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Facile Preparation of Aromatic Fluorides by the Fluoro-Dediazoniation of Aromatic Diazonium Tetrafluoroborates Using HF-Pyridine Solution

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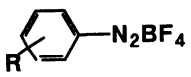
The fluoro-dediazoniation of ArN_2BF_4 using HF-pyridine solution has been successfully carried out either thermally or photochemically to afford the corresponding ArF in good yields. Particularly, the photochemically induced reaction in HF-pyridine was a useful tool for the preparation of ArF having polar substituents such as halogens, OH, OMe, CF_3, etc.

The decomposition of arenediazonium tetrafluoroborates salts (ArN_2BF_4) is the most convenient and practical method available for the controlled and regiospecific introduction of fluorine into aromatic rings.[1-4] However, it is not free from difficulties;[3] the yields of the corresponding aromatic fluorides (ArF) are not reproducible and greatly influenced by the substituents on the aromatic nucleus, and solvents used.[4] Particularly, the reaction of ArN_2BF_4, which have polar substituents with strong electron donating or withdrawing properties such as halogen, OH and so on at their ortho or para positions, is difficult to produce the corresponding ArF, and tarry matter is sometimes formed in significant amounts. Recently, we have reported the convenient one-pot diazotization of anilines ($ArNH_2$) followed by in situ thermal or photochemical fluoro-dediazoniation in HF combined with organic bases such as pyridine.[5,6] Also, the diazotization stage has been found to play the most important part in such one-pot deaminative fluorinations of $ArNH_2$ effectively yielding ArF.[7,8] Thus, we have examined the thermal or photochemical decomposition of ArN_2BF_4 in HF-pyridine solution. Representative experimental results are summarized in Table 1.

The thermal decomposition of ArN_2BF_4 having no polar substituent gave the corresponding ArF in good yields using HF-pyridine solution and temperatures characteristic of the substrates. However, most of ArN_2BF_4 having polar substituents had very sluggish reactions that afforded little ArF with significant amounts of unidentified tarry-like products. On the other hand, the reaction of these substrates was significantly accelerated photochemically to efficiently afford ArF in HF-pyridine at room temperature, except for a substrate with NO_2 at the ortho position.[9] The reductive dediazoniation of some of substrates took place affording Ar-H, but the formation of these was very small. Thus, this photochemically induced procedure is useful, particularly for the fluoro-dediazoniation of ArN_2BF_4 having polar substituents at their ortho and para positions, which is difficult to thermally occur. As a typical example, 4-fluoro-3-(trifluoromethyl)phenol, a useful herbicide,[10] was prepared in 84% yield from the corresponding ArN_2BF_4, which is always a sluggish thermal decomposition reaction.

Consequently, by employing HF-pyridine solution as the solvent, the fluoro-dediazoniation of ArN_2BF_4 has been successfully carried out , and extremely accelerated photochemically affording ArF in good yields. The application of other solvents combined with HF to the reaction is under active investigation.

Table 1. Thermal or Photochemical Decomposition of ArN_2BF_4 in HF-Pyridine

 R:	Conditions[a]				Products yield/%	
	Decomp.[b]	X_{HF}[c]	Temp/ ℃	Time/min	ArF	ArH
H	Δ	0.86	60	60	99.0[d]	0
2-F	Δ	0.86	160	60	0.6	0.2
"	hν	0.90	12	120	80.2	0.6
2-Cl	Δ	0.86	160	60	52.9	trace
"	hν	0.90	12	90	88.3	0.2
2-CF_3	Δ	0.86	90	60	73.5	0
"	hν	0.90	12	180	85.4	0
2-OH	Δ	0.86	60	130	6.6	0.4
"	hν	0.90	12	100	86.9	0
3-OH	hν	0.90	12	200	87.1	0
2-OMe	Δ	0.86	150	60	10.6	0.6
"	hν	0.90	12	80	92.7	0.2
3-Me, 4-OH	Δ	0.86	140	60	94.0	0
"	hν	0.90	12	100	93.8	0.4
2-CF_3, 4-OH	Δ	0.86	140	60	2.5	1.1
"	hν	0.90	12	200	83.8	0.1

a) ArN_2BF_4: 5-10 mmol, HF-pyridine: 5-10 ml.
b) Δ: Thermal decomposition, hν: Photochemical decomposition (Irradiation with 500W Hg lamp).
c) HF mole fraction in HF-pyridine. d) Ref. 7.

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