Fluorination of Nitro Compounds with Acetyl Hypofluorite

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Various types of nitro derivatives are fluorinated to form the $CFNO_2$ moiety in very good yields using acetyl hypofluorite (AcOF). The corresponding nitro anion, preferably prepared with NaOMe, is added quickly to a cold (−75 °C) $CFCl_3$ solution of AcOF, and although it contains water and acetic acid little or no protonation occurs because these proton donors are frozen. Many of the starting nitro derivatives were prepared by oxidizing the corresponding amino derivatives using the complex $HOF{\cdot}CH_3CN$, prepared by bubbling F_2 through aqueous acetonitrile.

The fact that nitro derivatives are useful building blocks in chemistry[1] has stimulated fluoroorganic chemists to try to prepare fluoronitro derivatives as well. Some of these compounds have pronounced biological activity[2] and others are used as building blocks in organic synthesis.[3] The number of methods for constructing these compounds, however, is limited. One of them consists of coupling reactions between two fragments, one of which contains the nitro moiety and the other the fluorine atom.[4] A unique example of irradiating TiO_2/AgF in the presence of a nitro compound also appeared recently.[5] Still, the main method employs perchloryl fluoride—$FClO_3$[6] —but unfortunately, it also leads to highly explosive byproducts.[7] One or two attempts to replace it with reagents from the N−F family have appeared,[8] but although some of these materials have the advantage of being "off the shelf" reagents, they are still very expensive and have to be made with F_2.

Acetyl hypofluorite, introduced to organic chemistry more than a decade ago,[9] possesses a much more active electrophilic fluorine than the reagents mentioned above. It is also much cheaper and easier to prepare, since it only requires the bubbling of dilute fluorine through a cold suspension of hydrated sodium acetate in either trichlorofluoromethane or acetonitrile[10] containing acetic acid. Unlike the previous methods it is also very useful tool for introducing the ^{18}F isotope into biologically active molecules for positron emitting tomography studying. In unrelated studies we have recently also developed a highly efficient methodology for oxidizing most type of amines to nitro derivatives using the $HOF{\cdot}CH_3CN$ complex, which like AcOF is easily made by bubbling dilute fluorine through aqueous acetonitrile.[11] These results prompted us to use acetyl hypofluorite for a systematic study targeted at making the rarely described *gem*-fluoronitro moiety.

We had seen in the past that the electrophilic fluorine in AcOF could substitute the acidic hydrogen of certain 1,3-dicarbonyl derivatives with fluorine without prior treatment with base.[12] This was found not to be the case with nitro derivatives, which proved to be unreactive toward AcOF, while reaction with elemental fluorine resulted mainly in tars. It was clear that in order to carry out this transformation, an anionic center would have to be created. However, AcOF is most conveniently produced in the presence of acetic acid and water, meaning that fluorination of anionic centers could be potentially problematic. There is always the possibility of carrying the gaseous acetyl hypofluorite, free of any proton donor, with a stream of nitrogen into the reaction vessel which contains the anion, but this procedure is somewhat tedious and part of the AcOF decomposes during the process. At low temperatures, however, the above proton donors are mostly frozen and we hoped that the extremely fast reaction between the anion and the AcOF in solution would shift the reaction toward the desired products.

Most of the optimization experiments were carried out with nitrocyclopentane (**1**) serving as a substrate. Sodium hydride or methoxide proved to be sufficiently strong bases for creating anions α to a nitro group. This obviated the need for the much stronger lithium bases which require strictly dry solvents, complicating the fluorination procedure. At first, in order to avoid possibly uncontrollable fast reactions, we added the trichlorofluoromethane solution of AcOF to the anion of **1**. Although the desired 1-fluoronitrocyclopentane (**2**) was formed, it was accompanied by a substantial amount of the starting material **1**. It seemed that the relatively long addition time offered a chance for the low concentration of protons in solution to compete with the electrophilic fluorine for the reaction with the anion. When, however, we added the anion to the cold (−75 °C) reaction vessel in which the AcOF was made, a gentle and yet immediate reaction took place, forming **2** in 85% yield. When the acetyl hypofluorite was prepared using an acetonitrile solution at −45 °C,[10] the yield of **2** was reduced to 75% since more acetic acid and water were

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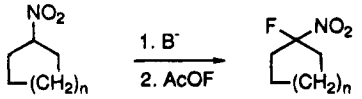
soluble in this solvent at that temperature than in trichlorofluoromethane at −75 °C.

As for bases, we also checked, in addition to sodium methoxide and sodium hydride, solid potassium carbonate. This proved suitable in some cases although it required much longer reaction times to form the anion in boiling methanol and the yields on average were 20% lower. The last variation we examined was a direct reaction with F_2 itself. As already mentioned, even fairly dilute fluorine has a destructive effect on **1**, but passing it through the anion solution did produce **2**, although in 55% yield only, along with considerable amounts of tars. Baum had already employed fluorine on some α-nitrocarbanions, producing the corresponding fluoronitro derivatives in yields mostly between 11 and 25%.[13]

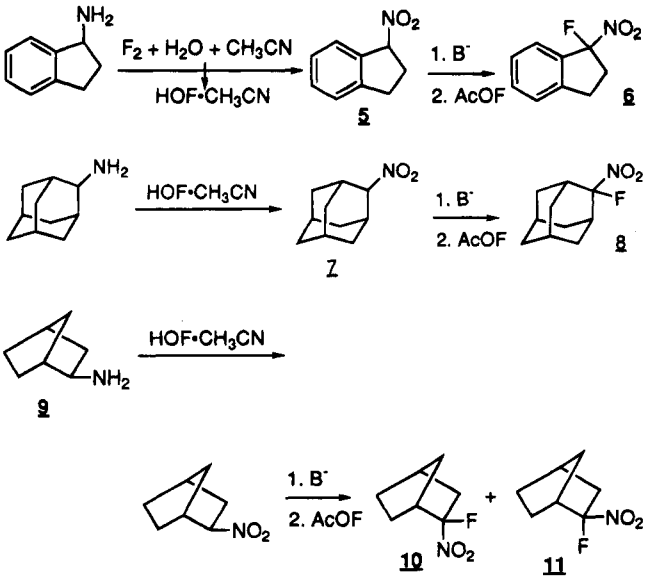
The advantage of AcOF over other fluorinating agents was not confined only to the ease of the reaction but also lay in the reaction yields. Nitrocyclohexane (**3**), for example, formed 1-fluoro-1-nitrocyclohexane (**4**) in 85% yield while the parallel reaction with perchloryl fluoride ($FClO_3$) gave only 42%.[14]

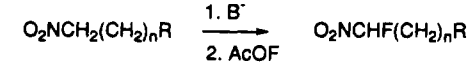


1 n = 1 **2**
3 n = 2 **4**

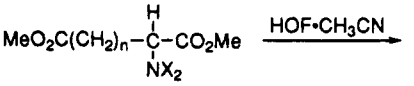
In order to explore the scope of the reaction, we reacted benzylic nitro compounds such as 1-nitroindane (**5**), which formed 1-fluoro-1-nitroindane (**6**), and bicyclic derivatives such as 2-nitroadamantane (**7**), converted to 2-fluoro-2-nitroadamantane (**8**), both in 90% yield. The fact that these reactions are very fast and do not require a large excess of AcOF helps to keep the aromatic ring in **5** intact, avoiding the potential aromatic fluorination for which acetyl hypofluorite is well known.[15] The two noncommercial starting nitro derivatives (**5** and **7**) were prepared in excellent yields via oxidation of the corresponding amino compounds with the HOF·CH_3CN complex.[11] A similar reaction sequence was performed with *exo*-2-aminonorbornane (**9**), which resulted eventually in a mixture of 65% *endo*-2-nitro-2-fluoronorbornane (**10**) along with an additional 6% of the exo-nitro stereoisomer **11**. The stereochemistry of **10** is mainly based on ^1H NMR which shows a doublet of $J_{HF} = 3$ Hz for the C-3 endo hydrogen and a doublet of doublets, $J_{HF} = 28$ Hz, $J_{HH} = 4$ Hz, for the C-3 exo hydrogen, coupling constants which fit the dihedral angles of the proposed configuration. In the ^{13}C NMR we find the C(6), as a doublet, $^3J_{CF} = 7$ Hz, which is typical of γ carbons in an anti configuration to the fluorine atom,[16] again in accordance to the structure of **10**. Such a stereochemical control preferring exo electrophilic attack is known in the bornane series.[17]

Straight chain aliphatic nitro derivatives react satisfactory as well: 1-fluoro-1-nitropentane (**13**) was prepared from 1-nitropentane (**12**) in quantitative yield (but with 70% mass balance). A somewhat surprising result was observed with molecules possessing two possible anionic centers, exemplified by ethyl 12-nitrododecanoate (**14**). After the treatment with excess of either sodium ethoxide or sodium hydride followed by addition of AcOF, only the fluoronitro derivative **15** was formed in 85% yield without any fluorine incorporation into the 2 position. This brings to mind the previously ascertained fact that AcOF reacts best with enolates only if they are prepared with LDA or similar strong bases under strictly dry conditions.[18] It does not mean, however, that the position α to the carboxylic group cannot be fluorinated. Dimethyl nitrosuccinate (**16**) and dimethyl nitroglutarate (**17**), obtained through the oxidation of dimethyl aspartate (**18**) and glutamate (**19**) with HOF·CH_3CN,[19] reacted smoothly to give the *gem*-fluoronitromethylene moiety α to the carboxylic group (**20** and **21**, respectively) in 85% yield.

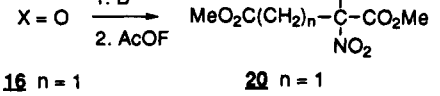




12 n = 4, R = H **13**
14 n = 10, R = COOEt **15**



18 X = H, n = 1
19 X = H, n = 2



16 n = 1 **20** n = 1
17 n = 2 **21** n = 2

Experimental Section

^1H NMR spectra were recorded with Bruker AC-200 and AM-360 WB spectrometers, with $CDCl_3$ as solvent and Me_4Si as internal standard. The proton broad band decoupled ^{13}C

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NMR spectra were recorded at 90.5 MHz. Here too, $CDCl_3$ served as a solvent and TMS as internal standard. The ^{19}F NMR spectra were measured at 338.8 MHz and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. Mass spectra were measured with a DuPont 21-491B instrument and GC/MS with a Varian-3400 equipped with a Finnigan Mat ITD-800 detector. High-resolution MS were carried out with a Finnigan Mat 711; IR spectra were recorded as neat films or in KBr pellets on a Nicolet 205 FTIR spectrophotometer.

General Procedure for Working with Fluorine. Fluorine is a strong oxidant and a very corrosive material. An appropriate vacuum line made from copper or monel in a well-ventilated area should be constructed for working with this element.[20] For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, simplifying the whole process. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple and we have had no bad experiences working with this element.

Preparation of AcOF and Its Reaction with α-Nitro Anions. A mixture of 15% F_2 in N_2 was bubbled into a cold (−75 °C) suspension of 10 g of AcONa·AcOH dispersed in 430 mL of $CFCl_3$ and 20 mL AcOH. The solvated salt could be made by leaving anhydrous AcONa over AcOH in a closed desiccator for at least 24 h. The amount of the AcOF thus obtained could be easily determined by reacting aliquots of the reaction mixture with aqueous KI solution and titrating the liberated iodine. After the desired concentration of AcOF was achieved, usually around 0.16 M (80 mmol), about 5 g of NaF was added in order to absorb, as much as possible, HF and other acids in solution. Meanwhile, about 100 mmol of MeONa in 15−20 mL of MeOH was reacted with 20−30 mmol of the desired nitro compound for 10 min at 65 °C. The solution of the α-nitro anion thus obtained was cooled to 0 °C and added in one portion to the stirred AcOF solution. After a few seconds the reaction was terminated by pouring the solution into 500 mL of thiosulfate solution, washing the organic layer with $NaHCO_3$ solution followed by water until neutral, drying the organic layer over $MgSO_4$, and finally evaporating the solvent. The products were usually either distilled or sublimed under reduced pressure. A few compounds have already been mentioned in the literature and in such cases only the physical properties which were not described previously are given.

General Procedure for Producing the Oxidant HOF·CH_3CN. Mixtures of 10% F_2 in nitrogen were used in this work. This mixture was passed at a rate of about 400 mL per minute through a cold (−10 °C) and vigorously stirred mixture of 400 mL of CH_3CN and 40 mL of H_2O. The formation of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. It is thus possible to achieve concentrations of more then a mol/L of the oxidizing reagent.

General Oxidation Procedure for Amines. About 20 mmol of an amine was dissolved in 20−40 mL of $CHCl_3$ or CH_2Cl_2. The mixture was added to the glass reactor containing 5 g of NaF and 60−70 mmol of the oxidizing HOF·CH_3CN in cold (−10 °C) aqueous CH_3CN (200 mL). The reaction was allowed to proceed for 10−15 min, and by that time most of the oxidizing compound had been consumed. It was neutralized with saturated sodium bicarbonate solution, poured into 1500 mL of water, extracted with CH_2Cl_2, and washed with $NaHCO_3$ and water until neutral. The organic layer was dried over $MgSO_4$, and the solvent was evaporated, preferably at room temperature. The crude product was usually purified by vacuum flash chromatography using Silicagel 60-H (Merck).

Fluorination of nitrocyclopentane (1) was performed as above. The resulting fluoro derivative **2**, distilled at 65 °C/30 mmHg, was obtained in 85% yield as an oil. IR: 1370, 1564 cm^{-1}. ^1H NMR: 2.6−2.1 (4 H, m), 1.93−1.87 (4 H, m). ^{19}F NMR: -114.8 (quintet, $J = 21$ Hz). ^{13}C NMR: 126.22 (d, $^1J_{CF} = 245$ Hz), 38.31 (d, $^2J_{CF} = 22.9$ Hz), 24.6. MS, *m/e*: 87 [(M − NO_2)$^+$], 67 [(M − NO_2 − HF)$^+$]. Anal. Calcd for $C_5H_8FNO_2$: C, 45.11; H, 6.06. Found: C, 45.61; H, 6.15.

Fluorination of nitrocyclohexane (3) was performed as described above. The resulting fluoro derivative **4**, which is known in the literature,[14] was obtained in 85% yield as an oil. IR: 1561 cm^{-1}. ^{19}F NMR: −128.24 (bs, $W_{h/2} = 88$ Hz). ^{13}C NMR: 119.84 (d, $^1J_{CF} = 240$ Hz), 33.55 (d, $^2J_{CF} = 23$ Hz), 23.89, 22.07. MS, *m/e*: 101 [(M − NO_2)$^+$], 81 [(M − NO_2 − HF)$^+$].

Oxidation of 1-aminoindane with HOF·CH_3CN to 1-nitroindan (5)[21] was achieved in 85% yield using the procedure described above. IR: 1365, 1552 cm^{-1}. ^1H NMR: 5.86 (1 H, dd, $J_1 = 7.7$ Hz, $J_2 = 2.4$ Hz). MS, *m/e*: 117 [(M − NO_2)$^+$].

Fluorination of 1-nitroindane (5) was performed as described above. The resulting fluoro derivative **6** was obtained in 90% yield as an oil. IR: 1360, 1563 cm^{-1}. ^1H NMR: 7.3−7.8 (4 H, m), 3.30 (2 H, m), 3.12 (1 H, m), 2.69 (1 H, m). ^{19}F NMR: −111.32 (bs). ^{13}C NMR: 145.4, 134.6, 132.4, 127.7, 125.5, 123.2, 125.08 (d, $^1J_{CF} = 243$ Hz), 36.4 (d, $^2J_{CF} = 21$ Hz), 29.5. MS (high res), *m/e*: [(M − NO_2)$^+$] calcd for C_9H_8F, 135.0610, found 135.0616, [(M − NO_2 − HF)$^+$]; calcd for C_9H_7, 115.0548, found 115.0556.

Oxidation of 2-aminoadamantane with HOF·CH_3CN to 2-nitroadamantane (**7**)[22] was achieved in 85% yield by the procedure described above. Mp: 166 °C (sublimation). ^1H NMR: 4.37 (1 H, bs). MS, *m/e*: 135 [(M − NO_2)$^+$].

Fluorination of 2-nitroadamantane (7) was performed as described above. The resulting fluoro derivative **8** was obtained in 85% yield and purified by sublimation at 90 °C/30 mmHg; mp 163 °C (closed capillary). IR: 1387, 1560 cm^{-1}. ^1H NMR: 2.75 (2 H, m), 2.07−1.76 (m, 12 H). ^{19}F NMR: −115.8 (bs, $W_{h/2} = 27$ Hz). ^{13}C NMR: 123.46 (d, $^1J_{CF} = 234$ Hz). MS, *m/e*: 153 [(M − NO_2)$^+$], 133 [(M − NO_2 − HF)$^+$]. Anal. Calcd for $C_{10}H_{14}FNO_2$: C, 60.29; H, 7.08; N, 7.03. Found: C, 60.23; H, 7.16; N, 6.79.

Oxidation of *exo*-2-aminonorbornane (9) with HOF·CH_3CN to *exo*-2-nitronorbornane[23] was achieved in quantitative yield by the procedure described above; oil. ^1H NMR: 4.40 (1 H, dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz). MS, *m/e*: 95 [(M − NO_2)$^+$].

Fluorination of *exo*-2-nitronorbornane was performed as described above. The resulting major fluoro derivative **10** was purified by sublimation at 90 °C/30 mmHg and obtained in 65% yield, mp 57 °C (closed capillary). IR: 1375, 1558 cm^{-1}. ^1H NMR: 2.73 (1 H, bd, $J = 10$ Hz), 2.57 (1 H, dd, $J_1 = 28$ Hz, $J_2 = 4$ Hz), 2.51 (1 H, d, $J = 3$ Hz). ^{19}F NMR: −107.9 (bd, $J = 28$ Hz). ^{13}C NMR: 126.8 (d, $^1J_{CF} = 245$ Hz), 46.8 (d, $^2J_{CF} = 21$ Hz), 41.3 (d, $^2J_{CF} = 19$ Hz), 38.02, 36.0, 26.2, 21.8 (d, $^3J_{CF\ (anti)} = 7$ Hz). MS, *m/e*: 113 [(M − NO_2)$^+$], 93 [(M − NO_2 − HF)$^+$]. Anal. Calcd for $C_7H_{10}FNO_2$: C, 52.83; H, 6.33; N, 8.8. Found: C, 52.77; H, 6.22; N, 8.3. The minor isomer **11** was only observed in GC/MS in 6% yield, but was not isolated.

Fluorination of nitropentane (12) was performed as above. The resulting fluoro derivative **13**,[24] distilled at 48 °C/11 mmHg, was obtained in 70% yield as an oil. IR: 1573 cm^{-1}. ^1H NMR: 5.82 (1 H, dt, $J_1 = 51$ Hz, $J_2 = 5$ Hz), 2.27−2.01 (2 H, m), 1.57−1.32 (4 H, m), 0.94 (3 H, t, $J = 7$ Hz). ^{19}F NMR: −147.5 (m). ^{13}C NMR: 111.2 (d, $^1J_{CF}$ 239 Hz), 32.82 (d, $^2J_{CF}$ 19 Hz), 24.7, 21.8, 13.5. MS, *m/e*: 89 [(M − NO_2)$^+$], 69 [(M − NO_2 − HF)$^+$].

Fluorination of ethyl nitrododecanoate (14) was performed as above. The anion of **14** was prepared using a 4-fold excess of NaH. A similar excess of AcOF was also used. The resulting fluoro derivative **15** was obtained in 85% yield as an oil and purified as fast as possible on a short basic alumina column using 5% EtOAc in petroleum ether. Prolonged absorption on alumina caused decomposition. IR: 1573, 1735 cm^{-1}. ^1H NMR: 5.81 (1 H, dt, $J_1 = 51$ Hz, $J_2 = 6$ Hz), 4.12 (2 H, q, $J = 7$ Hz), 2.29 (3 H, t, $J = 7$ Hz), 2.22−2.03 (m, 2 H), 1.68−1.21 (m, 18 H). ^{19}F NMR: −147.5 (m). ^{13}C NMR: 173.85,

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111.2 (d, $^1J_{CF}$ = 240 Hz), 60.13, 33.14 (d, $^2J_{CF}$ = 19 Hz). MS, *m/e*: 245 [(M − NO_2)$^+$]. Anal. Calcd for $C_{14}H_{26}FNO_4$: C, 57.73; H, 8.99. Found: C, 58.01; H, 9.25.

Fluorination of dimethyl nitrosuccinate (16)[19] was performed as described above. The resulting dimethyl 2-fluoro-2-nitrosuccinate (**20**) was obtained in 85% yield as an oil. IR: 1573, 1740, 1770 cm^{-1}. ^{1}H NMR: 3.95 (3 H, s), 3.70 (3 H, s) 3.60 (1 H, dd, J_1 = 21 Hz, J_2 = 7 Hz). ^{19}F NMR: −128.72 (t, J = 23 Hz). ^{13}C NMR: 165.6, 160.7 (d, $^2J_{CF}$ = 27 Hz) 110.6 (d, $^1J_{CF}$ = 254 Hz), 54.7, 52.7 38.8 (d, $^2J_{CF}$ = 21 Hz). MS (high res, CI), *m/e*: (M + 1)$^+$ calcd for $C_6H_9FNO_6$, 210.0413, found 210.0356.

Fluorination of dimethyl nitroglutarate (17)[19] was performed as described above. The resulting dimethyl 2-fluoro-2-nitroglutarate (**21**) was obtained in 86% yield as an oil. IR: 1573, 1770, 1745 cm^{-1}. ^{1}H NMR: 3.92 (3 H, s), 3.71 (3 H, s), 2.83 (2 H, m), 2.54 (2 H, m). ^{19}F NMR: −129.44 (t, J = 20 Hz). ^{13}C NMR: 170.95, 161.1 (d, $^2J_{CF}$ = 27 Hz), 113.1 (d, $^1J_{CF}$ = 252 Hz), 54.4, 52.0 29.1 (d, $^2J_{CF}$ 20 Hz), 26.51. MS, *m/e*: 224 (M + 1)$^+$, 192 [(M − OMe)$^+$], 177 [(M − NO_2)$^+$]. Anal. Calcd for $C_7H_{10}FNO_6$: C, 37.68; H, 4.52; N, 6.28. Found: C, 37.76; H, 4.48; N, 6.06.

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