Our proposed multiple-step addition–elimination mechanism for 1 also offers a plausible alternative explanation to certain anomalies noticed in the nitration of pyrene,[40,41] where unusually large amounts of dinitropyrenes, including the unexpected 1,3-dinitropyrene, are formed.

Although the synthetic applications of the nitration of PAH with NO_2 in organic solvents are attractive,[10,36,42] special attention should be given to the drying and choice of solvents, drying of the NO_2, temperature, and catalysts. As we have demonstrated, the operative reaction mechanisms are highly dependent on the experimental conditions.

Toxicological Implications. Fluoranthene (1) is one of the most abundant PAH in environmental samples.[43] The reaction of 1 with NO_2 is slower than with N_2O_5;[12,14] nevertheless, the reaction with NO_2 might be the most important contributor to the formation of 2NF due to the relatively higher concentrations of NO_2 in urban atmosphere.[44] There currently is evidence for a substantial contribution from a nonionic reaction pathway in atmospheric reactions to the total nitro-PAH that are in the urban environment.[4,8,9,13,14,45] The distribution of nitro-PAH obtained upon nitration with NO_2 under free-radical conditions (in solvents of low dielectric constant) may model the atmospheric (gas phase) reaction. For example, 2-nitrofluoranthene is one of the most important nitro-PAH in ambient polluted air,[46] and, as we have found, is the major product of the homolytic nitration of 1 with NO_2.[47] In contrast, 2-nitrofluoranthene is the only isomer not detected under nitrations mediated by the nitronium ion or a carrier thereof. The nitration of 1 with NO_2 under free-radical conditions also leads to the facile formation of highly mutagenic dinitrofluoranthenes.[15,48] Dinitrofluoranthenes have been detected as atmospheric pollutants; they display GC retention times similar to the more studied dinitropyrenes[41,49,50] and also have the same molecular weight and similar MS fragmentation patterns. Thus, what has previously been identified as dinitropyrenes by lower resolution gas chromatography may actually reflect the sum of dinitropyrenes and dinitrofluoranthenes.

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Supplementary Material Available: X-ray crystallographic data for 1,2-dinitrofluoranthene: complete tables of coordinates, bond distances and angles, coordinates for hydrogen atoms, and anisotropic thermal parameters (6 pages); listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(39) Squadrito, G. L.; Fronczek, F. R.; Watkins, S.; Church, D., F.; Pryor, W. A., manuscript in preparation.

(40) Ross, D. S.; Hum, G. P.; Schmitt, R. J., paper presented at the 192nd American Chemical Society National Meeting, Anaheim, CA, Sept 1986.

(41) A study on the nitration of pyrene with NO_2/N_2O_4 in nonparticipating solvents is currently in progress in our laboratories, Squadrito, G. L.; Wu, M.-D.; Church, D. F.; Pryor, W. A., unpublished results.

(42) Eberson, L.; Radner, F. Acc. Chem. Res. 1987, 20, 53–59.

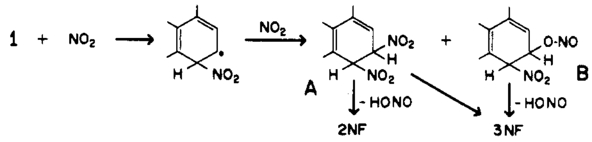
(43) Vogt, N. B.; Brakstad, F.; Thrane, K.; Nordenson, S.; Krane, J.; Aamot, E.; Kolset, K.; Esbensen, K.; Steinnes, E., *Environ. Sci. Technol.* **1987**, *21*, 35–44.

(44) Atkinson, R.; Winer, A. M.; Pitts, J. N., Jr. *Atm. Environ.* **1986**, *20*, 331–339.

(45) Another possible route to 2NF in polluted air is attack by the hydroxyl radical at C3, trapping of the resulting 2-hydroxy-2-hydro-3-fluoranthenyl radical by NO_2, and elimination of water.

(46) Greenberg, A.; Darack, F.; Wang, Y.; Harkov, R.; Louis, J.; Atherholt, T. Proc.-APCA (Air Pollution Control Association), 80th Annual Meeting, Vol. 6, pp 1–33.

(47) A referee has suggested that the 2NF/3NF ration could be controlled by trapping the 3-nitrofluoranthenyl radical either on nitrogen or oxygen by NO_2, as shown below.



However, nitro–nitrite addition intermediates lead to the formation of oxidation products (usually quinones or ketones), presumably via hydrolytic and/or thermolytic cleavages (for a review see, for example: Titov, A. I. *Tetrahedron* **1963**, *19*, 557–580). We have detected only traces of a fluoranthenequinone and of hydroxynitrofluoranthenes in a few experiments, suggesting that radical coupling of the 3-nitrofluoranthenyl radical with NO_2 at one of the oxygen atoms is not an important reaction pathway.

(48) Shane, B. S.; Squadrito, G. L.; Church, D. F.; Pryor, W. A., manuscript in preparation.

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(50) Tokiwa, H.; Otofuji, T.; Nakagawa, R.; Horikawa, K.; Maeda, T.; Sano, N.; Izumi, K.; Otsuka, H. In *Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust*; Ishinishi, N., Koizumi, A., McClellan, R. O., Stöber, W., Eds.; Elsevier: Amsterdam, 1986; pp 253–270.

Acyl Hypofluorites. A New Class of Organic Compounds

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Acyl hypofluorites, RCOOF, with hydrogen containing alkyl residues have been prepared from the corresponding carboxylic acid salts and F_2. For these compounds to have a reasonable stability, at least one electron-withdrawing group has to be attached to the α-position and lengthy chains should be avoided. All hypofluorites have an electrophilic fluorine which can readily react with an electron-rich double bond, as in tetralone enol acetate to give α-fluorotetralone.

There is considerable interest in compounds possessing the O–F bond since they are found to be strong electrophilic fluorinating agents. This bond is found mainly in two groups of compounds: fluoroxyperfluoro alkanes and perfluoroacyl hypofluorites. The first member of the fluoroxy family, CF_3OF, was initially prepared by Cady[1]

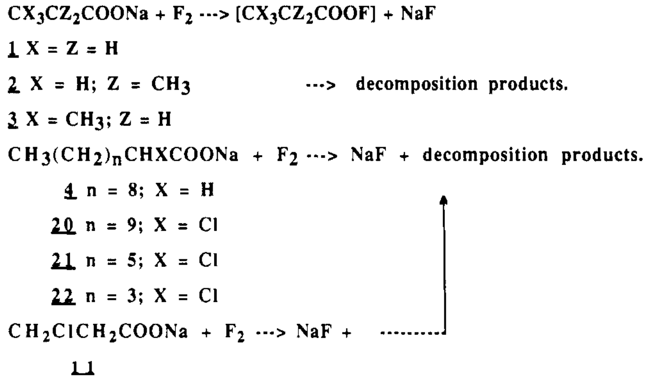
0022-3263/90/1955-2621$02.50/0

and later introduced by Barton to organic chemistry as an electrophilic fluorinating agent.[2] Shortly afterward CF_3OF and to a lesser extent CF_3CF_2OF[3] became subjects for numerous electrophilic as well as radical fluorination studies.[4] At the same time several other hydrogen-free fluoroxy compounds had been prepared and found to be stable for years to room temperature providing no external radical initiation took place.[5]

The perfluoroacyl hypofluorites did not receive as much attention. Again, Cady was the first to prepare and isolate CF_3COOF,[6] but during the following 15 years nobody reported it in organic chemistry. Some years ago we "rediscovered" this and some higher hypofluorites, prepared them by an easier procedure, and used them in organic and polymer chemistry.[7,8] The last use emphasizes the fact that radical decomposition of hypofluorites, $R_fCOOF \rightarrow R_f^\bullet + F^\bullet + CO_2$, is considerably easier then that of the fluoroxy derivatives.

It was generally accepted that the O–F-containing compounds derive their stability, low as it may be, from their perfluorinated alkyl chain. For instance, the presence of a single hydrogen as in CHF_2CF_2OF causes a rapid decomposition even at 0 °C.[9] The stability was mainly attributed to the electron-withdrawing power of the perfluoroalkyl group which would tend to strengthen the oxygen fluorine bond and also to the uniform fluorine "shield" protecting the carbon frame from radical attacks which might originate in the weak O–F moiety.[10] Such notions, widely accepted for many years as "common knowledge", discouraged chemists from a second, harder look into the matter. Some years ago, however, we succeeded in preparing for the first time the now widely used acetyl hypofluorite[11] and demonstrated that, despite its lack of perfluoroalkyl, it is stable enough to be employed in many chemical reactions.[12] Later it was unequivocally shown by us and Appelman that AcOF is indeed a real molecule[13] and the overall effect is not caused by just a series of consecutive reactions each contributing the elements of fluorine and the acetoxy group.[14] We report here on our efforts to make some new hypofluorites with various hydrogen-containing alkyl groups and at the same time determine the factors which can stabilize such compounds to a degree that they can be used in fruitful organic syntheses.

Following the successful preparation of AcOF from sodium acetate, the next natural step was to test the reaction of sodium propionate (**1**) with fluorine, with or without the presence of water and propionic acid.[15] The reaction produced only traces of an oxidizing hypofluorite and eventually, after adding slightly more than 1 molar equiv of fluorine, only sodium fluoride could be isolated and identified. It is reasonable to assume that the first step is indeed the formation of propionyl hypofluorite, but since the fluorine which is weakly bound to the oxygen atom can be in conformations where it is in close proximity to a hydrogen, it can react with it and eliminate the very stable HF. We hoped at first to avoid this decomposition pathway by replacing either the α- or the β-hydrogens with methyl groups. However, reacting sodium pivalate (**2**) or sodium *tert*-butylacetic acid (**3**) with fluorine afforded again no detectable oxidizing compounds, and only a quantitative formation of sodium fluoride and fragmentation of the alkyl radical to very volatile components was observed. This fragmentation is also evident when sodium undecanoate (**4**) is treated with fluorine. Attempts to identify nonvolatile compounds clearly showed that derivatives such as fluorodecane were not formed.


$CX_3CZ_2COONa + F_2$ ---> $[CX_3CZ_2COOF] + NaF$

1 X = Z = H

2 X = H; Z = CH_3 ---> decomposition products.

3 X = CH_3; Z = H

$CH_3(CH_2)_nCHXCOONa + F_2$ ---> NaF + decomposition products.

4 n = 8; X = H

20 n = 9; X = Cl

21 n = 5; X = Cl

22 n = 3; X = Cl

$CH_2ClCH_2COONa + F_2$ ---> NaF +

11

When, however, the α-hydrogens were replaced by chlorine atoms and sodium 2,2-dichloropropionate (**5**) was reacted with fluorine, a considerable amount of the oxidative 2,2-dichloropropionyl hypofluorite (**6**) was formed. This was then reacted at −78 °C with the enol acetate of tetralone (**7**) and the product, α-fluorotetralone (**8**), was obtained in 85% yield. This is typical of a reaction between any electrophilic fluorinating agent and enol acetates[16] and supports the existence of the O–F bond. An additional proof for the formation of the hypofluorite **6** could be found in its low-temperature ^{19}F NMR spectrum which displays a sharp singlet at +134 ppm, a characteristic signal of the O–F bond.

The next step was aimed at finding whether it was necessary to replace all the hydrogens in the α-position. We reacted, therefore, sodium 2,3-dichloropropionate (**9**) with fluorine with results similar to the previous case: the resulting hypofluorite **10** was stable enough for several hours at −78 °C[17] and performed the transformation **7** → **8** in 80% yield. We soon found that the second chlorine atom, on the β-carbon, does not play an important role in stabilizing the hypofluorite moiety. Thus sodium 3-chloropropionate (**11**) did not produce any oxidizing material when treated with F_2, but its isomer sodium 2-

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(6) Gard, G. L.; Cady, G. H. *Inorg. Chem.* **1965**, *4*, 594.

(7) (a) Rozen, S.; Menahem, Y. *J. Fluorine Chem.* **1980**, *16*, 19. (b) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672.

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(14) Such reactions are well known: thus a mixture of an *N*-haloamide and HF is a source for adding the elements of [X,F] across double bonds (Olah, G. A.; Nojima, M.; Kerekes, I. *Synthesis* **1973**, 780. Alvernhe, G.; Laurent, A.; Haufe, G. *Synthesis* **1987**, 562), while reacting CF_3OF with olefins in the presence of MeOH produces eventually the corresponding [MeO,F] adducts (Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Pechet, M. M. *J. Chem. Soc. Perkin Trans. 1* **1977**, 2604).

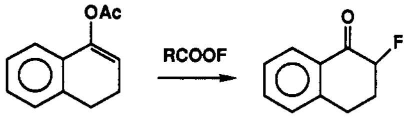
(15) The reason for the addition of the propionic acid and water is that adding acetic acid to AcONa greatly enhances the efficiency of the AcOF production. The corresponding acid and the water have also an essential role in directing the reaction toward hypofluorite formation rather than fluorooxy compounds. See discussion in refs 3a and 7.

(16) Rozen, S.; Lerman, O. *J. Am. Chem. Soc.* **1979**, *101*, 2782.

(17) The stability is checked by monitoring the oxidizing power of the hypofluorite which is determined iodometrically.

chloropropionate (**12**) reacted quickly with fluorine to give the relatively stable hypofluorite **13**, which also passed the test of fast reaction with tetralone enol acetate to give **8** in higher than 80% yield. Similarly, substituting only one of the α-hydrogens with chlorine was found to be enough to give stability to 2-chlorobutyryl hypofluorite (**14**), which was obtained from the corresponding sodium salt (**15**) and behaved similarly to the above hypofluorites.

Chlorine, however, is not the only substituent at the α-position enabling the formation of relatively stable hypofluorites. Sodium 2-nitrobutyrate (**16**) reacted quite efficiently with F_2 to form the hypofluorite **17**, as did monosodium monoethyl 2-ethylmalonate (**18**), which produced the corresponding hypofluorite **19**. Both **17** and **19** produced the expected α-fluoro ketone **8** from the enol acetate **7** in higher than 85% yield.



7 8

$CH_2ZCXClCOONa + F_2$ ---> $CH_2ZCXClCOOF$

5 X = Cl; Z = H	6 X = Cl; Z = H
9 Z = X = Cl	10 Z = X = Cl
12 Z = X = H	13 Z = X = H

$CH_3(CH_2)_nCHXCOONa + F_2$ ---> $CH_3CH_2CHXCOOF$

15 n = 1; X = Cl	14 n = 1; X = Cl
16 n = 1; X = NO_2	17 n = 1; X = NO_2
18 n = 1; X = COOEt	19 n = 1; X = COOEt
23 n = 2; X = Cl	25 n = 2; X = Cl
24 n = 2; X = COOEt	26 n = 2; X = COOEt

An important contribution to the stability of the O–F bond is obviously the electronegative group at the 2-position, but it seems that this is not the sole factor which has to be considered. Apparently another important point is the proximity in space of the other hydrogen atoms to the oxygen bound fluorine. Thus, reacting sodium α-chlorodecanoate (**20**) with fluorine does not produce any long-lasting oxidizing material, although the salt is fully consumed. Similarly with shorter chains of 8 or even 6 carbons, i.e. sodium α-chlorooctanoate (**21**) and -hexanoate (**22**), there are numerous conformations where the oxygen-bound fluorine can be very close to one of the chain hydrogens. It seems that with our reaction conditions, a five-carbon chain is the upper limit where hypofluorites with a monosubstituted alkyl residue can have a synthetically useful life time. Indeed, sodium α-chloropentanoate (**23**) and monosodium monoethyl propylmalonate (**24**) react successfully with fluorine to produce the corresponding hypofluorites (**25** and **26**) though in somewhat lower yield than with the previously discussed shorter chain homologs. What is more, their reaction with the enol acetate **7** is also less efficient, and the yield of the fluoro ketone **8** is only 40–50%. The lower yields reflect the lower stability of these five-carbon hypofluorites, where easy decomposition is a competitive route even to the fast reaction with an electron-rich enolacetate.

In conclusion, it seems that hydrogen-containing hypofluorites, other than AcOF, can be made and used in organic synthesis contrary to the general belief. The two stabilizing factors contributed by the perfluoroalkyl moiety, namely strengthening the O–F bond and shielding the carbon skeleton from possible radical attack, are definitely important. However there is enough tolerance to accommodate some variations in the chain attached to the hypofluorite. It seems that a single electron-withdrawing group such as chlorine, nitro, or carbethoxy is enough to strengthen the O–F bond, and, at −78 °C, the hydrogens on the first four carbons are not readily accessible for intramolecular radical HF elimination.

Experimental Section

^{1}H NMR spectra were recorded with a Bruker WH-360 spectrometer at 360 MHz with $CDCl_3$ as a solvent and Me_4Si as an 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. Since the hypofluorites were prepared in $CFCl_3$, their ^{19}F NMR spectra were measured after selectively suppressing the intense solvent signal using the 1331 sequence.[18]

General Fluorination Procedure. A description of the setup and the procedure for working with elemental fluorine has previously been described.[3a,7] It is worth stressing that F_2 and RCOOF should be treated with care, since they are strong oxidizers. The work should be conducted in an efficient hood or in a well-ventilated area. The toxicities of the various RCOOF compounds are not known, but some of the fluoroxy reagents are suspected to be strong poisons. If elementary precautions are taken, work with fluorine and its derivatives is safe and relatively simple. In the past we have had no bad experience working with this element.

General Procedure for Generating the Hypofluorites. A sodium salt (70 mmol) was mixed well with 30 mmol of the corresponding acid and 2 mL of water,[15] suspended in 400 mL of $CFCl_3$, cooled to −78 °C, and stirred well. About 80 mmol of fluorine diluted with nitrogen[19] (10% F_2/N_2) was then bubbled slowly through this suspension. The amount of the resultant hypofluorite was determined by reacting aliquots of the reaction mixture with aqueous KI and titrating the liberated iodine with thiosulfate. Usually 20–40 mmol of the hypofluorites were obtained, representing 25–50% yield based on the amount of the fluorine passed. Most of the salt was usually consumed and eventually converted into NaF. One should bear in mind though, that yields based on F_2 can vary greatly, since fluorine is not soluble in $CFCl_3$ and the reaction depends on the efficiency of dispersing the gas bubbles and the mixing of the suspension. We have found that both problems can be addressed quite efficiently by using a vibromixer with a hollow shaft equipped with a stirrer disk, both purchased from Chemap AG.

Fluorination of Tetralone Enol Acetate.[7a,16] A cold (−78 °C) CH_2Cl_2 solution of the enol acetate **7** was added in one portion to the hypofluorite solution (in excess by 20% to **7**). The mixture was stirred for 2 min, poured into thiosulfate solution, washed with water until neutral, and dried, and the solvent was evaporated. The resulting α-fluorotetralone was compared with an authentic sample.

Registry No. **5**, 127-20-8; **6**, 125973-26-4; **7**, 19455-84-6; **8**, 71019-06-2; **9**, 91999-76-7; **10**, 125973-27-5; **12**, 16987-02-3; **13**, 125973-28-6; **14**, 125973-29-7; **15**, 91778-96-0; **16**, 125973-25-3; **17**, 125973-30-0; **18**, 117643-93-3; **19**, 125973-31-1; **23**, 112812-47-2; **24**, 117643-94-4; **25**, 125973-32-2; **26**, 125973-33-3.

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(18) Turner, D. L. *J. Magn. Reson.* **1983**, *54*, 146.

(19) We found it more convenient to prepare our own mixtures of F_2/N_2 by charging a secondary cylinder with the appropriate amounts of F_2 and N_2. Passivated gauges for fluorine can be purchased from Matheson and Air Products. An infrequent user, however, may find it more convenient to purchase already premixed F_2/N_2 mixtures supplied also by the above companies.