Syntheses and Properties of *N*-Fluoropyridinium Salts

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Various stable *N*-fluoropyridinium salts with a non- or weakly nucleophilic counter anion such as TfO^-, FSO_3^-, BF_4^-, SbF_6^-, ClO_4^-, $CH_3SO_3^-$ etc., or with an electron-donating or -withdrawing substituent(s) on the pyridine ring were synthesized and their properties investigated. *N*-Fluoropyridinium-2-sulfonates, *N*-fluoroquinolinium triflate, and highly hindered *N*-fluoro-2,6-di-*t*-butylpyridinium salts were also synthesized. They were synthesized by counter anion displacement reactions of unstable pyridine-F_2 compounds, fluorination of salts of pyridines with protonic acids or silyl esters with F_2, and/or fluorination of Lewis acid complexes of pyridines. The scope of each method was examined in detail. Each of the *N*-fluoropyridinium salts was assigned as the first stable 1:1 salt structure of the pyridine nucleus and halogen atom on the basis of the spectral and elemental analyses. The stability depended on the nucleophilicity or basicity of the counter anions and electronic nature or position of the ring substituents. These results and NMR analyses clearly showed the unstable pyridine-F_2 compounds to have *N*-fluoropyridinium fluoride salt structure. Some *N*-fluoropyridinium triflates were hydrolyzed and the products were examined, suggesting a unique hydrolysis mechanism.

Although the reactions of pyridine and many substituted pyridines with Cl_2, Br_2, or I_2, producing molecular complexes with linear nitrogen-halogen-halogen atom structure, have been examined extensively, only limited attention has been directed to those of pyridines with molecular fluorine (F_2).[1] F_2 differes greatly from the other halogens[2] and so consequently, the products obtained from its reaction should be of considerable interest.

Simons first found that liquid pyridine smoothly and completely absorbs F_2 and when absorption is conducted at −40 °C, a dark brown solid separates from the liquid, which decomposes on warming to 0 °C.[3] He described that the thermally unstable solid was apparently a molecular complex between pyridine and F_2, $C_5H_5N \cdot F_2$.[3]

Meinert noted a solid, isolated by bubbling F_2 diluted with N_2 into a solution of pyridine in $CFCl_3$ at −80 °C followed by filtering at low temperature, to decompose violently above −2 °C.[4] He considered this solid to be a pyridine-F_2 compound with polar character. However, no spectral or other data on the structure of the pyridine-F_2 compound are presently not available, probably due to its explosive nature.

The authors found unstable pyridine-F_2 compounds to smoothly undergo counter anion displacement reactions with nonnucleophilic anions to give stable *N*-fluoropyridinium salts.[5] It was also found that insertion reactions of F_2 to salts or complexes of pyridines with protonic acids, silyl esters, or Lewis acids gave the *N*-fluoropyridinium salts. In this paper, syntheses of various *N*-fluoropyridinium salts by different methods and their properties are described in detail.

Experimental

General. Melting points were uncorrected. ^1H NMR spectra were measured on a Varian EM 390 or XL-100 NMR spectrometer or a Bruker AM-400 NMR spectrometer. ^{19}F NMR spectra were obtained on a Hitachi R-20B NMR spectrometer and the chemical shifts were given in ppm downfield from $CFCl_3$ as an internal standard. Both ^1H and ^{19}F NMR spectra were taken by using CD_3CN solvent, unless otherwise noted. IR spectra were measured on a JASCO A-202 diffraction grating infrared spectrometer. Mass spectra were recorded on a Hitachi RMU-6MG mass spectrometer at 70 eV or a Hitachi M-80A mass spectrometer by EI (electron impact ionization) method or SIMS (secondary ion mass spectrometry) method. Unless otherwise noted, the data by EI method are given.

Materials. A 20% F_2–80% N_2 cylinder was purchased from Kanto Denka Kagaku Company (Japan). Since the content of HF in the fluorine was very low (0.2—0.3%), it was used without a NaF trap. 3-Chloro-5-trifluoromethylpyridine and 3,5-bis(trifluoromethyl)pyridine were given by Ishihara Sangyo Company (Japan). 2-[(1*R*,3*R*,4*S*)-Menthyloxy]pyridine (bp 112 °C/0.2 mmHg, 1 mmHg=133.322 Pa, $[\alpha]_D^{20}=-110.7$ (c=0.994, $CHCl_3$)) was prepared by treatment of 2-chloropyridine with (−)-menthol by the action of NaH in tetrahydrofuran (THF) under reflux for 19 h. 2-(Fluoromethyl)-4,6-dimethylpyridine was prepared from 2,4,6-trimethylpyridine by oxidation with 35% H_2O_2 in acetic acid, rearrangement reaction with Ac_2O, alkaline hydrolysis, and fluorination with (diethylamino)sulfur trifluoride. 6-Chloropyridine-2-sulfonic acid was prepared by treatment of 2,6-dichloropyridine with sodium sulfite. Dry CH_3CN was made by distillation over CaH_2 and used immediately. Other solvents used were dried by usual methods and stored over molecular sieves.

Synthesis of *N*-Fluoropyridinium Salts 1—46. [CAUTION!]. Since F_2 is a highly oxidizing and toxic gas, the experimenter should familiarize him- or herself with the precautions necessary for the safe handling of F_2.[6] The use of diluted F_2 in an inert gas (N_2 or Ne) is considerably safer than pure F_2.

Apparatus: As shown in Fig 1, the apparatus used for the fluorination consisted of a 20% F_2–80% N_2 cylinder, a N_2 cylinder, two flow meters (Hastings Mass Flowmeters Model CST), a Pyrex®-glass reactor, and valves made of

† From Onoda Cement Company.

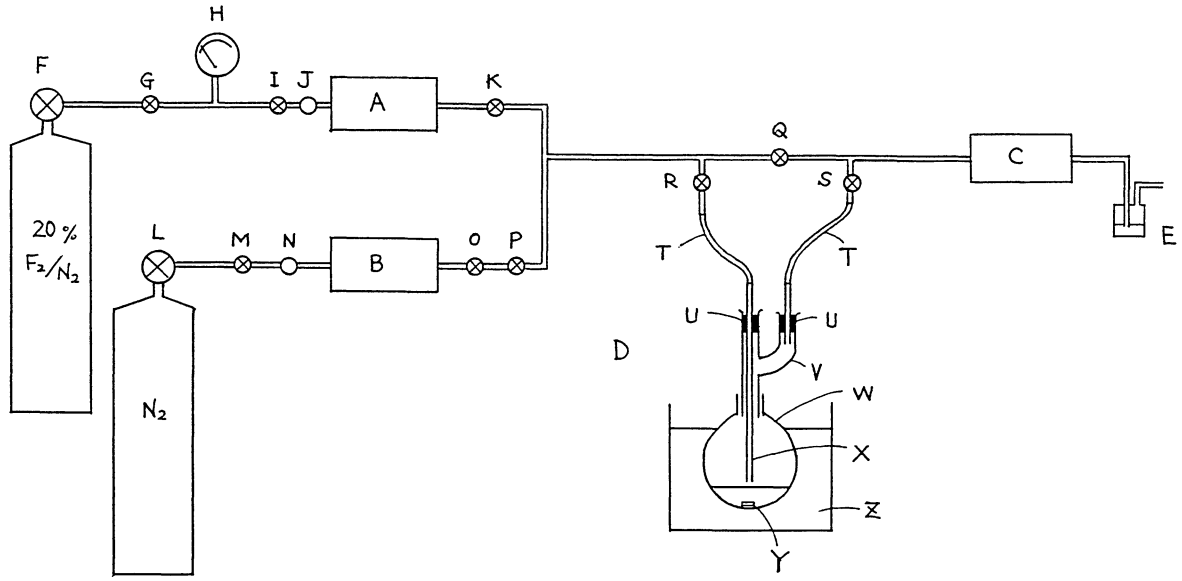


Fig. 1. Apparatus for fluorination.
A: A flow meter (Hastings Mass Flowmeter Model CST-M). B: A flow meter (Hastings Mass Flowmeter Model CST). C: An alumina trap. D: A reactor. E: A bubble counter containing perfluorotributylamine. F: A pressure regulator for fluorine (Takachiho F_2 Regulator Model 7630H). G,I, K,O,P: Valves made of stainless steel. H: A pressure gauge made of stainless steel. J,N: Filters made of stainless steel. L: A pressure regulator for nitrogen. M,Q,R,S: Valves made of brass. T: A Viton® tube. U: A Teflon® cork. V: An adaptor made of Pyrex®-glass. W: A round-bottomed flask made of Pyrex®-glass. X: A Pyrex®-glass tube. Y: A Teflon®-coated stirring bar. Z: A bath of −40 °C.

stainless steel or brass. The cylinders, the flow meters, and the valves were connected with stainless steel or copper tubes. The 20% F_2-N_2 cylinder was equipped with a pressure regulator (Takachiho F_2 Regulator Model 7630H) that was designed for fluorine service. The glass reactor was connected to the outlet of further diluted F_2 (10% F_2-N_2) by using a Viton® tube. The gas outlet of the reactor was connected to a granular alumina trap to consume the F_2 gas. The designed concentration of F_2 in N_2 and the flow rates of a F_2-N_2 mixture gas were adjusted by the flow meters.

Method A (a two-step procedure): **General Procedure;** a 50-mL reaction flask was charged with 3 mmol of a pyridine and 6 mL of dry CH_3CN. The system was purged with N_2 and the reaction mixture was immersed in a cooling bath of −40 °C. A 10% F_2-90% N_2 mixture gas was introduced at a flow rate of 30 mL min^{-1} just above the surface of the rapidly stirred solution. Total amount of F_2 used was 9 mmol. After the flow of F_2 was stopped, N_2 only was flowed through the system at rate of 15 mL min^{-1} for 30 min while keeping the reaction mixture at −40 °C. After that, 3 mmol of TfOH (a reactant shown in Tables 1 and 2) was added into the reaction mixture and it was stirred for 1 h at −40 °C. The post-treatment for *N*-fluoropyridinium triflate (**1a**) was as follows; 50 mL of diethyl ether (Et_2O) was added into the reaction mixture and warmed to room temperature. The resulting solid was collected by filteration to give a solid of 0.306 g, which was sufficiently washed with 1 ml of dry ethyl acetate (AcOEt) to give 0.242 g (33%) of pure **1a**.

Method B (a one-step procedure): **General Procedure;** a solution of 3 mmol of a pyridine, 3 mmol of NaOTf (a reactant shown in Tables 1 and 2), and 6 mL of dry CH_3CN was fluorinated in the same manner as described in Method A. The reaction mixture was then warmed to room temperature, filtered through Celite to remove NaF formed, and evaporated up to dryness at room temperature. The resulting solid was washed with dry AcOEt to give 0.554 g (75%) of **1a**. Analytically pure crystals were obtained by recrystallization from CH_3CN-AcOEt at room temperature. When KOTf was used in place of NaOTf, 12 mL of dry CH_3CN was used as a solvent.

Method C: General Procedure; a solution of a pyridinium hydrogen salt or a *N*-silylpyridinium salt which was in situ prepared by mixing 3 mmol of a pyridine and 3 mmol of a protonic acid or a silyl ester (a reactant shown in Tables 1 and 2) in 6 mL of dry CH_3CN, was treated with 10% F_2-N_2 at −40 °C in the same manner as described in Method A (CAUTION!; a 2% F_2-98% N_2 mixture gas should be used for fluorination of *N*-trimethylsilylpyridinium triflates). The post-treatment for **1a** was as follows; the reaction solution was completely evaporated up to dryness at room temperature and the residue was washed with dry AcOEt to give pure crystals of **1a**.

Method D: General Procedure; a solution of a pyridine-Lewis acid complex, which was in situ prepared by mixing 3 mmol of a pyridine and 3 mmol of a Lewis acid (a reactant shown in Tables 1 and 2) in 6 mL of dry CH_3CN, was treated with 10% F_2-N_2 at −40 °C in the same manner as described in Method A. The reaction mixture was warmed to room temperature and evaporated up to dryness at room temperature. For **29b**, the residue was crystrallized from CH_3CN-Et_2O, giving 79% of **29b**.

Tables 1 and 2 summarize the results. Melting points, spectral data, and elemental analyses of the *N*-fluoropyridinium salts synthesized by the above methods are shown below. Their ^{19}F NMR data will be shown and discussed elsewhere.

***N*-Fluoropyridinium Triflate (1a):** Mp 185—187 °C (recrystallization solvent CH_3CN-Et_2O); ^{19}F NMR δ=48.8 (1F, bs, NF), −77.6 (3F, s, CF_3); ^1H NMR δ=8.32 (2H, dt, $J_{3\text{-}H\text{-}F}$=4.8 Hz, $J_{3\text{-}H\text{-}2\text{-}H}$=$J_{3\text{-}H\text{-}4\text{-}H}$=7.0 Hz, 3-H), 8.77 (1H, dt, $J_{4\text{-}H\text{-}F}$=2.0 Hz, $J_{4\text{-}H\text{-}3\text{-}H}$=7.0 Hz, 4-H) , 9.33 (2H, dd, $J_{2\text{-}H\text{-}F}$= 16.0 Hz, $J_{2\text{-}H\text{-}3\text{-}H}$=7.0 Hz, 2-H); MS *m/z* 227 (M^+−HF), (SIMS method) 98 (M^+−OTf). Found: C, 29.17; H, 1.99; N, 5.66; F, 30.49; S, 13.21%. Calcd for $C_6H_5F_4NO_3S$: C, 29.16; H, 2.04; N, 5.67; F, 30.75; S, 12.97%.

***N*-Fluoropyridinium Fluorosulfate (1b):** Mp 120—125 °C (CH_3CN-Et_2O); MS *m/z* 177 (M^+−HF). Anal. ($C_5H_5F_2NO_3S$) C, H, N.

***N*-Fluoropyridinium Methanesulfonate (1c):** Mp 140—142 °C; MS *m/z* 173 (M^+−HF). Anal. ($C_6H_8FNO_3S$), C, H, N.

***N*-Fluoropyridinium Trichloromethanesulfonate (1d):** Mp 205.5—207 °C (with decomp) (CH_3CN); MS *m/z* 277, 275 (M^+−HF). Anal. ($C_6H_5Cl_3FNO_3S$) C, H, N.

***N*-Fluoropyridinium Nonafluorobutanesulfonate (1e):** Mp 111—112 °C (AcOEt-Et_2O); MS *m/z* 377 (M^+−HF). Anal. ($C_9H_4F_{10}NO_3S$) C, H, N.

***N*-Fluoropyridinium Tetrafluoroborate (1f):** Mp 196.8—198 °C (CH_3CN-AcOEt, or CH_3CN); MS *m/z* 104. Anal. ($C_5H_5BF_5N$) C, H, N.

***N*-Fluoropyridinium Hexafluorophosphate (1g):** Decomp 202 °C (THF); MS *m/z* 174, 172, 107, 97. Anal. ($C_5H_5F_7NP$) C, H, N.

***N*-Fluoropyridinium Hexafluoroarsenate (1h):** Decomp 230 °C (CH_3CN-Et_2O); MS *m/z* 97. Anal ($C_5H_5F_7NAs$) C, H, N.

***N*-Fluoropyridinium Hexafluoroantimonate (1i):** Decomp 293 °C (CH_3CN-Et_2O); MS *m/z* 278, 276. Anal. ($C_5H_5F_7NSb$) C, H, N.

***N*-Fluoropyridinium Perchlorate (1j):** Mp 225—227.5 °C (with decomp) (CH_3CN); MS *m/z* 156, 155, 97, 79. Anal. ($C_5H_5ClFNO_4$) C, H, N.

***N*-Fluoro-2-methylpyridinium Triflate (2):** Mp 119.5—120.5 °C (CH_3CN-Et_2O); ^1H NMR δ=2.90 (3H, d, $J_{H\text{-}F}$=4.5 Hz, CH_3), 9.23 (1H, dd, *J*=15.0, 7.5 Hz, 6-H).

***N*-Fluoro-3-methylpyridinium Triflate (3):** Oil; ^1H NMR δ=2.55 (3H, s, CH_3); MS *m/z* 241 (M^+−HF). Anal. ($C_7H_7F_4NO_3S$) C, H, N.

***N*-Fluoro-4-methylpyridinium Triflate (4):** Mp 84—88 °C (AcOEt); ^1H NMR δ=2.70 (3H, s, CH_3); MS *m/z* 241 (M^+−HF). Anal. ($C_7H_7F_4NO_3S$) C, H, N.

***N*-Fluoro-2,6-dimethylpyridinium Triflate (5):** Mp 126—128 °C (CH_3CN-THF); ^1H NMR δ=2.83 (6H, d, $J_{H\text{-}F}$=4.8 Hz, CH_3); MS *m/z* 255 (M^+−HF). Anal. ($C_8H_9F_4NO_3S$) C, H, N.

***N*-Fluoro-3,5-dimethylpyridinium Triflate (6):** Mp 51—54 °C (CH_2Cl_2); ^1H NMR δ=2.57 (6H, s, CH_3), 9.02 (2H, d, *J*=16.5 Hz, 2-H); MS *m/z* 255 (M^+−HF). Anal. ($C_8H_9F_4NO_3S$) C, H, N.

***N*-Fluoro-2,4,6-trimethylpyridinium Triflate (7a):** Mp 168—170 °C (CH_3CN-Et_2O); ^1H NMR δ=2.58 (3H, s, 4-CH_3), 2.75 (6H, d, $J_{H\text{-}F}$=3.5 Hz, 2-CH_3), 7.73 (2H, d, *J*=6.5 Hz, 3-H); MS *m/z* 269 (M^+−HF), (SIMS method) 288 (M^+−1), 140 (M^+−OTf). Anal. ($C_9H_{11}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,4,6-trimethylpyridinium Fluorosulfate (7b):** Mp 162—164 °C (with decomp) (CH_3CN-Et_2O). Anal. ($C_8H_{11}F_2NO_3S$) C, N, H.

***N*-Fluoro-2,4,6-trimethylpyridinium (+)-10-Camphorsulfonate (7c):** Mp 135—136.5 °C (CH_3CN-AcOEt); $[\alpha]_D^{22}$=29.51 (*c*=0.664, CH_3CN); ^1H NMR δ=0.80 (3H, s, CH_3), 1.10 (3H, s, CH_3), 2.57 (3H, s, 4-CH_3), 2.78 (6H, d, *J*=4.5 Hz, 2-CH_3), 7.77 (2H, d, *J*=6.0 Hz, 3-H); MS (SIMS method) *m/z* 140 (M^+−OTf). Anal. ($C_{18}H_{26}FNO_4S$) C, H, N.

***N*-Fluoro-2,4,6-trimethylpyridinium Tetrafluoroborate (7d):** Mp 215—217 °C (with decomp) (CH_3CN-Et_2O); MS (SIMS method) *m/z* 228 (M^+−1), 140 (M^+−BF_4). Anal. ($C_8H_{11}BF_5N$) C, H, N.

***N*-Fluoro-2,3,5,6-tetramethylpyridinium Triflate (8):** Mp 136—138 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=2.45 (6H, s, 3-CH_3), 2.68 (6H, d, $J_{H\text{-}F}$=4.5 Hz, 2-CH_3), 8.05 (1H, s, 4-H); MS *m/z* 283 (M^+−HF). Anal. ($C_{10}H_{13}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,3,4,5,6-pentamethylpyridinium Triflate (9):** Mp 97—97.5 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=2.10 (6H, s, 3-CH_3), 2.35 (3H, s, 4-CH_3), 2.73 (6H, d, $J_{H\text{-}F}$=4.5 Hz, 2-CH_3); MS *m/z* 168 (M^+−OTf). Anal. ($C_{11}H_{15}F_4NO_3S$) C, H, N.

***N*-Fluoro-4-*t*-butylpyridinium Triflate (10):** Mp 116—118 °C (CH_3CN-Et_2O); ^1H NMR δ=1.42 (9H, s, *t*-Bu); MS *m/z* 268 (M^+−HF). Anal. ($C_{10}H_{13}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,6-di-*t*-butylpyridinium Triflate (11):** Mp 112—114 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=1.59 (18H, d, $J_{H\text{-}F}$=2.0 Hz, 2×*t*-Bu); MS *m/z* 210 (M^+−OTf). Anal. ($C_{14}H_{21}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,4,6-tri-*t*-butylpyridinium Triflate (12):** Mp 238—239 °C (with decomp) (CH_2Cl_2-Et_2O); ^1H NMR δ=1.43 (9H, s, 4-*t*-Bu), 1.58 (18H, d, $J_{H\text{-}F}$=1.5 Hz, 2,6-*t*-Bu), 7.82 (2H, d, *J*=7.5 Hz, 3-H); MS *m/z* 266 (M^+−OTf). Anal. ($C_{18}H_{29}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,6-di-*t*-butyl-4-methylpyridinium Triflate (13):** Mp 158—159 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=1.55 (18H, d, *J*=2.0 Hz, 2,6-*t*-Bu), 2.63 (3H, s, CH_3), 7.83 (2H, d *J*=7.5 Hz, 3-H); MS *m/z* 224 (M^+−OTf). Anal. ($C_{15}H_{23}F_4NO_3S$) C, H, N.

***N*-Fluoro-1,2,3,4,5,6,7,8-octahydroacridinium Triflate (14):** Mp 150—152 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=8.02 (1H, s, 4-H); MS *m/z* 206 (M^+−OTf). Anal. ($C_{14}H_{17}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,6-bis(methoxymethyl)pyridinium Triflate (15):** Mp 56—58 °C (CH_2Cl_2-Et_2O); ^1H NMR δ=3.58 (6H, s, CH_3), 4.78 (4H, s, CH_3); MS *m/z* 186 (M^+−OTf). Anal. ($C_{10}H_{13}F_4NO_3S$) C, H, N.

***N*-Fluoro-2,4,6-tris(methoxymethyl)pyridinium Triflate (16):** Crystalline solid; ^1H NMR ($CDCl_3$) δ=3.50 (3H, s, 4-OMe), 3.57 (6H, s, 2, 6-OMe), 4.72 (2H, bs, 4-CH_2), 4.95 (4H, bs, 2, 6-CH_2), 7.95 (2H, d, $J_{H\text{-}F}$=6.0 Hz, 3, 5-H); MS *m/z* 230 (M^+−OTf).

***N*-Fluoro-2-(benzoyloxymethyl)pyridinium Triflate (17):** Mp 94—96 °C (AcOEt); ^1H NMR δ=5.82 (2H, d, $J_{H\text{-}F}$=1.5 Hz, CH_2O), 9.28 (1H, dd, *J*=16.5, 7.5 Hz, 6-H); MS *m/z* 361 (M^+−HF). Anal. ($C_{13}H_9F_4NO_5S$) C, H, N.

***N*-Fluoro-2,6-bis(acetoxymethyl)pyridinium Triflate (18):** Mp 125—127 °C (AcOEt-Et_2O); ^1H NMR δ=2.17 (6H, s, CH_3), 5.56 (4H, d, $J_{H\text{-}F}$=3.0 Hz, CH_3); IR (Nujol on NaCl) 1765 cm^{-1} (CO); MS *m/z* 271 (M^+−OTf). Anal. ($C_{12}H_{13}F_4NO_7S$) C, H, N.

***N*-Fluoro-2-fluoromethyl-4,6-dimethylpyridinium Triflate (19):** Mp 160—162 °C (CH_3CN-Et_2O); ^1H NMR δ=2.62 (3H, s, 4-CH_3), 2.80 (3H, d, $J_{H\text{-}F}$=4 Hz, 2-CH_3), 5.81 (2H, dd, $J_{H\text{-}F}$=45 Hz, $J_{H\text{-}NF}$=1 Hz, CH_2); MS *m/z* 258 (M^+−HF). Anal. ($C_9H_{10}F_5NO_3S$) C, H, N.

***N*-Fluoro-2-methoxypyridinium Triflate (20):** Mp 95—96 °C (CH_3CN-Et_2O); ^1H NMR δ=4.38 (3H, s, CH_3); MS *m/z* 128 (M^+−OTf), 113 (M^+−OTf−Me), (SIMS method) 128 (M^+−OTf). Anal. ($C_7H_7F_4NO_4S$) C, H, N.

***N*-Fluoro-3-methoxypyridinium Triflate (21):** Oil; ^{1}H NMR δ=4.07 (3H, s, CH_3); MS *m/z* 257 (M^+−OTf).

***N*-Fluoro-4-methoxypyridinium Triflate (22):** Mp 32 °C (AcOEt-Et_2O); ^{1}H NMR δ=4.12 (3H, s, CH_3); MS *m/z* 257 (M^+−HF). Anal. ($C_7H_7F_4NO_4S$) C, H, N.

***N*-Fluoro-2-[(1*R*,3*R*,4*S*)-menthyloxy]pyridinium Triflate (23):** Mp 111—111.5 °C (with decomp) (CH_2Cl_2-Et_2O); $[\alpha]_D^{20}$=−77.7 (*c*=4.16, $CHCl_3$); ^{1}H NMR δ=0.83 (3H, d, *J*=6.6 Hz, CH_3), 0.98 (6H, d, *J*=6.6 Hz, CH_3), 4.93 (1H, td, *J*=9.6, 4.5 Hz, CH-O), 7.52 (1H, m, 5-H), 7.89 (1H, td, *J*=9.0, 1.5 Hz, 3-H), 8.45 (1H, ddd, *J*=9.0, 7.8, 1.5 Hz, 4-H), 8.83 (1H, ddd, *J*=17.4, 7.8, 1.5 Hz, 6-H); MS (SIMS method) *m/z* 252 (M^+−OTf). Anal.($C_{16}H_{23}F_4NO_4S$) C, H, N.

***N*-Fluoro-4-phenylpyridinium Triflate (24):** Mp 130.5—132.5 °C (CH_3CN-Et_2O); ^{1}H NMR δ=7.64 (3H, m, 3′-H, 4′-H), 7.90 (2H, m, 2′-H); MS *m/z* 303 (M^+−HF). Anal. ($C_{12}H_9F_4NO_3S$) C, H, N.

***N*-Fluoro-2-fluoropyridinium Triflate (1:1 salt with LiOTf) (25):** Decomp ca. 145 °C (in a sealed tube) (CH_3CN-Et_2O); ^{1}H NMR δ=9.25 (1H, m, 6-H). Anal. ($C_7H_4F_8LiNO_6S_2$) C, H, N.

***N*-Fluoro-2-chloropyridinium Triflate (26):** Mp 149—151 °C (AcOEt); ^{1}H NMR δ=9.42 (1H, ddd, *J*=16.0, 6.7, 1.5 Hz, 6-H); MS *m/z* 263, 261 (M^+−HF), (SIMS method) 134, 132 (M^+−OTf). Anal. ($C_6H_4ClF_4NO_3S$) C, H, N.

***N*-Fluoro-3-chloropyridinium Triflate (27):** MP 108—109 °C (CH_3CN-CH_2Cl_2); ^{1}H NMR δ=9.60 (1H, ddd, *J*=14.5, 2.5, 1.8 Hz, 2-H); MS *m/z* 263, 261 (M^+−HF). Anal. ($C_6H_4ClF_4NO_3S$) C, H, N.

***N*-Fluoro-2,6-dichloropyridinium Triflate (28):** Mp 151—153 °C (CH_3CN-Et_2O) (mp 126 °C was indicated by thermometric analysis conducted by Dr. Takao Iida of Onoda Cement Co.); MS *m/z* 169, 167, 165 (M^+−HOTf), 151, 149, 147 (M^+−OTf−F). Anal. ($C_6H_3Cl_2F_4NO_3S$) C, H, N.

***N*-Fluoro-3,5-dichloropyridinium Triflate (29a):** Mp (in a sealed tube) 118.5—121 °C (CH_3CN-Et_2O); ^{1}H NMR δ=9.61 (2H, dd, *J*=14.0, 1.8 Hz, 2-H); MS *m/z* 299, 297, 295 (M^+−HF), (SIMS method) 166 (M^+−OTf). Anal. ($C_6H_3Cl_2F_4NO_3S$) C, H, N.

***N*-Fluoro-3,5-dichloropyridinium Tetrafluoroborate (29b):** Mp 208—209 °C (CH_3CN-Et_2O); MS *m/z* 169, 167, 165 (M^+−HBF_4). Anal. ($C_5H_3BCl_2F_5N$) C, H, N.

***N*-Fluoropentachloropyridinium Triflate (30a):** Mp 122—123 °C (CH_3CN); MS *m/z* 274, 272, 270, 268 (M^+−OTf). Anal. ($C_6Cl_5F_4NO_3S$) C, H, N.

***N*-Fluoropentachloropyridinium Tetrafluoroborate (30b):** Mp (in a sealed tube) 198—200 °C (CF_3COOH-AcOEt); MS *m/z* 293, 291, 289, 287 (M^+−BF_3). Anal. ($C_5BCl_5F_5N$) C, H, N.

***N*-Fluoro-3-chloro-5-(trifluoromethyl)pyridinium Triflate (31):** Mp 105—108 °C (THF-CH_2Cl_2); ^{1}H NMR δ=9.95 (2H, dm, J_{H-F}=14 Hz, 2-H, 6-H); MS *m/z* 343, 341, 199 (M^+−F−Tf), 197 (M^+−F−Tf). Anal. ($C_7H_3ClF_7NO_3S$) C, H, N.

***N*-Fluoro-3,5-bis(trifluoromethyl)pyridinium Triflate (32):** Mp 193—195 °C (CH_3CN-Et_2O); ^{1}H NMR δ=10.19 (2H, d, *J*=13.5 Hz, 2-H); MS *m/z* 375, 363 (M^+−HF). Anal. ($C_8H_3F_{10}NO_3S$) C, H, N.

***N*-Fluoro-3-acetoxypyridinium Triflate (33):** Mp 111.5—112.5 °C (CH_3CN-Et_2O); ^{1}H NMR δ=9.46 (1H, dm, *J*=16.0 Hz, 2-H); IR (Nujol on NaCl) 1780 cm^{-1} (CO); MS *m/z* 243, 187, 186, 137, 135, 113, (SIMS method) 156 (M^+−OTf). Anal. ($C_8H_7F_4NO_5S$) C, H, N.

***N*-Fluoro-2-(methoxycarbonyl)pyridinium Triflate (34):** Mp 115—166 °C (CH_3CN-Et_2O); ^{1}H NMR δ=4.16 (1H, s, CH_3); IR (Nujol on NaCl) 1740 cm^{-1} (CO); MS *m/z* 137, 107, 79, 78. Anal. ($C_8H_7F_4NO_5S$) C, H, N.

***N*-Fluoro-3-(ethoxycarbonyl)pyridinium Triflate (35):** Mp 115—116 °C (THF-CH_2Cl_2); ^{1}H NMR δ=1.42 (3H, t, *J*=7.0 Hz, CH_3), 5.52 (2H, q, *J*=7.0 Hz, CH_2); IR (Nujol on NaCl) 1735 cm^{-1} (CO); MS *m/z* 299 (M^+−HF). Anal. ($C_8H_7F_4NO_5S$) C, H, N.

***N*-Fluoro-4-(methoxycarbonyl)pyridinium Triflate (36):** Solid (recrystallization failed); ^{1}H NMR δ=4.07 (3H, s, CH_3); IR (Nujol on NaCl) 1740 cm^{-1} (CO).

***N*-Fluoro-2,6-bis(methoxycarbonyl)pyridinium Triflate (37):** Mp 140—143 °C (CH_3CN-Et_2O); ^{1}H NMR δ=4.13 (6H, s, CH_3), IR (Nujol on NaCl) 1770 cm^{-1} (CO); MS *m/z* 227, 137, 69, 59. Anal. ($C_{10}H_9F_4NO_7S$) C, H, N.

***N*-Fluoro-3,5-bis(methoxycarbonyl)pyridinium Triflate (38):** Mp 144—147 °C (CH_3CN-Et_2O); ^{1}H NMR δ=4.08 (6H, s, CH_3); IR (Nujol on NaCl) 1760 cm^{-1} (CO); MS *m/z* 343 (M^+−HF). Anal. ($C_{10}H_9F_4NO_7S$) C, H, N.

***N*-Fluoro-2,4,6-tris(methoxycarbonyl)pyridinium Triflate (1:1 Salt with LiOTf) (39):** Decomp ca. 145 °C (CH_3CN-Et_2O); ^{1}H NMR δ=4.05 (3H, s, 4-CH_3), 4.12 (6H, s, 2-CH_3); IR (Nujol on NaCl) 1780 (CO), 1750 (CO) cm^{-1}. Anal. ($C_{13}H_{11}F_7LiNO_{12}S_2$) C, H, N.

***N*-Fluoro-2-acetylpyridinium Triflate (40):** Mp 151—152 °C (CH_3CN-Et_2O); ^{1}H NMR δ=2.77 (3H, s, CH_3).

***N*-Fluoro-4-acetylpyridinium Triflate (41):** Pale yellow oil; ^{1}H NMR δ=2.72 (3H, s, CH_3); IR (Nujol on NaCl) 1715 cm^{-1} (CO); MS *m/z* 269 (M^+−HF).

***N*-Fluoro-2-cyanopyridinium Tetrafluoroborate (42):** Mp 114—116 °C (CH_3CN-AcOEt); ^{1}H NMR δ=9.58 (1H, dd, *J*=15, 6 Hz, 6-H); MS *m/z* 122 (M^+−HBF_4), 95, 49, (SIMS method) 195, 121, 93, 75, 57. Anal. ($C_6H_4BF_5N_2$) C, H, N.

***N*-Fluoro-3-cyanopyridinium Triflate (43):** Mp 63—67 °C (AcOEt); ^{1}H NMR δ=9.88 (1H, ddd, *J*=13.5, 2.5, 1.4 Hz, 2-H); IR (Nujol on NaCl) 2255 cm^{-1} (CN); MS *m/z* 252 (M^+−HF). Anal. ($C_7H_4F_4N_2O_3S$) C, H, N.

***N*-Fluoro-4-cyanopyridinium Triflate (44):** Mp 137—140 °C (CH_3CN-Et_2O); ^{1}H NMR δ=9.52 (2H, dd, *J*=14, 7 Hz, 2-H); MS *m/z* 252 (M^+−HF). Anal. ($C_7H_4F_4N_2O_3S$) C, H, N.

***N*-Fluoro-2,6-dicyanopyridinium Triflate (45):** Mp (in a sealed tube) 123—132 °C (with decomp) (CH_3CN-Et_2O); ^{1}H NMR δ=9.02 (3H, m, 3-H, 4-H); IR (Nujol on NaCl) 2260 cm^{-1} (CN); MS *m/z* 147, 129. Anal. ($C_8H_3F_4N_3O_3S$) C, H, N.

***N*-Fluoro-4-nitropyridinium Triflate (46):** Mp (in a sealed tube) 55—59 °C (AcOEt-Et_2O); ^{1}H NMR δ=9.68 (2H, dd, *J*=13, 7.5 Hz, 2-H); IR (Nujol on NaCl) 1555, 1355 cm^{-1} (NO_2); MS *m/z* 272 (M^+−HF). Anal. ($C_6H_4F_2N_2O_5S$) C, H, N.

Synthesis of *N*-Fluoroquinolinium Triflate (49). This salt was prepared in 16% yield according to Method B. Mp (in a sealed tube) 144—154 °C (with decomp) (CH_3CN-AcOEt); ^{1}H NMR δ=9.28 (1H, d, $J_{4-H-3-H}$=8 Hz, 4-H), 9.69 (1H, dd, J_{2-H-F}=18 Hz, $J_{2-H-3-H}$=7 Hz, 2-H); MS *m/z* 277 (M^+−HF), (SIMS method) 148 (M^+−OTf). Anal. ($C_{10}H_7F_4NO_3S$) C, H, N.

Synthesis of *N*-Fluoropyridinium-2-sulfonates 52 and 53. Typical Procedure; a mixture of 0.209 g (1.08 mmol) of 6-chloro-2-pyridinesulfonic acid in 2.1 mL of H_2O-CH_3CN

(1/20 v/v) was fluorinated at −25 °C in a similar manner as Method A. Total amount of F_2 was 3.24 mmol. After the fluorination, 25 mL of THF was added into the reaction mixture at −25 °C under stirring and it was warmed to room temperature. The resulting crystals were collected by filtration and dried to give 0.177 g (77%) of *N*-fluoro-6-chloropyridinium-2-sulfonate (**53**). Analytically pure crystals were obtained by the recrystallization from CH_3CN-Et_2O.

***N*-Fluoropyridinium-2-sulfonate (52):** 81%; Decomp 232—235 °C (CH_3CN); ^1H NMR (400 MHz) δ=9.04 (1H, ddd, J=14.5, 7.0, 1 Hz, 6-H); MS m/z 177 (M^+). Anal. ($C_5H_4FNO_3S$) C, H, N.

***N*-Fluoro-6-chloropyridinium-2-sulfonate (53):** 77%; Mp 171—173 °C (CH_3CN-Et_2O); MS m/z 112 (M^+−F−SO_3). Anal. ($C_5H_3ClFNO_3S$) C, H, N.

Hydrolysis of *N*-Fluoropyridinium Salts 1a, 28, 29a, 30a, and 49. A *N*-fluoropyridinium salt was added into a stirred water at room temperature. The amount of water used was ca. 2 mL to 1 mmol of a *N*-fluoropyridinium salt and 5.2 mmol of **1a**, 1.6 mmol of **28**, 5.3 mmol of **29a**, 4 mmol of **30a**, and 0.34 mmol of **49** were used for the hydrolysis experiments. The reaction mixture was stirred at room temperature for 14 d (**1a**), 6 h (**28**), ca. 10 min (**29a**), 0.5 h (**30a**), and ca. 10 min (**49**) and then neutralized to pH 7 with $NaHCO_3$. The hydrolysis products were isolated by usual post-treatments. The results are described in Result section. The structural assignment of the products was carried out by analyzing their spectral data. 2-Pyridinol and 2-quinolinol were in agreement with authentic samples. The data of other products are shown in the following.

3,5-Dichloro-2-pyridinol (56): ^1H NMR δ=7.42 (1H, d, J=3.0 Hz, 4 or 5-H), 7.61 (1H, d, J=3.0 Hz, 4 or 5-H); IR (KBr) 3100 (NH), 1695 cm^{-1} (CO); MS m/z 167, 165, 163 (M^+).

***N*-Fluoro-6-chloro-2-pyridone (57):** Mp 74 °C; ^{19}F NMR ($CDCl_3$) δ=−44.6 (s, NF); ^1H NMR ($CDCl_3$) δ=6.26 (1H, ddd, J=7.5, 4.5, 2.0 Hz, 3-H), 6.66 (1H, ddd, J=9.5, 8.0, 2.0 Hz, 5-H), 7.26 (1H, dd, J=9.5, 7.5 Hz, 4-H); IR (KBr) 1680 cm^{-1} (CO); MS m/z 149, 147 (M^+). Anal. (C_5H_3ClFNO) C, H, N.

2,6-Dichloro-4-pyridinol (58): ^1H NMR ($CDCl_3$) δ=6.79 (s); IR (KBr) 3100—3000 cm^{-1} (OH); MS m/z 167, 165, 163 (M^+).

***N*-Fluoro-3,4,5,6-tetrachloro-2-pyridone (59):** Mp 102—104 °C (CCl_4); ^{19}F NMR ($CDCl_3$) δ=−33.0 (s, NF); IR (Nujol on NaCl) 1680 cm^{-1} (CO); MS m/z 255, 253, 251, 249 (M^+). Anal. (C_5Cl_4FNO) C, H, N.

Alkaline Hydrolysis of *N*-Fluoropyridinium Triflate (1a). Into a stirred solution of 10 mL of aq KOH (1 mol dm^{-3}) was by portions added 1.29 g (5.21 mmol) of **1a**. After 2 h, the reaction mixture was neutralized to pH 7 with $NaHCO_3$ and extracted with CH_2Cl_2. GC and GC-Mass analyses of the organic layer showed that 2-pyridyl triflate and 2-fluoropyridine were produced in 0.5 and 0.6% yields, respectively. A column (2 m×2 mm) packed with PEG-6000 (15%) on Uniport B was used for the GC analysis. The post-treatment of the organic layer gave 0.246 g (50%) of 2-pyridinol.

Alkaline Hydrolysis of *N*-Fluoro-2,4,6-trimethylpyridinium Triflate (7a). Into a stirred solution of 10 mL of aq KOH (2.9 mol dm^{-3}) was by portions added 1.48 g (5.11 mmol) of **7a**. An exothermic reaction occurred. After it ceased, the usual post-treatment was carried out to give 170 mg (24%) of 2-hydroxymethyl-4,6-dimethylpyridine (**54**) and 166 mg (23%) of 2-fluoromethyl-4,6-dimethylpyridine (**55**). Spectral data of **54** and **55** were in agreement with those of each authentic sample.

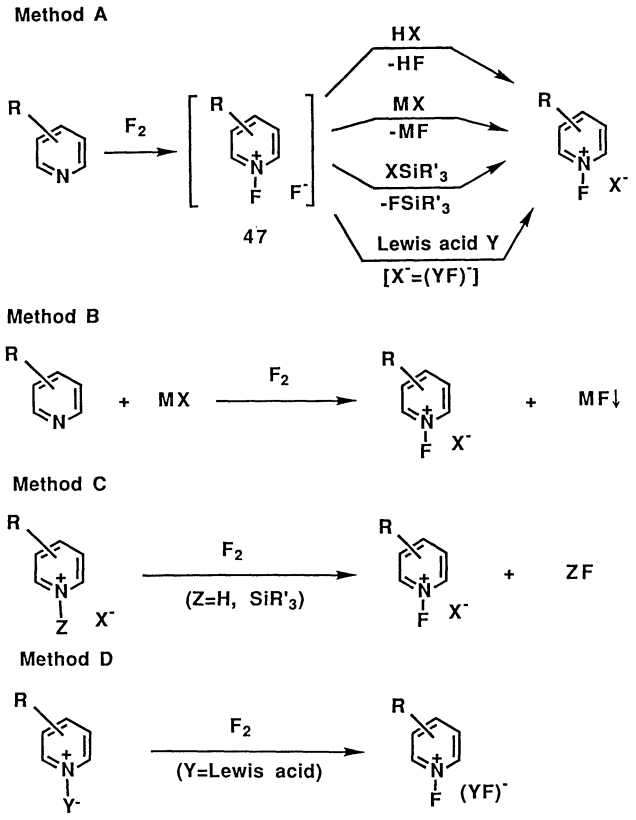
Reaction of *N*-Fluoro-2,4,6-trimethylpyridinium Triflate (7a) with Triethylamine or Sodium Hydride. Into a stirred solution of 1 mmol of triethylamine or sodium hydride (50% in oil) in 2 mL of a dry solvent was added 0.289 g (1 mmol) of **7a** at room temperature under argon atmosphere. After 10 min., the reaction mixture was analyzed by ^{19}F NMR. The results are described in Result section. The assignment of product **60** was carried out by the spectral analysis of the isolated product.

3-Fluoro-2,4,6-trimethylpyridine (60): Oil; ^{19}F NMR ($CDCl_3$) δ=−137.1 (bs); ^1H NMR ($CDCl_3$) δ=2.24 (3H, d, J=1.5 Hz, 4-CH_3), 2.45 (3 H, d, J=0.5 Hz, 6-CH_3), 2.46 (3H, d, J=3.2 Hz, 2-CH_3), 6.82 (1H, d, J=5.3 Hz, 4-H); IR (neat) 2940, 1620, 1470, 1230, 1215, 1160, 1025, 928, 860, 755 cm^{-1}. Found: m/z 139.0780 (M^+). Calcd for $C_8H_{10}FN$: M, 139.0796.

Thermal Stability. The sample was heated in a NMR tube under air in an oil bath of which temperature was set and monitored by ^{19}F NMR.

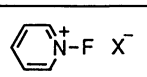
Results

Syntheses of *N*-Fluoropyridinium Salts. Various *N*-fluoropyridinium salts **1**—**46** were synthesized in varying yields as follows; by the fluorination of a pyridine and subsequent acid, metal salt of an acid, silyl ester, or Lewis acid treatment (Method A), fluorina-



Scheme 1.

Table 1. Syntheses of *N*-Fluoropyridinium Salts **1** with a Different Counter Anion

Run			Method[a]	Reactant	Yield of **1**[b] / %
1	X=OTf	**1a**	B	LiOTf	87
2	X=OTf	**1a**	B	NaOTf	75
3	X=OTf	**1a**	B	KOTf	63
4	X=OTf	**1a**	C	TfOH	66
5	X=OTf	**1a**	C[c]	TfOH	96
6	X=OTf	**1a**	A	TfOH	33
7	X=OTf	**1a**	A[d]	NaOTf	32
8	X=OTf	**1a**	A	$TfOSiMe_3$	29
9	X=OTf	**1a**	C	$TfOSiMe_3$	40
10	X=OSO_2F	**1b**	A	FSO_3H	45
11	X=OSO_2CH_3	**1c**	C[e]	CH_3SO_3H	79
12	X=OSO_2CH_3	**1c**	C	$CH_3SO_3SiMe_3$	42
13	X=OSO_2CCl_3	**1d**	B	CCl_3SO_3Na	83
14	X=$OSO_2C_4F_9{}^n$	**1e**	B	n-$C_4F_9SO_3Na$	87
15	X=BF_4	**1f**	B	$NaBF_4$	78
16	X=BF_4	**1f**	A	$BF_3 \cdot OEt_2$	33
17	X=PF_6	**1g**	B	$NaPF_6$	83
18	X=AsF_6	**1h**	B	$NaAsF_6$	66
19	X=SbF_6	**1i**	B	$NaSbF_6$	85
20	X=SbF_6	**1i**	B	$LiSbF_6$	93
21	X=SbF_6	**1i**	A	SbF_5	35
22	X=ClO_4	**1j**	B	$NaClO_4$	69

a) See Experimental Section. The fluorination was conducted in CH_3CN at −40 °C unless otherwise noted. b) Isolated yields. c) The fluorination was carried out at −20 °C. d) In place of CH_3CN, $CFCl_3$ was used as a solvent in the first fluorination step which was carried out at −78 °C. The solvent of the second step at −40 °C was a 1 : 2 mixture of $CFCl_3$ and CH_3CN. e) The fluorination was carried out at −20 °C by using H_2O-CH_3CN (1/20) solvent. The post-treatment for **1c** was as follows; a large amount of THF was added to the reaction mixture cooled at −20 °C and the resulting precipitates of **1c** was collected by filtration.

tion of a mixture of a pyridine and metal salt of an acid (Method B), fluorination of a pyridinium hydrogen salt or a *N*-silylpyridinium salt (Method C), or fluorination of a pyridine-Lewis acid complex (Method D), as outlined in Scheme 1. The results are summarized in Tables 1 and 2.

According to Method A, the first treatment of pyridine in CH_3CN with 10% F_2-N_2 mixture gas at −40 °C and successive treatment with TfOH (Tf=CF_3SO_2), fluorosulfuric acid, trimethylsilyl triflate, $BF_3 \cdot OEt_2$, or SbF_5 gave the corresponding N-fluoropyridinium salts **1** in 29—45% yields. In case of a more basic pyridine, 2,4,6-trimethylpyridine, the first fluorination step was conducted in the presence of a 4—10 equivalent amount of NaF added as a HF trapping agent (modified Method A) to lessen the formation of 2,4,6-trimethylpyridinium hydrogen triflate (**48**).

Method B, a one-step procedure, afforded good yields of *N*-fluoropyridinium salts. Thus a mixture of pyridine and metal salt of a strong acid such as NaOTf, CCl_3SO_3Na, $NaBF_4$, n-$C_4F_9SO_3Na$, $NaPF_6$, $NaAsF_6$ etc. in CH_3CN was treated with 10% F_2-N_2 mixture gas at −40 °C to produce *N*-fluoropyridinium salt **1** in 63—93% yields, as shown in Table 1. As fluorination proceeded, metal fluoride appeared gradually in the form of precipitates. Table 2 shows that by Method B, the synthesis of a large number of *N*-fluoropyridinium salts possessing an electron-donating or -withdrawing atom(s) or group(s) on the pyridine ring can be effectively carried out using substituted pyridines.

In the Method B fluorination of pyridine, LiOTf, NaOTf, and KOTf were used to obtain 87, 75, and 62% yields of *N*-fluoropyridinium triflate (**1a**), respec-

Table 2. Syntheses of a Variety of Substituted *N*-Fluoropyridinium Salts **2**—**46**

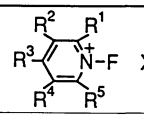
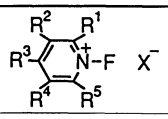
Run								Method[c]	Reactant	Yield[d] / %
	No.[a]	X[b]	R^1	R^2	R^3	R^4	R^5			
1	**2**	OTf	Me	H	H	H	H	B	NaOTf	60
2	**3**	OTf	H	Me	H	H	H	B	NaOTf	—[e]
3	**4**	OTf	H	H	Me	H	H	B[f]	NaOTf	90
4	**5**	OTf	Me	H	H	H	Me	B	NaOTf	69
5	**6**	OTf	H	Me	H	Me	H	A[g]	NaOTf	60
6	**7a**	OTf	Me	H	Me	H	Me	B	LiOTf	22
7	**7b**	OSO_2F	Me	H	Me	H	Me	A	FSO_3H	56[h]
8	**7c**	OSO_2Camph	Me	H	Me	H	Me	A[f]	$NaOSO_2$Camph[i]	50
9	**7d**	BF_4	Me	H	Me	H	Me	B[f]	$NaBF_4$	70
10	**8**	OTf	Me	Me	H	Me	Me	B[f]	NaOTf	9
11	**9**	OTf	Me	Me	Me	Me	Me	B[f]	NaOTf	12
12	**10**	OTf	H	H	*t*-Bu	H	H	B[f]	NaOTf	86
13	**11**	OTf	*t*-Bu	H	H	H	*t*-Bu	B[f]	NaOTf	12
14	**12**	OTf	*t*-Bu	H	*t*-Bu	H	*t*-Bu	B[f]	NaOTf	1.3
15	**13**	OTf	*t*-Bu	H	Me	H	*t*-Bu	B[f]	NaOTf	5
16	**14**	OTf	$-(CH_2)_4-$		H	$-(CH_2)_4-$		B	KOTf	48
17	**15**	OTf	CH_2OMe	H	H	H	CH_2OMe	B	NaOTf	85
18	**16**	OTf	CH_2OMe	H	CH_2OMe	H	CH_2OMe	B	NaOTf	73
19	**17**	OTf	CH_2OCOPh	H	H	H	H	B	NaOTf	84

Table 2. (Continued)

Run							Method[c]	Reactant	Yield[d]
	No.[a]	X[b]	R^1	R^2	R^3	R^4	R^5			%
20	**18**	OTf	CH_2OAc	H	H	H	CH_2OAc	B	NaOTf	74
21	**19**	OTf	CH_2F	H	Me	H	Me	B	KOTf	75
22	**20**	OTf	OMe	H	H	H	H	B	NaOTf	73
23	**21**	OTf	H	OMe	H	H	H	B[f]	NaOTf	62
24	**22**	OTf	H	H	OMe	H	H	B[f]	NaOTf	87
25	**23**	OTf	OMenth[j]	H	H	H	H	B	NaOTf	57
26	**24**	OTf	H	H	Ph	H	H	B	NaOTf	41
27	**25**	OTf	F	H	H	H	H	B	LiOTf	23[k]
28	**26**	OTf	Cl	H	H	H	H	B	NaOTf	71
29	**27**	OTf	H	Cl	H	H	H	C	$TfOSiMe_3$	79
30	**28**	OTf	Cl	H	H	H	Cl	B[l]	LiOTf	38
31	**28**	OTf	Cl	H	H	H	Cl	C[m]	TfOH	62
32	**28**	OTf	Cl	H	H	H	Cl	C	TfOH	56
33	**29a**	OTf	H	Cl	H	Cl	H	B	LiOTf	77
34	**29a**	OTf	H	Cl	H	Cl	H	B	NaOTf	27
35	**29b**	BF_4	H	Cl	H	Cl	H	D	$BF_3 \cdot OEt_2$	79
36	**30a**	OTf	Cl	Cl	Cl	Cl	Cl	C[n]	TfOH	85
37	**30a**	OTf	Cl	Cl	Cl	Cl	Cl	C	TfOH	32
38	**30b**	BF_4	Cl	Cl	Cl	Cl	Cl	D[n]	BF_3	87
39	**31**	OTf	H	Cl	H	CF_3	H	C	$TfOSiMe_3$	71
40	**31**	OTf	H	Cl	H	CF_3	H	C	$TfOSiMe_2Ph$	71
41	**32**	OTf	H	CF_3	H	CF_3	H	C	$TfOSiMe_3$	68
42	**33**	OTf	H	OAc	H	H	H	B	NaOTf	90
43	**34**	OTf	COOMe	H	H	H	H	C	$TfOSiMe_3$	86
44	**35**	OTf	H	COOEt	H	H	H	C	$TfOSiMe_3$	69
45	**36**	OTf	H	H	COOMe	H	H	C	$TfOSiMe_3$	—[e]
46	**37**	OTf	COOMe	H	H	H	COOMe	B	NaOTf	72
47	**37**	OTf	COOMe	H	H	H	COOMe	B	LiOTf	78
48	**38**	OTf	H	COOMe	H	COOMe	H	C	$TfOSiMe_3$	60
49	**39**	OTf	COOMe	H	COOMe	H	COOMe	B	LiOTf	15[k]
50	**40**	OTf	$COCH_3$	H	H	H	H	B	NaOTf	72
51	**41**	OTf	H	H	$COCH_3$	H	H	B	LiOTf	96
52	**42**	BF_4	CN	H	H	H	H	B	$LiBF_4$	78
53	**43**	OTf	H	CN	H	H	H	B	LiOTf	84
54	**44**	OTf	H	H	CN	H	H	B	LiOTf	94
55	**45**	OTf	CN	H	H	H	CN	B	LiOTf	50
56	**46**	OTf	H	H	NO_2	H	H	B	LiOTf	86

a) Compound numbers. b) Counter anion part of *N*-fluoropyridinium salts. c) See Experimental Section. Fluorination was conducted in CH_3CN at −40 °C unless otherwise noted. d) Isolated yields. e) Good yields. f) Modified Method using added NaF. g) This reaction was carried out in the similar manner as Run 7 in Table 1. Thus, $CFCl_3$ was used as a solvent in the first fluorination step. h) A crude yield. i) Sodium (+)-10-camphorsulfonate. j) (1*R*,3*R*,4*S*)-Menthyloxy group. k) Products were isolated as 1 : 1 salts with LiOTf. l) This reaction was carried out in dry propionitrile solvent at −60 °C. m) This reaction was carried out in dry propionitrile at −78 °C. n) Fluorination with 20% F_2-N_2 was conducted in CF_3COOH at room temperature (ca. 10 °C).

tively. With 2,4,6-trimethylpyridine, LiOTf gave only a 22% yield of *N*-fluoro-2,4,6-trimethylpyridinium triflate (**7a**). In this reaction, two by-products, **48** (26%) and *N*-fluoro-2-fluoromethyl-4,6-dimethylpyridinium triflate (**19**) (5%) were found. As seen in Table 3, the yield of **7a** depended on the nature of metal triflate used, and KOTf greatly increased **7a** and decreased the by-product **48**. Salt **7a** was obtained in highest yield and **48** suppressed completely by KOTf in H_2O-CH_3CN (1/100) solvent. No significant change was noted in the yields of **19**. Runs 5 and 6 in Table 3 show better yields of **7a** by modified Method B in which the fluorination was conducted in the presence of a 4—10 equivalent amount of NaF added. Salt **7a** could be separated easily from **48** by recrystallization, though its complete separation from **19** was difficult.

Pure *N*-fluoro-2,3,5,6-tetramethylpyridinium triflate (**8**) and -pentamethylpyridinium triflate (**9**) were isolated in very low yields by the modified Method B. Considerable amounts of the corresponding pyridinium hydrogen salts were formed in these reactions.

Table 3. Reaction Conditions for Preparation of *N*-Fluoro-2,4,6-trimethylpyridinium Triflate (**7a**)

Run	Method[a)]	MOTf	Solv.	Additive[b)]	Yield[c)]/%		
					7a	**48**	**19**
1	B	LiOTf	CH_3CN	—	22	26	5
2	B	NaOTf	CH_3CN	—	39	23	7
3	B	KOTf	CH_3CN	—	71	5	8
4	B	KOTf	H_2O-CH_3CN(1/100)	—	81	0	7
5	B[d)]	NaOTf	CH_3CN	NaF(4 equiv)	52	20	9
6	B[d)]	NaOTf	CH_3CN	NaF(10 equiv)	57	15	8

a) See Experimental Section. b) Figures in parentheses mean equivalent amounts of NaF based on 2,4,6-trimethylpyridine. c) Yields of **7a** were isolated yields. The yields of **48** and **19** were determined by ^1H NMR of the crude reaction products, based on the isolated yields of **7a**. d) This method was specified as modified Method B.

Highly hindered pyridines, 2,6-di-*t*-butylpyridine and its derivatives were fluorinated according to the modified Method B to give *N*-fluoro-2,6-di-*t*-butylpyridinium triflate (**11**), *N*-fluoro-2,4,6-tri-*t*-butylpyridinium triflate (**12**), and *N*-fluoro-2,6-di-*t*-butyl-4-methylpyridinium triflate (**13**). The yields, however, were quite low. During the reactions, the corresponding pyridinium hydrogen salts and tars were also formed. The separation of these pure *N*-fluoro salts from the protonated pyridinium salts was successfully carried out by treatment of a CH_2Cl_2 solution of the mixture with aq $NaHCO_3$ followed by recrystallization. Method B using KOTf in the aq CH_3CN solvent improved the yields only to a very slight extent.

The yields of *N*-fluoropyridinium salts possessing an electron-withdrawing ring-substituent(s) by Method B varied depending on the metal salts used, or on the nature, ring-position and number of substituents. Apparently, lithium salts give better yields than sodium or potassium salts. *N*-Fluoro-3,5-dichloropyridinium triflate (**29a**) was obtained in 77% yield using LiOTf, but in 22% yield by NaOTf. Isomeric *N*-fluoro-2,6-dichloropyridinium triflate (**28**) was prepared in only a 38% yield by LiOTf.

As the pyridine nitrogens became weak in basicity, efficiency of the fluorination decreased. When 2,4,6-tris(methoxycarbonyl)pyridine and 2-fluoropyridine were fluorinated by Method B using LiOTf, *N*-fluoro-2,4,6-tris(methoxycarbonyl)pyridinium triflate (**39**) and *N*-fluoro-2-fluoropyridinium triflate (**25**) were isolated in low yields as 1 : 1 crystals with unreacted LiOTf.

Method C fluorination of salts of pyridine, 2,6-dichloropyridine, and pentachloropyridine with triflic acid gave **1a** (66%), **28** (56—62%), and *N*-fluoropentachloropyridinium triflate (**30a**) (32%), respectively, while the corresponding salt **48** of 2,4,6-trimethylpyridine failed to produce **7a** under the same conditions. In the latter case, a large amount of the starting **48** was found to remain. The yield of **1a** was improved by the fluorination at elevated temperature and was high at −20 °C (96%, Run 5 in Table 1). The fluorination of the salt of extremely low basic pentachloropyridine was most efficiently carried out at room temperature using trifluoroacetic acid as a solvent to obtain **30a** in 85% yield.

By Method C, the reaction of *N*-(trimethylsilyl)-pyridinium triflate, easily obtained from pyridine and trimethylsilyl triflate, with F_2 in CH_3CN at −40 °C led to the formation of **1a** in 40% yield. In this reaction, trimethylsilyl fluoride, as another product, was detected by ^{19}F NMR of the reaction mixture. As can be seen from Table 2, Method C is suitable for pyridine itself or pyridines possessing an electron-withdrawing substituent(s). A pyridinium salt with the electron-donating groups, *N*-trimethylsilyl-2,4,6-trimethylpyridinium triflate did not produce **7a** under the same reaction conditions.

Care must be taken when fluorinating *N*-(trimethylsilyl)pyridinium salts. When the very dilute 2% F_2-N_2 was used for the fluorination, there was no *explosion* while at 5% or more, there ensued a violent gas-phase reaction. This may possibly have resulted from a gas-phase reaction of the volatile by-product, trimethylsilyl fluoride, with F_2, since no *violent reaction* occurred with *N*-(dimethylphenylsilyl)pyridinium triflate by which nonvolatile dimethylphenylsilyl fluoride was produced as the by-product (Run 40 in Table 2).

Method D fluorination of a BF_3 complex of 3,5-dichloropyridine formed tetrafluoroborate **29b** in 79% yield while only a trace of **1f** could be formed from pyridine-BF_3 complex under the same conditions. *N*-Fluoropentachloropyridinium tetrafluoroborate (**30b**) was synthesized in 87% yield by Method D fluorination with 20% F_2-N_2 in trifluoroacetic acid at room temperature.

N-Fluoropyridinium trifluoroacetate, regarded as a salt with a weakly nucleophilic counter anion, was produced by Method A using sodium trifluoroacetate or trimethylsilyl trifluoroacetate. The pure salt could not be obtained owing to its failure to be crystallized. The ^1H NMR of the crude product was in good agreement with that of the *N*-fluoropyridinium moiety of **1a** and ^{19}F NMR showed an N-F peak at δ=48.4. *N*-Fluoropyridinium methanesulfonate

(**1c**), a salt with another weakly nucleophilic counter anion, was isolated in good yield according to Method C (Runs 11 and 12 in Table 1). The synthesis of *N*-fluoropyridinium acetate, a salt possessing a considerably strongly nucleophilic counter anion, was attempted by Method B using sodium acetate (NaOAc). Treatment of an equimolar mixture of pyridine and NaOAc in CH_3CN with 10% F_2-N_2 at −40 °C produced new precipitates, probably NaF, but the reaction mixture immediately became dark on rising to room temperature. *N*-Fluoropyridinium acetate may thus possibly be present at low temperature but decomposes with its increase.

A higher homologue of pyridinium salts, *N*-fluoroquinolinium triflate (**49**), was synthesized in 16% yield by Method B using NaOTf. The low yield obtained may possibly have been due to the considerably low stability of **49** toward moisture.

N-Fluoropyridinium-2-sulfonate (**52**) and *N*-fluoro-6-chloropyridinium-2-sulfonate (**53**), counter anion-bound salts, were synthesized as stable crystals in 81 and 77% yields by treating 2-pyridinesulfonic acid (**50**) and 6-chloro-2-pyridinesulfonic acid (**51**) with 10% F_2-N_2 in H_2O-CH_3CN (1/20) solution at −25 °C, respectively.

Hydrolysis Experiment. *N*-Fluoropyridinium salt **1a** was dissolved in water and decomposed very slowly at room temperature. When a solution of **1a** in water stood for 14 days at room temperature, **1a** decomposed completely to give 2-pyridinol in 66% yield. The half decay for its decomposition in heavy water at room temperature was 13 days. Its hydrolysis was accelerated by alkali. Salt **1a** was thus readily hydrolyzed with aq KOH solution at room temperature. GC and GC-Mass analyses of a reaction mixture showed traces of 2-pyridyl triflate (0.5%) and 2-fluoropyridine (0.6%) to form in addition to 2-pyridinol which was isolated in 50% yield.

2,4,6-Trimethyl salt **7a** dissolved in water without decomposing. It remained intact after 30 days at room temperature in heavy water, but decomposed immediately with aq KOH solution to give 2-(hydroxymethyl)-4,6-dimethylpyridine (**54**) and 2-(fluoromethyl)-4,6-dimethylpyridine (**55**) in 24 and 23% yields, respectively. Treatment of **7a** with triethylamine in CH_2Cl_2 and THF afforded a new fluoro product, 3-fluoro-2,4,6-trimethylpyridine (**60**), in addition to **55** in total 62 and 63% yields, respectively. The ratios of **55**/**60** were 2/1 in CH_2Cl_2 and 1/1 in THF. The treatment with NaH in CH_2Cl_2 gave **55**/**60**=8/1 (total yield; 60%).

In water, 3,5-dichloro salt **29a** decomposed immediately and exothermally to give 3,5-dichloro-2-pyridinol (**56**) in 82% yield. 2,6-Dichloro salt **28** decomposed slowly in water, compared to **29a**, to give *N*-fluoro-6-chloro-2-pyridone (**57**) and 2,6-dichloro-4-pyridinol (**58**) in 35 and 7% yields, respectively. Pentachloro salt **30a** decomposed rapidly in water, affording *N*-fluoro-3,4,5,6-tetrachloro-2-pyridone (**59**) in 62% yield. *N*-Fluoroquinolinium salt **49** decomposed immediately in water, so that 2-hydroxyquinoline was obtained in 68% yield.

Thermal Stability. *N*-Fluoropyridinium salts with nonnucleophilic counter anions are generally stable crystals with high melting points. *N*-Fluoropyridinium salt **1a** and 2,4,6-trimethyl salt **7a** remained intact after 5 h at 150 °C, but melted and decomposed within a few minutes at 190 °C. 3,5-Dichloro salt **29a** remained spectroscopically intact after 6 h at 100 °C, though its crystals turned pale brown. Salt **29a**, however, melted and decomposed in less 1 min at 190 °C and in ca. 45 min at 150 °C. These salts may thus be considered to retain their stability for prolonged periods at temperatures less than their melting points, but decompose rapidly or slowly above their melting points.

Solubility. *N*-Fluoropyridinium salts in most cases are freely soluble in polar solvents such as acetonitrile, but insoluble or sparingly soluble in nonpolar organic solvents. The solubilities of *N*-fluoropyridinium triflate **1a**, tetrafluoroborate **1f**, hexafluoroantimonate **1i**, and perchlorate **1j** in CH_2Cl_2 are 0.63, 0.05, 0.09, and 0.035 mg cm^{-3}, respectively. Thus, triflate **1a** has relatively high solubility in this series. Salts having bulky ring-substituents or counter anions such as **10, 11, 12, 14, 15, 16, 18, 23,** or **7c** are soluble in CH_2Cl_2. The solubility of **1a** in THF is 1.71 mg cm^{-3}.

Discussion

Syntheses of *N*-Fluoropyridinium Salts. The pyridine-F_2 compounds produced with pyridine or substituted pyridines and F_2 smoothly underwent the counter anion displacement reactions to give stable *N*-fluoropyridinium salts. They also reacted smoothly with Lewis acids to give *N*-fluoropyridinium salts. The products were determined to have completely ionic structures on the basis of their spectral and elemental analyses. From these results, it appears quite likely that unstable pyridine-F_2 compounds have the *N*-fluoropyridinium fluoride salt structure **47**, which is in agreement with the fact that fluorine atoms have extremely poor two-coordinating ability.[7]

At room temperature, the ^1H NMR spectrum of a homogeneous CH_3CN solution prepared by treating pyridine with 10% F_2-N_2 in CH_3CN at −40 °C, was totally consistent with that of *N*-fluoropyridinium salts. Its ^{19}F NMR showed two peaks at 48.2 and −175 ppm (strong peak), these corresponding to the N-F chemical shifts of the *N*-fluoropyridinium salts and F^- or HF, respectively. An unidentified small peak at 57.4 ppm, however, was also detected. In a concentrated solution, some other small peaks were noted in the range of −63—−100 ppm. Subsequent cooling of the CH_3CN solution to −40 °C followed by treatment with $BF_3 \cdot OEt_2$ gave tetrafluoroborate **1f** in

31% yield, which was the same as that (33%) obtained while keeping the reaction mixture at −40 °C during the treatment.

Since F^- forms a tight hydrogen bond with HF, the pyridine-F_2 compound may quite likely be present as *N*-fluoropyridinium fluoride stabilized by HF, in the form as $[C_5H_5N\text{-}F]^+F^-(HF)_n$. A large part of this compound remained intact in the solution even after standing for 11 days at room temperature.

A comparison of the HF-stabilized salt with the explosive pyridine-F_2 solid, as reported by Meinert,[4] was considered pertinent to the present study. The unstable solid also gave triflate **1a** (32%) and NaF on treatment with NaOTf at low temperature (Run 7 in Table 1). It is thus evident from these data that the unstable solid is *N*-fluoropyridinium fluoride not stabilized by HF, which is most likely formed by immediate precipitation and without the formation of HF as a by-product due to the use of $CFCl_3$ as a solvent inactive toward F_2 under such reaction conditions.

Quantitative ^{19}F NMR analysis indicated the HF-stabilized *N*-fluoropyridinium fluoride to be formed in about a 45% yield, based on the starting pyridine. HF may have been produced by decomposition of the unstable *N*-fluoropyridinium fluoride formed at the first stage and by side-reactions brought about by the extremely reactive F_2. The decomposition reaction would explain well why one-step Method B, in which the unstable *N*-fluoropyridinium fluoride during its formation can immediately react with metal salts of acids, gave good yields of *N*-fluoropyridinium triflates and other salts, while the two-step Method A gave only low yields.

By Method B, in which metal triflates are used, the yield of **1a** increased from 62% to 75% to 87% in the order, KOTf<NaOTf<LiOTf. As noted in the preparation of 3,5-dichloro salt **29a**, the effect of the lithium salt was great in the fluorination of pyridines having electron-withdrawing substituents particularly at β- or γ-positions. It was shown in the related study that *N*-fluoropyridinium salts having an acidic α-proton(s) undergo novel base-initiated decomposition and that even KF causes the decomposition of **1a**, though at a slow rate.[8] The results of the hydrolysis experiments indicated decompostion to occur more easily with *N*-fluoropyridinium salts possessing electron-withdrawing substituents which made the α-proton more acidic. Method B gives metal fluoride as another product as fluorination proceeds. Since their reactivity as a base should decrease in the order of KF>NaF>LiF, the high yields obtained with LiOTf may be attributed to extremely low reactivity of LiF; LiF does not actually decompose any of the formed *N*-fluoropyridinium salts.

To the contrary, in the fluorination of 2,4,6-trimethylpyridine, the yield of product **7a** decreased from 71% to 39% and then to 22% as the metal triflate varied from KOTf to NaOTf and to LiOTf, as shown in Table 3. This may be explained by the decreasing order (KF>NaF>LiF) of the HF-trapping ability of resulting metal fluorides, which can suppress the formation of the by-product **48**. That KOTf in aq CH_3CN completely inhibited **48** is due to the fact that water can act as an additional HF-trapping agent. The effect of NaF as an additive in modified Methods A and B also supports this mechanism. The by-product **19** may be produced by further fluorination of decomposition product **55**, which was shown to form on treatment of **7a** with a base.

N-Fluoropyridinium salts could also be synthesized by insertion reactions of F_2 to proton or silyl salts or Lewis acid-complexes of some pyridines. Thus, pyridinium hydrogen triflate (**63**) and 2,6-dichloro- and pentachloropyridinium hydrogen triflates (**64**) and (**65**) were inserted by F_2 at their N^+-H bonds in CH_3CN at −40 °C to give salts **1a**, **28**, and **30a**, respectively. However, the same treatment of salt **48** of 2,4,6-trimethylpyridine failed to provide **7a**. 3,5-Dichloropyridine-BF_3 complex (**66**) gave a good yield of **29b**, but pyridine-BF_3 complex only a trace of **1f**. It would thus follow that the successful fluorine insertion to N^+-H or N^+-BF_3^- bonds of **63**—**66** is due to their relatively weak bonding. Similarly, the insertion reaction of F_2 into N^+-Si bonds depends on the strength of N^+-Si bonding. The reaction thus proceeded well in the case of the *N*-trimethylsilyl salts of pyridine itself or lower basic pyridine derivatives, while the corresponding silyl salt of more basic 2,4,6-trimethylpyridine did not give **7a** under the same conditions.

In regard to steric hindrance, it should be of considerable interest to fluorinate highly hindered pyridines such as 2,6-di-*t*-butylpyridine and its analogues. Such hindered pyridines react with protonic acid but not with other electrophiles such as BF_3 or methyl iodide by conventional procedure due to steric hindrance between the bulky groups and reactants. They react with methyl iodide or methyl fluorosulfate only under very high pressure of 5000—6000 atm at 90 °C to give stable *N*-methylpyridinium salts.[9] Since van der Waal's radius of fluorine atom (1.47 Å) is close to that of a hydrogen atom (1.20 Å), fluorine should be capable of penetrating into a hindered nitrogen site, as it does in the case of a hydrogen atom.

By the modified Method B, the expected *N*-fluoro-2,6-di-*t*-butyl salts **11**, **12**, and **13** could be obtained along with large amounts of the corresponding pyridinium hydrogen triflates. These *N*-fluoro salts are stable crystals with high melting points, and not sensitive to moisture.

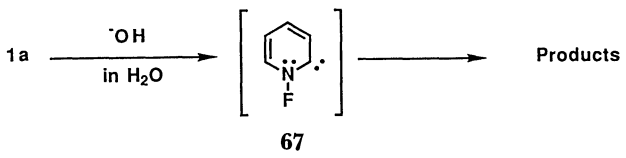
Thus, except for the hydrogen atom, fluorine is the first atom to be inserted into highly crowded nitrogen sites at atmospheric pressure. It is thus clear that, in contrast to the chlorine atom, fluorine atom is capable of substituting all or any hydrogen atom in compounds even though greatly hindered.

Structures and Properties of *N*-Fluoropyridinium Salts. The halogen cations, Cl^+, Br^+, and I^+, have a strong tendency toward two coordination.[10] They thus combine with pyridine or its derivatives to form two kinds of compounds, depending on the nature of the counter anions. One is ionic 2 : 1 salts of pyridine nucleus (Py) and the halogen atom (X) with noncoordinating counter anions such as ClO_4^- or SbF_6^-, as shown by $[Py_2X]^+ClO_4^-$ or SbF_6^-. The other is 1 : 1 covalent molecular complexes with strongly coordinating anions such as carboxylate anions, PyXOCOR.[11] Moderate counter anions such as NO_3^- form both types of compounds, $[Py_2X]^+NO_3^-$ and $PyXONO_2$.

All synthesized *N*-fluoropyridinium compounds possessing non- or weakly coordinating counter anions are concluded to possess completely ionic 1 : 1 structures, $[PyF]^+Y^-$ (Y^-; counter anion). The ease of formation and high stability of 1 : 1 salts contrast sharply with other halogens having the two-coordination form. The reason for this must surely be the low polarizability or lack of d-orbitals of the fluorine atom, or the great difficulty of positive fluorine F^+ formation.[2]

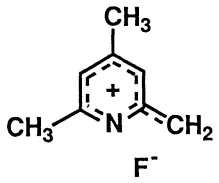
N-Fluoropyridinium fluoride is an unstable solid with an explosive nature, while *N*-fluoropyridinium salts possessing nonnucleophilic counter anions are stable crystals with high melting points. *N*-Fluoropyridinium methanesulfonate (**1c**), a salt having a weakly nucleophilic counter anion, is also stable crystals which melt at 140—142 °C. *N*-Fluoropyridinium trifluoroacetate is also stable at room temperature though its pure salt could not be isolated in the present study. But *N*-fluoropyridinium acetate, a salt having a strongly coordinating or considerably nucleophilic counter anion, was shown by the present data to decompose at room temperature. The stability of *N*-fluoro salts thus clearly depends on the basicity or nucleophilicity of the counter anions. Salts **1** with nonnucleophilic counter anions except for $^-OSO_2F$ are nonhygroscopic crystals.

Electron-withdrawing substituents on the pyridine ring lessen the stability of *N*-fluoropyridinium salts. Particularly 2-fluoro salt **25** and 2,6-dicyano salt **45** were sensitive to moisture. Hydrolysis experiments have afforded some further evidence. The hydrolysis of **1a** in water proceeded quite slowly while that of 3,5-dichloro salt **29a**, rapidly to give 2-pyridinol **56**. Its isomer, 2,6-dichloro salt **28**, was hydrolyzed somewhat slowly, giving other types of hydrolysis products, *N*-fluoro-2-pyridone **57** and 4-pyridinol **58**. Thus, the activating effect of a chlorine atom is outstanding, as is also the blocking effect of an α-chlorine atom. The latter effect suffices to explain why **28** is more stable than **29a** in air in spite of more activation of the N–F moiety of **28**. It should be clear now that, although extremely activated, pentachloro salts **30a** and **30b**, in which all positions are blocked, still possess relatively high stability.



67

Scheme 2.



69

Fig. 2.

The hydrolysis of *N*-fluoropyridinium salts contrasts sharply with that of other pyridinium salts having electron-withdrawing groups at the nitrogen sites. *N*-Cyano, -nitro, -nitroso and -(2,4-dinitrophenyl)pyridinium salts and pyridine–SO_3 complex have all been shown to undergo ring opening reaction by alkaline hydrolysis, giving glutaconaldehyde or its derivatives.[14] The mechanism of this is said to be the addition of a hydroxide anion to the α-position. This marked difference may possibly arise from the very different reaction mechanism of *N*-fluoropyridinium salts. As indicated in the related study, *N*-fluoropyridinium salts react with a base to generate a unique carbene **67** (Scheme 2).[8] The detection of traces of 2-pyridyl triflate and 2-fluoropyridine in the alkaline hydrolysis of **1a** supports this mechanism. In the hydrolysis in water, H_2O may serve as a base.

Treatment of **7a** with aq alkaline solution and with a base in an organic solvent afforded different types of products, **54**, **55**, or **60**. They can be explained by an ion pair intermediate **69** (Fig. 2) resulting from deprotonation of **7a**, similar to those for rearrangement reactions of 2- and 4-methylpyridine *N*-oxides.[15]

Conclusions

N-Fluoropyridinium salts provide a new chemistry of pyridine–halogen compounds. Their syntheses can be conducted by counter anion displacement reactions of unstable *N*-fluoropyridinium fluorides and/or insertion reactions of F_2 with salts or complexes of pyridines with protonic acids, silyl esters, and Lewis acids. Their structures and stability characterization, and hydrolysis experiments indicate unique characters of fluorine. The results of this study demonstrate the presence of a new interesting pyridinium salt system based on the superlative nature of fluorine and thus extend the concept of pyridine and fluorine chemistry.

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