ELSEVIER

Journal of Fluorine Chemistry 78 (1996) 95–96

JOURNAL OF FLUORINE CHEMISTRY

Preliminary note

Deaminative fluorination of anilines using potassium hydrogen fluoride and silicon tetrafluoride

Masanori Tamura *, Motonari Shibakami, Shigeru Kurosawa, Takashi Arimura, Akira Sekiya *

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Received 11 December 1995; accepted 11 January 1996

Abstract

It has been found that the combination of potassium hydrogen fluoride and silicon tetrafluoride works as an efficient fluorinating agent for the deaminative fluorination of anilines. A one-pot diazotization of anilines followed by fluoro-dediazoniation proceeds with this combination of the reagents and *t*-butyl nitrite to afford fluoroarenes.

Keywords: Deaminative fluorination; Aniline derivatives; Metal fluoride salt

Recently we have demonstrated that the combination of potassium hydrogen fluoride (KHF_2) and silicon tetrafluoride (SiF_4) works as an efficient reagent for hydrofluorination of unsaturated compounds, and the corresponding fluorides are obtained by the reaction at room temperature in high yields [1]. Herein, we report a new method of deaminative fluorination of anilines using KHF_2 and SiF_4.

Deaminative fluorination of anilines is a useful method for the synthesis of aromatic fluorides [2,3]. The Baltz–Schiemann reaction [4] is a representative method, but the isolation of diazonium fluoroborates is necessary, and reproducibility of yields of the desired fluoroarenes is poor [3]. To overcome these difficulties, a one-pot diazotization and fluoro-dediazoniation of anilines using hydrogen fluoride (HF) or organic base–HF reagents, such as pyridine–HF, had been investigated [3,5,6]. However, these reagents are corrosive, although pyridine–HF is less so than anhydrous hydrogen fluoride itself, and a large amount of these reagents was used as solvent. Thus we have investigated the one-pot deaminative fluorination of anilines using KHF_2 and SiF_4 (Scheme 1).

$$ArNH_2 \xrightarrow[\text{room temp.}]{KHF_2,\ SiF_4} \xrightarrow[\text{room temp.}]{t\text{-BuONO}} \xrightarrow{\Delta} ArF$$

Scheme 1.

As an initial attempt, the reaction of aniline (1 mmol) with KHF_2 (6 mmol), SiF_4 (4 mmol), and *t*-butyl nitrite (1.2 mmol) was carried out at room temperature for 16 h. After the reaction mixture was heated at 60 °C, fluorobenzene was obtained in 50% yield. The yield increased to 64% when *t*-butyl nitrite was added after the reaction of aniline with KHF_2 and SiF_4. Thus the deaminative fluorination of aniline was attempted under various reaction conditions in this method (Table 1). The best result was obtained when 6 mmol of KHF_2 and 4 mmol of SiF_4 were used to 1 mmol of aniline (entry 3). The reaction also proceeded when another diazotization agent, $NaNO_2$ (entry 6), or other alkali metal hydrogen fluorides, $NaHF_2$ and NH_4HF_2 (entries 7 and 8), were used, but the use of *t*-butyl nitrite and KHF_2 gave a better result.

The deaminative fluorination of various aniline derivatives was examined under these reaction conditions, and the results are summarized in Table 2. The corresponding fluoroarenes were obtained in fair yields. When *o*-chloroaniline, *p*-anisidine or *p*-nitroaniline was reacted, however, the yield of fluoroarene was low.

Concerning the reaction route, since HF is released [1] from KHF_2 and SiF_4, diazotization of aniline derivatives would proceed with HF and *t*-butyl nitrite to afford arenediazonium fluorides, and its thermal decomposition would give fluoroarenes. Arenediazonium hexafluorosilicate $(ArN_2)_2SiF_6$, which can form from arenediazonium fluoride and SiF_4, would not be the intermediate of this reaction, because thermal decomposition of the intermediate proceeds at 60 °C in

---

* Corresponding authors. E-mail: tamuranimc.go.jp.

[1] The generation of HF was observed from the reaction between KHF_2 and SiF_4, see Ref. [1].

PII S0022-1139(96)03406-9

Table 1
Deaminative fluorination of aniline with MHF_2, SiF_4, and RONO [a]

Entry	MHF_2	Amount [b] of MHF_2 (mmol)	Amount [b] of SiF_4 (mmol)	RONO	Yield [c] (%)
1	KHF_2	3	2	*t*-BuONO	46
2	KHF_2	6	2	*t*-BuONO	39
3	KHF_2	6	4	*t*-BuONO	64
4	KHF_2	6	6	*t*-BuONO	12
5	KHF_2	9	6	*t*-BuONO	16
6	KHF_2	6	4	$NaNO_2$	60
7	$NaHF_2$	6	4	*t*-BuONO	47
8	NH_4HF_2	6	4	*t*-BuONO	45

[a] After aniline was agitated with MHF_2 and SiF_4 at room temperature for 16 h, RONO (1.2 mmol relative to aniline) was added and the mixture was agitated at room temperature for 1 h, and then it was heated at 60 °C for 1 h.

[b] Amount of the reagent relative to 1 mmol of aniline.

[c] Yield was determined by gas chromatography.

Table 2
Deaminative fluorination of aniline derivatives [a]

Entry	Substrate	Yield [b] (%)
1	$C_6H_5NH_2$	64 (45)
2	*o*-CH_3-$C_6H_4NH_2$	61 (39)
3	*m*-CH_3-$C_6H_4NH_2$	55 (37)
4	*p*-CH_3-$C_6H_4NH_2$	62 (31)
5	*o*-Cl-$C_6H_4NH_2$	14
6	*m*-Cl-$C_6H_4NH_2$	42 (30)
7	*p*-Cl-$C_6H_4NH_2$	39 (22)
8	*p*-CH_3OCO-$C_6H_4NH_2$	45 (32)
9	*p*-CH_3O-$C_6H_4NH_2$	16
10	*p*-NO_2-$C_6H_4NH_2$	5 [c]

[a] After substrate (1 mmol) was agitated with KHF_2 (6 mmol) and SiF_4 (4 mmol) at room temperature for 16 h, *t*-butyl nitrite (1.2 mmol) was added and the mixture was agitated at room temperature for 1 h, and then it was heated at 130 °C (Entry 1; 60 °C) for 1 h.

[b] Yield was determined by gas chromatography unless otherwise noted. In parentheses are isolated yields.

[c] Yield was determined by ^{19}F NMR ($C_6H_5CF_3$ was used as internal standard).

the case of the reaction of aniline [2], and the decomposition of benzenediazonium hexafluorosilicate needs a much higher temperature [7].

A typical experimental procedure is as follows. The substrate (1 mmol) and KHF_2 (6 mmol) were placed in a stainless steel reactor equipped with a stop valve. SiF_4 (4 mmol) was introduced into the reactor at − 196 °C from a vacuum line. The reactor was allowed to warm up to ambient temperature and shaken vigorously for 16 h. *t*-Butyl nitrite was introduced into the reactor in the same way. The reactor was shaken vigorously for 1 h at ambient temperature and then heated to the desired temperature (Table 2) for 1 h. The crude product was transferred from the reactor using a vacuum line system and dissolved in dichloromethane. The yield of fluoroarene was determined by gas chromatography or ^{19}F NMR analysis of the solution of the crude product. After it was dried and concentrated, the product was purified by bulb-to-bulb or trap-to-trap distillation [8] and identified by IR, ^1H NMR and ^{19}F NMR spectroscopy.

In conclusion, we have demonstrated that deaminative fluorination of aniline derivatives proceeds with KHF_2, which is easy to handle and less corrosive than other reagents such as amine–hydrogen fluoride, and SiF_4 to afford corresponding fluoroarene. This is a quite new method for deaminative fluorination using a metal fluoride salt.

---

[2] It has been reported that benzenediazonium fluoride, which is prepared by the reaction of aniline with pyridine–HF, decomposes at 60 °C to afford fluorobenzene, see Ref. [6].

References

[1] M. Tamura, M. Shibakami, S. Kurosawa, T. Arimura and A. Sekiya, *J. Chem. Soc., Chem. Commun.* (1995) 1891.

[2] A. Roa, *Org. React.*, *5* (1949) 193.

[3] N. Yoneda, *Tetrahedron*, *47* (1991) 5329.

[4] G. Baltz and G. Schiemann, *Chem. Ber.*, *60* (1927) 1186.

[5] G.A. Olah, J.T. Welch, Y.D. Vanker, M. Nojima, I. Kerekes and J.A. Olah, *J. Org. Chem.*, *44* (1979) 3872.

[6] T. Fukuhara, N. Yoneda, T. Sawada and A. Suzuki, *Synth. Commun.*, *17* (1987) 685.

[7] P.H. Cheek, R.H. Wiley and A. Roe, *J. Am. Chem. Soc.*, *71* (1949) 1863.

[8] A. Sekiya and K. Ueda, *Chem. Lett.*, (1990) 609.