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Preliminary Note

N-HALOGENO-COMPOUNDS. PART 10. N-FLUOROQUINUCLIDINIUM TRIFLATE

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SUMMARY

Direct fluorination of quinuclidine at ca. -33 °C in acetonitrile containing lithium trifluoromethanesulphonate (triflate) gives N-fluoroquinuclidinium triflate (2) in excellent yield. Similar fluorination of quinuclidine in trichlorofluoromethane at -78 °C, followed by treatment of the resultant N-fluoroquinuclidinium fluoride (1) with trimethylsilyl triflate, also yields the new triflate, but in somewhat lower yield (80%). N-Fluoroquinuclidinium triflate (2) is much more convenient to use as an electrophilic fluorinating agent than the fluoride (1) owing to its non-hygroscopic nature.

N-Fluoroquinuclidinium fluoride (**1**) [1,2], a stable white solid obtainable in ca. 90% yield by direct fluorination of quinuclidine in trichlorofluoromethane at -78 °C, has aroused interest recently as a mild electrophilic fluorinating agent for organic substrates possessing carbanionic character [1,2]. Unfortunately, particularly from the viewpoint of using it to effect site-selective fluorination via alkali-metal derivatives or Grignard reagents, it is extremely hygroscopic. Wishing to convert it simply to a more easily-handled reagent with the same fluorinating characteristics, we have examined the effect of replacing the fluoride counterion with other anionic species, including BF_4^- [cf.3], Ph_4B^- [cf.4] and TfO^- ($CF_3SO_3^-$)[cf.3]. Conversion of **1** to its triflate analogue (**2**) proved to be the most straightforward approach and also solved the hygroscopicity problem.

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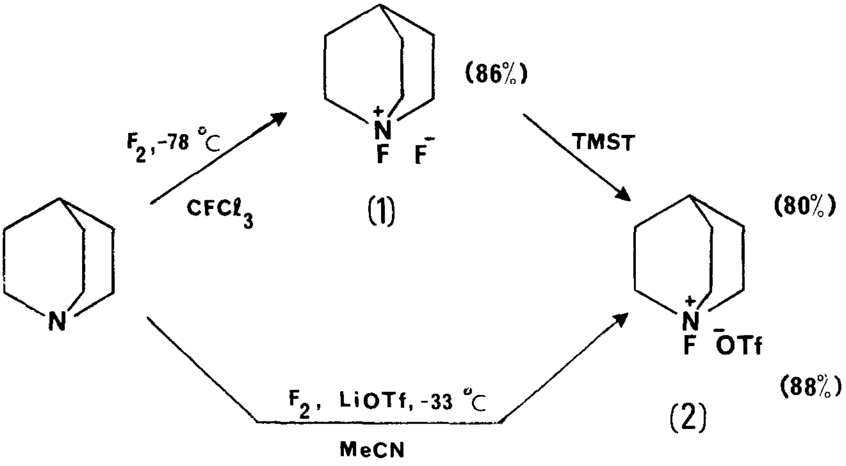
Analytically-pure (C,H,F,S and N) *N*-fluoroquinuclidinium triflate (2) was first obtained by treating the corresponding fluoride (1) with trimethylsilyl triflate in acetonitrile at room temperature. The reaction proceeded rapidly, and the new triflate (2) was isolated in 80% yield. A more efficient ('one-pot') procedure was then developed in which a solution of quinuclidine in cold (-30 to -35 °C) acetonitrile containing lithium triflate was treated with neat fluorine at low pressure to give the new organic triflate (2) directly in almost quantitative yield.



N-Fluoroquinuclidinium triflate (2) is a white, seemingly non-hygroscopic solid that chars without melting when heated to temperatures above 180 °C in air. It possesses the same fluorinating power as *N*-fluoroquinuclidinium fluoride (1) [1,2] but is far easier to use because it can be stored and manipulated normally, *i.e.* without having to take the rigorous precautions to exclude air demanded by the moisture-seeking nature of the fluoride (1).

Preparation of N-Fluoroquinuclidinium Triflate (2)

(*a*) From N-fluoroquinuclidinium fluoride (1)

Trimethylsilyl trifluoromethanesulphonate (2.98 g, 13.4 mmol) (Aldrich) was injected into a cold (-196 °C) evacuated Pyrex Rotaflo tube (200 cm^3) containing *N*-fluoroquinuclidinium fluoride (2.0 g, 13.4 mmol) in acetonitrile (60 cm^3) and a PTFE-coated magnetic stirrer follower. The tube was sealed and left at room temperature overnight with the stirrer activated. After removal of fluorotrimethylsilane (b.p. 18 °C; collected at -196 °C and identified by ^{19}F n.m.r. spectroscopy), the liquid remaining in the reaction vessel was evaporated (Rotavapor) and the solid residue was dissolved in the minimum quantity of AnalaR acetone. Addition of pure dry chloroform to the acetonic solution caused *N*-fluoroquinuclidinium triflate (2) to precipitate. This was recovered by filtration and dried to give the pure salt (nc) (3.0 g, 10.75 mmol, 80%) (Found : C, 34.4; H, 4.7; F, 27.2; N, 5.0; S, 11.1. $C_8H_{13}F_4NO_3S$ requires: C, 34.4; H, 4.7; F, 27.2; N, 5.0; S, 11.5%) {^1H n.m.r. spectrum almost identical with that of *N*-fluoroquinuclidinium fluoride (1) [2], and δ_F [(Perkin-Elmer R32 (84.6 MHz); soln. in D_2O; ext. CF_3CO_2H ref.] + 134.5 (broadened s, $\overset{+}{N}F$), +0.2 (s, $CF_3SO_3^-$) p.p.m. *m*/*z* (AEI MS902; EI at 70 eV) 148 (top mass peak) (10%), 130 [$C_7H_{13}FN^+$ (*M* - OTF), 100%]}.

In a more convenient manner, and using dry-box techniques (N_2 atmosphere), *N*-fluoroquinuclidinium fluoride (1) (2.40 g 16.11 mmole) was added to a magnetically stirred solution of trimethylsilyl triflate (3.58 g, 16.12 mmol) in dry acetonitrile (60 cm^3) contained in a flask equipped with a water-cooled reflux condenser fitted with a guard tube ($CaCl_2$). The mixture was stirred under nitrogen for 2 hours then evaporated (Rotavapor). The residual solid was purified as described above to give *N*-fluoroquinuclidinium triflate (2) (3.52 g, 12.6 mmol, 78%) with correct n.m.r. parameters.

(*b*) Directly from quinuclidine

Using exactly the same techniques and apparatus employed to prepare *N*-fluoroquinuclidinium fluoride (1) from quinuclidine and elemental fluorine at low pressure [2], fluorine (0.95 g, 25 mmol) was passed during 5.5 hours into vigorously stirred, cold (-30 to -35 °C), dry acetonitrile (200 cm^3) containing quinuclidine (Aldrich; 2.38 g, 21.4 mmol), lithium triflate (Aldrich; 3.345 g, 21.4 mmol), and powdered molecular sieve (5A; 0.5 g, to scavenge any HF formed via attack of F_2 on C-H bonds in the quinuclidine or the solvent). The product was filtered to remove lithium fluoride and molecular sieve then evaporated (Rotavapor); the residual solid was worked-up as in method (a) above to provide N-fluoroquinuclidinium triflate (**2**) (5.26 g, 18.85 mmol, 88%), shown to contain a trace of fluoride ion by ^{19}F n.m.r. spectroscopy [δ_F (soln. in D_2O) -51.2 (s) p.p.m.].

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1 R.E. Banks, R.A. Du Boisson, and E. Tsiliopoulos, J.Fluorine Chem., **32** (1986) 461.

2 R.E.Banks, R.A. Du Boisson, W.D. Morton, and E. Tsiliopoulos, J.Chem.Soc., Perkin Trans I, 1988, in the press.

3 T.Umemoto and K. Tomita, Tetrahedron Lett., **27** (1986) 3271. (N-fluoropyridinium triflates etc.).

4 I.V. Vigalok, G.G. Petrova, and S.G. Lukashina, J.Org.Chem. USSR, **19** (1983) 1203 (N-butyl-N-fluoro-2,2,6,6-tetramethylpiperidinium tetraphenylborate).