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N-Halogeno compounds
Part 19 [1]: Electrophilic fluorinating agents of the multiple mono-N-fluoro class derived from nitrogen heterocycles

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Abstract

Bis(4-fluoro-1,4-diazoniabicyclo[2.2.2]oct-1-yl)-ethane and -propane tetratriflates (**4**, **5**), and 1,1′-difluoro-4,4′-bipyridinium ditriflate (**6**) were prepared by solution-phase direct fluorination of bis(4-aza-1-azoniabicyclo[2.2.2]oct-1-yl)-ethane or -propane ditriflate (**10**, **11**), and 4,4′-bipyridine respectively. The same technique was employed to convert the complex 4,4′-bipyridine · 2BF$_3$ to the mono-NF derivative $F_3B \cdot NC_5H_4\text{-}C_5H_4N^+\text{-}F\ BF_4^-$ (**7**) and its monomethylated analogue $(4\text{-}NC_5H_4)C_5H_4N^+\text{-}CH_3\ TfO^-$ to $F\text{-}^+NC_5H_4\text{-}C_5H_4N^+\text{-}CH_3\ (TfO^-)_2$ (**8**). The results of site-specific electrophilic fluorination of some model substrates (1-morpholinocyclohexene, phenol, 2-naphthol, anisole, di- and tri-methoxybenzene) with **5**, **7** and **8** are presented.

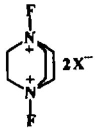
Keywords: Electrophilic fluorination; N-Fluoro reagents; Bis(N-fluoroammonium) salts

1. Introduction

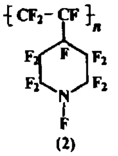
Except for a preliminary report [1] on 1,4-difluoro-1,4-diazoniabicyclo[2.2.2]octane salts (**1**, bis(NF)-TEDA salts, TEDA ≡ triethylenediamine) and information concerning polymeric versions of perfluoro-N-fluoropiperidine (e.g. **2**) [2] and N-fluoropyridinium salts (e.g. **3**) [3], the literature seems devoid of accounts detailing the synthesis and use of electrophilic fluorinating agents of the N–F class containing more than one N-fluoro substituent per molecule. This paper describes the chemistry of several such compounds (**4–6**) made some years ago during developmental work on NF-TEDA reagents [4] (including **1** [1]). Information is also presented here concerning mono-NF analogues (**7**, **8**) of the 'double' Umemoto [5] reagent **6**.

2. Synthesis of NF compounds 4–8

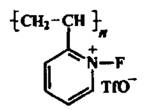
Established methods [6,7] developed for the direct (i.e. using F$_2$) solution-phase fluorination of analogues of the substrates used here were employed, namely passage of fluorine diluted with nitrogen (ca. 10% F$_2$ by volume) through a vigorously stirred solution of starting material in well cooled CH$_3$CN or a CFCl$_3$–CHCl$_3$ blend, and a corresponding closed-system method employing neat F$_2$ at low pressure (less than or equal to 20 mmHg). Although the latter method requires far more sophisticated apparatus [7] and a more experienced operator, its merits vis-à-vis the flow method have proved invaluable in our wide-ranging small-scale exploratory work on N–F reagents: syntheses achieved using this technique can usually be translated with confidence to the flow method on a larger scale (see for example Ref. [8]). All the new products (**4–8**) reported here were prepared by the closed-system fluorination technique, and further samples of the TEDA-based compounds **4** and **5** were also made using the flow method.



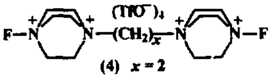
(1)
$X^- = TfO^-, BF_4^-, PF_6^-, FSO_3^-$



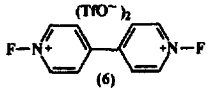
(2)



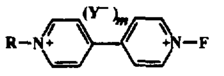
(3)



(4) $x = 2$
(5) $x = 3$



(6)



(7) $R = BF_3^-, Y^- = BF_4^-, m = 1$
(8) $R = CH_3, Y^- = TfO^-, m = 2$

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[1] Part 18: R.E. Banks, M.K. Besheesh, S.N. Mohialdin-Khaffaf and I. Sharif, *J. Chem. Soc., Perkin Trans. 1* (1996) 2069.

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Closed-system fluorination of 4,4′-bipyridine followed by in situ addition of lithium triflate (to avoid isolation of the difluoride salt counterpart of **6**, which presumably will be explosive, like its mononuclear analogue *N*-fluoropyridinium fluoride [5]), gave the expected bis-$^{+}$NF salt **6** in 67% yield. The non-aromatic bis(*N*-fluoroammonium) triflates **4** and **5**, which are analogues of mono-$^{+}$NF members of the TEDA-based Selectfluor™ series of reagents [4,9], were isolated in greater than 85% and 80% yield respectively, following flow fluorination of the corresponding diquat salts (**10** and **11**) in acetonitrile at ca. −40 °C in the presence of lithium or potassium triflate. These starting materials were made from TEDA by conventional methods, as follows: $2N(CH_2CH_2)_3N + TsOCH_2CH_2OTs \rightarrow [N(CH_2CH_2)_3N^{+}\text{-}CH_2]_2\ 2TsO^{-}$ (**9**) $\rightarrow$ (with LiOTf) $[N(CH_2CH_2)_3N^{+}\text{-}CH_2]_2\ (TfO^{-})_2$ (**10**); $2N(CH_2CH_2)_3N + TfOCH_2CH_2CH_2OTf \rightarrow [N(CH_2CH_2)_3N^{+}\text{-}CH_2]_2CH_2\ (TfO^{-})_2$ (**11**).

A single attempt to prepare the bis(tetrafluoroborate) analogue of **6** by flow fluorination of the 4,4′-bipyridine–boron trifluoride complex $(F_3B\cdot NC_5H_4)_2$ (**12**) gave only the mono-$^{+}$NF product **7** (cf. closed-system fluorination of $F_3B\cdot N(CH_2CH_2)_3N\cdot BF_3 \rightarrow$ **1** ($X^{-} \equiv BF_4^{-}$) [1]). Not unexpectedly, the monomethylated derivative $4\text{-}NC_5H_4\text{-}C_5H_4N^{+}\text{-}CH_3\ TfO^{-}$ (**13**) of 4,4′-bipyridine gave only the mono-NF derivative **8** when fluorinated in a closed system in the presence of lithium triflate. Neither **7** nor **8** were obtained in analytically pure form (C, H, F and N determinations were performed), hence their identities rest on the results of NMR analyses (^{1}H, ^{19}F).

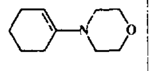
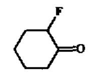
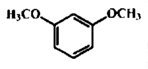
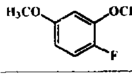
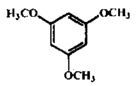
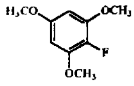
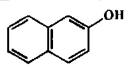
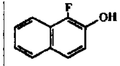
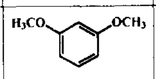
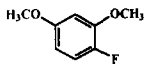
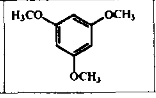
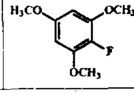
3. Electrophilic fluorination of organic substrates with NF compounds 5, 7 and 8

The results of a limited study of site-specific electrophilic fluorination reactions carried out with **5**, **7** and **8** are presented in Table 1. The substrates used were selected from lists of 'model molecules' normally employed to compare new 'F^{+}' transfer reagents with established reagents. Our principal aim was to assess qualitatively how reagents **5** and **8** (impure) compared with the analogous Selectfluor™ reagent $CH_3\text{-}{}^{+}N(CH_2CH_2)_3N^{+}\text{-}F\ (TfO^{-})_2$ (**15**) [4].

Fluorination of 1-morpholinocyclohexene and phenol with the 'double' Selectfluor-type reagent **5** gave, not unexpectedly, virtually the same results as with its mono-NF analogue **15**. However, experiments with anisole, which was employed previously as a test substrate to establish that **15** is less reactive than its chloromethyl analogue $ClCH_2\text{-}{}^{+}N(CH_2CH_2)_3N^{+}\text{-}F\ (TfO^{-})_2$ [4], clearly differentiated **8** and **15**; thus, with a 1:1 molar ratio of substrate:reagent at 80 °C in dry acetonitrile for 15 h, yields of a ca 1:1 mixture of *o*-fluoroanisole and *p*-fluoroanisole were shown by ^{19}F NMR analysis to be 55% and 100% respectively. Also, the more reactive substrate 2-naphthol underwent fluorination considerably more readily with **15** (a 71% yield of the 1-fluoro derivative was achieved at 20 °C in less than 1 h in CH_3CN) than with **8** (see Table 1).

Table 1

Electrophilic fluorinations carried out with $[F\text{-}{}^{+}N(CH_2CH_2)_3N^{+}\text{-}CH_2]_2CH_2\ (TfO^{-})_2$ (**5**), $4,4'\text{-}F_3B\cdot NC_5H_4\text{-}H_4C_5N^{+}\text{-}F\ BF_4^{-}$ (**7**), and $4,4'\text{-}CH_3\text{-}{}^{+}NC_5H_4\text{-}H_4C_5N^{+}\text{-}F\ (TfO^{-})_2$ (**8**)

NF Reagent[a]	Substrate[a]	Reaction Conditions[b]	Product(s)	yield/%, unchanged substrate/%[c]
5		20 °C overnight in CH_2Cl_2, acid (1M-HCl aq.) workup		57[d]; ND
5	C_6H_5OH	20 °C, 15 h in CH_3OH	*ca.* 1.5:1 2- and **4-FC_6H_4OH**	52[d]; ND
7		20 °C, 20 h in CH_3CN[e]		52; 35[f]
7		20 °C, 18 h in CH_3CN[e]		61[g]; ND
8	$C_6H_5OCH_3$	80 °C, 15 h in CH_3CN[e]	*ca.* 1:1 2- and **4-$FC_6H_4OCH_3$**	55[g]; ND
8		80 °C, 15 h in CH_3CN[e]		60[g]; ND
8		20 °C, 15 h in CH_3CN; then at 60 °C for 20 h[e]		40; 54[f]
8		20 °C, 18 h in CH_3CN[e]		50[g]; ND

[a] Reactant ratios equal or close to 1:1 (molar) were used on a 0.25–1.00 mmol scale, except in the case of **5** when the ratio was 0.5:1 (reagent:substrate).

[b] Conditions were not optimized.

[c] ND means not determined.

[d] Yield of isolated product.

[e] Carried out in a sealed (Rotaflo) tube under anaerobic conditions.

[f] Determined by GLC (calibrated) analysis.

[g] Determined by ^{1}H and/or ^{19}F NMR spectroscopy.

4. Experimental details

4.1. ^{19}F NMR data

Chemical shifts extracted from ^{1}H and ^{19}F NMR spectra are given in ppm (positive values downfield) from external Me_4Si and external CF_3CO_2H respectively.

4.2. Starting materials

Commercial samples (Aldrich) of triethylenediamine (TEDA), 4,4′-bipyridine, melamine, lithium and potassium triflate, triflic anhydride, methyl triflate, trifluoroacetic anhydride, ethylene glycol di-*p*-tosylate, propane-1,3-diol, and boron trifluoride etherate were used as received.

4.3. Fluorination apparatus and techniques

Closed-system fluorinations with neat fluorine at low pressure (less than or equal to 20 mmHg) were carried out as described in detail previously [7]. Flow fluorinations were performed with a ca. 10% (by volume) fluorine-in-nitrogen mixture using apparatus employed earlier for fluorinating aqueous substrates [6], except that the product cold traps were removed. Fluorine was generated electrolytically with an ICI-type fluorine cell [7]. Aldrich HPLC-grade acetonitrile or trichlorofluoromethane–chloroform mixtures were used as reaction solvents.

*4.4. 1,2-bis(4-aza-1-azoniabicyclo[2.2.2]oct-1-yl)ethane ditriflate (**10**)*

A stirred mixture of ethylene glycol ditosylate (7.40 g, 20.0 mmol), TEDA (4.48 g, 40.0 mmol) and dry acetonitrile (50 cm^3) was heated at 80 °C under reflux for 3 h, then cooled to room temperature and filtered to remove the 1,2-bis(4-aza-1-azoniabicyclo[2.2.2]oct-1-yl)ethane ditosylate (**9**) (5.70 g after being dried in vacuo, 9.60 mmol, 48%). Found: C, 56.3; H, 7.4; N, 9.4. Calculated for $C_{28}H_{42}N_4S_2O_6$: C, 56.6; H, 7.1; N, 9.4%. m.p. 270–272 °C. Treatment of a sample (3.00 g, 5.05 mmol) of this ditosylate in dry acetonitrile (50 cm^3) with lithium triflate (1.56 g, 10.0 mmol; the reaction mixture was stirred under nitrogen at room temperature overnight, then filtered to remove the lithium tosylate which precipitated and the filtrate evaporated) provided the corresponding ditriflate (**10**, n.c.) (1.84 g, 3.30 mmol, 67% after purification by dissolution in acetonitrile and reprecipitation with diethyl ether), m.p. 280–282 °C, δ_H (300 MHz, in D_2O) 3.30 (t, ring CH_2), 3.58 (t, ring CH_2), 5.18 (s, CH_2CH_2) ppm (relative intensity 3:3:1), δ_F (84.6 MHz, in D_2O) 0.2 ($CF_3SO_3^-$) ppm.

*4.5. 1,3-Bis(4-aza-1-azoniabicyclo[2.2.2]oct-1-yl)propane ditriflate (**11**)*

Dichloromethane (10 cm^3) containing propane-1,3-diol (3.04 g, 40 mmol) and pyridine (6.94 g, 88 mmol) was added dropwise to a stirred solution of triflic anhydride (24.8 g, 88 mmol) in cold (0 °C) dichloromethane (20 cm^3). The mixture was stirred at 0 °C for 30 min then filtered through a 4 cm bed of silica to remove pyridinium triflate. The filtrate was concentrated in vacuo at room temperature to provide a viscous orange liquid, presumed to be the di-ester $TfOCH_2CH_2CH_2OTf$ [10] (7.2 g, 21 mmol, 53%); this was diluted with dichloromethane (10 cm^3) and added dropwise to a stirred solution of TEDA (4.6 g, 41 mmol) in cold (0 °C) dichloromethane (20 cm^3), causing the immediate appearance of a white precipitate. After the addition was complete, the reaction mixture was stirred at room temperature for 3 h then filtered; the white precipitate thus recovered was washed with a small amount of dichloromethane, dried in vacuo, and shown by elemental analysis and NMR spectroscopy to be 1,3-bis(4-aza-1-azoniabicylo[2.2.2]oct-1-yl)propane ditriflate (**11**, n.c.) (11.2 g, 19.8 mmol, 49.5% based on propane-1,3-diol). Found: C, 36.0; H, 5.4; F, 20.3; N, 9.6. Calculated for $C_{17}H_{30}F_6N_4O_6S_2$: C, 36.2; H, 5.3; F, 20.2; N, 9.9%. m.p. 194 °C (decomp.), δ_H (300 MHz, in CD_3CN) 2.30 (m, $CH_2C\mathit{H}_2CH_2$), 3.15 (m, ring CH_2), 3.21 (m, $C\mathit{H}_2CH_2C\mathit{H}_2$), 3.35 (m, ring CH_2) ppm (relative intensity 1:6:2:6), δ_F (84.6 MHz, in CD_3CN) 0.0 ($CF_3SO_3^-$) ppm.

*4.6. 1-Methyl-4-(4-pyridyl)pyridinium triflate (**13**)*

A mixture of methyl triflate (0.45 g, 2.74 mmol) and 4,4′-bipyridine (0.43 g, 2.75 mmol) in HPLC-grade acetonitrile (15 cm^3), prepared at 0 °C under dry nitrogen, was stirred magnetically overnight (under N_2) then evaporated (Rotavapor). This gave a ca. 2:1 (by ^{1}H NMR analysis) mixture of the required monomethylated product (**13**) and the corresponding diquaternary salt (**14**), which were separated by heating the mixture under reflux with ethanol and then (without cooling) filtering off the insoluble 1,1′-dimethyl-4,4′-bipyridinium ditriflate (**14**, n.c.) (0.24 g, 0.5 mmol, 36%). Found: C, 34.7; H, 2.9; F, 23.2; N, 6.0. Calculated for $C_{14}H_{14}F_6N_2O_6S_2$: C, 34.7; H, 2.9; F, 23.55; N, 5.8%. m.p. 257 °C (decomp.), δ_H (300 MHz, in D_2O) 4.57 (s, $^+NCH_3$), 8.58 (d, 2,2′,6,6′-H), 9.10 (d, 3,3′,5,5′-H) ppm (relative intensity 3:2:2, $^3J_{HH}$ 6 Hz), δ_F (84.6 MHz, in D_2O) −0.20 ($CF_3SO_3^-$) ppm. Evaporation (Rotavapor) of the filtrate gave tolerably pure 1-methyl-4-(4-pyridyl)pyridinium triflate (**13**, n.c.) (0.50 g, 1.56 mmol, 57%). Found: C, 43.8; H, 3.5; F, 18.7; N, 8.4. Calculated for $C_{12}H_{11}F_3N_2O_3S$: C, 44.9; H, 3.4; F, 17.8; N, 8.75%. m.p. 135 °C, δ_H (220 MHz, in D_2O) 4.47 (s, $^+NCH_3$), 7.92, 8.40, 8.77, 8.92 (all $2H$ d) ppm, δ_F (84.6 MHz, D_2O) −0.10 ($CF_3SO_3^-$) ppm, m/z 322 ($(M+2)^+$, 1%), 171 ($(M\text{-}OTf)^+$, 2%), 157 ($C_{10}H_9N_2^+$, 14%), 156 ($C_{10}H_8N_2^+$, 100%).

5. Preparation of *N*-fluoro compounds

*5.1. 1,2-Bis(4-fluoro-1,4-diazoniabicyclo[2.2.2]oct-1-yl)ethane tetratriflate (**4**)*

Fluorine diluted with nitrogen (10% by volume of F_2) was passed slowly through a cold (ca. −40 °C) vigorously stirred solution of 1,2-bis(4-aza-1-azoniabicyclo[2.2.2]oct-1-yl)-ethane ditriflate (**10**, 1.65 g, 3.00 mmol) and lithium triflate (0.90 g, 6.00 mmol) in dry acetonitrile (200 cm^3). When uptake of fluorine slowed markedly (the exit gas was tested with damp KI paper), the reaction mixture was purged with nitrogen then filtered (microglass fibre paper) to remove lithium fluoride. Evaporation of the filtrate (Rotavapor) provided tolerably pure 1,2-bis(4-fluoro-1,4-diazoniabicyclo-[2.2.2]oct-1-yl)ethane tetratriflate (**4**, n.c.) (2.37 g, 2.68 mmol, 89%). Found: C, 23.7; H, 2.9; N, 6.5. Calculated for $C_{18}H_{28}F_{14}N_4O_{12}S_4$: C, 24.3; H, 3.2; N, 6.3%. m.p. 185–188 °C (decomp.), δ_H (300 MHz, in CD_3CN) 4.82 (t, ring CH_2), 5.00 (q, ring CH_2), 5.24 (s, CH_2CH_2) ppm (relative intensity 3:3:1), δ_F (80 MHz, in CD_3CN) 125.7 (broadened s, ^+NF), 0.15 (s, $CF_3SO_3^-$) ppm (relative intensity 1:6).

5.2. 1,3-Bis(4-fluoro-1,4-diazoniabicyclo[2.2.2]oct-1-yl)propane tetratriflate (5)

Flow fluorination of 1,3-bis(4-aza-1-azoniabicyclo-[2.2.2]oct-1-yl)propane ditriflate (**11**) (3.0 g, 5.3 mmol) in cold (ca. −40 °C) acetonitrile (200 cm^3) containing potassium triflate (1.99 g, 10.6 mmol), as described above (Section 5.1), gave, after filtration of the reaction solution and removal of solvent from the filtrate, a yellowish oil, which, when stirred with a small amount of a 1:1 v/v mixture of ethanol and diethyl ether, partly solidified. The white solid was separated by filtration, dried in vacuo, and identified as 1,3-bis(4-fluoro-1,4-diazoniabicyclo[2.2.2]oct-1-yl)-propane tetratriflate (**5**, n.c.) (3.8 g, 4.2 mmol, 80%). Found: C, 25.4; H, 3.6; F, 29.1; N, 6.2. Calculated for $C_{19}H_{30}F_{14}N_4O_{12}S_4$: C, 25.3; H, 3.3; F, 29.5; N, 6.2%. m.p. 169–171 °C, δ_H (220 MHz, in CD_3CN) 3.37 (m, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 3.62 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2$), 4.30 (m, ring CH_2), 4.70 (m, ring CH_2) ppm (relative intensity 1:2:6:6), δ_F (80 MHz, in CD_3CN) 125.8 (broadened s, $^+$NF), 0.20 (s, $CF_3SO_3^-$) ppm. The yield of this product (**5**) increased to 91% when the fluorination of **11** was repeated with neat fluorine at a pressure of 10–20 mmHg in a closed-system apparatus.

5.3. 1,1′-Difluoro-4,4′-bipyridinium ditriflate (6)

A cold (−78 °C) vigorously stirred solution of 4,4′-bipyridine (0.9, 5.8 mmol) in a 1.35:1.0 (by volume) mixture (200 cm^3) of trichlorofluoromethane and AnalaR chloroform was treated with neat fluorine at 10–20 mmHg pressure in a closed-system fluorinator [7] until uptake of the halogen became imperceptible (5 h). The unchanged fluorine was pumped out of the reactor via a KI trap [8] and the vacuum broken with dry nitrogen so that a cold (ca. −35 °C) solution of lithium triflate (1.8 g, 11.5 mmol) in dry acetonitrile (30 cm^3) could be injected into the reactor. The temperature of the reaction mixture was then allowed to rise to ca. −40 °C before ca. 150 cm^3 of solvent was removed in vacuo and the remaining mixture filtered. The insoluble material thus recovered was shaken with dry acetonitrile (50 cm^3) and the solution obtained (after filtration to remove the insoluble LiF present) evaporated (Rotavapor), leaving a yellowish solid. This residue was triturated with dry acetone to provide a white sample (recovered by filtration and washed with a small volume of acetone, then dried in vacuo) of 1,1′-difluoro-4,4′-bipyridinium ditriflate (**6**, n.c.) (1.9 g, 3.9 mmol, 67%). Found: C, 29.2; H, 1.7; F, 30.4; N, 5.7; S, 13.1. Calculated for $C_{12}H_8F_8N_2O_6S_2$: C, 29.3; H, 1.6; F, 30.9; N, 5.7; S, 13.0%. m.p. 134–135 °C, δ_H (300 MHz, in D_2O) 8.60 (m), 9.10 (m) ppm (relative intensity 1:1), δ_F (84.6 MHz, in D_2O) 122.2 ($^+$NF, computed for TFA by adding 76.6 to a measured δ_{CFCl_3} value of 45.6 ppm), −0.9 (s, $CF_3SO_3^-$) ppm, *m/z* 343 (top mass peak, (M-TfO)$^+$, 9%), 157 ($C_{10}H_8N_2^+$, 100%).

5.4. 1-Fluoro-4-(4-pyridyl)pyridinium-trifluoromonoborane tetrafluoroborate (7)

Flow fluorination (10% F_2 in N_2 by volume) of a cold (−35 °C) vigorously stirred solution of 4,4′-bipyridine-bis(trifluoromonoborane) (**12**, 8.56 g, 29.3 mmol; analysis C 40.7, H 2.9, F 36.9, N 9.6; calculated for $C_{10}H_8B_2F_6N_2$: C 41.1, H 2.7, F 39.1, N 9.6%; prepared in 94% yield by treating 4,4′-bipyridine with BF_3–Et_2O, cf. [11]), followed by evaporation of the reaction mixture, gave (according to ^{1}H and ^{19}F NMR analysis) a mixture of starting material (**12**) and the required product (**7**). The latter was extracted with cold acetonitrile to yield (after evaporation of MeCN and vacuum drying) 6.00 g (18.2 mmol, 62%) of impure 1-fluoro-4-(4-pyridyl)pyridinium-trifluoromonoborane tetrafluoroborate (**7**, n.c.). Found: C, 36.6; H, 3.2; F, 43.1; N, 7.6. Calculated for $C_{10}H_8B_2F_8N_2$: C, 36.4; H, 2.4; F, 46.1; N, 8.5%. m.p. 200–205 °C (decomp., the sample appeared to soften at ca. 170 °C), which was identified by NMR analysis δ_H (300 MHz, in CD_3CN) 8.32, 8.46, 8.84, 9.35 ppm (all 2*H* multiplets), δ_F (84.6 MHz, same solution) 125.5 (broadened s, $^+$NF), −72.7 (s, BF_3 and BF_4^-) ppm.

5.5. 1-Fluoro-1′-methyl-4,4′-bipyridinium ditriflate (8)

Closed-system fluorination (F_2 at 10–20 mmHg) [8] of 1-methyl-4-(4-pyridyl)pyridinium triflate (**13**, 0.40 g, 1.25 mmol) in cold (−35 °C) HPLC grade acetonitrile (50 cm^3) containing lithium triflate (0.20 g, 1.25 mmol) gave, after removal of LiF (by filtration) then solvent (by evaporation) from the product, an impure sample (0.50 g, 1.02 mmol, 82%; analysis C 28.6, H 2.3, F 28.2, N 4.9; calculated for $C_{13}H_{11}F_7N_2O_6S_2$: C 32.0, H 2.25, F 27.25, N 5.7%) of 1-fluoro-1′-methyl-4,4′-bipyridinium ditriflate (**8**, n.c.), m.p. 170 °C (decomp.) which was identified by NMR spectroscopy, δ_H (220 MHz, in CD_3CN) 5.21 (s, $^+NCH_3$), 9.25 (d, 2*H*), 9.45 (m, 2*H*), 9.73 (d, 2*H*), 10.30 (m, 2*H*), δ_F (84.64 MHz, same solution) 124.5 (broadened s, $^+$NF), −0.50 (s, $CF_3SO_3^-$) ppm.

5.6. Electrophilic fluorinations with N–F reagents 5, 7 and 8

Reactions were carried out using techniques described previously in reports on studies of *N*-fluoroquinuclidinium salts [7,8], NF-TEDA salts (Selectfluor$^{\mathrm{TM}}$ reagents) [4], and the *N*-fluorotrifluoromethylsulfonamido derivative of pentafluoropyridine [12]. No new organofluorine compounds were prepared, so the identities of all the products (see Table 1) and often the yields/isomer ratios rest on the results of ^{19}F NMR analysis.

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References

[1] R.E. Banks and M.K. Besheesh, *J. Fluorine Chem.*, *74* (1995) 165.

[2] R.E. Banks and E. Tsiliopoulos, *J. Fluorine Chem.*, *34* (1986) 281.

[3] T. Umemoto and K. Tomita, *Jpn. Kokai Tokkyo Koho JP 63-295610*, May 1987 (to Sagami Chemical Research Center and Onoda Cement Co.), *Chem. Abs.*, *110* (1989) 213695g.

[4] R.E. Banks, *U.S. Patent 5,086,178*, February 1992 (to Air Products and Chemicals Inc.), *Chem. Abs.*, *116* (1992) 194355b. R.E. Banks, S.N. Mohialdin-Khaffaf, G.S. Lal, I. Sharif and R.G. Syvret, *J. Chem. Soc., Chem. Commun.*, (1992) 595. R.E. Banks, M.K. Besheesh, S.N. Mohialdin-Khaffaf and I. Sharif, *J. Chem. Soc., Perkin Trans. 1*, (1996) 2069.

[5] See for example, T. Umemoto, K. Harasawa, G. Tomizawa, K. Kawada and K. Tomita, *Bull. Chem. Soc. Jpn.*, *64* (1991) 1081 and references cited therein.

[6] R.E. Banks, R.N. Haszeldine and J.P. Lalu, *J. Chem. Soc. C*, (1966) 1514.

[7] R.E. Banks, R.A. Du Boisson, W.D. Morton and E. Tsiliopoulos, *J. Chem. Soc., Perkin Trans. 1*, (1988) 2805.

[8] R.E. Banks and I. Sharif, *J. Fluorine Chem.*, *55* (1991) 207.

[9] G.S. Lal, Selectfluor^{TM} (F-TEDA-BF_4): a new broad-spectrum selective fluorinating agent. In R.E. Banks (ed.), *Fluorine in Agriculture*, Fluorine Technology Ltd, Manchester, 1994, Conference paper 16.

[10] C.D. Beard, K. Baum and V. Grakauskas, *J. Org. Chem.*, *38* (1973) 3673.

[11] R.E. Banks, M.K. Besheesh, S.N. Mohialdin-Khaffaf and I. Sharif, *J. Fluorine Chem.*, *78* (1996) 43.

[12] R.E. Banks and A. Khazaei, *J. Fluorine Chem.*, *46* (1990) 297.