Pergamon

*Tetrahedron*, Vol. 52, No. 1, pp. 23-36, 1996
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/96 $15.00 + 0.00

0040-4020(95)00867-5

# Facile Preparation of Aromatic Fluorides by Deaminative Fluorination of Aminoarenes Using Hydrogen Fluoride Combined with Bases.

**Norihiko Yoneda* and Tsuyoshi Fukuhara**

Division of Molecular Science, Graduate School of Engineering,
Hokkaido University, Sapporo, 060 Japan

**Abstract** : One-pot deaminative fluorination of aminoarenes including heteroaromatics, namely, diazotization of aminoarenes followed by *in situ* fluoro-dediazoniation of the corresponding diazonium ions, was successfully accomplished to produce fluoroarenes in high yields by using hydrogen fluoride combined with base solutions. The diazotization stage has been found to play the most important part in yielding fluoroarenes effectively. It was greatly influenced by the composition of the HF solution and enhanced by employing appropriate amounts of bases such as pyridine under carefully controlled conditions. The fluoro-dediazoniation stage was effectively accelerated photochemically to afford fluoroarenes having polar substituents such as hydroxyl, nitro and so on in high yields.

## Introduction

The characteristics of the fluorine atom, its size which is bioisosteric with both the hydrogen atom and the hydroxyl group and its unique electronic properties, provide peculiar biological properties to aromatic fluorides (ArF).[1] Thus, ArF appear in a broad variety of molecules having the enormous activity as antibiotics, anti-folate, sedatives, estrogen receptor imaging agents and so on.[2] The common problem associated with the synthesis of these multiform materials is the introduction of fluorine onto the aromatic rings, because the synthesis of ArF efficiently and in high yields is very difficult. Various preparative methods for the ring-fluorinated aromatic compounds have been reported so far.[3] They can be representatively classified into three categories. Firstly, substitutive fluorination of ring C-H bonds in ArH by an F cation or radical generation reagents.[4] Secondly, halogen (or nitro group) exchange fluorination of ring C-X bonds in ArX (X: Halogen or $NO_2$) by fluoride ion generation reagents,[5] and thirdly, deaminative fluorination of ring C-$NH_2$ bonds in aminoarenes $ArNH_2$.[6] The difficulties in substitutive fluorination are regulation of exothermic reactions and lack of regiospecificity, and those in halogen or $NO_2$-exchange fluorination generally require severe conditions of high temperature and long reaction time and a limitation of substrate ArX which must have a strong electron-withdrawing group on the aromatic rings. The deaminative fluorination procedure of $ArNH_2$ is composed of diazotization of aminoarenes to produce arenediazonium tetrafluoroborates ($ArN_2BF_4$) and fluorinative decomposition (fluoro-dediazoniation) of the corresponding $ArN_2BF_4$.[6] The later stage, known as the Balz-Schiemann reaction, is the classical but most convenient and practical method available for a controlled, regiospecific introduction of fluorine onto aromatic rings. However, many difficulties also arise in this method such as a difficult preparation and isolation of some $ArN_2BF_4$ having polar substituents and troublesome decomposition of $ArN_2BF_4$ for a controlled synthetic procedure, so that the reproducibility of yields of the desired ArF is at times very poor.[6]

On the other hand, the use of hydrogen fluoride (HF) for the diazotization of $ArNH_2$ greatly simplified the transformation of $ArNH_2$ to ArF to allow ready *in situ* fluoro-dediazoniation of intermediate diazonium salts.[7] This procedure offered the advantage of not requiring the preparation and isolation of the intermediate diazonium salts to provide a convenient one-pot deaminative fluorination of $ArNH_2$ as a more practical method for the preparation of ArF. So far, however, its application on an industrial scale is restricted to simple $ArNH_2$ such as aniline and toluidines.[7]

Recently, this procedure has been greatly improved to produce ArF in good yields while depressing the formation of undesirable tarry matter by the use of HF with bases (HF-Base).[8] Olah and his collaborators reported the diazotization of $ArNH_2$ at room temperature for 1h and *in situ* dediazoniation at 85 °C for 1h in HF-30% pyridine solution employing an autoclave to produce 30-90% yields of ArF.[9] Interestingly, $ArNH_2$

having some substituents such as $NO_2$ and $CF_3$ underwent the deaminative fluorination in non-regiospecific fashion affording a mixture of isomers of the corresponding ArF. The mechanism in such a non-regiospecific reaction was proposed to involve an intermediate benzyne.[10] This might be caused by metals contained in the autoclave. Bases other than pyridine were also reported to depress the formation of side products to improve the yields of ArF.[11] More recently, by carrying out the reaction in a vessel made of PFA[12], most of the $ArNH_2$ compounds gave the corresponding ArF in very high yields in HF-pyridine solution (HF-Pyr).[13] Nevertheless, even in such an attractive procedure, the yield of ArF is greatly influenced by a substituent on the aromatic nucleus, and tarry matter is at times formed in considerable amounts, particularly in the reaction of substrates having polar substituents such as OH, $NO_2$ and so on. Currently, however, no simple explanation can be offered for the formation of unusual by-products including tarry matter which renders it difficult to apply this method satisfactorily for facile preparation of ArF. The reaction can be postulated to involve the initial formation of arenediazonium species ($ArN_2^+$) (diazotization step (Stage [A])) and its subsequent decomposition (fluoro-dediazoniation step (Stage [B])) *in situ* in the HF-solution. The acidity of the reaction media should influence both Stages [A] and [B]. So far, the dediazoniation step has been regarded as being very important for improving the yield of ArF to suppress any undesirable products in such a one-pot procedure.[13,14]

We will now report recent progress in studies on one-pot deaminative fluorination of $ArNH_2$ for the facile preparation of ArF in the presence of HF combined with base solutions.

## Results and discussion

### 1. *Deaminative Fluorination of $ArNH_2$ in HF.*

One-pot deaminative fluorination of $ArNH_2$, namely, the diazotization of aniline (**1**), *p*-toluidine (**2**), *p*-chloroaniline (**3**), *p*-nitroaniline (**4**), and *p*-aminophenol (**5**) with $NaNO_2$ at 0 °C for 20 min (Stage [A]) followed by *in situ* thermal treatment of the resultant solution for 1 h (Stage [B]), was carried out using HF. The effects of the composition of moles of HF to one mole of $ArNH_2$ ($N$) in the reaction solution on the yields of ArF are shown in Table 1.

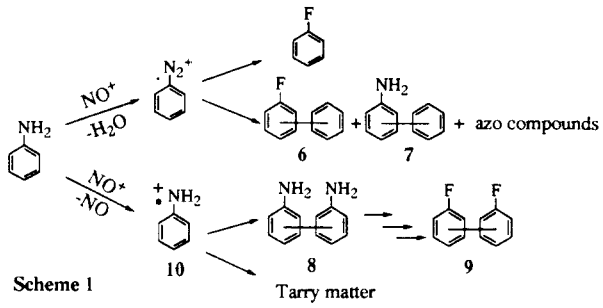
Table 1. Effects of HF/$ArNH_2$ Molar Ratio on the Yields of ArF in the Reaction of $ArNH_2$ in HF[a]

| R—⟨⟩—$NH_2$ | | Stage [B][b] | ArF Yield / % | | | | | |
|---|---|---|---|---|---|---|---|---|
| R | | Temp / °C | $N$[c] / 20 | 25 | 30 | 40 | 50 | 60 |
| H | 1 | 55 | 86 | 80 | 58 | 39 | 33 | 30 |
| $CH_3$ | 2 | 70 | 85 | 55 | 35 | – | 20 | 8 |
| Cl | 3 | 90 | 91 | 84 | 78 | 74 | – | 57 |
| $NO_2$ | 4 | 110 | 55 | 61 | – | 58 | – | 54 |
| OH | 5 | 140 | 0 | 0 | 0 | 0 | 0 | – |

a) Stage [A]: $ArNH_2$ 5-25 mmol, $ArNH_2/NaNO_2$= 1/1.1 (molar ratio), 0 °C for 20 min. b) 1h. c) HF/$ArNH_2$ molar ratio at Stage [A].

The yields of ArF were remarkably influenced by $N$ in the reactions of **1**, **2**, and **3** but little in the reaction of **4**. The decreasing $N$ in a solution brought about difficulty in dissolving $NaNO_2$ in HF, and the amount of the highest limit of $ArNH_2$ to HF which enables the reaction to proceed smoothly was found to be $N \geq 20$. Stage [B] required the characteristic temperatures dependent upon $ArNH_2$ in order to afford the corresponding ArF and the maximum yields of ArF were obtained around 85~90% by carrying out Stage [B] of **1** at 55 °C, of **2** at 70 °C and of **3** at 90 °C, and 65% in the case of **4** at 110 °C for 1 h in each case by employing the solution with a composition of $N$=20. The reaction of **5**, on the other hand, did not afford the corresponding ArF by carrying out Stage [B] at 20-140 °C under the conditions of $N$ = 20~50 but gave 1,4-benzoquinone together with a fairly large amount of tarry matter accompanying the generation of nitrogen oxide (NO).[15] The increasing of $N$ in the reactions of **1**, **2**, **3**, and **4** brought about the increasing formation of side products. As a representative example, when the solution prepared at Stage [A] in the reaction of **1** with $N$=90 was heated at a temperature higher than 50 °C for 30 min, fluorobenzene (PhF) boiled off together with NO and a considerable amount of HF which condensed in a cooled trap during the reaction. After quenching the reaction mixture with ice-water, 15-30% yields (reproducibility is poor) of PhF were obtained

together with fairly large quantities of a deep brown tarry matter (40% or more)[17] and small amount of side products such as monofluorobiphenyls (**6**), monoaminobiphenyls (**7**), azo compounds, diaminobiphenyls (**8**), and difluorobiphenyls (**9**).[19] Compounds **6**, **7** and azo compounds can be formed by the reactions of the intermediate $PhN_2^+$ with PhF or with unaltered **1**. The generation of NO suggests the oxygenation of **1** with $NO^+$ to give an anilinium cation radical (**10**) and may play an important role in the formation of **8**, **9**, and tarry matter as shown in Scheme 1.




Scheme 1

*2. The rates of diazotization of $ArNH_2$ in HF*

The effects of $N$ on the rate of diazotization of $ArNH_2$ at 0 °C for 20 min (Stage [A]) are shown in Table 2. In case of **3** and **4**, the corresponding $ArN_2^+$ was obtained in good or almost quantitative yields in a solution with a composition of $N$=30 or less but decreased with the increasing value of $N$ to increase unaltered $ArNH_2$. Pronounced decreasing yields of $ArN_2^+$ with increasing $N$ were observed in the reaction of **1** and **2**. In order to study the products formed in Stage [A], **2** was employed as a substrate to make NMR spectroscopic analysis easier.[20] The results are shown in Table 3.

**Table 2.** Effects of $HF/ArNH_2$ Molar Ratio on the Yields of $ArN_2^+$ at Stage [A] in the Diazotization of $ArNH_2$ in HF[a]

| R—⟨⟩—$NH_2$ | | $ArN_2^+$ Yield / % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R | | $N$[b] / 20 | 25 | 30 | 35 | 40 | 45 | 50 | 60 |
| H | **1** | 88 | 48 | 21 | – | 8 | – | 4 | 0 |
| $CH_3$ | **2** | 85 | 44 | 19 | – | 7 | – | 4 | 0 |
| Cl | **3** | 98 | 95 | 92 | 82 | 48 | 17 | 9 | 1 |
| $NO_2$ | **4** | 99 | 97 | 96 | 95 | 88 | 80 | 31 | 2 |

a) $ArNH_2$ 5 mmol, $NaNO_2$ 5.5 mmol, 0 °C for 20 min. b) $HF/ArNH_2$ molar ratio.

The NMR spectrum of the amino group in unaltered **2** in the resultant solution of Stage [A] with a composition of $N$=20~25 or less at 0~20 °C gave a broad singlet at δ=8.00~7.90 indicating the rapid proton exchange with the ammonio group, with increasing formation of the corresponding $ArN_2^+$ with time. In a solution with a composition of $N$=40 or more at 0 °C, exclusive protonation of the amino group in the substrate to form an ammonio group took place, whose NMR spectra showed a triplet pattern with an N-H coupling constant of 50 Hz, without the formation of the corresponding $ArN_2^+$. Such a solution having a high value of $N$, in which the nitrosation of $ArNH_2$ is difficult to carry out, gave a fair amount of $ArN_2^+$ on heating up to 40 °C or on diluting with water or organic bases such

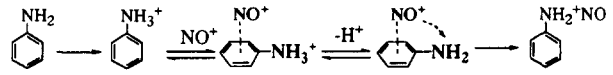
**Table 3.** Products Found in the Diazotization of *p*-Toluidine in HF

| Conditions[a] | | | Products[b] composition / % | | | |
|---|---|---|---|---|---|---|
| $N$[c] | °C | min | *p*-$TolNH_3^+$ | *p*-$TolN_2^+$ | Others | *p*-TolF |
| 5[d] | 5 | 0 | 29.5 | 70 | 0.5 | 0 |
| 10 | 5 | 120 | 18 | 80 | 5 | Trace |
| 25 | 0 | 0 | 85 | 15 | 0 | 0 |
| 25 | 0 | 120 | 46 | 49 | 5 | Trace |
| 25 | 20 | 20 | 34 | 57 | 9 | Trace |
| 25 | 20 | 60 | 15 | 77 | 8 | Trace |
| 40 | 0 | 0 | 100 | 0 | 0 | 0 |
| 40 | 20 | 60 | 96 | 3.3 | 1.7 | 0 |
| 40 | 40 | 60 | 37 | 53 | 14 | Some[f] |
| 40[e] | 0 | 0 | 0 | 91 | 9 | 0 |
| 60 | 0 | 120 | 100 | 0 | 0 | 0 |

a) *p*-Toluidine 20 mmol; $NaNO_2$ 21 mmol. b) *p*-$TolNH_3^+$; *p*-Tolylammonium ion, *p*-$TolN_2^+$; *p*-Methylbenzenediazonium ion, *p*-TolF; *p*-Methylfluorobenzene. c) HF/*p*-Toluidine (molar ratio). d) $NaNO_2$ did not disolve in HF completely. e) Water (100 mmol) was added to this solution. f) Less than 3%.

as pyridine, ether and so on. In a solution with a composition of $N \leq 25$, on the other hand, the diazotization of **2** was found to take place remarkably to afford $ArN_2^+$ even at 0 °C. This may be because of the dilution of HF by the base **2**, which reduces the acidity of the reaction mixture to accelerate the diazotization of **2**. This evidence indicates that a stronger protonation towards the amino group in $ArNH_2$ tends to prevent its nitrosation with $NO^+$ to form the corresponding *N*-nitroso anilinium ion (**11**).

The diazotization rate of $ArNH_2$ is reported to decrease with the increasing acidity of the reaction medium with an $H_0$ value higher than -4.[21-23] Such a rate decrease at high acidities was explained by assuming that the rate-limiting step is the deprotonation of **11** to afford $ArN_2^+$.[23] It is concluded that $ArNH_3^+$, not free $ArNH_2$, always takes part in the initial stage of the nitrosation in strong acids.[22] Namely, as shown in the following Eq., the nitrosating entity $NO^+$ associates with the $\pi$-electrons of the aromatic rings having an ammonio group followed by the deprotonation of such a dicationic charge-transfer complex to rearrange the $NO^+$ to the amino group forming **11**.




**11**

Judging from the NMR spectroscopic observations of the HF solution prepared in Stage [A] of **2** with a composition of variable *N*, however, the nitrosating entity $NO^+$ seems to attack the free $ArNH_2$, which coexists with $ArNH_3^+$ at equilibrium in a solution with a composition of $N \leq 25$, resulting in the formation of $ArN_2^+$ as shown in Scheme 1. Thus, the rate of the diazotization of $ArNH_2$ in highly acidic solution of HF with an $H_0$ value of -15[24] depends on the degree of protonation of the amino group, because exclusive formation of $ArNH_3^+$without **11** or $ArN_2^+$ was observed in a solution with a composition of $N \geq 40$ at 0 °C. Raising the temperature of the solution with a such composition, however, may bring about free $ArNH_2$ to some extent to allow the successive reaction with $NO^+$ affording the corresponding cation radical **10** with the generation of NO which in turn undergoes highly variable reactions to give a significant amount of tarry matter as shown in Scheme 1.

The formation rate of $ArN_2^+$ is also greatly influenced by the substituent on $ArNH_2$ as shown in Table 2. The amino group in **3** and **4** having relatively lower basicity than that in **1** and **2**, insufficient to cause its protonation, can undergo nitrosation more readily to afford $ArN_2^+$ in high yields in a solution with a composition of $N$=30. The yields of ArF shown in Table 1, however, are not in accordance with the yields of the corresponding $ArN_2^+$ formed at Stage [A] shown in Table 2, particularly in the reaction of **1**, **2**, and **3** in a solution with a composition of $N$>30. This apparent discrepancy between the yields of ArF and $ArN_2^+$ in similar solutions comes from the change in the composition of the reaction mixture at Stage [B] by releasing HF noticeably with increasing temperature. This in turn brought about decreasing acidity of the reaction mixture to accelerate the diazotization of unaltered $ArNH_2$ followed by the fluoro-dediazoniation of $ArN_2^+$. In the reaction of **4**, the yield of ArF was only 65% but is nevertheless a quantitative yield of $ArN_2^+$ in a solution with a composition of $N$=20. This is because the decomposition of $ArN_2^+$ originating from **4** required a high temperature such as 110 °C to cause undesirable reactions giving a considerable amount of unidentified products.

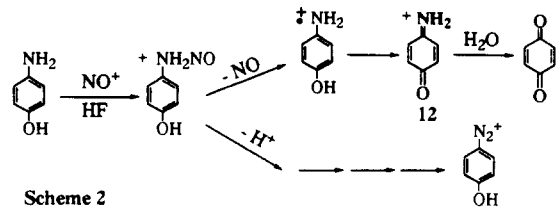
In the reaction of **5**, the desired ArF, *p*-fluorophenol, was not produced at all but 1,4-benzoquinone was obtained together with a fairly large amount of tarry matter accompanying the generation of NO under the conditions at Stage [B]. A considerable amount of the benzoquinone monoiminium ion (**12**) was found together with unaltered protonated **5**, *p*-hydroxy anilinium ion, by NMR spectroscopic observation of the solution prepared at Stage [A] in the reaction of substrate **5** as shown in Table 4. This evidence indicates that, as shown in

**Table 4.** Effects of HF/$ArNH_2$ Molar Ratio on the Products Comopsition in the Reaction of *p*-Aminophenol[a)]

| N[b)] | Products Composition / % | | |
|---|---|---|---|
| | HO-⟨⟩-$N_2^+$ | O=⟨⟩=$NH_2^+$ | HO-⟨⟩-$NH_3^+$ |
| 20 | 15 | 82 | 3 |
| 25 | 10 | 70 | 20 |
| 30 | 7 | 68 | 24 |
| 35 | 6 | 71 | 23 |
| 40 | 1 | 70 | 29 |

a) *p*-Aminophenol 5 mmol, $NaNO_2$ 5.5 mmol, 0 °C for 20 min.
b) HF/$ArNH_2$ molar ratio.

Scheme 2, the hydroxyl group on the ring at the *para* position seems to accelerate the oxygenation of $ArNH_2$ with $NO^+$ generating NO preferentially under the conditions in Stage [A] to give **12**. The formation of benzoquinone after quenching the resultant solution with ice-water can be well explained by the hydrolysis of **12**. On the other hand, by diluting the solution at Stage [A] with the addition of another bases such as pyridine, transformation of **5** to the corresponding $ArN_2^+$, *p*-hydroxybenzenediazonium ion, was found to occur in the resultant solution by NMR spectroscopic analysis.




Scheme 2

3. *Deaminative fluorination of $ArNH_2$ in HF Combined with Bases.*

By employing the solution of HF combined with bases such as pyridine, ether or water, whose composition is stable at atmospheric pressure and up to 60 °C,[25] the reaction of **1** was carried out under the conditions of $N$=90 in Stage [A] at 0 °C for 1 h and in Stage [B] at 55 °C for 1 h. The results are shown in Table 5.

Although the deaminative fluorination of **1** took place very sluggishly in HF to produce PhF in poor yields with the formation of a considerable amount of tarry matter, a quantitative deaminative fluorination of **1** took place successfully to produce PhF using HF combined with organic bases such as pyridine. In the case where ethers and water were employed, however, reductive deamination products and phenol were also produced with a decreasing yield of PhF.

As shown in Table 6, the one-pot deaminative fluorination of **1**, **2**, **3**, and **4** was greatly affected by the HF mole fraction ($X_{HF}$) in the solution of HF combined with pyridine (HF-Pyr). The effect of $X_{HF}$ of the solution on the deaminative fluorination of **2**, **3**, and **4**

**Table 5.** One-pot Deaminateve Fluorination of Aniline[a] in Sstable HF-base Solutions at 55° C

| Base | HF-Base[b] | | | Yield of PhF / %[f] |
|---|---|---|---|---|
| | Wt. %[c] | Molar Ratio[d] | $X_{HF}$[e] | |
| — | — | — | 1.0 | 15[g] |
| Pyridine | 30 | 9.2 | 0.90 | 99 |
| 2-Hydroxypyridine | 36 | 8.5 | 0.89 | 99 |
| 2-Methylpyridine | 31 | 10.4 | 0.91 | 99 |
| Pyradine | 28 | 10.3 | 0.91 | 94 |
| Melamine | 32 | 13.8 | 0.93 | 76 |
| 2,4,6-Trimethyltriazine | 36 | 10.8 | 0.92 | 98 |
| 2,4,6-Triphenyltriazine | 33 | 31.4 | 0.97 | 98 |
| Ethyl ether | 42 | 5.0 | 0.83 | 80 |
| THF | 43 | 4.8 | 0.83 | 14 |
| $H_2O$ | 23 | 3.0 | 0.75 | 85 |

a) Aniline 5 mmol, HF 450 mmol. Stage [A]: 0 °C for 1 h. Stage [B]: 55 °C for 1 h. b) Stable composition of HF-Base at 55 °C. c) wt% of base. d) HF/Base. e) HF mole fraction. f) GC yields g) With considerable amount of tarry amtter.

**Table 6.** Effects of $X_{HF}$[a] in HF-pyridine on the Yields of ArF in the Deaminative Fluorination of $ArNH_2$[b]

| R | | Stage [B][c] | ArF Yield / % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Temp. / °C | $X_{HF}$[a] / 0.63 | 0.72 | 0.76 | 0.80 | 0.83 | 0.86 | 0.90 | 0.95 | 1.00 |
| H | 1 | 55 | 11 | 20 | 39 | 81 | 91 | 99 | 99 | 58 | 18 |
| *p*-$CH_3$ | 2 | 70 | - | 2 | 25 | 71 | 95 | 99 | 98 | 49 | 10 |
| *p*-Cl | 3 | 90 | - | 1 | 39 | 40 | 95 | 99 | 99 | 69 | 45 |
| *p*-$NO_2$ | 4 | 110 | - | 0 | - | 2 | 65 | 99 | 99 | 78 | 59 |
| *p*-OH | 5 | 140 | - | - | 0 | 13 | 70 | 66 | 10 | 1 | - |
| *m*-OH | | 60 | - | - | 28 | 61 | 92 | 99 | 97 | 72 | 60 |
| *o*-OH | | 140 | - | - | 0 | 0 | 0 | 0 | 0 | 0 | - |

a) HF mole fraction in HF-pyridine. b) Stage [A]: $ArNH_2$ 5 mmol, $NaNO_2$ 5.5 mmol, HF 450 mmol, 0 °C for 20 min. c) 1h.

showed a tendency almost similar to that of the reaction of **1** affording the corresponding ArF in good yields

under the conditions using HF-Pyr with a composition of $0.83 \leq X_{HF} \leq 0.90$. The reaction using HF-Pyr with a composition of $X_{HF}<0.83$ took place very sluggishly to afford the corresponding ArF in low yields. For example, the reaction of **1** using HF-Pyr with a composition of $X_{HF}=0.63$ (70wt% pyridine in HF-Pyr) gave PhF in a yield of 11% with the considerable formation of phenylpyridines in yield of 55% and 2-, or 4-phenylazoanilines in a yields of 8% in total (ratio 1:5) with unidentified variable products. When the solution with a composition of $X_{HF}=0.86$ (40 wt% pyridine) prepared at Stage[A] was held at 20 °C, on the other hand, the deaminative fluorination of **1** took place gradually in yields of 5% for 1 h and 30% for 24 h without the formation of undesirable products. Interestingly, by allowing the ice-water quenched reaction mixture in Stage [A] to stand for some hours at 20 °C, PhOH was produced together with PhF in yields of 51% and 27% for 24 h, and 57% and 31% for 48 h. A quantitative yield of PhF was obtained by heating the solutions with a composition of 0.86 (40wt% pyridine)$\leq X_{HF} \leq$0.90 (30wt% pyridine) in Stage [B] at 55 °C for 30 min. A quantitative yield of PhF was also obtained by immediate heating of the solution with a composition of $X_{HF}=0.86$ prepared in Stage [A] at 90 °C for 15 min or longer without releasing HF from the reaction mixture. However, on immediate heating of the reaction mixture with a composition of $X_{HF} \geq 0.90$ at 90 °C, the generation of considerable amounts of HF was observed together with some amount of NO resulting in a decreased yield of PhF (e.g. 83%, $X_{HF}=0.90$) and increased formation of tarry matter and some amounts of 8 and fluoronitrobenzenes. This is because HF in the solution with a composition of $X_{HF}>0.86$ is unstable in combination with pyridine and is readily released at 90 °C. By allowing the solution with a composition of $X_{HF}=0.90$ prepared in Stage [A] to stand at 0 °C for 1 h and 2 h, an increasing yield of PhF to 89% and 95% respectively was observed by the subsequent heating of the reaction mixture at 90 °C for 15 min. These results suggest that increasing $X_{HF}$ in HF-Pyr served to slow down the rate of diazotization of **1**. However, immediate heating of the solution with a composition of $X_{HF}=0.90$ at 55 °C gave PhF sufficiently without the occurrence of undesirable reactions, because the diazotization rate of unaltered **1** in HF-Pyr with a composition of $X_{HF}=0.90$ may increase with increasing temperature and seems to be reconciled with the fluoro-dediazoniation rate of the resultant $PhN_2^+$ under these conditions. In the case of using HF-Pyr with a composition of $X_{HF}>0.90$, however, the yield of PhF was decreased with an accompanying formation of a fairly large amount of tarry matter indicating the sluggish formation of $ArN_2^+$ in Stage [A] at 0 °C for 1 h.

As shown in Table 6, *m*-aminophenol underwent deaminative fluorination readily to afford the corresponding ArF in quantitative yield under the conditions of Stage [B] at 60 °C in HF-Pyr with a composition of $0.83<X_{HF}<0.90$. However, *o*-aminophenol did not afford the corresponding ArF in HF-Pyr under similar conditions. On the other hand, **5** afforded benzoquinone in fairly good yield with little formation of the corresponding ArF in HF-Pyr with a composition of $X_{HF} \geq 0.90$ by carrying out Stage [A] at -50 °C for 30 min and Stage [B] at 20~100 °C for another 1 h. Heating the solution with a composition of $X_{HF} \geq 0.90$ at 140 °C in Stage [B] brought about the formation of a considerable amount of tarry matter. However, use of the solution with a composition of $0.80<X_{HF}<0.90$ for the reaction of **5** brought about the formation of a lower amount of benzoquinone at 20~120 °C, and fairly good yields of *p*-fluorophenol (70% at the most in HF-Pyr with a composition of $X_{HF}=0.83$) were produced by carrying out Stage [B] at 140 °C for 1 h. The yield of *p*-fluorophenol was also influenced by the temperature at Stage [A] as shown in Table 7.

Similar results were also observed in the reaction of methylated aminophenols to produce the corresponding ArF. On the other hand, in the reaction of *p*-aminophenols having electron-withdrawing groups such as nitro and carboxyl at their 2-position using HF-Pyr with a composition of $0.80 \leq X_{HF}$ in Stage [A] at 20 °C for 30 min, the corresponding quinonediazides[26] were obtained in good yields without the formation of benzoquinones as shown in Table 8.

**Table 7.** Effects of Temperature at Stage [A] on the Reaction of *p*-Aminophenol in HF-pyridine[a)]

| Temp/°C | *p*-Fluorophenol Yield / %[b)] |
|---|---|
| -70 | 42 |
| -60 | 70 |
| -50 | 68 |
| -40 | 50 |
| -30 | 32 |

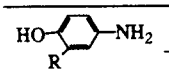
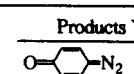
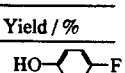
a) Stage [A]: *p*-Aminophenol 5 mmol, $NaNO_2$ 5.5 mmol, HF 900mmol, $X_{HF}$ 0.86, Time 30 min. b) Stage [B]: 140 °C for 1 h.

When such a solution was heated in

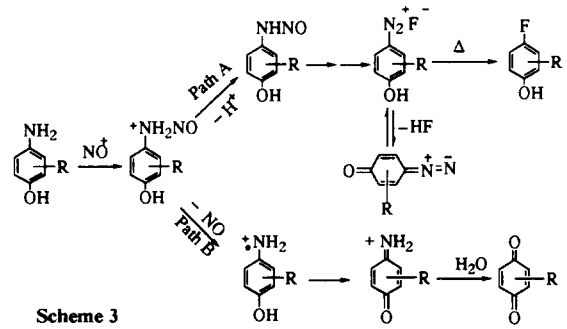
Stage [B] at 140 °C for 1 h, and then quenched with ice-water, the corresponding ArF was obtained in good yields. Judging from these experimental results, one-stage deaminative fluorination of $ArNH_2$ having a hydroxyl group at its *para* position using HF-Pyr solution may be illustrated as in Scheme 3.

Conclusively, the composition of HF-Pyr and the temperature at Stage [A] play an important role in Path [A] in Scheme 3, which gives *N*-nitrosoaminophenols by the deprotonation of the initially formed *N*-nitrosoanilinium cations to cause the diazotization of $ArNH_2$. Otherwise, Path [B] proceeds to form a radical cation by the generation of NO from the initially formed *N*-nitrosoanilinium cations, which in turn give benzoquinones by subsequent hydrolysis. Electron-withdrawing substituents such as carboxyl or nitro groups at the 2-position in the substrate favor the Path [A] to form the corresponding quinonediazides, which equilibrated with $ArN_2^+$ to cause thermal fluorinative decomposition readily to

Table 8. Products Found in the Reaction[a] of 2-Substituted-4-aminophenols

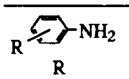
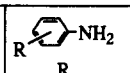
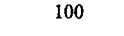
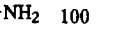
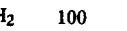
|  R | Stage [B][b] Temp / °C | $X_{HF}$[c] | Products Yield / %  |  |
|---|---|---|---|---|
| COOH | 20 | 0.80 | 74 | 0 |
| " | " | 0.90 | 95 | 0 |
| " | " | 1.00 | 90 | 0 |
| " | 140 | 0.80 | 0 | 19 |
| " | " | 0.86 | 0 | 96 |
| " | " | 0.90 | 0 | 98 |
| $NO_2$ | 20 | 0.86 | 80 | 0 |
| " | 140 | 0.90 | 0 | 70 |

a) Stage [A]: $ArNH_2$ 5 mmol, $NaNO_2$ 5.5 mmol, 0 °C for 20 min. b) 1h. c) HF mole fraction in HF-pyridine.



Scheme 3

Table 9. One-pot Deaminative Fluorination of $ArNH_2$ in HF-Pyridine[a]

|  R | Stage [B] Temp. / °C | ArF Yield / %[b] | Others[c] |  R | Stage [B] Temp. / °C | ArF Yield / %[b] | Others[c] |
|---|---|---|---|---|---|---|---|
| H | 55 | 99 (51-90) | − | *o*-$NH_2$ | 130 | low ( − ) | ++ |
| *o*-$CH_3$ | 55 | 99 (45-65) | − | *m*-$NH_2$ | 100 | 78[d] (31-54) | − |
| *m*- or *p*-$CH_3$ | 70 | 98 (69-87) | − | *p*-$NH_2$ | 120 | 65[d] (35-58) | + |
| *o*-$OCH_3$ | 150 | 17 (31-64) | ++ | *o*-$NO_2$ | 130 | low (7-17) | ++ |
| *m*-$OCH_3$ | 55 | 87 (32-52) | − | *m*-$NO_2$ | 120 | 93 (31-54) | − |
| *p*-$OCH_3$ | 130 | 71 (47-73) | + | *p*-$NO_2$ | 110 | 92 (35-58) | − |
| *o*-Cl | 160 | 72 (60-65) | + | *o*-OH | 160 | low ( − ) | ++ |
| *m*-Cl | 80 | 98 (83) | − | *m*-OH | 60 | 99 ( − ) | − |
| *p*-Cl | 110 | 92 (63) | − | *p*-OH | 140 | 70 ( − ) | + |
| *o*-$CO_2H$ | 90 | 72 (7) | + | 4-OH, 2- or 3-$CH_3$ | 140 | 92 ( − ) | − |
| *m*-$CO_2H$ | 80 | 95 (5) | − | 4-OH, 3-$CO_2H$ | 140 | 90 ( − ) | − |
| *p*-$CO_2H$ | 100 | 89 (32) | − | 4-OH, 3-$NO_2$ | 140 | 60 ( − ) | + |
| *o*-$CF_3$ | 90 | 76 ( − ) | + | 4-  | 100 | 80[d] (44-80) | − |
| *m*-$CF_3$ | 90 | 95 (64-80) | − | 4-$CH_2$-  | 100 | 95[d] (58) | − |
| *p*-$CF_3$ | 80 | 85 ( − ) | + | 4-O-  | 100 | 95[d] (10) | − |

a) Stage [A]: $ArNH_2$ 5 mmol, $NaNO_2$ 5.5 mmol, HF-pyr $X_{HF}$=0.86, 0 °C for 20 min. Stage [B]: 1 h.
b) Parentheses are the reported yields in the following reaction.[6] $ArNH_2 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF$
c) Tarry matter: − ; None or Trace, + ; Some, ++ ; A large amount. d) Difluoro compounds.

afford the corresponding fluorophenols.

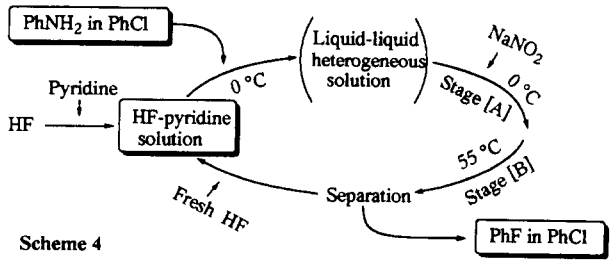
As shown in Table 9, one-pot deaminative fluorination of most $ArNH_2$ gave the corresponding ArF in good or quantitative yields, except for some $ArNH_2$ having polar substituents such as methoxy, hydroxy, nitro at their *ortho* position, when the reaction was carried out by above outlined procedure using HF-Pyr with a composition of $0.80 \leq X_{HF} \leq 0.90$.

4. *Facile Continuous Operation of Deaminative Fluorination of Aniline.*

It should be noted that one-pot deaminative fluorination of **1** took place efficiently to afford PhF in high yields by employing HF-Pyr with a composition of $0.80 \leq X_{HF} \leq 0.90$ even under the conditions of an extremely large excess HF such as $N$=90, which may have enabled us to carry out the continuous operation. Thus, the reaction of **1** has been studied[13] by employing a liquid-liquid two-phase mixture of chlorobenzene and HF-Pyr with a composition of $X_{HF}$=0.90 as shown in Scheme 4.

After completion of the reaction, the PhF produced was located in the chlorobenzene layer which was free of HF.[27] Thus, the agent layer separated from the chlorobenzene layer may be used for the next run with or without another addition of fresh HF as summarized in Table 10.

When no addition of fresh HF was made prior to the next run, the yield of PhF in each repeated run gradually decreased. Such deterioration of agent activity may be attributed to the formation of water in the diazotization of **1** with $NaNO_2$ with the consumption of HF itself. Thus, fresh HF was added repeatedly to the recovered HF layer[28] to permit carrying out the deaminative fluorination of **1** continuously without a remarkable decrease in the yield of PhF.




Scheme 4

Table 10. Repeated Use of HF-pyridine in the Reaction of Aniline[a)]

| without fresh HF | | with fresh HF[b)] | |
|---|---|---|---|
| Number of repeated run | Yield of PhF / % | Number of repeated run | Yield of PhF / % |
| 1 | 99 | 1-5 | 97 |
| 2 | 99 | 6-10 | 95 |
| 3 | 79 | 11-15 | 90 |
| 4 | 83 | 16-20 | 90 |

a) Stage [A]: Aniline 5 mmol in 30 ml chlorobenzene, $NaNO_2$ 5 mmol, Intial amount of HF and pyridine is 450 mmol and 49 mmol respectively. 0 °C for 20 min. Stage [B]: 55 °C for 1 h. b) Amount of HF is 40 mmol in each run.

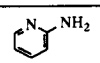
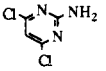
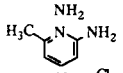
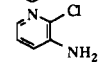
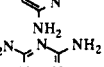
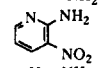
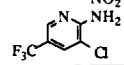
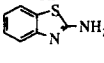
5. *Deaminative Fluorination of Heteroaromatic Amines*

Because amino heteroaromatic compounds such as aminopyridines may play the part of an organic base in HF, the amino group located on the hetero aromatic rings underwent diazotization very readily in HF without bases accompanied by subsequent fluoro-dediazoniation very efficiently giving the corresponding heteroaromatic fluorides in good yields under moderate conditions as shown in Table 11.

It should be noted that this procedure is very useful for the preparation of fluoropyridines because in only a few cases have fluoropyridines been reported by the decomposition of the corresponding $ArN_2BF_4$ in poor or low yields.[6,29-33] HF-Pyr, which is convenient to handle, was also employed in the reaction of aminopyridines.[34] Particularly, in the reaction of aminopyridines with electron-withdrawing substituents with relatively low basicity, use of HF-Pyr with a composition of $X_{HF}$=0.80 was recommended in order to prevent undesirable side reactions and facilitate the handling of HF solution. The desired fluoropyridines were liberated by addition of a large amount of cold water without neutralization after the completion of the reaction because their basicity may not strong enough for the solution in the acid layer. Unexpectedly, 2-fluoro-6-methylpyridine, in contrast to 2-, 3-, and 4-fluoropyridines, was also liberated from the acid layer without the neutralization. Interestingly, 2-amino-4-nitropyridine gave the corresponding fluoride very readily and in high yields under moderate conditions at Stage [B], despite the very sluggish deaminative fluorination of 2-

nitroaniline as described before. Relative deaminative fluorination rates of 2,4-dinitroaniline, *p*-nitroaniline, 2-, 3-, and 4-aminopyridines to aniline were determined by the amount of nitrogen gas generated at Stage [B] to be 0.0001 or less, 0.001, 48,000, 11, and 110 respectively under the conditions of Stage [A] at -78 °C and Stage [B] at 20 °C using HF-Pyr with a composition of $X_{HF}$=0.90 and $N$=20. The discrepancy observed in the reactions between the heteroaromatics and the usual aromatics is not well elucidated.

Table 11. One-pot Deaminative Fluorination of Heterocyclic Aminoarenes in HF or HF-pyridine[a)]

| Substrate | Acid | Stage [B][b)] Temp. / °C | ArF Yield / %[c)] | | Substrate | Acid | Stage [B][b)] Temp. / °C | ArF Yield / %[c)] | |
|---|---|---|---|---|---|---|---|---|---|
|  | HF | 25 | 91 | (10) |  | HF | 25 | 50 | (–) |
| | HF-Pyr | 25 | 94 | | | HF-Pyr. | 25 | 55 | |
|  | HF | 40 | 93 | (42) |  | HF | 40 | 65 | (–) |
| | HF-Pyr | 40 | 96 | | | HF-Pyr. | 40 | 80 | |
|  | HF | 60 | 90 | (–) |  | HF-Pyr. | 20 | 72 | (–) |
| | HF-Pyr | 60 | 95 | | | | | | |
|  | HF-Pyr | 0 | 95 | (–) |  | HF-Pyr. | 90 | 60 | (–) |
|  | HF-Pyr | 20 | 89 | (–) |  | HF-Pyr. | 50 | 45 | (–) |
|  | HF-Pyr | 20 | 97 | (–) | | | | | |
|  | HF-Pyr | 20 | 99 | (–) |  | HF-Pyr. | 50 | 75 | (–) |

a) Stage [A]: Substrate 5 mmol, HF 450 mmol, $NaNO_2$ 5.5 mmol, $X_{HF}$=0.86. 0 °C for 20 min. b) 1 h. c) Parentheses are the reported yields in the following reaction.[6] $ArNH_2 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF$

## 6. *Photo-induced Deaminative Fluorination of $ArNH_2$*

Certain $ArNH_2$ having polar substituents such as hydroxyl, amino, nitro, methoxy and so on, particularly at the *ortho* position, always required high temperature in Stage [B] and were inclined to form undesirable by-products with considerably lower yields of ArF. *o*-Anisidine, for example, did not afford the expected ArF at all when Stage [A] was carried out in the presence of HF-Pyr with compositions of $X_{HF}$=0.90 and 0.80 at 20 °C for 6 h with stirring as shown in Table 12.

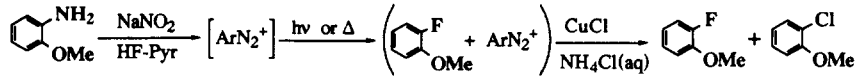
Table 12. Products Found in the Solution after the Addition of aq. $NH_4Cl/CuCl$[a)] to the Reaction Mixure of *o*-Anisidine with $NaNO_2$ in HF-pyridine

| Stage [A][b)] $X_{HF}$ | Stage [B] | | | Products Yield / %  |  | $ArN_2^+$ / %[d)] |
|---|---|---|---|---|---|---|
| | | Temp. / °C | Time / h | | | |
| 0.90 | - | 20 | 6 | 0 | 21 | 21 |
| 0.90 | - | 150 | 1 | 17[e)] | 0 | - |
| 0.80 | - | 20 | 6 | 0 | 62 | 62 |
| 0.80 | - | 130 | 1 | 19[e)] | 0 | - |
| 0.90 | irrad.[c)] | 20 | 6 | 20 | 0 | 20 |
| 0.80 | irrad.[c)] | 20 | 6 | 43 | 20 | 63 |
| 0.80 | irrad.[c)] | 20 | 18 | 73 | 5 | 78 |

a) $NH_4Cl$(aq)(50%): 20 ml, CuCl: 0.2 mmol, 20 °C for 5 h. b) 20 °C for 1 h, *o*-anisidine 5 mmol, $NaNO_2$ 5.5 mmol, HF 450 mmol. c) 300 watt high pressure Hg-lamp. d) Estimated amount of $ArN_2^+$ formed in Stage [A] (the summation of amount of *o*-fluoroanisol and *o*-chloroanisol). e) With a considerable amount of unknown products.

By heating these solutions with a composition of $X_{HF}$=0.80 and 0.90 at 130

°C or higher for 1 h, the remarkable generation of HF with NO, particularly in the case of $X_{HF}$=0.90, was observed, and only 19% and 17% yields of the corresponding ArF were respectively produced with a considerable amount of tarry matter. However, as shown in following Eq., the addition of $NH_4Cl$ and CuCl to the resulting reaction mixtures of Stage [A] brought about the formation of the corresponding ArCl (the Sandmeyer reaction) in yields of 21% and 62% respectively.



The Sandmeyer reaction of $ArN_2BF_4$ was found to take place very readily and quantitatively to afford ArCl in HF-Pyr solution with $X_{HF}$>0.80,[37] therefore, the yields of ArCl obtained by the above outlined procedure may correspond to the amount of $ArN_2^+$ formed at Stage [A] in the reaction of *o*-anisidine. Thus, the fluorinative decomposition of the initially formed $ArN_2^+$ in the solutions at Stage [A], which requires a temperature of 130 °C or higher, was invariably accompanied by undesirable reactions with the formation of the expected ArF in poor yields. However, when these solutions with compositions of $X_{HF}$=0.80 and 0.90 obtained in Stage [A] were irradiated at 20 °C for 6 and 18 h by a 300 watt high pressure Hg-lamp and then aqueous $NH_4Cl$ with CuCl was added to the resultant solutions, the formation of ArF and ArCl was observed in yields of 43% and 20%, and 73% and 5% respectively without the formation of tarry matter.

Most of the ArF compounds, having polar substituents, as shown in Table 13, were produced in good yields by carrying out Stage [B] under irradiation in the presence of HF-Pyr with a composition of $X_{HF}$=0.86. The undesirable coupling reactions of $ArN_2^+$ with pyridine in HF-Pyr invariably take place on thermal treatment of the reaction mixture with a composition of $X_{HF}$<0.86 at Stage [B] to decrease the formation of the desired ArF. However, photo-induced deaminative fluorination of $ArNH_2$, for example **5**, was found to take place most effectively in HF-Pyr with $X_{HF}$=0.86 to give the corresponding ArF in a yield of 80% with minimal formation of undesirable products. When γ-collidine or ethyl ether was used as the base, the hydrogen abstraction from their α-carbon seems take place to give reductive products.[38] These by-products may be formed by the reaction of the aryl radical ($Ar^•$). The reaction can be understood to proceed *via* the initial formation of aryl cation ($Ar^+$) [39] or/and aryl radical $Ar^•$ by the irradiation of $ArN_2^+$ in HF combined with base solutions.[40] The nucleophilic activity of fluoride ion ($F^-$) in HF is known to be much more enhanced by the presence of organic bases.[8,41] Thus, the reaction of $Ar^+$ with $F^-$ might occur more effectively to afford ArF in HF combined base solutions than that conducted in pure HF.

**Table 13.** Photochemically Induced Deaminative Fluorination of $ArNH_2$ in HF-pyridine[a)]

| R-C$_6$H$_3$-NH$_2$ R | Stage [B][b)] temp. / °C | time / h | ArF yield / %[d)] | R-C$_6$H$_3$-NH$_2$ R | Stage [B][b)] temp. / °C | time / h | ArF yield / %[d)] |
|---|---|---|---|---|---|---|---|
| *o*-$CH_3O$ | 20 | 18[c)] | 73 (0) | *o*-COOH | 13 | 6 | 58 (0) |
| " | 150 | 1 | — (17)[e)] | *p*-COOH | 13 | 18 | 23 (0) |
| *m*-$CH_3O$ | 13 | 2 | 89 (Some) | *o*-$CF_3$ | 13 | 18 | 62 (0) |
| *p*-CH3O | 13 | 2 | 23 (0) | *o*-OH | 13 | 6 | 38 (0) |
| " | 13 | 18 | 70 — | *m*-OH | 13 | 6 | 86 (Some) |
| *o*-F | 20 | 6 | 82 (0) | *p*-OH | 13 | 6 | 80 (0) |
| *o*-$NO_2$ | 13 | 18 | 27 (0) | 2-$CH_3O$, 4-$NO_2$ | 20 | 18 | 64 (0) |
| *p*-$NO_2$ | 13 | 18 | 62 (0) | " | 20[g)] | 6 | 0 (0) |
| *p*-$NH_2$ | 13 | 18 | 62[f)] (0) | " | 20[h)] | 6 | 22 (0) |
| | | | | " | 20[i)] | 6 | 41[j)] (0) |

a) HF-Pyr with $X_{HF}$=0.86. b) Irradiation by 500 watt high pressure Hg-lamp. c) 300 watt high pressure Hg-lamp. d) Parentheses are the yield of ArF without irradiation. e) With a considerable amount of tarry matter. f) F-C$_6$H$_4$-F. g) HF-Pyr with $X_{HF}$=0.57. h) HF-γ-Collidine with $X_{HF}$=0.90. i) HF-Ethyl ether with $X_{HF}$=0.71. j) 2-Pyridyl-4-nitroanisol (40%) was found.

Although the photochemically induced fluoro-dediazoniation of $ArN_2BF_4$ salts to produce ArF was attempted by Rutherfords, and Cohen's groups respectively,[42] the present procedure was convenient for obtaining ArF more effectively without the isolation and the purification of $ArN_2BF_4$ obtained from the

corresponding $ArNH_2$. It is also noteworthy that deaminative fluorination of $ArNH_2$ having amino, halogen, methoxy, hydroxy or nitro groups in the *ortho* position, which proceeds sluggishly thermally to produce ArF in very poor yields, was also accelerated photochemically to afford the desired product with minimal formation of by-products.

## Experimental

General. All precautions which apply to the use of anhydrous hydrogen fluoride should likewise be applied to the use of HF combined organic base solutions (HF-Base). The recommended procedure for an HF burn is to sluice with water, pack with ice and obtain medical attention as quickly as possible. HF was purchased from Hashimoto Chemical Industry Co. Ltd. and freshly distilled prior to use. $NaNO_2$ was purchased from Wako Pure Chemical. $ArNH_2$ were used directly as purchased Tokyo Chemical Industry Co, Ltd., THOKEM Products Co. Ltd., Yuki Gosei Kagaku Co. Ltd., and Mitsubishi Kagaku Co. Ltd. Organic solvents were the best commercial grade and used directly. $^1$H-NMR spectra were recorded on a JEOL JNM A 400 II, Bruker SL 400 (400 MHz) or Hitachi R-1900 (90 MHz) NMR spectrometer, $^{19}$F-NMR spectra were recorded on a Hitachi R-1900 (84.6 MHz) NMR spectrometer. $^1$H-NMR chemical shifts are expressed in parts per million (δ scale) downfield from TMS; $^{19}$F-NMR chemical shifts are expressed in parts per million (δ scale) downfield from hexafluorobenzene. GLC-Mass were recorded with Hewlett Packard 5970 series or Hitachi 023 (Column: OV-1 25 m, 50~250 °C)-Finnigan ITD 800 mass spectrometer. IR spectra were measured using a Hitachi 260-30 IR spectrometer. Vapor phase chromatography analysis was performed on a Hitachi 023 equipped with both flame ionization and thermal conductivity detector using an 2 m column (10% OV-1). Elemental analysis were performed by the Hokkaido university analytical center.

Preparation of HF-Base solutions. Solutions of HF with organic bases were prepared by the addition of the prescribed amount of HF distilled from a commercial cylinder into a organic base by portions under stirring in a 100 cm$^3$ polyethylene bottle equipped with a reflux condenser under nitrogen at -78 °C. Great care should be required since vigorous exothermic reactions are usually observed in the preparation of HF-Base solutions.

Deaminative fluorination procedure. As a general one-pot deaminative fluorination procedure of $ArNH_2$, in a 100~250 cm$^3$ PFA[12] made reactor equipped with a reflux condenser and/or a cooled trap, prescribed amount of $ArNH_2$ (5~25 mmol) was added to HF or HF-Base at 0 °C, of which quantities are shown in Tables in the text. Then the mixture was allowed to stand at room temperature (if necessary at 30~45 °C) until $ArNH_2$ was completely dissolved. After cooling down to lower than -30 °C, 5~30 mmol of $NaNO_2$ (usually 1.1 equivalent amount of $ArNH_2$) was added to a solution of $ArNH_2$ in HF or HF-Base. The addition of $NaNO_2$ to the HF-Base solution did not result in a vigorous rise temperature as was observed in the case of HF. Thus, clean and almost colorless solutions were readily obtained by these of HF-Pyr with a composition of $X_{HF} \leq 0.90$. If necessary, the temperature of the solution was raised to room temperature (Stage [A]) and maintained for 15 min or longer to dissolve $NaNO_2$. The reaction mixture was then heated to the prescribed temperatures (50~140 °C) for 30 min or longer in an oil bath under stirring (Stage [B]). During the course of raising the temperature, an evolution of nitrogen gas was observed at the characteristic temperatures dependent upon $ArNH_2$ to indicate the occurrence of dediazoniation of $ArN_2^+$. In order to force the dediazoniation to completion, the reaction was usually carried out at a 10 °C higher temperature than at that observed in the first evolution of nitrogen. The reaction mixture was then quenched with ice-water and the products were extracted with ether, $CH_2Cl_2$, $CCl_4$, chlorobenzene or pentane. In case of using HF-Base, products extracted with organic solvents were washed with aqueous NaCl to remove organic bases such as pyridine. After neutralizing the solvent layer with $NaHCO_3$ and drying over $MgSO_4$, the products were identified by ordinary spectroscopic methods.

Reaction of 4-Aminopyridine. After an addition of $NaNO_2$ to 4-aminopyridine in HF (N=90) at -78 °C, the stirred solution was allowed to stand 0 °C for 30 min and then stand at 20~60 °C for 15~30 min under stirring. By quenching the resultant solution with ice-water, followed by the neutralization with cold saturated $NaHCO_3$, the crude product obtained by extraction with $CH_2CCl_2$ was dried over $MgSO_4$ refluxed in the presence of $CaH_2$ for 3 h, and evaporated. Distillation (104~105 °C) afforded 80% or more of 4-fluoropyridine, which must be stored in a sealed tube since it is sensitive to moisture changing from colorless to yellow giving polymeric products.

Continuous operation of deaminative fluorination of aniline. HF-Pyr solution composed of 450 mmol of HF and 50 mmol of pyridine was added drop wise to 5 mmol of $PhNH_2$ in 30 cm$^3$ of PhCl at 20 °C under vigorous stirring in a reaction vessel of 200 cm$^3$ equipped with a reflux condenser. Then 5~5.5 mmol of $NaNO_2$ was added to the solution and heated at 50~55 °C for 30 min. After the completion of the reaction, the mixture separated into two layers. The desired PhF was found in PhCl layer to be free from HF. The HF-Pyr layer separated from the organic layer was subjected to the next run for 5 mmol of $PhNH_2$ in 30 cm$^3$ of PhCl.

Photo-induced deaminative fluorination. An experimental arrangement for photo-induced deaminative fluorination of $ArNH_2$ in HF-Base solutions is illustrated in Fig. 1.

A solution prepared at Stage [A] in the PFA made bottle (100 cm$^3$) was irradiated by a 300 or 500 watt high pressure Hg-lamp (Eikohsha Co., Ltd.) by showering a cooling water to remain at lower than 20 °C for the durations specified in Tables 12 and 13. Exhausted gas, $N_2$, was washed with aqueous NaCl solution and collected

to gas holder. The resultant solution was worked up in the manner described before.
NMR spectroscopic analysis of intermediates formed in Stage [A]. The NMR spectra of the reaction mixtures of Stage [A] were taken on a Bruker MSL 400 NMR spectrometer using a tube made of FEP (3$\phi$) inserted in the usual NMR sample tube (5$\phi$) with TMS as external standard.

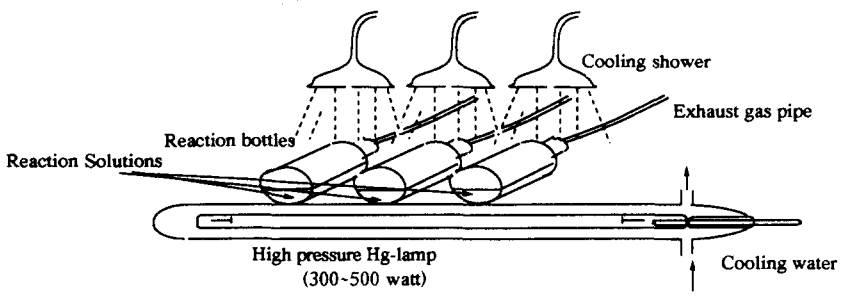



Fig. 1 Apparatus of Photo-induced deaminative fluorination

Spectra data. 4-Fluoropyridine: $^1$H-NMR: δ 8.60 (m, 2 H), 7.05 (m, 2 H). $^{19}$F-NMR: δ 59.36 (m). IR (neat) 3040, 1580, 1495, 1415, 1250, 1205, 815. MS: m/z (relative intensity) 97 ($M^+$ 100), 70 (85), 51 (31). HRMS: Found; m/z 97.0328 Calcd for $C_5H_4NF$; M 97.0328. 2-Fluoro-3-nitropyridine: $^1$H-NMR: δ 8.52 (m, 2 H), 7.45 (m, 1 H). $^{19}$F-NMR: δ 94.36 (s). IR (neat) 3080, 1590, 1525, 1455, 1440, 1350, 1290, 1235, 1150, 1085, 870, 820, 755, 660. MS: m/z (relative intensity) 142 ($M^+$ 50), 96 (100), 76 (49), 69 (50), 51 (29). HRMS, Found: m/z 142.0157 Calcd for $C_5H_3N_2FO_2$: M 142.0178. 2-Fluoro-3-chloro-5-trifluoromethylpyridine: $^1$H-NMR: δ 8.42 (m, 1 H), 8.08 (m, 1 H). $^{19}$F-NMR: δ 99.88 (s, 3 F), 96.90 (s, 1 F). IR (neat) 3080, 1595, 1465, 1405, 1330, 1300, 1240, 1170, 1140, 1090, 1075, 920, 895, 745, 705, 625. MS: m/z (relative intensity) 201, 199 ($M^+$ 23, 100), 180 (30), 149 (27), 69 (48). HRMS, Found: m/z 198.9837 Calcd for $C_6H_2NF_4Cl$: M 198.9812. 2,6-Difluoro-4-phenyl-*s*-triazine: $^1$H-NMR: δ 8.52 (m, 2 H), 7.68 (m, 1 H), 7.56 (m, 2 H). $^{19}$F-NMR: δ 126.60 (s). IR (nujol) 3060, 1605, 1590, 1575, 1560, 1540, 1440, 1380, 1305, 1240, 1060, 1000, 895, 820, 780, 710, 680, 660. MS: m/z (relative intensity) 193 ($M^+$ 100), 192 (59), 103 (60), 76 (56), 51 (31). HRMS, Found: m/z 193.0459 Calcd for $C_9H_5N_3F_2$: M 193.0452. 2-Fluoro-6-methylpyridine: $^1$H-NMR: δ 7.66 (m, 1 H), 7.03 (m, 1 H), 6.72 (m, 1 H), 2.50 (s, 3 H). $^{19}$F-NMR:δ 93.85 (s). IR (neat) 3070, 2920, 1600, 1570, 1445, 1280, 1260, 1220, 1140, 1080, 1010, 985, 930, 785, 720. MS: m/z (relative intensity) 111 ($M^+$ 100), 91 (59), 84 (24), 64 (15). HRMS, Found: m/z 111.0479 Calcd for $C_6H_6NF$: M 111.0485. 2-Fluoropyrimidine: $^1$H-NMR: δ 8.67 (dd, 2 H, J=2, 4 Hz), 7.30 (m, 1 H). $^{19}$F-NMR: δ 118.26 (s). IR (neat) 1575, 1555, 1445, 1410, 1210, 1190, 1180, 855, 815, 780, 635. MS: m/z: (relative intensity) 98 ($M^+$ 100), 71 (93), 52 (29). HRMS, Found: m/z 98.0279 Calcd for $C_4H_3N_2F$: M 98.0280. 2-Fluorobenzothiazol: $^1$H-NMR: δd 7.78 (m, 2 H), 7.42 (m, 2 H). $^{19}$F-NMR: δ 89.36. IR (neat) 3060, 1600, 1555, 1445, 1435, 1310 1240, 1225, 1060, 1015, 985, 750, 725, 640. MS: m/z: (relative intensity) 153 ($M^+$ 100), 107 (17), 63 (20). HRMS, Found: m/z 153.0038 Calcd for $C_7H_4NFS$: M 153.0048. 2-Chloro-3-fluoropyridine: $^1$H-NMR: δ 8.23 (m, 1 H), 7.49 (m, 1 H), 7.28 (m, 1 H). $^{19}$F-NMR: δ 43.53 (m). IR (neat) 3060, 1580, 1450, 1420, 1270, 1210, 1120, 1080, 795, 710, 675. MS: m/z (relative intensity) 133, 131 ($M^+$, 29, 100), 96 (86), 76 (33), 69 (18). HRMS, Found: m/z 132.9924 (M+2) Calcd for $C_7H_4NFS$: M 132.9908. 2-Fluoro-4,6-dichloropyrimidine: $^1$H-NMR: δ 7.04 (d, 1 H, J=2 Hz). $^{19}$F-NMR: δ 120.89 (s). IR (nujol) 3080, 1550, 1460, 1390, 1265, 1115, 965, 850, 825, 770, 665. MS: m/z: (relative intensity) 170, 168, 166 ($M^+$ 8, 56, 100), 131 (49), 869 (44), 51 (29). HRMS, Found: m/z 165.9502 Calcd for $C_7H_4NFS$: M 165.9501. 2,6-Dimethyl-4-fluoropyrimidine: $^1$H-NMR: δ 6.64 (m, 1 H), 2.67 (s, 3 H), 2.54 (s, 3 H). $^{19}$F-NMR: δ 99.44 (s). IR (neat) 3080, 2930, 1595, 1565, 1445, 1410, 1385, 1360, 1345, 1210, 1155, 1045, 940, 845, MS: m/z (relative intensity) 126 ($M^+$ 100), 111 (11), 85 (19). HRMS, Found: m/z 126.0581 Calcd for $C_7H_4NFS$: M 126.0594. 2-Fluoro-4-chloro-6-methylpyrimidine: $^1$H-NMR: δ 7.17 (d, 1 H, J=3 Hz), 2.56 (s, 3 H). $^{19}$F-NMR: δ 118.21 (s). IR (neat) 3080, 1580, 1550, 1440, 1370, 1325, 1140, 1040, 975, 885, 775, 660. MS: m/z (relative intensity) 148, 146 ($M^+$ 24, 100), 111 (15), 66 (34). HRMS, Found: m/z 146.0029 Calcd for $C_7H_4NFS$: M 148.0037. *p*-Methylanilinium ion: $^1$H-NMR (HF/amine=60 (molar ratio)): δ 8.10 (t, 3 H (-$NH_3^+$), $J_{HN}$=54 Hz), 7.81 (m, 4 H), 2.84 (s, 3 H). *p*-Methylanilinium ion: $^1$H-NMR (HF/amine=20 (molar ratio)): δ 7.90 (s, 3 H (-$NH_3^+$)), 7.20 (d, 2 H, J=8), 7.15 (d, 2 H, J=8), 2.03 (s, 3 H). *p*-Chloroanilinium ion: $^1$H-NMR (HF/amine=20 (molar ratio)): δ 7.91 (s, 3 H (-$NH_3^+$)), 7.75 (d, 2 H, J=8), 7.10 (d, 2 H, J=8). *p*-Nitroanilinium ion: $^1$H-NMR (HF/amine=20 (molar ratio)): δ 8.21 (s, 3 H (-$NH_3^+$)), 8.59 (d, 2 H, J=8), 7.38 (d, 2 H, J=8). *p*-Hydroxyanilinium ion: $^1$H-NMR (HF/amine=20 (molar ratio)): δ 8.02 (s, 3 H (-$NH_3^+$)), 7.60 (d, 2 H, J=8), 6.82 (d, 2 H, J=8). Anilinium ion: $^1$H-NMR (HF/amine=20 (molar ratio)): δ 8.10 (s, 3 H (-$NH_3^+$)), 7.81-7.23 (m, 5 H). *p*-Methylbenzenediazonium ion: $^1$H-NMR (HF/amine/$NaNO_2$=20/1/1.1 (molar ratio)): 8.42 (d, 2 H, J=8 Hz), 7.01

(d, 2 H, J=8 Hz), 2.84 (s, 3 H). *p*-Chlorobenzenediazonium ion: $^1$H-NMR (HF/amine/$NaNO_2$=20/1/1.1 (molar ratio)): 8.20 (d, 2 H, J=8 Hz), 7.84 (d, 2 H, J=8 Hz). *p*-Nitrobenzenediazonium ion: $^1$H-NMR (HF/amine/$NaNO_2$ =20/1/1.1 (molar ratio)): 8.87 (d, 2 H, J=8 Hz), 8.63 (d, 2 H, J=8 Hz). *p*-Benzoquinone monoiminium ion: $^1$H-NMR (HF/amine/$NaNO_2$=20/1/1.1 (molar ratio)): δ 10.75 (t, 2 H (-$NH_2^+$), $J_{HN}$=57 Hz), 7.58 (d, 2 H, J=8 Hz), 7.08 (d, 2 H, J=8 Hz). 3-Carboxyquinonediazide: $^1$H-NMR (DMSO-$d_6$): δ 9.08 (m, 1 H), 7.96 (m, 1 H), 6.64 (m, 1 H). IR (nujol) 2160, 1600, 1495, 1450, 1300, 1120, 1045, 810. 3-Nitroquinonediazide: $^1$H-NMR (DMSO-$d_6$): δ 8.98 (m, 1 H), 8.17 (m, 1 H), 6.83 (m, 1 H). IR (nujol) 2170, 1590, 1460, 1375, 1120, 1005, 840. 2-Carboxy-4-Fluorophenol: $^1$H-NMR: δ 10.55 (s, 1 H), 7.95 (m, 1 H)6.69 (m, 2 H). $^{19}$F-NMR: δ 38.25 (s). IR (nujol) 3280, 1660, 1600, 1440, 1250, 1205, 1135, 980, 850, 775, 615. MS: m/z:(relative intensity) 156 ($M^+$ 34), 138 (98), 110 (100), 82 (62), 57 (33). HRMS, Found: m/z 156.0220 Calcd for $C_7H_5O_3F$: M 156.0223. 2-Nitro-4-Fluorophenol: $^1$H-NMR: δ 10.36 (s, 1 H), 7.82 (m, 1 H), 7.36 (m, 1 H), 7.15 (m, 1 H). $^{19}$F-NMR: δ 40.57 (s). IR (nujol) 3280, 1590, 1540, 1460, 1240, 1205, 945, 845, 785. MS: m/z:(relative intensity) 157 ($M^+$ 100), 140 (7), 127 (19), 99 (41), 83 (64), 57 (80). HRMS, Found: m/z 157.0181 Calcd for $C_6H_4O_3NF$: M 157.0175.

Most ArF other than those shown above were identified by direct comparison with the corresponding authentic samples.

***Acknowledgements***: Support of the research in this field by Grants-in-aid (No. 04555200) from the Ministry of Education, Science, and Culture, Japan is warmly acknowledged. Thanks are due to TOHKEM Products Co. Ltd., Mitsubishi Kagaku Co. Ltd., Yuki Gosei Kagaku Co. Ltd., Asahi Denka Co. Ltd., Central Grass Co. Ltd., and Tokai Denka Co. Ltd., for an offer of aminoarenes and financial supports.

## References and Notes

1) (a) Boudakian, M. M. "Encyclopedia of Chemical Technology" Vol. 11, 4th Ed. John Wiley & Sons Inc. p. 565, 1994. (b) Olah, G. A.; Chambers, R. D.; Prakash, G. K. S. "Synthetic Fluorine Chemistry " John Wiley & Sons Inc. 1992. (c) Wilkinson, J. A. *Chem. Rev.* **1992**, *92*, 505. (d) German, L.; Zemskov, S. (Eds.) "New Fluorinating Agents in Organic Synthesis" Springer-Verlag, 1989. (e) Liebman, J. F. "Fluorine-Containing Molecul" VCH Publishers Inc. 1988. (f) Banks, R. E. "Organofluorine Chemicals and their Industrial Applications" John Wiley & Sons Inc. 1979. (g) Ishikawa, N.; Kitazume, T. *J. Synth. Org. Chem. Jpn.* **1976**, *34*, 173.

2) (a) Welch, T. J. "Fluorine in Bioorganic Chemistry" John Wiley & Sons Inc. p. 234, 1991. (b) Welch, T. J. *Tetrahedron* **1987**, *43*, 3123.

3) (a) Meurs, J. H. H.; Eilenberg, W. *Tetrahedron* **1991**, *47*, 705. (b) Meurs, J. H. H.; Sopher, D. W.; Eilenberg, W. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 927. (c) Hewitt, C. D.; Silvester M. J. *Aldrichimica Acta* **1988**, *21*, 3. (d) Knunyants, I. L.; Yakobson, G. G. "Syntheses of Fluoroorganic Compounds" Springer-Verlag Tokyo, 1985. (e) Christe, K. O.; Pavlath, A. E. *J. Org. Chem.* **1965**, *30*, 3170.

4) (a) Stavber, S.; Zupan, M. *J. Org. Chem.* **1985**, *50*, 3609. (b) Lerman, O.; Tor, Y.; Rozen, S. *Ibid.* **1984**, *49*, 806. (c) Anand, S. P.; Quarterman, L. A.; Christian, P. A.; Hyman, H. H.; Filler, R. *Ibid.* **1975**, *40*, 3796. (d) Grakauskas, V. *Ibid.* **1969**, *34*, 2835.(e) Puy, M. V. D. *Tetrahedron Lett.* **1987**, *28*, 255. (f) Umemoto, T.; Kawada, K.; Tomita, K. *Ibid.* **1986**, *27*, 4465. (g) Appelman, E. H.; Basile, L. J.; Hayatsu, R. *Tetrahedron* **1984**, *40*, 189. (h) Stavber, S.; Zupan, M. *J. Chem. Soc. Chem. Commun.* **1981**, 148. (i) Kollonitsch, J.; Barash, L.; Doldouras, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7494. (j) Shaw, M. J.; Hyman, H. H.; Filler, R. *Ibid.* **1969**, *91*, 1563.

5) (a) Okazoe, T.; Yokokoji, O.; Kumai, S. 14th Symposium of Japan Fluorine Chemistry, Kyoto, Oct. 1989, Abstr. No. O-50. (b) Yoshida, Y.; Kimura, Y. *Chem. Lett.* **1988**, 1355. (c) Clark, J. H.; Macquarrie, D. J. *Tetrahedron Lett.* **1987**, *28*, 111. (d) Tanabe, T. 8th Symposium of Japan Fluorine Chemistry, Nigata, Oct. 1982, Abstr. No. 1Q-06. (e) Ishikawa, N.; Kitazume, T.; Yamazaki, T; Mochida, Y.; Tatsuno, T. *Chem. Lett.* **1981**, 761. (f) Kitazume, T.; Ishikawa, N. *Ibid.* **1978**, 283. (g) Finger, G. C.; Starr, L. D.; Dickerson, D. R.; Gutowsky, H. S.; Hamer, J. *J. Org. Chem.* **1963**, *28*, 1666. (h) Fuller, G. J. *J. Chem. Soc.* **1965**, 6264. (i) Ueda, K.; Hashiguchi, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 688.

6) (a) Roe, A. *Org. React.* Vol 5, R. Adams (Ed.), John Wiley & Sons Inc. 1949. (b) Milner, D. J. *Synth. Commun.* **1992**, *22*, 73. (c) Silvester, M. J. *Aldrichimica Acta* **1991**, *24*, 31. (d) Hand, E. S.; Baker, D. C. *Synthesis* **1989**, 905. (e) Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572. (f) Ferraris, J. P.; Saito, G. *J. Chem. Soc, Chem. Commun.* **1978**, 992. (g) Suschitzky, H. I. *Adv. Fluorine Chem.* **1965**, *1*, 4. (h) Ferm, R. L.; Werf, C. A. V. *J. Am. Chem. Soc.* **1950**, *72*, 4809. (i) Flood, D. T. *Org. Synth.* Coll. Vol. *2*, John Wiley & Sons Inc., p. 295, 1945.

7) Ishikawa, N. *Petrotech* **1987**, *10*, 543.

8) Yoneda, N. *Tetrahedron* **1991**, *47*, 5329.

9) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

10) Olah, G. A.; Welch, J. T. *J. Am. Chem. Soc.* **1975**, *97*, 208.

11) Boudakian, M. M. U.S.Patent, 4,096,196, **1978**; *Chem. Abstr.* **1978**, *90*, 103597n.

12 Tetrafluoroethylene-perfluoroalkylvinylether co-polymer.

13) Fukuhara, T.; Yoneda, N.; Sawada, T.; Suzuki, A. *Synth. Commun.* **1987**, *17*, 685.

14) Moilliet, J. S. *J. Fluorine Chem.* **1987**, *35*, 38

15) NO was identified in GLC (Hitachi 063-tcd, column: Molecular sieves 5A, 2m, 110 °C).[16]

16) Trowell, J. M. *Anal. Chem.* **1965**, *37*, 1152.

17) Tarry matter (Found: C,82.37; H,4.97; N,10.64; F,2.06%; IR (KBr) 3390 (N-H), 3030, 1620, 1500, 1300, 820 (*p*-substituted aryl)) was insoluble in both $CH_2Cl_2$ and aqueous layer and was composed of black particles that resembled sand. The empirical formula of this material was $C_6H_{4.3}N_{0.7}F_{0.1}$, which is similar to that of polyaniline ($C_6H_{4.5\sim5.0}N$).[18]
18) Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules* **1988**, *21*, 1297.
19) Side products are 2% or less amount of biaryls such as biphenyl, phenyl fluorobenzenes, fluorophenyl fluorobenzenes, aminophenyl fluorobenzenes, and aminophenyl anilines together with 3% or less of phenylazoanilines. The composition of difluorobiphenyls was determined by GLC-Mass to be 2,2'- and 2,4'-difluorobiphenyls as major (80% in total) and 4,4'-difluorobiphenyl as minor products.
20) In order to elucidate the rate of diazotization of $ArNH_2$ in HF, *p*-toluidine was employed as a substrate to make NMR spectroscopic analysis easier, since the chemical shifts of protons on the aromatic ring of *p*-toluidine which gave typical AA'XX' spectra were observed to shorten its $\Delta\nu_{AX}$ in HF solution. Here the increasing amount of HF made $\Delta\nu_{AX}$ smaller to give a singlet peak in the solution of *p*-toluidine with a composition of $N>60$.
21) de Fabrizio, E. C. R.; Kalatzis, E.; Ridd, J. H. *J. Chem. Soc. (B)* **1966**, 533.
22) Zollinger, H. *Helv. Chim. Acta* **1988**, *71*, 1661.
23) Casado, J.; Castro, A.; Iglesias, E.; Pena, M. E.; Tato, J. V. *Can. J. Chem.* **1986**, *64*, 133.
24) (a) Gillespie, R. J; Liang, J. *J. Am. Chem. Soc.* **1988**, *110*, 6053. (b) O'Donnell, T. A. *J. Fluorine Chem.* **1984**, *25*, 75.
25) At temperatures higher than 60 °C, HF released from the solution.
26) (a) Danek, O.; Smobl, D.; Knizek, I.; Mouzova, S. *Call. Czech. Chem. Comm.* **1967**, *32*, 1642. (b) Fukuhara, T.; Yoneda, N.; Takamura, K.; Suzuki, A. *J. Fluorine Chem.* **1991**, *51*, 299.
27) When chlorobenzene was added to the HF-Pyr, the solution was found to result in a liquid-liquid two phase mixture. Chlorobenzene layer was found to be free form HF, since no evolution of carbon dioxide was observed when $NaHCO_3$ was added to the layer.
28) By the reaction of one mole of aniline, two moles of HF are consumed and two moles of $H_2O$ are formed. The HF-$H_2O$ solution which is free of volatile HF at 55 °C was found to have three molar ratio of HF/$H_2O$. Thus, the requisite amount of fresh HF was determined to be 8-fold moles if aniline charged in each run.
29) (a) Zollinger, H. "Azo and Diazo Chemstry, Aliphatic and Aromatic Compounds" Iterscience, 1961. (b) Sanders, K. H.; Allen, R. L. M. (Eds) "Aromatic Diazo Compounds" 3rd Ed., Edward Arnold, London, p. 744, 1985.
30) Beaty, R. D.; Musgrave, W. K. R. *J. Chem. Soc.* **1952**, 852.
31) Wibaut, J. P.; Holemes-Damminga, W. J. *Bull. Soc. Chem. France* **1958**, 428.
32) Deasi, P. B. *J. Chem. Soc. Perkin I* **1973**, 1865.
33) The halogen-exchange fluorination method of ArCl with KF is an allowed approach for preparing fluoropyridines but required severe conditions of high temperature (240 °C) for prolonged time (12 h), and 4-fluoropyridine was difficult to obtain through the reaction.[35,36]
34) Fukuhara, T.; Yoneda, N.; Suzuki, A. *J. Fluorine Chem.* **1988**, *38*, 435.
35) Finger, G. C; Starr, L. D. *J. Am. Chem. Soc.* **1959**, *81*, 2674.
36) Ogawa, T.; Takaoka, A.; Ishikawa, N. 11th Symposium of Japan Fluorine Chemistry, Nagoya, Oct. 1986, Abstr., No. 2E-15.
37) The addition of $NH_4Cl$ and CuCl to HF-Pyr solutions of $ArN_2BF_4$ or $ArN_2Cl$, which are produced independently from $ArNH_2$, was found to give ArCl in quantitative yield at 20 °C for 30 min.
38) Burri, P.; Loewenschuss, H.; Zollinger, H.; Zwolinski, G. K. *Helv. Chim. Acta* **1974**, 57, 395.
39) (a) Becker, H. G. O.; Israel, G. *J. Pract. Chem.* **1979**, 321, 579. (b) Maskill, H.; McCrudden, K. *Croatica Chemica Acta* **1992**, *65*, 567.
40) Clear evidence for the formation of $Ar^+$ from $ArN_2^+$ by irradiation has not been obtained yet in our experiments. One electron transfer mechanism in the formation of $Ar^\bullet$ by irradiation might be an adequate explanation for our reactions. We are grateful to Prof. Sonoda, T. (Kyushu Univ. Jpn) for his helpful discusions.
41) (a) Yoneda, N.; Fukuhara, T.; Nagata, S.; Suzuki, A. *Chem. Lett.* **1985**, 1693. (b) Fukuhara, T.; Yoneda, N.; Abe, T.; Nagata, S.; Suzuki, A. *Nippon Kagaku Zashi* **1985**, 1951. (c) Fukuhara T.; Sasaki, T.; Yoneda, N.; Suzuki, A. Bull. Chem. Soc. Jpn. **1990**, *36*, 2058.
42) (a) Patai, S. "The Chemistry of Diazonium and Diazo Groups" Vol. 1. John Wiley & Sons Inc., p. 341, 1978. (b) Rutherford, K. G.; Remond, W.; Rigaminti, J. *J. Org. Chem.* **1961**, *26*, 5140. (c) Kirk, K. L.; Cohen, L. A. *J. Am. Chem. Soc.* **1971**, *93*, 3060.

(*Received* 2 *July* 1995)