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N-FLUOROPYRIDINIUM TRIFLATE AND ITS ANALOGS, THE FIRST STABLE 1:1 SALTS OF PYRIDINE NUCLEUS AND HALOGEN ATOM

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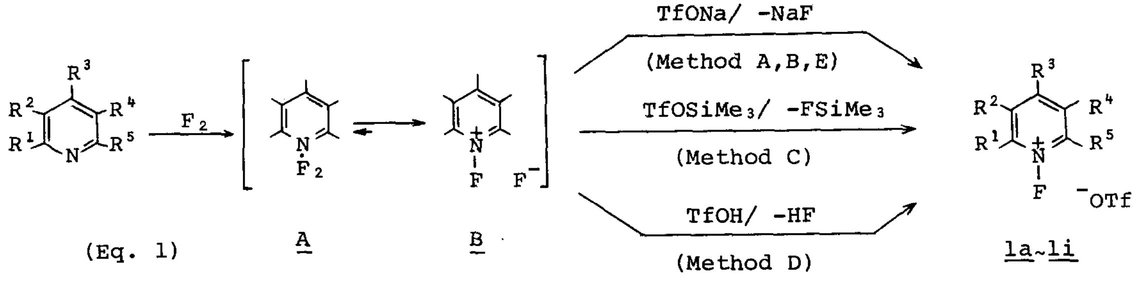
N-Fluoropyridinium salts having non-nucleophilic counter-anions and their derivatives were synthesized by treating pyridine-F_2 adducts with strong Brønsted acids, their salts or trimethylsilyl esters, or Lewis acids, or by allowing F_2 to react with N-trimethylsilylpyridinium salts.

The nature of the bonding between a halogen atom and a pyridine nitrogen atom, which shares the lone paired electrons, has been of great interest for a long time from the viewpoint of molecular complex, charge-transfer complex studies, or reconsideration of the bonding related to halogens.1) It is well known that a iodine, bromine, or chlorine cation combines with pyridine to form not 1:1 salt $[PyX]^+$ but a stable 1:2 salt $[Py_2X]^+$ (Py=pyridine).1,2) Thus the halogen cations have a strong tendency towards two-coordination. The compounds of the type PyXY (Y=anion part) isolated so far are essentially covalent compounds or molecular complexes.2) However there are no data about the fluorine compounds. The corresponding nitrogen-fluorine bonding is very interesting since a fluorine atom is remarkably different from other halogen atoms because of its highest electronegativity, great difficulty in the formation of a fluorine cation, or the lack of d-orbitals.3) Meinert reported that fluorine (F_2) diluted with N_2 was bubbled into a solution of pyridine in $CFCl_3$ at -80°C to form Py-F_2 adduct as moisture-sensitive, unstable white precipitates and that it decomposed violently at more than -2°C to leave redbrown oil containing 2-fluoropyridine.4) However no physical or spectral data on the adduct itself was reported. He also suggested that the adduct had an ionic structure in a polar solvent from electrolysis experiment.4) We now wish to report about the



(Eq. 1) A B 1a~1i

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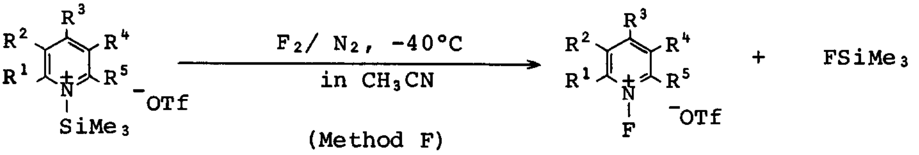
synthesis and properties of the first stable 1:1 salts, N-fluoropyridinium salts.

We thought that the instability of Py-F_2 would be due to some nucleophilicity of F^- in a possible ionic form (B, Eq. 1) and might be improved by exchanging F^- for a non-nucleophilic anion. The adduct prepared in $CFCl_3$ at -75° C was allowed to react with sodium triflate in dry CH_3CN at -40°C for 2 h to give N-fluoropyridinium triflate 1a as very stable white crystals[5] in 67% yield (Method A). It was found that 1a was synthesized conveniently by the reaction of F_2/N_2 (1/9) with pyridine in CH_3CN at -40°C followed by treatment with sodium triflate (71%, Method B). Instead of sodium triflate in Method B, trimethylsilyl triflate and triflic acid could be used successfully with the formation of trimethylsilyl fluoride and hydrogen fluoride [Method C (45% for 1a) and D (44% for 1a)], respectively. Most conveniently 1a was prepared by bubbling F_2/N_2 (1/9) into a solution of pyridine in CH_3CN at -40°C in the presence of sodium triflate (80%, Method E). The results of our reactions support that the pyridine-fluorine compound is in the ionic form B (Eq. 1) in CH_3CN, which is in agreement with the suggestion of Meinert.[4]

We also found a new insertion reaction of fluorine into a N-Si bond. 1a was prepared by the reaction of F_2/N_2 (1/9) with N-trimethylsilylpyridinium



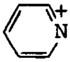
1

(Eq. 2)

triflate at -40°C (78%, Method F) (Eq. 2).

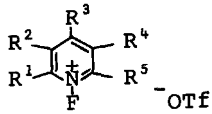
N-Fluoropyridinium salts possessing several kinds of counter-anions were prepared by our methods using $NaPF_6$, $NaClO_4$, $NaSbF_6$ etc. (Table 1). Borate 2

Table 1 N-Fluoropyridinium salts with several kinds of counter-anions

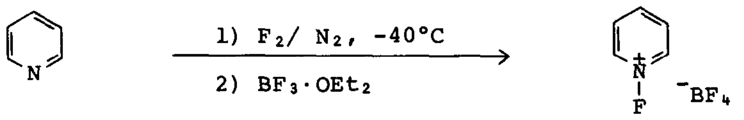
	 N-F $^-$X	Method	Yield(%)	Mp(°C)	^{19}F-NMR(ppm)[a)]
1a	X=OTf	A-F	44-80	185-187	-48.75
2	BF_4	G	69	90-91	-48.75
3	PF_6	B	34	202 (decomp)	-48.58
4	ClO_4	B	72	225-227.5 (with decomp)	-48.75
5	SbF_6	B	51	>300	-48.82
6	$OSO_2C_4F_9{}^n$	E	77	111-112	-48.37

a) In CD_3CN, $CFCl_3$ as int. standard, negative values mean downfield shift from $CFCl_3$.

Table 2 Substituted N-fluoropyridinium triflates

		Method	Yield (%)	Mp (°C)	^{19}F-NMR[a)] (ppm)
1b	R^1=Me, $R^{2\sim5}$=H	E	60	119.5-120.5	-37.13
1c	$R^{1,5}$=Me, $R^{2\sim4}$=H	E	73	126-128	-24.75
1d	$R^{1,3,5}$=Me, $R^{2,4}$=H	E	49	164-166	-17.25
1e	R^1=OMe, $R^{2\sim5}$=H	E	73	111.5-112.5	-0.75
1f	R^2=Cl, $R^{1,3\sim5}$=H	F	79	108-109	-50.59
1g	$R^{2,4}$=Cl, $R^{1,3,5}$=H	C,D,F	62,41,55	99.5-101	-52.13
1h	R^2=COOMe, $R^{1,3\sim5}$=H	F	69	115-116	-50.02
1i	$R^{1,5}$=COOMe, $R^{2\sim4}$=H	E,F	72,68	140-143	-25.50

a) See a) in Table 1.



(Eq. 3)

(Method G)

2 69%

was prepared by the reaction of fluorine with pyridine followed by the addition of Lewis acid BF_3OEt_2 (69%, Method G) (Eq. 3).

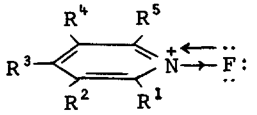
Physical or chemical properties of N-fluoropyridinium salts should closely be correlated with the electron density of lone paired electrons at the nitrogen site of the pyridine nucleus. A series of N-fluoropyridinium triflates having electron-donating or -withdrawing substituents were prepared by our methods (Table 2). It is worth noting that even dimethyl 2,6-pyridinedicarboxylate with much lower electron density at the nitrogen site afforded the corresponding salt 1i.

The structural assignment of the N-fluoro salts was made from spectral analyses (^{1}H- and ^{19}F-NMR and Mass) and elemental analyses,[5)] which were in accord with the assigned 1:1 salts. The easy formation of the 1:1 salts of fluorine atom and pyridine nucleus is in sharp contrast to other halogens forming the 1:2 salts. It must be owing to low polarizability[6)] or the lack of d-orbitals of the fluorine atom, or the great difficulty in the formation of F^+. ^{1}H-NMR of 1a showed signals at δ 9.33, 8.77, and 8.32 at much lower field than those of pyridine itself, which were assigned as α-H, γ-H, and β-H, respectively. The coupling constants between F and H, J(α-H-F)=16.0 Hz, J(β-H-F)=4.8, and J(γ-H-F)=2.0, were observed. It demonstrated the existence of the N-F bond. ^{19}F-NMR showed -48.75 ppm as a broad singlet. There was no difference in the

^{19}F-chemical shifts of 1a and 2-6, indicating that the salts have completely ionic structure. The mass spectrum (SIMS method) of 1a exhibited a base peak at 98 (m/z) corresponding to N-fluoropyridinium cation.

In general, all the salts synthesized above are thermally stable and non-hygroscopic crystals. 1g and 1i having two electron-withdrawing groups are not so stable as other salts. They have still high oxidation potential. For example, 1a can oxidize I$^-$ and Br$^-$ to iodine and bromine, respectively.

Although the high electronegativity of the fluorine atom bonding to the positive nitrogen atom should cause the destabilization of the whole system compared to other halogens, the N-fluoro salts revealed high stability. Evidently such high stability depends primarily on the strong N-F bonding$^{7)}$ which may be additionally reinforced by some possible back-donation$^{8)}$ of p-electrons on the fluorine atom to the positive nitrogen site, that is, the electron-deficient π-system.



The ^{19}F-chemical shifts of N-F were sensitive to the substituents on the pyridine nuclei (Table 1 and 2). Electron-donating groups caused upfield shift compared to that of 1a, while electron-withdrawing ones brought about downfield shift. It is related to the electron density at the nitrogen sites. Only an exception was 1i of which N-F chemical shift appeared at -25.50 ppm upfield from that of 1a. That may be because steric or other neighboring effect of methoxycarbonyl groups overcame the inductive or resonance effect. In 1h in which there is no such neighboring effect, the signal appeared at -50.02 ppm downfield from 1a.

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5) 1a (Recryst. from CH$_3$CN-Et$_2$O); C:29.26, H:2.04, N:5.70, F:30.49, S:13.21%. Calcd for C$_6$H$_5$NF$_4$O$_3$S; C:29.10, H:2.00, N:5.70, F:30.70, S:12.95%.

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