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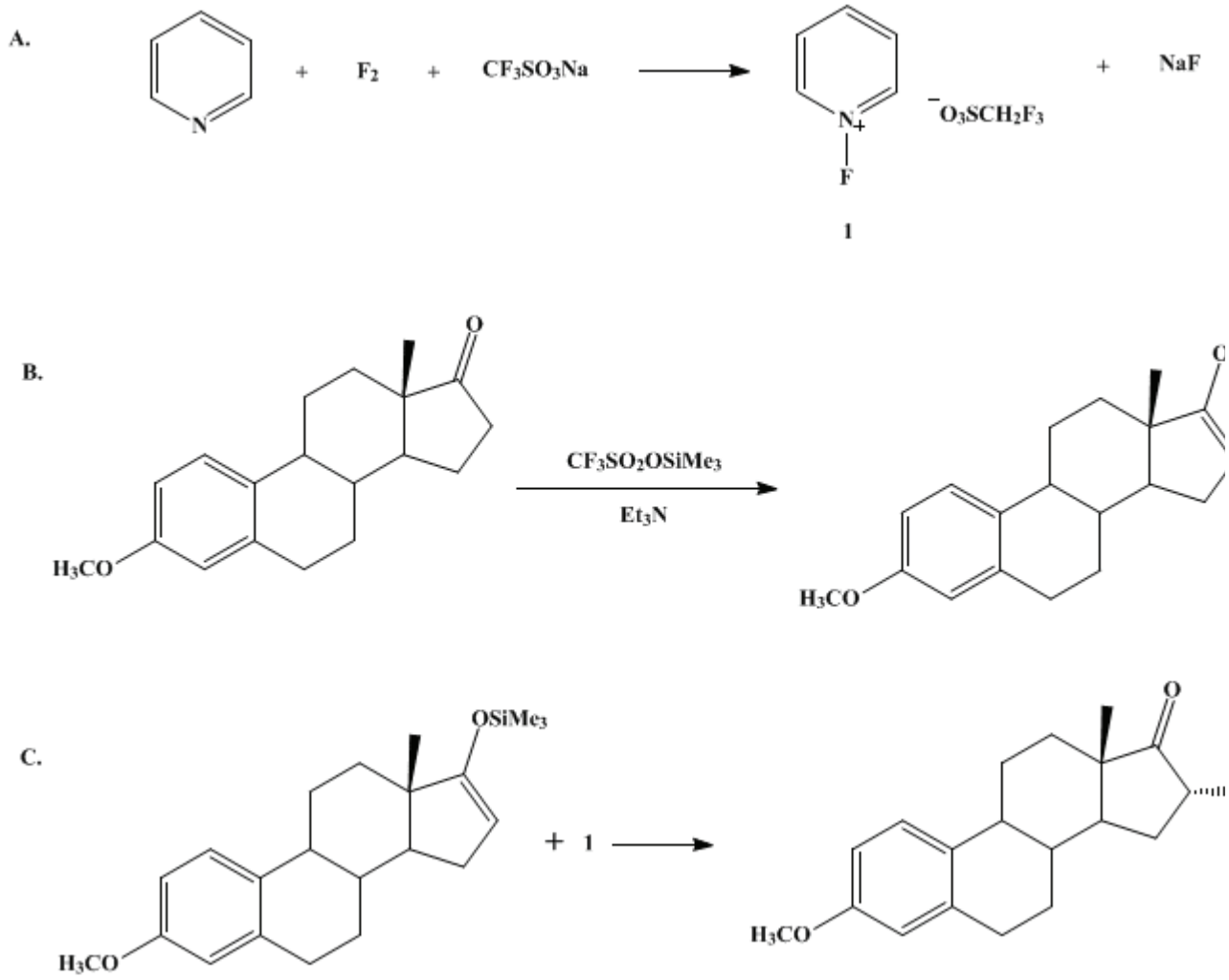
N-FLUOROPYRIDINIUM TRIFLATE: AN ELECTROPHILIC FLUORINATING AGENT

[Pyridinium, 1-fluoro-, salt with trifluoromethanesulfonic acid (1:1)]



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Checked by Shlomo Rozen and Bruce E. Smart.

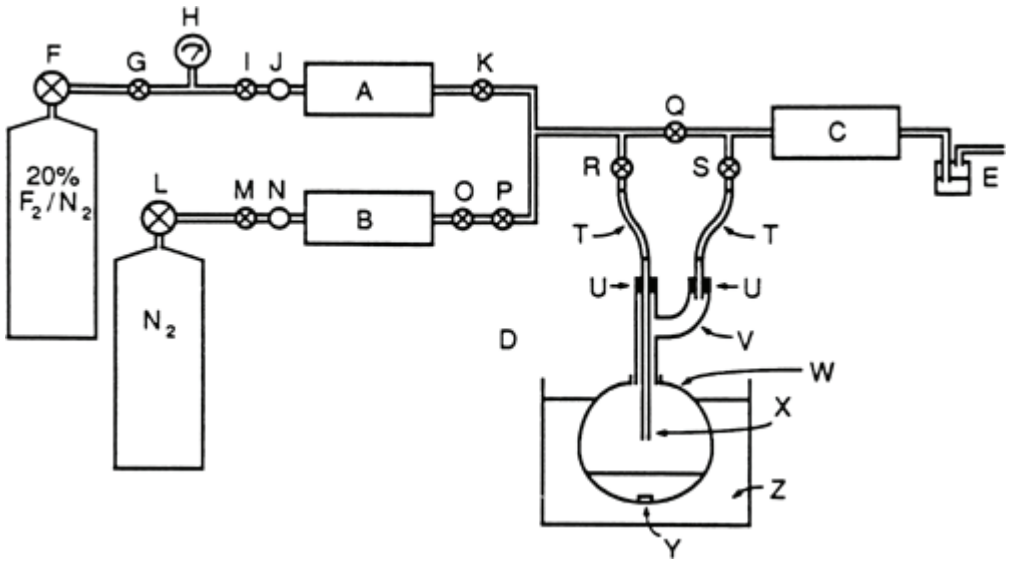
1. Procedure

Caution! Molecular fluorine is a very toxic and corrosive gas. The following reaction should be carried out in an efficient fume hood, and the experimenter should be familiar with the precautions necessary for safe handling of fluorine.[3] Since molecular fluorine diluted with an inert gas is much safer to handle than pure fluorine, the use of a fluorinel nitrogen mixture comprising no more than 20% fluorine is recommended.

A. *N-Fluoropyridinium triflate* ***(1).*** The reaction is carried out in the apparatus shown in Figure 1. The pressure regulator on the cylinder containing a mixture of 20% fluorine/80% nitrogen (Note 1), and the pressure gauge and flowmeter on the fluorine line are specifically designed for fluorine service (Note 2). The fluorine and nitrogen cylinders, pressure regulators, flowmeters, valves, and filters are connected with stainless-steel tubing. The Pyrex glass reaction vessel is connected to the metal tubing

via Viton® tubing, and the fluorine gas is introduced into the vessel through a Pyrex glass tube (7 mm o. d.). The gas outlet from the reaction vessel is connected to a granular alumina trap which consumes molecular fluorine.

Figure 1. A—flowmeter (Matheson model 7825); B—flowmeter (Hastings model CST); C—alumina trap; D—reactor system; E—bubble counter containing perfluorotributylamine; F—pressure regulator (Matheson model 63–5512); G, I, K, O, P—stainless-steel values; H—pressure gauge (Matheson model 63–5512); J, N—stainless-steel filters; L—pressure regulator for nitrogen; M, Q, R, S—brass valves; T—Viton tubing; U—Teflon corks; V—Pyrex Claisen Adapter; W—Pyrex flask; X—Pyrex tube; Y—Teflon-coated stirring bar; Z— −40°C cooling bath.



The 300-mL, round-bottomed reaction flask is charged with 4.74 g (0.06 mol) of pyridine (Note 3), 10.3 g (0.06 mol) of sodium triflate (Note 4), and 80 mL of dry acetonitrile (Note 5). The system is purged with nitrogen, and the reaction mixture is chilled and maintained at −40°C. The flow of dilute fluorine is started, and the flow rates from the nitrogen and fluorine cylinders are adjusted to introduce a 10% fluorine/90% nitrogen mixture at a rate of 90 mL/min just above the surface of the rapidly stirred solution (Note 6). When a total of 2.7 L of fluorine (0.12 mol) is introduced (Note 7), the flow of fluorine is discontinued and nitrogen only is flowed through the system at a rate of 45 mL/min for 30 min while keeping the reaction mixture at −40°C. The reaction mixture is then warmed to room temperature and filtered through a pad of Celite to remove the sodium fluoride. The filtrate is concentrated to dryness with a rotary evaporator without heating. The crystalline residue is washed with 30 mL of dry ethyl acetate to give 11.0–12.0 g (74–81%) of crude product, mp 178–181°C. The crude material is dissolved in 18 mL of dry acetonitrile at room temperature, and 36 mL of dry diethyl ether is added. The precipitated crystals are collected by filtration under nitrogen (Note 8) to give 10.0–10.3 g (68–70%) of pure *N*-fluoropyridinium triflate, mp 182°C (Note 9),(Note 10),(Note 11).

B. *3-Methoxy-17-trimethylsiloxy-1,3,5(10), 16-estratetraene.* A 125-mL, two-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer is purged with argon and charged with 6.8 g (0.024 mol) of estrone 3-methyl ether (Note 12), 50 mL of dry benzene, and 4.0 mL (2.9 g, 0.029 mol) of triethylamine. The solution is stirred, 4.9 mL (5.6 g, 0.025 mol) of trimethylsilyl triflate (Note 13) is added through a syringe, and the mixture is refluxed for 1.5 hr. The reaction mixture is allowed to cool to room temperature, whereupon it separates into two layers. Dry hexane (40 mL) is added, and the upper hexane–benzene layer is separated, washed successively with saturated sodium bicarbonate and water, and then dried over magnesium sulfate. The drying agent is removed by filtration, and the filtrate is transferred to a 125-mL, round-bottomed, tared flask. The solution is evaporated to a constant weight with a rotary evaporator, initially at water-aspirator pressure and then at 0.5–1 mm, to leave 8.6 g (100%) of pale-yellow enol trimethylsilyl ether. This material is used immediately in Part C without purification (Note 14).

C. *16α-Fluoro-3-methoxy-1,3,5(10)-estratrien-17-one (16α-fluoroestrone 3-methyl ether)*. The 125-mL, round-bottomed flask containing the enol silyl ether from Part B is purged with argon, and 50 mL of dry dichloromethane is added. *N*-Fluoropyridinium triflate **(1)** (6.5 g, 0.026 mol) is added in one portion, and the mixture is stirred at 20–25°C for 8 hr (Note 15). The reaction mixture is poured into water and extracted with three 60-mL portions of dichloromethane. The combined organic extracts are washed with saturated sodium bicarbonate and then with water, and dried over magnesium sulfate. The drying agent is removed by filtration and the solution is evaporated to dryness with a rotary evaporator. The resulting pale-yellow solid is column-chromatographed on silica gel (250 g, 60 × 4.5-cm column) using dichloromethane eluant (Note 16) to give 950 mg (14%) of estrone 3-methyl ether starting material and 4.8 g (66%) of 16α-fluoroestrone 3-methyl ether as a colorless solid, mp 157°C (Note 17), (Note 18),(Note 19).

2. Notes

1. A cylinder containing 20% fluorine/80% nitrogen was obtained from Air Products & Chemicals, Inc.
2. The checkers used a Matheson model B15F-679 single-stage pressure regulator, a model 63-5512 pressure gauge, and a model 7825 flowmeter. Information on equipment designed to handle fluorine can be found in the bulletin Tech-Brief TB-115, published by Matheson Gas Products.
3. Anhydrous pyridine (≥99%) packaged under nitrogen was purchased from Aldrich Chemical Company, Inc., and used without further purification.
4. Sodium trifluoromethanesulfonate (triflate) was prepared from trifluoromethanesulfonic acid (Aldrich Chemical Company, Inc.) as follows. A solution of 26.5 g (0.66 mol) of sodium hydroxide in 50 mL of water was added dropwise to 100 g (0.67 mol) of triflic acid chilled in an ice bath. The solution was concentrated to dryness with a rotary evaporator, and the residual solid was recrystallized from 65 mL of acetonitrile. The collected solid is dried at 80°C under vacuum for 24 hr to give 90 g of pure sodium triflate.
5. Acetonitrile was distilled from calcium hydride under nitrogen immediately before use.
6. A powerful magnetic stirrer was used to obtain a stirring rate of about 80 rps. The checkers also used a VIBRO-Mixer E1 (Chemapec, Inc.). The checkers found that the yield was unaffected if the fluorine is introduced below rather than above the surface of the solution.
7. A substantial excess of fluorine over the theoretical, equimolar amount is needed to complete the reaction because of the low solubility of fluorine. The amount of fluorine required can vary depending on the scale of reaction, the flow rate, and the efficiency of mixing.
8. The submitters carried out the filtration procedure in air. Filtration in wet air should be avoided.
9. The submitters report obtaining 13.2 g of crude product, mp 181–184°C, and 12.0 g (81%) of recrystallized material, mp 185–187°C.
10. The product obtained by the checkers is pure by NMR analyses. *N*-Fluoropyridinium triflate **(1)** has the following spectral properties: ^{1}H NMR (CD_3CN) δ: 8.32 (m, 2 H), 8.77 (m, 1 H), 9.33 (dd, 2 H, J = 16.7); ^{19}F NMR (CD_3CN) δ: 48.8 (bs, 1 F, N-F), −77.6 (s, 3 F, CF_3): IR (Nujol on NaCl plate) cm^{-1}: 3140 (s), 3120 (s), 3080 (s), 3050 (s), 1600 (m), 1485 (s), 1475 (s), 1330 (w), 1270 (s), 1250 (s), 1220 (s), 1200 (s), 1175 (s), 1160 (s), 1090 (m), 1055 (w), 1020 (s), 805 (m), 770 (s), 755 (m), 630 (s).
11. *N*-Fluoropyridinium triflate is stable and can be stored indefinitely under a dry atmosphere. It slowly decomposes in water. The submitters report that it has a half-life of 13 days in D_2O at room temperature.
12. Estrone 3-methyl ether [3-methoxyestra-1,3,5(10)-trien-17-one] was purchased from Sigma Chemical Company.
13. Trimethylsilyl triflate was obtained from Aldrich Chemical Company, Inc. and used without further purification.
14. The product exhibits the following partial spectral data: ^{1}H NMR ($CDCl_3$) δ: 0.21 (s, 9 H, CH_3Si), 0.87 (s, 3 H, 18-CH_3), 3.77 (s, 3 H, OCH_3), 4.53 (m, 1 H, 16-H). This silyl enol ether is sensitive to hydrolysis, and the submitters recommend that it be isolated in the same flask that is used for its subsequent reaction in Part C.
15. Crystals of **1** gradually disappear as the reaction proceeds, and the mixture turns orange and finally becomes homogeneous when the reaction is completed.
16. Each fraction was monitored by thin-layer chromatography on silica gel (Merck Silica Gel 60 F-254). The R_f values (dichloromethane) of the product and starting estrone 3-methyl ether are 0.53 and 0.40, respectively.
17. The product has the following characteristic spectral properties: ^{1}H NMR (360 MHz, $CDCl_3$) δ: 0.95

(s, 3 H, 18-CH_3), 3.77 (s, 3 H, OCH_3), 5.13 (dd, 1 H, J = 50.6, 7.3, 16 β-H), 6.64 (d, 1 H, J = 2.7, 4-H), 6.72 (dd, 1 H, J = 8.6, 2.7, 2-H), 7.19 (d, 1 H, J = 8.6, 1-H); ^{19}F NMR ($CDCl_3$) δ: −192.7 (m); IR (KBr) cm^{-1}: 2900, 2850, 1750, 1600, 1500, 1460, 1440, 1310, 1240, 1030, 1000: MS *m/e* (relative intensity) 304 (2.7), 303 (21.5), 302 (M^+) (100), 301 (3.7).

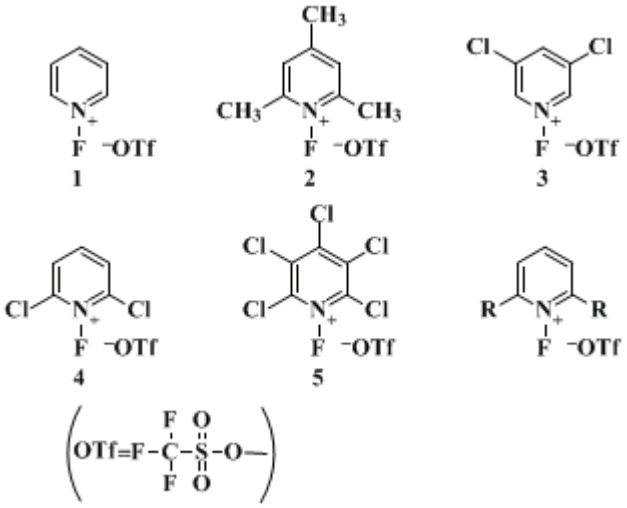
18. The product contains about 4% of the 16β-fluoroestrone epimer; ^{1}H NMR (360 MHz, $CDCl_3$) δ: 4.76 (dt, J = 50, 8; 16α-H); ^{19}F NMR ($CDCl_3$) δ: −185.3 (dd, J = 50, 22; 16β-F).

19. Identical yields of recovered starting material and product were obtained when Parts B and C were run on 2.5 times the scale. The submitters report obtaining a 78% yield of product, mp 145–149°C (recrystallized from ethyl acetate/hexane after chromatography) containing a small but unspecified amount of its epimer, along with 11% recovered starting material and 12% 2-pyridyl triflate, which is a decomposition product of **1**. Anal. calcd. for $C_{19}H_{23}O_2F$: C, 75.47; H, 7.66. Found: C, 75.52; H, 7.81.

3. Discussion

Electrophilic fluorinating agents such as F_2,[4] CF_3OF,[5] $FClO_3$,[6] CF_3COOF,[7] CH_3COOF,[8] XeF_2,[9] and $CsSO_4F$[10] require the use of special equipment and techniques because of their explosive, toxic, unstable, or hygroscopic nature. *N*-Fluoroperfluoropiperidine,[11] *N*-fluoropyridone,[12] and *N*-fluoro-*N*-alkyltoluenesulfonamides[13] are easy to handle, but their low reactivity limits the scope of their applications. Recently, a variety of fluorinating agents have been developed; *N*-fluoroquinuclidinium salts,[14] *N*-fluorobis[(trifluoromethyl)sulfonyl]imide,[15] *N*-fluorosultams,[16] *N*-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazole 1,1-dioxide,[17] perfluoro-[*N*-fluoro-*N*-(4-pyridyl)methanesulfonamide],[18] *N*-fluoro-*o*-benzenedisulfonimide,[19] *N*-fluorobenzenesulfonimide,[20] and *N*-fluorotriethylenediammonium salts.[21]

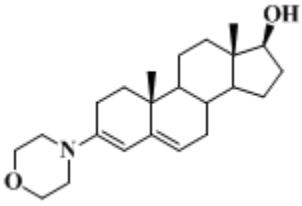
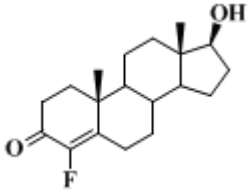
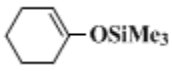
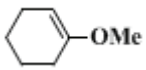
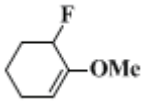
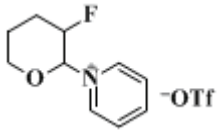
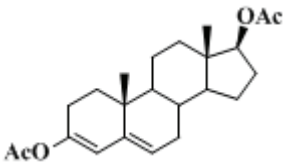
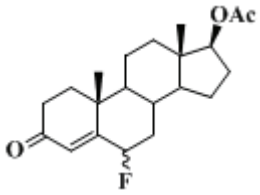
N-Fluoropyridinium trifluoromethanesulfonate (triflate) and its analogs are widely applicable, stable fluorinating agents with varying degrees of power and selectivity in fluorinations.[22 23 24 25 26 27 28 29 30 31] The procedure given here represents a general method for preparing substituted *N*-fluoropyridinium triflates. *N*-Fluoropyridinium salts with a different counter anion such as BF_4, PF_6, or ClO_4 can be prepared in good yields by the same method. However, depending on the ring substituents or counteranions, the modified or other methods should be adopted.[24,25] Counteranion-bound *N*-fluoropyridinium salts **6** and **7** are prepared in good yields by fluorination of the corresponding pyridinesulfonic acids with 10% F_2/N_2 in aqueous acetonitrile at −20°C.[24,25]



The reactivity of the *N*-fluoropyridinium salts can be adjusted by varying the substituents on the pyridine ring. Triflates **1–5**, whose fluorinating power increases in the order **2** < **1** < **3** < **4** < **5**, are the most generally useful reagents. Salts **6 and 7**, power order **6** < **7**, are the highly selective reagents. Other useful *N*-fluoropyridinium salts were described in the paper.[23] The reagents are all stable, crystalline materials and thus can be handled routinely. However, it should be noticed that the relative stability of the *N*-fluropyridinium salts decreases with increasing fluorinating power. Examples of fluorinations which illustrate their use are given in Table I. The weakest reagent, **2**, is most suited for fluorinating

reactive or easily oxidized compounds, such as carbanions, enamines, and sulfides, whereas the most potent reagents **4** and **5** are preferred for fluorinating alkenes and aromatic rings. Salt **1** of intermediate reactivity is effective with moderately electron-rich substrates, such as enol alkyl ethers, enol silyl ethers, and activated vinyl acetates. Salt **3** is useful with activated aromatic compounds but an elevated reaction temperature is required.

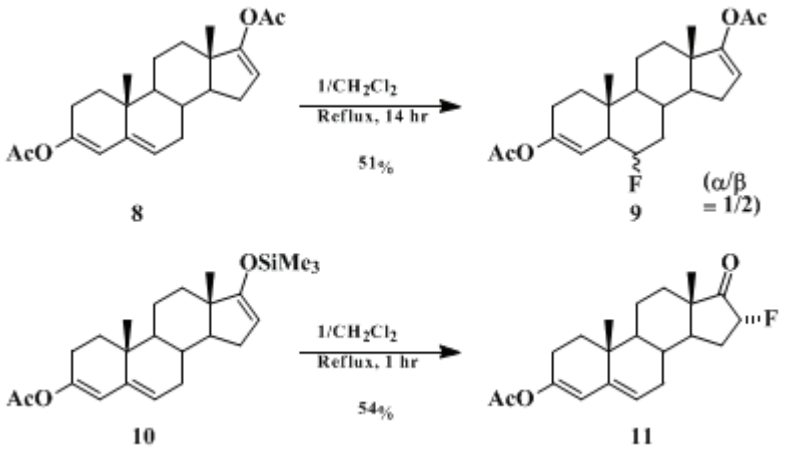
TABLE I
ELECTROPHILIC FLUORINATIONS WITH *N*-FLUOROPYRIDINIUM TRIFLATES

Substrate	Reagent[a]	Conditions	Product	Yield (%)[b]
n-$C_{12}H_{25}MgCl$	**2**	0°C, 30 min in Et_2O	n-$C_{12}H_{25}F$	75[c]
$NaCH(COOEt)_2$	**2**	0°C, 0.1 hr in THF	$CHF(COOEt)_2$	73
$CH_2(COOEt)_2$	**2**[d]	$AlCl_3$,[e] 80°C 24 hr in CH_2ClCH_2Cl	$CF_2(COOEt)_2$	76[f]
			p-$ClC_6H_4SCH_3$	**2**
	**2**	(1) −15°C, 1 hr in CH_2Cl_2/CH_3CN (1/4)		54
	 **1**			RT, 7 hr in CH_2Cl_2
	**1**	60°C, 30 min in CH_2ClCH_2Cl		63[f]
	**1**	Reflux, 7 hr in CH_2Cl_2		86[h]
	**1**	Reflux, 10 hr in CH_2Cl_2		71[f]
PhH	**5**	Reflux, 2 hr in CH_2Cl_2	Ph-F	48[f]
PhOH	**4**	RT, 5 hr in CH_2Cl_2	F-C_6H_4OH (*o:p*)	49[c,j] (1.3:1)
PhOH	**6**	Reflux, 1.5 hr in $CHCl_2CH_2Cl$	*o*-F-C_6H_4OH	45[c,j]
PhNHCOOEt	**3**	Reflux, 5.5 hr in CH_2ClCH_2Cl	F-$C_6H_4NHCOOEt$ (*o:p*)	51[j] (2.6:1)
PhNHCOOEt	**7**	Reflux, 72 hr in CH_2ClCH_2Cl	F-$C_6H_4NHCOOEt$ (*o:p*)	66[j] (12:1)
		RT, 1 hr in		

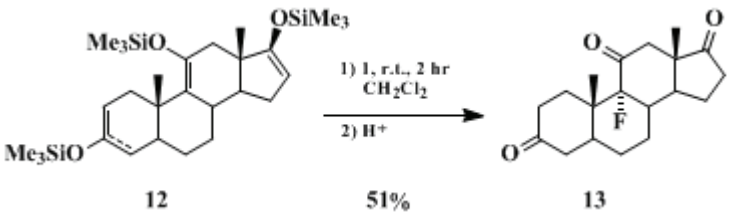
$PhCH{=}CH_2$	**5**	AcOH	$PhCH(OAc)CH_2F$	72

[a]Equimolar *N*-fluoropyridinium triflate unless noted otherwise.
[b]Isolated yields unless noted otherwise. Yield calculations based on the used amounts of triflates.
[c]GLPC yields.
[d]2 Equivalents of **2.**
[e]0.4 Equivalents of $AlCl_3$.
[f]^{19}F NMR yields.
[g]1.5 Equivalents of dihydropyran.
[h]*cis/trans* = 1/1.
[i]α/β = ½.
[j]A considerable amount of the starting substrate (16–38%) was recovered.
[j]α/β = ½.

N-Fluoropyridinium triflate shows high regioselectivity in its fluorinations, as evidenced by the results in Schemes 1 and 2. With steroids **8** and **10**, each having two reactive sites, **1** reacts to give exclusively the 6-fluoro steroid **9** and the 16-fluoro steroid **11**, respectively. Thus **1** can distinguish between a conjugated and a nonconjugated vinyl acetate, and between an enol silyl ether and a conjugated vinyl acetate in its fluorinations. The present procedure for converting estrone enol silyl ether to 16α-fluoroestrone also shows that **1** selectively reacts with an enol silyl ether moiety in the presence of an activated aromatic ring.



The fluorination of **12**, easily prepared from the corresponding triketo steroid, with an equimolar amount of **1** (Scheme 2) shows the remarkable ability of **1** to distinguish disubstituted from trisubstituted enol silyl ethers. The 9α-fluoro steroid **13** is produced in 51% yield (78% based on recovered triketo steroid) and the combined yield of the other products is only 4.6%.[23] It thus is apparent that **1** reacts almost exclusively with the trisubstituted enol ether moiety. The new, selective direct fluorination at the 9α-position holds considerable promise as a means to prepare biologically important 9α-fluoro steroids.[32]



Salt **6** or **7** affords exclusive or greatly preferential ortho-fluorination of phenol and aniline derivatives (Table I). Some fluorinations may be stereoselective. When allowed to react with 3, 17β-diacetoxy-3,5-androstadiene, **1** gives a 1 : 2 mixture of α- and β-fluorination at 6-position, while the

bulky salt **2** affords a 1 : 8.5 mixture of them, resulting from less hindered fluorination.[23] A diastereoselective fluorination of a chiral enolate with salt **2** was reported.[30]

With the increasing importance of organofluorine compounds in the development of new materials, pharmaceuticals, and agricultural chemicals, *N*-fluoropyridinium salts should find extensive use as mild and selective fluorinating agents.

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

fluorinel nitrogen

N-fluoro-o-benzenedisulfonimide

N-fluorobenzenesulfonimide

N-fluorotriethylenediammonium

9α-fluoro steroids

Pyridinium, 1-fluoro-, salt with trifluoromethanesulfonic acid (1:1)

Benzene (71-43-2)

ethyl acetate (141-78-6)

diethyl ether (60-29-7)

aniline (62-53-3)

acetonitrile (75-05-8)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

phenol (108-95-2)

Salt (7647-14-5)

nitrogen (7727-37-9)

pyridine (110-86-1)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

sodium fluoride (7681-49-4)

vinyl acetate (108-05-4)

dihydropyran

hexane (110-54-3)

vinyl (2669-89-8)

triethylamine (121-44-8)

argon (7440-37-1)

calcium hydride (7789-78-8)

9α-fluoro

Fluorine (7782-41-4)

triflate

trifluoromethanesulfonic acid,
triflic acid (1493-13-6)

silyl (13765-44-1)

trimethylsilyl ether (107-46-0)

silyl ether (13597-73-4)

trimethylsilyl triflate (27607-77-8)

N-fluoropyridinium,
N-fluropyridinium

sodium triflate,
Sodium trifluoromethanesulfonate (2926-30-9)

perfluorotributylamine (311-89-7)

estrone 3-methyl ether,
3-methoxyestra-1,3,5(10)-trien-17-one

16α-Fluoro-3-methoxy-1,3,5(10)-estratrien-17-one,
16α-fluoroestrone 3-methyl ether (2383-28-0)

16β-fluoroestrone

2-pyridyl triflate (65007-00-3)

estrone enol silyl ether

16α-fluoroestrone

17β-diacetoxy-3,5-androstadiene

N-Fluoropyridinium triflate,
N-Fluoropyridinium trifluoromethanesulfonate (107263-95-6)

N-Fluoroperfluoropiperidine (836-77-1)

N-fluoropyridone

N-fluoroquinuclidinium

N-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazole 1,1-dioxide (124170-23-6)

perfluoro-[N-fluoro-N-(4-pyridyl)methanesulfonamide]

3-Methoxy-17-trimethylsiloxy-1,3,5(10), 16-estratetraene