Ltd., Tokushima, 771-01, Japan

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FACILE CONVERSION OF ARENEDIAZONIUM SALTS TO THE CORRESPONDING
FLUOROARENES USING BORON TRIFLUORIDE DIETHYL ETHER COMPLEX

Kōichi Shinhama, Shinji Aki, Takuya Furuta,
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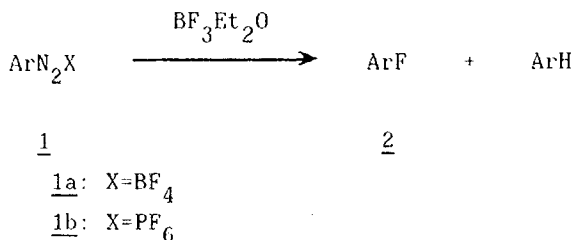
Process Research Div., Second Tokushima Factory,
Otsuka Pharmaceutical Co., Ltd., Tokushima, 771-01 Japan

Abstract: The conversion of various arenediazonium salts 1 to the corresponding fluoroarenes 2 has been achieved in good yields under mild conditions in boron trifluoride diethyl ether complex.

In recent years, preparation of fluoroarenes has been a subject of extensive studies.¹⁻⁵⁾ The Balz-Schiemann reaction, fluoro-dediazoni-ation of arenediazonium tetrafluoroborate salts, provides one of the most convenient methods for a regiospecific introduction of fluorine into aromatic rings.^{6,7)} This procedure, however, involves thermal decomposition of diazonium salts, which could be hazardous and may suffer ill-reproducibility depending on the substrates. Olah et al.⁵⁾ have circumvented the high temperature thermal decomposition of diazonium salts by employing a hydrogen fluoride-organic base

mixture (e.g. 70% w/w HF, 30% w/w pyridine) as the dediazonation solvent. The mixture is an amine-poly(hydrogen fluoride)complex in equilibrium with a certain amount of free hydrogen fluoride.⁵⁾ The acid mixture has been utilized for various types of fluorination reactions.²⁻⁵⁾ Thus, the conversion of aminoarenes to the corresponding fluoroarenes through diazonium salts can be achieved in many cases with yield better than those obtained with the conventional Balz-Schiemann reaction. However, the requirement of special equipments, such as FEP vessels,^{1,4)} to handle strongly corrosive hydrogen fluoride reagents may be a problem in ordinary laboratories. We wish to report here a practical dediazonation procedure employing a non-protonic solvent, boron trifluoride diethyl ether complex.

A variety of arenediazonium tetrafluoroborates 1a or hexafluorophosphates 1b, obtainable from the corresponding aminoarenes in high yield, undergo a smooth thermal decomposition in boron trifluoride diethyl ether complex at a low temperature (20-125°C) affording the corresponding fluoroarenes 2 with minimum formation of the by-product ArH. The boron trifluoride adduct appears to be an excellent solvent in view of its appropriate boiling point (126°C) and thermal and photochemical stability. As shown in the Table, a variety of substituted benzenediazonium salts gave the corresponding fluoro compounds upon heating in this solvent with yields ranging from excellent to moderate.



The dediazonation reaction can be accelerated by photo-irradiation. Thus the reaction temperature can be lowered

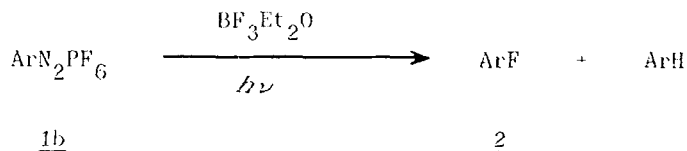
Table

Conversion of Diazonium Salts 1 to the Corresponding Fluoroarenes 2 in Boron Trifluoride Diethyl Ether Complex

Diazonium Salt <u>1</u>	Reaction Temp. (°C)	Reaction Time (hr)	Yield of <u>2</u> (%)		lit. ⁶⁾
			a)	b)	
4-NO ₂ -C ₆ H ₄ N ₂ BF ₄	120-125	1	72	91	40-58
3-NO ₂ -C ₆ H ₄ N ₂ BF ₄	120-125	1	39		43-54
3-NO ₂ -4-Me-C ₆ H ₃ N ₂ PF ₆	120-125	1	69	87	
2-(EtO ₂ C-)C ₆ H ₄ N ₂ PF ₆	120-125	1	85		68-87
4-(EtO ₂ C-)C ₆ H ₄ N ₂ PF ₆	120-125	1	57	71	
4-Cl-C ₆ H ₄ N ₂ PF ₆	120-125	1	62		
2,3-Cl ₂ -C ₆ H ₃ N ₂ PF ₆	35-37	4	66 ^{c)}		
2,4-Br ₂ -5,6-Me ₂ -C ₆ H ₂ N ₂ PF ₆	120-125	1	89		
2,4-F ₂ -3-Me-C ₆ H ₂ N ₂ PF ₆	23-25	8	82 ^{c)}		
4-MeO-C ₆ H ₄ N ₂ PF ₆	120-125	1	44 ^{d)}		
2-Me-C ₆ H ₄ N ₂ PF ₆	120-125	1	72		90
3-Me-C ₆ H ₄ N ₂ PF ₆	120-125	1	65	74	87
4-Me-C ₆ H ₄ N ₂ PF ₆	120-125	1	54		
2,6-Me ₂ -C ₆ H ₃ N ₂ PF ₆	120-125	1	64		
2,3-Me ₂ -C ₆ H ₃ N ₂ PF ₆	20-30	5	62		
α-C ₁₀ H ₇ N ₂ PF ₆	120-125	1	63		60-98

a) Isolated yield. b) HPLC yield. c) The mixture was irradiated with ultraviolet light. d) 4-Ethoxyfluorobenzene (16%) was obtained as the by-product.

drastically as shown in the Table. A couple of typical experimental procedures are shown below. The amounts of by-products ArH were less than the thermal reaction described above.



Experimental

All the boiling points were uncorrected. Analytical determinations by HPLC were performed on a Shimadzu LC-6A liquid chromatograph with a TSK gel ODS-120T column. $^1\text{H-NMR}$ spectra were taken at 200 MHz on a Varian XL-200 NMR spectrometer. IR spectra were recorded with a Perkin Elmer 1600 series FTIR apparatus. Mass spectra were recorded with a Shimadzu GCMS-QP1000 spectrometer.

The thermal conversion of diazonium salts 1 to the corresponding fluoroarenes 2 in boron trifluoride diethyl complex

The following is a typical run. A stirred suspension of 2,6-dimethylenediazonium hexafluorophosphate (14.4 g, 60 mmol) and boron trifluoride diethyl ether complex (50 ml) was heated for 1 hr at 120 to 125 °C under nitrogen. Then the reaction mixture was cooled, diluted with ethyl acetate and poured onto ice. The organic layer was washed with water and dried (Na_2SO_4). The solution was concentrated and distilled (bp 55-58 °C/38 mmHg) to give 4.88 g (64%) of 2-fluoro-m-xylene.

Various other arenediazonium salts 1 were also shown to undergo facile decomposition to the corresponding fluoroarenes 2 upon heating in boron trifluoride diethyl ether complex. All the products were identified by comparing their IR and NMR

spectra and boiling points with those of authentic compounds. The results are summarized in the Table.

The photochemical conversion of diazonium salts 1 to the corresponding fluoroarenes 2 in boron trifluoride diethyl complex

The following is a typical run. A stirred suspension of 2,3-dichlorobenzediazonium hexafluorophosphate (5.81 g, 18.2 mmol) and boron trifluoride diethyl ether complex (130 ml) was irradiated with ultraviolet light for 4 hr at -10 to 5 °C by using a high pressure mercury lamp (Riko Kagaku Sangyo K.K. type UVL-100P). The reaction mixture was diluted with ethyl acetate and poured onto ice. The organic layer was dried (Na_2SO_4), concentrated and distilled (bp 70-72 °C/28 mmHg) giving 1.98 g (66%) of 2,3-dichlorofluorobenzene. The structure of the product was identified by IR and NMR spectroscopies.

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