velocity of the reaction of 1-**Br** at infinite [Br^-], where the solvolysis reaction would proceed solely by the capture of the ion-pair intermediate [2·Br^-]. This limiting velocity is only 0.06% (±0.02%) of the value of k_{solv} = 0.049 s^{-1} for the solvolysis reaction of 1-**Br** in the absence of bromide ion.

The substitution of bromide ion for perchlorate ion is expected to destabilize **2** relative to 1-**Br** because of the specific bromide ion salt effect (see above). This would be expected to lead to a decrease in k_{calc} for the reaction of 1-**Br** through the carbocation intermediate **2**. There is a 42% decrease in the observed first-order rate constant for the solvolysis of 1-**I** when 5.00 M NaBr is substituted for $NaClO_4$ at I = 6.00 ($NaClO_4$). If there were a similar specific bromide ion salt effect on k_{calc} (Table I), then (k_{obsd}–k_{calc}) would be increased to 9.0 × 10^{-5} s^{-1}.

The magnitude of (k_{obsd}–k_{calc}) at a given concentration of bromide ion depends on the association constant for formation of the ion pair from free ions ($K_{ass} = k_d/k_{-d}$) and on the relative reactivities of the free carbocation and the ion pair toward solvent (k_s/k_s'). Equation 6 gives a simple relationship between $K_{ass}(k_s'/k_s)$ and kinetic parameters determined in this work: $k_{solv} = 0.049\ s^{-1} = k_1k_{-d}/(k_{-1} + k_{-d})$; $k_{Br}/k_s = 77\ M^{-1} = k_dk_{-1}/[k_s(k_{-1} + k_{-d})]$. Substitution

$$\frac{k_{obsd} - k_{calc}}{k_{solv}/(k_{Br}/k_s)} = (3 \times 10^{-5}\ s^{-1})/(6.4 \times 10^{-4})\ M = (k_s'/k_s)K_{ass} \quad (6)$$

of an estimated[11] value of K_{ass} = 0.3 M^{-1} into eq 6 gives k_s'/k_s = 0.16, using the average value of ($k_{obsd} - k_{calc}$) = 3 × 10^{-5} $s^{-1} = k_1k_s'/k_{-1}$ (Figure 4), and k_s'/k_s = 0.4, using ($k_{obsd} - k_{calc}$) = 9.0 × 10^{-5} s^{-1} obtained by correcting for the estimated bromide ion salt effect on k_{calc}.

The values of ($k_{obsd} - k_{calc}$) in Figure 4 are consistent with a reaction in which the ion-pair intermediate [2·Br^-] is slightly less reactive toward water than the free carbocation **2** (k_s'/k_s = 0.16–0.4). A value of k_s'/k_s = 0.33 can be calculated from data of Ritchie, based on the 3-fold difference in the rate constants for the addition of water to a trityl carbocation with an *o*-sulfonyl methyl ester substituent and the analogous intramolecular trityl carbocation–sulfonate ion pair.[12]

Summary

The solvolysis reaction of 1-**Br** proceeds through the highly unstable carbocation intermediate **2**, which has an estimated half-life in water of ca. 30 ns. In spite of the high reactivity of **2**, the ion-pair intermediate [2·Br^-] of the reaction of 1-**Br** escapes to form free ions before there is a significant reaction of solvent ($k_d > 300k_s'$, Scheme III). The Winstein model for solvolysis reactions includes three types of carbocation intermediates, each of which may be captured by solvent.[2] The present results show that the reaction of solvent with an ion pair of the highly reactive carbocation **2** is normally not an important reaction. They are consistent with the proposal that, for solvolysis reactions in water, nucleophilic reagents generally react with the *liberated* carbocation intermediates.[3-5]

In the following exceptional cases a direct reaction between solvent and an ion-pair intermediate of a solvolysis reaction may be observed experimentally: (1) when the addition of large concentrations of the leaving group ion acts, by mass action, to convert a large fraction of the free carbocation to the ion pair; and (2) when $k_s' \geq k_{-d}$ (Scheme III), the ion pair will react directly with solvent, before there is significant escape to form free ions. The rate constant for capture of the 1-(4-methylphenyl)ethyl carbocation by 50:50 (v/v) trifluoroethanol/water is estimated to be k_s = 6 × 10^9 s^{-1}.[11] The reactions of 1-(4-methylphenyl)ethyl derivatives in this solvent generate ion-pair intermediates whose capture by solvent accounts for ~30% of the solvolysis reaction products, and the data are consistent with $k_{-d} \approx 1.6 \times 10^{10}$ s^{-1} for diffusional separation of the ion-pair intermediate to free ions.[11]

Acknowledgment. This work was supported in its early stages by a Bristol Meyers Co. Grant of Research Corporation and more recently by Grant GM 39754 from the National Institutes of Health. I gratefully acknowledge their support.

Registry No. 1-Br, 104395-39-3; 1-I, 104395-41-7; bromide, 24959-67-9.

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N-Fluorobis[(perfluoroalkyl)sulfonyl]imides: Reactions with Some Olefins via α-Fluoro Carbocationic Intermediates[1]

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N-Fluorobis[(perfluoroalkyl)sulfonyl]imides are a new class of electrophilic fluorinating agents. Reaction of $(CF_3SO_2)_2NF$ (1) with olefins gave various products, depending on the reaction conditions and the structure of the substrate. In solvents of higher nucleophilicity such as H_2O, acetic acid, aqueous HCl, and $(HF)_nPy$, α-fluorohydrins or their acetates, α,β-chlorofluoro- and α,β-difluoroalkanes were obtained. In acetic acid, *trans*-stilbene and tetraphenylethylene produced the rearranged, nonfluorinated aldehyde and ketone. Evidence is presented for the reactions proceeding via a one-electron transfer mechanism involving α-fluorocarbocationic intermediates.

Selectively fluorinated organic compounds are of current interest due to the rapidly increasing number of examples of useful biological activity.[2] Strategic fluorinations using a variety of electrophilic fluorination reagents including F_2,[3] CF_3OF,[4] C_2F_5OF,[5] RCO_2F,[6] R_fCO_2F,[7] XeF_2,[8] and

(1) Part of this work was presented at 12th International Symposium on Fluorine Chemistry, Santa Crutz, CA, Aug 7–12, 1988; Abstract No. 416.

(2) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier Biomedicinal Press: New York, 1982.

(3) (a) Purrington, S. T.; Kagan, B. S. *Chem. Rev.* **1986**, *86*, 997. (b) Purrington, S. T.; Woodward, D. L. *J. Org. Chem.* **1990**, *55*, 3423.

0022-3263/92/1957-0629$03.00/0

Table I. Effect of Solvent, Molar Ratio, and Temperature on Reaction of 4 with 1

entry	molar ratio olefin/1	solvent	temp (C)	products[a] 5	6	7
1	10	$CDCl_3$	22	77	10	
2	7	CH_2Cl_2	0	40	47	
3	7	$CF_2ClCFCl_2$	0	65[b]		
4	3	CH_2Cl_2	0	12	28	50

[a] Yields were determined by ^{19}F NMR unless otherwise stated. [b] GC yield.

$CsSO_4F$[9] have been successfully carried out. These reagents compliment nucleophilic fluorination reagents such as DAST[10] and various sources of fluoride anion.[11] Applications of electrophilic fluorination reagents have been limited to a considerable degree by the challenging experimental conditions required for their safe use.

Recently, a variety of *N*-fluoro compounds have been introduced as electrophilic fluorination reagents.[12] By varying the substituents on nitrogen, a broad spectrum of reactivity is possible and the reagents are easy to handle safely without special equipment. The most reactive and versatile reagents of this class appear to be the *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides[13] which are effective in the fluorination of aromatics, carbanions,[13] and α-fluorination of functionalized carbonyl compounds.[12a,b] *N*-Fluorobis[(trifluoromethyl)sulfonyl]imide, $(CF_3SO_2)_2NF$ (1), is especially attractive due to its excellent long-term stability, favorable physical properties (bp 90–91 °C), and high reactivity.

Most of the work with *N*-fluoro reagents has dealth with the fluorination of enolates or enol acetates and carbanions, but little has been done concerning their reactivity with double bonds.[12d] We wish to report the reaction of 1 with some alkenes.

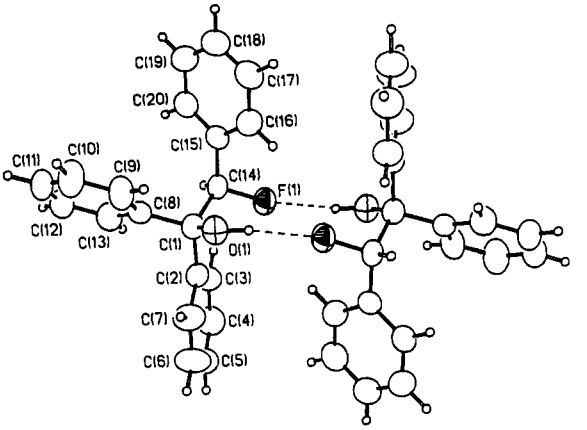
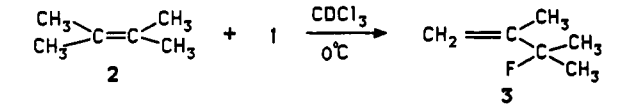


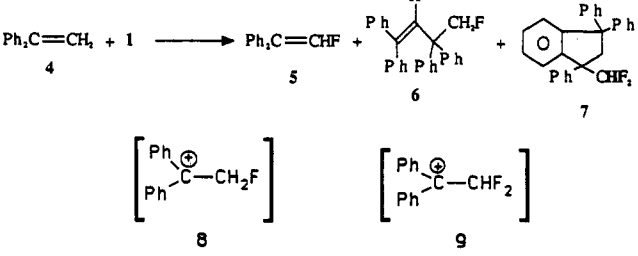
Figure 1. Thermal ellipsoid plot (50% probability) of a hydrogen-bonded dimer of molecules of **13**.

Results and Discussion

Reaction in Solvents of Low Nucleophilicity. 1 undergoes rapid reaction with electron-rich olefins in various solvents of low nucleophilicity such as $CHCl_3$, CH_2Cl_2, Freon-113, THF, Et_2O, etc. Usually, very complicated product mixtures are formed. With excess olefin, some fluorinated product can be isolated. For example, in the reaction of tetramethylethylene with 1 at a molar ratio of 10:1, product **3** could be detected by NMR. The fluorine atom was found at −139.05 ppm (sep d, J = 22.1, 11.7 Hz) in the ^{19}F NMR. The two allylic methyl groups were located at 1.28 ppm with a coupling constant of 21.8 Hz and the vinylic protons near 5.0 ppm with appropriate multiplicity.



The effects of solvent, reactant ratios, and temperature on the reaction of 1,1-diphenylethylene **4** with **1** were investigated in some detail. The results are shown in Table I. It appeared that these reactions involve a carbocation intermediate **8**, which could eliminate a proton to form the fluorinated olefin **5** or attack the starting olefin **4** to give the dimer **6**. The monofluoro olefin **5** reacted further with **1** to yield an α,α-difluorocarbocation **9**, which attacked the starting olefin **4** to afford the substituted indane **7**.



This latter reaction resembles the dimerization of the same olefin under acidic conditions.[14] Thus, the strong acid $(CF_3SO_2)_2NH$[15] reacted with **4** to form **10**.

Trifluoromethyl hypofluorite reacts with **4** to give an even more complex mixture of products.[16] The elec-

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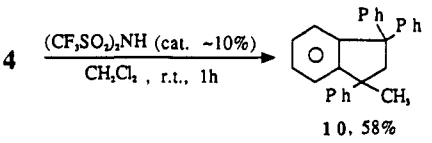
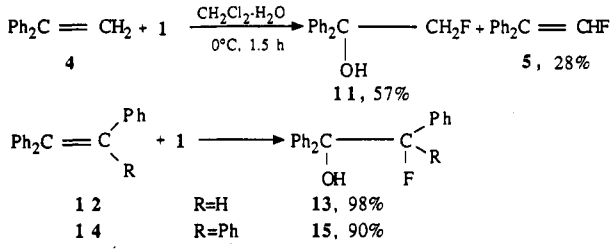


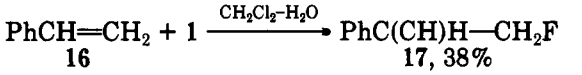
tron-deficient olefins, represented by 1,2-dichloroethylene, diethyl maleate, and cinnamonitrile, did not react with **1** under the same conditions.

Reaction in Solvents of High Nucleophilicity. The reaction of **1** with olefins in more polar solvents was investigated in an attempt to improve the fluorinations and, possibly, to capture the carbocation intermediates by the solvent.

A. In H_2O. **1** does not react with H_2O because it is insoluble in pure H_2O. However, **1** reacts with H_2O on addition of a polar cosolvent like THF or CH_3CN.[17] In CH_2Cl_2–H_2O, however, stabilized α-fluorocarbocations are captured by H_2O to produce α-fluorohydrins. If the α-

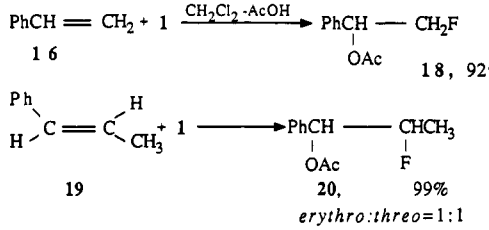


fluorocarbocation is stabilized by only one phenyl group, the yield of fluorohydrin is low. For example, when styrene **16** reacted with **1** in CH_2Cl_2–H_2O, only a 38% yield of fluorohydrin **17** was isolated and the major products were unidentified oligomers containing CH_2F groups. Identi-

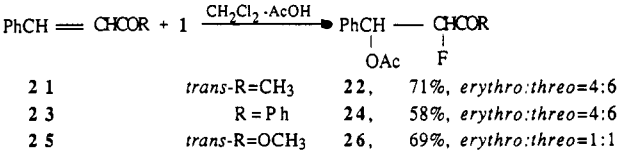


fication of the fluorohydrins was established by the usual spectral data, and **13** was unequivocally identified by X-ray diffraction. An ortep of the hydrogen bonded dimer in the crystal is shown in Figure 1.

B. In AcOH. **1** is soluble in AcOH to provide a homogeneous medium and AcO^- is a good nucleophile. Fortunately, AcOH does not react with **1** even under reflux.[17] Reactions of styrene **16** and *trans*-β-methylstyrene **19** in AcOH gave the β-acetoxy-α-fluoro addition products in high yields. **1** in AcOH even reacts with deactivated



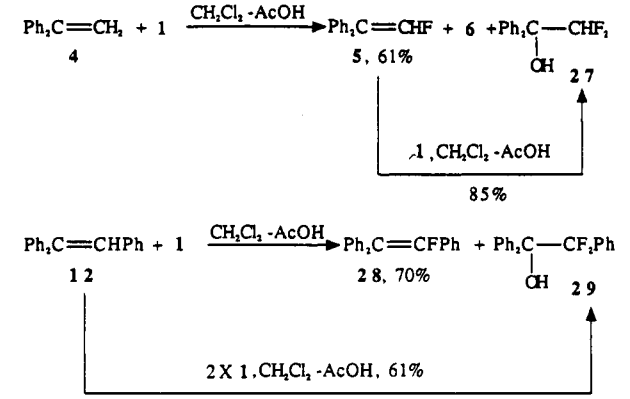
α,β-unsaturated carbonyls **21–25**, which are normally unreactive with the usual electrophiles,[6a] to afford β-acetoxy-α-fluoro derivatives. In these reactions, no stereoselectivity was observed, supporting once again the proposed carbocation intermediates.



Interestingly, the ^1H NMR of **18** was highly solvent dependent. In $CDCl_3$ the CH_2F protons exhibit an ABX spin system, but in DMSO-d_6 the spectrum is first order and nearly first order in CD_3CN. **17** exhibits similar spectra due to hydrogen bonding between F and OH,[18] but this is unlikely for **18** and the cause of the observed behavior is not obvious.

The stereochemistry of the products was determined by their NMR spectra (^1H and ^{19}F). The relative values of the $^3J_{HH}$, $^3J_{HF}$, and $^3J_{FF}$ coupling constants could be applied to assign the *erythro* and *threo* isomers.[7a,19] Usually, when a pair of very electronegative atoms such as F, F or F, O are found vicinal to each other, the gauche conformation is preferred and $^3J_{HH}$ (*threo*) > $^3J_{HH}$ (*erythro*).[20] In compound **20**, the vicinal F and OAc should be gauche and the $^3J_{HH}$ values of 6.7 and 3.8 Hz imply trans hydrogens for one diastereomer (*threo*) and gauche hydrogens for the other (*erythro*). In compounds **22**, **24**, and **26**, the vicinal F and OAc are gauche, but the magnitude of the small $^3J_{HH}$ values, 3–4Hz, indicates that there is a preference for the rotamers with gauche hydrogens. The $^3J_{HF}$ values, on the other hand, are significantly different, implying that the larger $^3J_{HF}$ should belong to the diastereomer with the vicinal H and F trans (*threo*) and the smaller one to the gauche isomer (*erythro*). The stereochemistry assigned by this analysis is consistent with the reported *threo*-**24** and *erythro*-**26**.[6a]

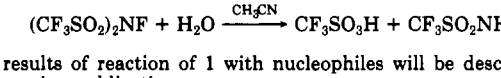
Olefins **4** and **12** react with **1** in AcOH to produce vinylic fluorinated alkenes as the major products, along with α,α-difluorohydrins. When alkene **5** reacted with a second equivalent of **1**, α,α-difluorohydrin **27** was formed in 85% yield. When **12** reacted with 2 equiv of **1**, α,α-difluorohydrin **29** was also isolated in 62% yield, along with 19% $Ph_2CHCOPh$ **30**. These results suggest that the vinylic alkenes **5** or **28** react with **1** to give β-acetoxy-α,α-difluoro derivatives, which undergo hydrolysis to the α,α-difluorohydrin.



Reaction of **1** with *trans*-stilbene (**31**) and tetraphenylethylene (**14**), however, led to rearrangement to form

(16) Patrick, T. B.; Cantrell, G. L.; Inga, S. M. *J. Org. Chem.* **1980**, *45*, 1409.

(17) The following reaction between **1** and H_2O took place in CH_3CN:



The results of reaction of **1** with nucleophiles will be described in a forthcoming publication.

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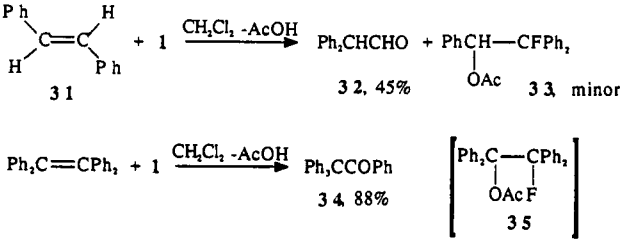
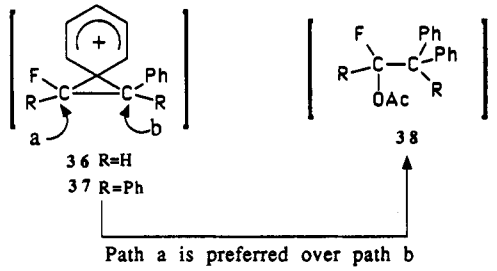
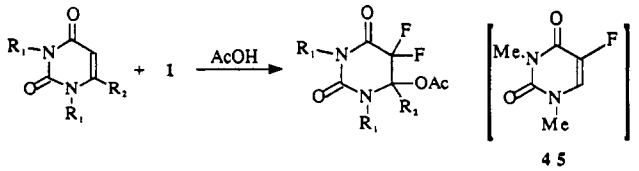
the nonfluorinated aldehyde **32** and ketone **34**. In these



cases, it is apparent that the phenonium ions **36** and **37** are preferred over the open benzylic ions **8** and **9**. The question arises as to which carbon of these phenonium ions is more easily attacked by the nucleophiles. Barton and Hesse[4a,21] and Rozen[5,7a] suggested that CF_3O^-, $CF_3CO_2^-$, and $CH_3CO_2^-$ would attack the carbon without fluorine (path b) to give the vicinal fluorine and nucleophilic addition products like **33** and **35** (not observed). Our results, however, clearly show that the carbon with the fluorine atom (path a) is the preferred site of attack by the nucleophile giving the geminal fluorine and nucleophile addition product, represented by **38**, which is unstable and collapses to the carbonyl compounds (**32** and **34**) by elimination of acyl fluoride. This result is expected because fluorine should cause the α-carbon to possess a relatively greater positive charge making it more prone to attack by nucleophiles.



Uracil (**39**) did not react with **1** at 22 °C in AcOH, probably due to its insolubility, but when heated at 45 °C for 12 h, the difluoro analogue **42**[22,23] was observed by ^{19}F NMR. However, **42** could not be isolated because it decomposed during workup and purification. 1,3-Dimethyluracil (**40**) reacts with 2 equiv of **1** at 22 °C to form **43** in 85% yield. When 1 equiv of **1** was used, the 5-fluorouracil **45** and difluoro derivatives **43** (major) were formed, and unreacted **40** was recovered. In the event that the initial addition product bears a hydrogen at C-5, this atom may be eliminated to generate a 5-fluorouracil followed by another attack of fluorine at C-5 and incorporation of solvent at C-6. Methyl orotate **41** could not be fluorinated even at 70 °C.



45

39	R_1=R_2=H	42, could not be isolated
40	R_1=Me, R_2=H	43, 85%
41	R_1=H, R_2=CO_2Me	44, no reaction

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(22) Visser, G. W. M.; Boele, S.; von Halteren, B. W.; Knopes, G. H. J. N.; Herscheid, J. D. M.; Brinkman, G. A.; Hoekstra, A. *J. Org. Chem.* **1986**, *51*, 1466 and references cited therein.
(23) Barton, D. H. R.; Bubb, W. A.; Hesse, R. H.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2095.

Scheme I

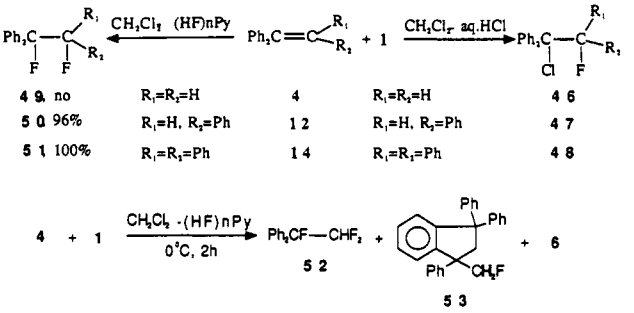


Table II. ^{19}F NMR of Chlorofluoroalkanes and Fluorohydrins

chlorofluoroalkanes	yield[a] (%)	^{19}F NMR	fluorohydrins	^{19}F NMR
46	81	−204.40 (t, J = 47.5 Hz)	11	−218.97 (t, J = 47.9 Hz)
47	90	−166.78 (d, J = 44.4 Hz)	13	−180.80 (d, J = 44.8 Hz)
48	76	−126.14 (s)	15	−142.93 (s)

[a] Determined by ^{19}F NMR.

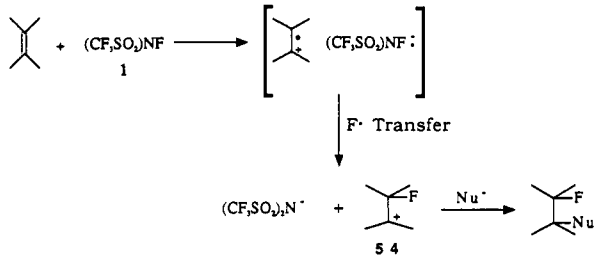
C. In Aqueous HCl and in $(HF)_nPy$. In order to further clarify the reactivity of the α-fluorocarbocation, aqueous HCl and $(HF)_nPy$ were tried as solvents. It was hoped that this would be a good method for synthesis of vicinal dihalo alkanes if the α-fluorocarbocation could be trapped by chloride and fluoride in the solvents. A variety of combinations of *N*-haloelectrophiles such as *N*-bromosuccinimide (NBS) and fluoride ion sources have been utilized effectively for the addition of XF across double bonds.[11f,24] No reverse addition, however, of an electrophilic fluorinating reagent and halide ion across double bonds has been reported. In general, the direct addition of fluorine to double bonds is difficult, but some success has been achieved using dilute elemental fluorine.[3a,7c,14,25]

In CH_2Cl_2–aqueous HCl, alkenes **4**, **12**, and **14** react with **1** at 22 °C to form **46**–**48** (Scheme I). These products could not be purified by silica gel chromatography due to hydrolysis of the chloride, dehydrochlorination, and/or phenyl group migration during the purification. The chlorofluoro alkanes were readily identified by the downfield chemical shift in the ^{19}F NMR compared with the corresponding fluorohydrin (Table II). For example, in the reaction of **12**, an 80% yield of fluorohydrin **13** was obtained after chromatography. However, olefin **16** did not react with **1** in CH_2Cl_2–aqueous HCl, while some high boiling point products without fluorines were formed in the reaction of olefin **21**.

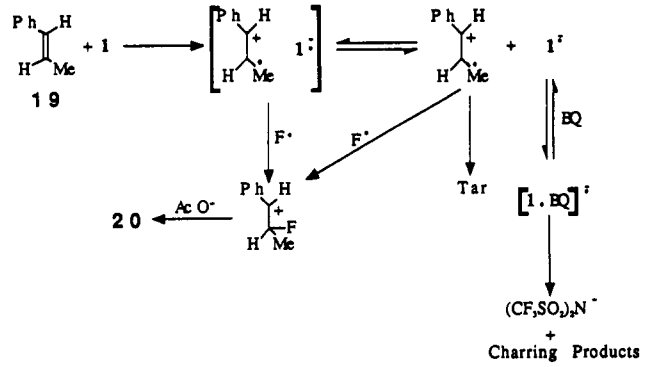
Olefins **12** and **14** react with **1** in CH_2Cl_2–$(HF)_nPy$ at 0 °C to yield the α,β-difluoroalkanes **50** and **51** in high yield. Reaction of **4** did not give **49** but gave instead the trifluoro analogue **52** and dimers **53** and **6** (**Scheme I**). Olefin **16** did not react with **1** in CH_2Cl_2–$(HF)_nPy$ at 0 °C, but at 22 °C, attack of fluoride on the sulfonyl group in **1** took

(24) (a) Maeda, M.; Abe, M.; Kojima, M. *J. Fluorine Chem.* **1987**, *34*, 337. (b) Chehid, I.; Chadboun, M. M.; Baklouti, A. *Tetrahedron Lett.* **1989**, *30*, 3167. (c) Shimizu, M.; Nakahara, Y.; Yoshioka, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1881. (d) Eddarir, S.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett.* **1991**, *32* 69. (e) Kuroboshi, M.; Hiyama, T. *Tetrahedron Lett.* **1991**, *32*, 1215. (f) Barluenga, J.; Camps, P. J.; Gonzalez, J. M.; Suarez, J. L.; Asensio, G. *J. Org. Chem.* **1991**, *56*, 2234.
(25) For indirect introduction of fluorines into double bonds see: (a) Bowers, A.; Holton, P. G.; Denot, E.; Loza, M. C.; Urquiza, R. *Ibid.* **1962**, *84*, 1050. (b) Barton, D. H. R.; Danks, J. L.; Ganguly, A. K.; Hesse, R. H.; Tarzia, G.; Pechet, M. M. *J. Chem. Soc., Chem. Commun.* **1976**, 101. (c) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

Scheme II



Scheme III



place to form CF_3SO_2F and CF_3SO_2NHF.[17] Reaction of **19** at 0 °C gave a viscous red liquid with a complicated ^{19}F NMR spectrum and the products were not identified. Without **1**, olefins **12**, **14**, and **19** did not react with $(HF)_nPy$ in CH_2Cl_2.[25c]

Proposed Reaction Mechanism. There have been few studies on the mechanism of reaction of *N*-fluoro compounds.[12d,26] For the reaction of fluoroxy compounds with unsaturated substrates, three pathways have been proposed: (1) an electrophilic reaction;[4a] (2) a free-radical reaction;[4c] (3) a single electron transfer.[22] Our initial investigation suggested that the reaction of *N*-fluoro compounds with double bonds might proceed through an electron-transfer mechanism (Scheme II).[12d] Support for this hypothesis is now more firmly established based on the following facts and observations. (1) All of the foregoing results provide good evidence in support of the formation of an α-fluoro carbocation intermediate **54**. (2) The polarity of the solvent is very important. Polar solvents such as acetic acid accelerate the reaction because electron transfer is often preceded by the formation of a charge-transfer complex between the substrate and the reagent, and the polar solvents favor the separation of charge and ion pair formation. (3) Reaction of alkenes, e.g., cyclohexene, 1-octene, and 2,3-dihydro-2*H*-pyran, with **1** led to highly colored products, most of which contain little or no fluorine and exhibit an infrared absorption near 1730 cm^{-1}. If the oxidation potential of the substrate is too high, the resultant radical cation combines with a nucleophile followed by a radical reaction like hydrogen abstraction, polymerization, etc.[27] (4) *p*-Dinitrobenzene, an efficient electron transfer quencher, inhibits the reaction of *trans*-β-methylstyrene (**19**) with **1** to an 80% conversion of **1**, compared with 100% conversion in the absence of p-dinitrobenzene. (5) In the presence of 1,4-benzoquinone (BQ), **19** consumed all of **1** but produced the addition product **20** in only 48% isolated yield. Unidentified solids insoluble in H_2O and CH_2Cl_2 were formed along with tars containing phenyl and methyl groups (^1H NMR) soluble in CH_2Cl_2. BQ is used to scavenge $O_2^{\cdot-}$. In this case, BQ combined with the radical anion of **1** and led to charred products (Scheme III). In the absence of alkene, no reaction took place between BQ and **1** under the same reaction conditions (0 °C, 2 h), but products similar in appearance were formed when the mixture was stirred at 22 °C for 3 days. (6) The fragmentation of the radical anion of **1** would presumably afford fluoride ion and the bis[(trifluoromethyl)sulfonyl]imide radical $(CF_3SO_2)_2N^{\cdot}$ because of the high-electron affinity of a fluorine atom. But in all the above reactions the bis[(trifluoromethyl)sulfonyl]imide anion $(CF_3SO_2)_2N^-$ is formed, indicating that the radical anion of **1** preferentially transfers a fluorine atom. In fact, it has been observed that the radical $(CF_3SO_2)_2N^{\cdot}$ is unstable toward the loss of CF_3[15] and we found no evidence of the expected products from this reaction path.

In summary, *N*-fluorobis[(trifluoromethyl)sulfonyl]imide (**1**) is a powerful electrophilic fluorinating reagent. It reacts with many types of alkenes in solvents of varying nucleophilicity to yield products which can be rationalized on the basis of fluoro carbocation intermediates. The latter are postulated to arise through an electron transfer mechanism. Ultimate proof of this proposed mechanism must await detection and identification of the intermediates.

Experimental Section

Melting points are uncorreted. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded at 200.13, 188.31, and 75.47 MHz, respectively. Chemical shifts are reported for $CDCl_3$ solution in ppm positive downfield from internal TMS for ^1H NMR and ^{13}C NMR and from internal $CFCl_3$ for ^{19}F NMR. Mass spectra were measured at 70 eV for electron impact (EI) and with methane for chemical ionization (CI). X-ray analysis of **13** was performed on a crystal obtained form hexane–CH_2Cl_2.[28] Column chromatography was performed on silica gel 60A (100–200 mesh). All of the starting olefins were obtained from Aldrich Chemical Co. and used as received. *N*-Fluorobis[(trifluoromethyl)sulfonyl]imide (**1**) was prepared according to literature methods.[13] Purity of all products was established by ^1H NMR and by ^{13}C and ^{19}F NMR and melting point, where appropriate.

General Procedure for the Reaction of 1 with Alkenes. Into a solution of the starting alkene in the appropriate solvent under N_2, **1** in CH_2Cl_2 was added dropwise during a period of 10–20 min with stirring. Reactions were followed by ^{19}F and ^1H NMR. After the reaction appeared to be completed, the mixture was diluted with CH_2Cl_2, rinsed with aqueous $NaHCO_3$ and saturated aqueous sodium chloride, and then dried over Na_2SO_4. The crude products were separated by column or preparative thin-layer chromatography on silica gel.

Reaction of 1,1-Diphenylethylene (4) in CH_2Cl_2. A 5-g (27.7-mmol) portion of **4** reacted with 0.9 g (3 mmol) of **1** in 25 mL of CH_2Cl_2 at rt for 1 h. Pure samples of **6** and **7** were obtained when hexane–Freon-11–CH_2Cl_2 (2.5:2.5:1) and hexane–CH_2Cl_2 (4:1) were used as eluents, respectively.

4-Fluoro-1,1,3,3-tetraphenyl-1-butene (6):[16] ^1H NMR δ 4.63 (2 H, d J = 47.5 Hz, CH_2F), 6.7–6.8 (4 H, m, phenyl H and

(26) After this paper was submitted, we became aware of further work concerning the mechanism of reaction of N–F compounds with enolates. It is argued that, with enolates, reactions proceed by SN_2 at fluorine and do not involve electron transfer in the formation of fluorinated products. Differding, E.; Ruegg, G. M. *Tetrahedron Lett.* **1991**, *32*, 3815. Differding, E.; Wehrli, M., *Tetrahedron Lett* **1991**, *32*, 3819.

(27) *Electrooxidation in Organic Chemistry*; Yoshida, K., Ed.; Wiley-Interscience: New York, 1984.

(28) **X-ray Analysis of 13.** A colorless crystal with dimensions of 0.15 × 0.20 × 0.55 mm was used for data collection at ambient temperature (21 ± 1 °C) on a Nicolet R3mV diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystal data: $C_{20}H_{17}OF$, fw = 292.37 g/mol, monoclinic, $P2_1/n$ (no. 14, nonstandard), a = 12.480 (3) Å, b = 5.854 (2) Å, c = 21.155 (7), Å, β = 98.26 (2)°, V = 1529.6 (8) Å^3, Z = 4, D_{calc} = 1.27 g/cm^3. Least-squares refinement, based on 1182 observed reflections ($I > 3\sigma(I)$), yielded final residuals of R = 0.0457, R_w = 0.0544, and S = 1.18. Additional details of the X-ray analysis of **13** have been deposited as supplementary material.

C=CH), 7.1–7.2 (2 H, m, phenyl H), 7.3 (15 H, s, phenyl); ^{19}F NMR δ -214.42 (td, J = 47.4, 2.3 Hz); ^{13}C NMR δ 54.8 (d, J = 18.0 Hz, Ph_2CCF), 87.6 (d, J = 178.9 Hz, CF), 126.6–129.6 (=CH in phenyl ring and =CH), 133.8 (d, J = 4.5 Hz, Ph_2C=), 139.7, 143.2, 143.6, 145.2 (tertial C in phenyl ring).

1-(Difluoromethyl)-1,3,3-triphenylindan (7): ^{1}H NMR δ 3.35, 3.43 (2 H, AB type, J_{AB} = 13.7 Hz, CH_2), 5.95 (1 H, t, J = 56.5 Hz, CHF_2), 6.6–7.45 (19 H, m, phenyl H); ^{19}F NMR δ -117.38, -120.69 (d-AB type, J_{AB} = 274.4 Hz, $J_{HF(gem)}$ = 56.4 Hz, CHF_2); ^{13}C NMR δ 52.4 (CH_2), 59.2 (t, J = 19.1 Hz, PhCCF), 60.6 (Ph_2C), 118.6 (t, J = 248.9 Hz, CHF_2), 125.8–129.8, 139.4, 141.4, 142.1, 148.0, 150.4 (phenyl C); MS m/e (EI) inten, assign) 397 (17.1, M + 1), 396 (64.9, M), 345 (100, M - CHF_2), 319 (34.6, M - C_6H_5), 267 (84.0, M - C_6H_5 - CHF_2 - 1), 265 (66.3, $C_{21}H_{13}$), 252 (57.4, $C_{20}H_{12}$.

1-Methyl-1,3,3-triphenylindan (10).[14,29] Into a solution of **4** (2.5 g, 13.9 mmol) in 10 mL CH_2Cl_2 at rt was added a solution of $(CF_3SO_2)_2NH$ (0.5 g, 1.8 mmol) dissolved in 6 mL of CH_2Cl_2 with stirring for 1 h. The reaction mixture, which became green on addition of the acid, was washed with H_2O and dried over Na_2SO_4. After purification with hexane–CH_2Cl_2 (4:1) as eluent, 1.45 g (58%) of white solid was obtained, mp 142–144.5 °C: ^{1}H NMR δ 1.54 (3 H, s, CH_3), 3.10, 3.39 (2 H, AB type, J_{AB} = 13.5 Hz, CH_2), 7.02–7.31 (19 H, m, phenyl H); ^{13}C NMR δ 28.9 (CH_3), 51.2 (CH_2), 61.0 (PhC), 61.4 (PhC), 125.0–128.8, 147.5, 148.5, 148.9, 149.3, 150.5 (phenyl C); MS m/e (EI) 360 (65.6, M), 345 (100, M - CH_3), 283 (50, M - C_6H_5); m/e (CI) 283 (100, M - C_6H_5).

1,1-Diphenyl-2-fluoroethanol (11). A 1-g (5.55-mmol) portion of **4** reacted with 1.8 g (5.95 mmol) of **1** in 50 mL of CH_2Cl_2 and 10 mL of H_2O at 0 °C for 1.5 h. Quantitative analysis by ^{19}F NMR with $CFCl_3$ as internal standard showed that the crude product consisted of **5** and **11** in yields of 28% and 57%, respectively. The pure sample of **11** was obtained by preparative TLC with CH_2Cl_2–Et_2O (5:1) as eluent: ^{1}H NMR δ 3.12 (1 H, d, J = 1.6 Hz, OH), 4.76 (2 H, d, J = 47.7 Hz, CH_2F), 7.1–7.4 (10 H, m, phenyl H); ^{19}F NMR δ -218.97 (t, J = 47.9 Hz, CH_2F); ^{13}C NMR δ 77.7 (d, J = 18.6 Hz, C-O), 87.3 (d, J = 180.3 Hz, CF), 126.6, 127.6, 128.2, 142.4, 142.5 (phenyl C). These data are not in agreement with that reported in ref. 30.

2-Fluoro-1,1,2-triphenylethanol (13). A 1.3-g (5.07-mmol) portion of triphenylethylene (**12**) was stirred with 1.8 g (5.92 mmol) of **1** in 40 mL of CH_2Cl_2 and 10 mL of H_2O at 0 °C for 1.5 h. When CH_2Cl_2–Et_2O (5:1) was used as eluent, 1.46 g (98%) of **13** was obtained, mp 153–155 °C: IR (cm^{-1}) (Nujol mull) 3562 (OH); ^{1}H NMR δ 2.69 (1 H, d, J = 1.3 Hz, OH), 6.31 (1 H, d, J = 44.8 Hz, CFH), 6.9–7.5 (15 H, m, phenyl H); ^{19}F NMR δ -180.80 (d, J = 44.8 Hz, CFH); ^{13}C NMR δ 79.9 (d, J = 23.4 Hz, CO), 96.2 (d, J = 183.1 Hz, CF), 126.6–129.1, 135.1 (d, J = 21.3 Hz), 142.7, 142.8 (phenyl C); MS m/e (EI) 183 (69.9, Ph_2COH), 105 (100, PhCO), 77 (55.7, C_6H_5); m/e (CI) 275 (16.5, M - OH), 273 (9.7, M - F), 195 (19.7, M - F - C_6H_5), 183 (100, Ph_2COH), 105 (58.1, PhCO).

2-Fluoro-1,1,2,2-tetraphenylethanol (15). A 1-g (3.0-mmol) portion of tetraphenylethylene (**14**) was stirred with 0.96 g (3.2 mmol) of **1** in 40 mL of CH_2Cl_2 and 10 mL H_2O at 0 °C for 1.5 h. Workup gave 1 g (90%) of pure **15**, mp 180 °C dec: IR (cm$^-$) (Nujol mull) 3574 (OH); ^{1}H NMR δ 2.81 (1 H, broad, OH), 7.0–7.5 (20 H, m phenyl H); ^{19}F NMR δ -142.93 (s, CF); ^{13}C NMR δ 81.7 (d, J = 26.6 Hz, CO), 101.4 (d, J = 187.3 Hz, CF), 126.7–128.1, 140.9, 141.4, 143.6, 143.7 (phenyl C); MS m/e (EI) 183 (100, Ph_2COH), 165 (23.1, Ph_2C-1), 105 (84.0, PhCO), 77 (29.7, Ph); m/e (CI) 351 (32.1, M - OH), 348 (37.7, M - HF), 332 (19.5, M - F - OH), 272 (47.0, M - HF - C_6H_5), 183 (100, Ph_2COH), 167 (34.0, Ph_2C + 1), 166 (30.2, Ph_2C), 165 (40.9, Ph_2C - 1), 105 (67.4, PhCO).

2-Fluoro-1-phenylethanol (17).[18,31] A 0.16-g (1.5-mmol) portion of styrene (**16**) was stirred with 0.50 g (1.7 mmol) of **1** in 4 mL of CH_2Cl_2 and 2 mL of H_2O at rt for 24 h. Purification with petroleum ether–AcOEt (4:1) as eluent gave 80 mg (38%) of **17**: ^{1}H NMR δ 3.20 (1 H, broad, OH), 4.41 (2 H, dm, J = 47.4 Hz, CFH), 5.01 (1 H, ddd, J = 14.0, 8.0, 4.0 Hz, CHO), 7.39 (m, phenyl H); ^{19}F NMR δ -221.05 (td, J = 47.5, 14.5 Hz, CFH).

1-Acetoxy-2-fluoro-1-phenylethane (18).[12d] A 0.16-g (1.5-mmol) portion of styrene (**16**) reacted with 0.45 g (1.5 mmol) **1** in 4 mL of CH_2Cl_2 and 2 mL of AcOH at rt for 24 h. Purification with petroleum ether–AcOEt (3:1) as eluent gave 0.25 g (92%) of **20**, colorless liquid: IR (cm^{-1}) (neat) 1738 (C=O); ^{1}H NMR δ 2.13 (3 H, s, CH_3CO), 4.56 (2 H, dm, J = 47.1 Hz, CFH_2), 6.03 (1 H, ddd, J = 16.3, 7.1, 3.8 Hz, CHO), 7.35 (5 H, s, phenyl H); ^{19}F NMR δ -222.58 (td, J = 47.1 Hz, J = 16.3 Hz, CFH_2, which collapsed to a doublet (J = 16.6 Hz) when subjected to decoupling from protons at 4.56 ppm and collapsed to a triplet (J = 46.0 Hz) when decoupled from protons at 6.03 ppm); MS m/e (CI) 305 (9.6, 2M - AcO), 207 (13.5, 2M - 2AcO - 2HF - 1), 183 (34.6, M + 1), 162 (51.7, M - HF), 149 (21.7, M - CFH_2), 123 (100, M - AcO), 120 (42.5, M - F - Ac), 107 (12.8, PhCHOH), 105 (17.3, PhCO).

1-Acetoxy-2-fluoro-1-phenylpropane (20).[12d] A 0.18-g (1.5-mmol) portion of *trans*-β-methylstyrene (**19**) reacted with 0.48 g (1.5 mmol) of **1** in 4 mL of CH_2Cl_2 and 2 mL of AcOH at 0 °C for 2 h. Purification with petroleum ether–CH_2Cl_2 (2:1) as eluent gave 0.29 g (99%) of **20**, colorless liquid: IR (cm^{-1}) (neat) 1737 (C=O); ^{1}H NMR for *erythro* isomer δ 1.29 (3 H, dd, J = 23.7, 6.4 Hz, CH_3, which collapsed to a doublet when it was decoupled from the fluorine at -183.81 ppm), 2.13 or 2.11 (3 H, s, CH_3CO), 4.85 (1 H, dm, J = 47.6 Hz, CHF), 5.84 (1 H, dd, J = 17.7, 3.8 Hz, CHO), 7.34 (5 H, s, phenyl H); for *threo* isomer δ 1.20 (3 H, dd, J = 23.7, 6.4 Hz, CH_3, which collapsed to a doublet when decoupled from the fluorine at -181.64 ppm), 2.11 or 2.13 (3 H, s, CH_3CO), 4.85 (1 H, dm, J = 47.6 Hz, CHF), 5.79 (1 H, dd, J = 15.1, 6.7 Hz, CH-O), 7.34 (5 H, s, phenyl H); ^{19}F NMR for *erythro* isomer δ -183.81 (dqd, J = 47.5, 23.9, 17.7 Hz, CFH); for *threo* isomer δ -181.64 (dqd, J = 47.8, 24.0, 15.0 Hz, CFH); MS m/e (CI) 312 (7.5, 2M - AcOH), 285 (30.7, 2M - AcOH - CH_3CFH), 273 (66.3, 2M - 2AcOH - 1), 235 (52.8, 2M - 2AcO - 2F - 1), 197 (5.4, M + 1), 176 (23.7, M - HF), 149 (51.6, M - $CHFCH_3$), 137 (100, M - AcO), 134 (29.7, M - F - Ac), 107 (27.3, PhCHOH).

4-Acetoxy-3-fluoro-4-phenyl-2-butanone (22). A 0.22-g (1.5-mmol) portion of *trans*-4-phenyl-3-buten-2-one (**21**) reacted with 0.51 g (1.7 mmol) of **1** in 4 mL of CH_2Cl_2 and 2 mL of AcOH at rt for 3 days. Purification using petroleum ether–AcOEt (7:1) as eluent gave 0.24 g (71%) of **22**. NMR showed two isomers: *erythro* and *threo* (4:6): IR (cm^{-1}) (neat) 1739 and 1748 (C=O); ^{1}H NMR for *erythro* isomer δ 1.95 (3 H, d, J = 5.2 Hz, CH_3CO), 2.08 (3 H, s, CH_3CO), 5.07 (1 H, dd, J = 50.9, 3.3 Hz, CHF), 6.12 (1 H, dm, CHOAc), 7.34–7.40 (5 H, m, phenyl H); for *threo* isomer δ 2.13 (3 H, s, CH_3CO), 2.30 (3 H, d, J = 4.8 Hz, CH_3CO), 4.86 (1 H, dd, J = 47.8, 2.6 Hz, CHF), 6.12 (1 H, dm, CHOAc), 7.34–7.40 (5 H, m, phenyl H); ^{19}F NMR for *erythro* isomer δ -199.85 (ddq, J = 51.0, 24.9, 5.0 Hz, CFH); for *threo* isomer δ -202.19 (ddq, J = 47.8, 27.1, 4.7 Hz, CFH); MS m/e (EI) 162 (7.3, M - F - CH_3CO), 122 (9.3, M - CH_3CO - CH_3CO_2), 107 (15.7, PhCHO + 1), 43 (100, CH_3CO); m/e (CI) 267 (20.6, M + CH_3CO), 225 (4.4, M + 1), 204 (4.5, M - HF), 189 (10.4, M - HF - CH_3), 147 (100, M - C_6H_5), 145 (74.6, M - F - AcO).

3-Acetoxy-2-fluoro-3-phenylpropiophenone (24). A 0.25-g (1.2-mmol) portion of benzalacetophenone (**23**) reacted with 0.36 g (1.2 mmol) of **1** in 4 mL of CH_2Cl_2 and 2 mL of AcOH at rt for 24 h. Separation using petroleum ether–AcOEt (7:1) as eluent gave about 80 mg of unreacted chalcone and 0.20 g (58%) of **24**, which is a mixture of *erythro* and *threo* isomers at the ratio of 4:6: IR (cm^{-1}) (neat) 1685, 1732 and 1750 (C=O); ^{1}H NMR for *erythro* isomer δ 2.03 (3 H, s, CH_3), 5.95 (1 H, dd, J = 49.0, 4.0 Hz, CHF), 6.30 (1 H, dd, J = 21.6, 4.0 Hz, CHOAc), 7.25–7.95 (5 H, m, phenyl H); for *threo* isomer[6a] 1.98 (3 H, s, CH_3), 5.65 (1 H, dd, J = 47.6, 3.9 Hz, CHF), 6.35 (1 H, dd, J = 23.3, 3.9 Hz, CHOAc), 7.25–7.95 (5 H, m, phenyl H); ^{19}F NMR for *erythro* isomer δ -200.30 (dd, J = 48.9, 21.9 Hz, CFH); for *threo* isomer[6a] -197.36 (dd, J = 47.7, 23.1 Hz, CFH); MS m/e (CI) 269 (19.1, M - F), 224 (12.0, M - F - CH_3CO), 105 (100, PhCO).

Methyl 3-Acetoxy-2-fluoro-3-phenylpropionate (26). A 0.24-g (1.5-mmol) portion of *trans*-methylcinnamate (**25**) reacted with 0.51 g (1.7 mmol) of **1** in 4 mL of CH_2Cl_2 and 2 mL of AcOH at rt for 4 days. Purification with petroleum ether–CH_2Cl_2 (1:2) as eluent gave 0.25 g (69%) of **26**, a mixture of *erythro* and *threo* (1:1): IR (cm^{-1}) (neat) 1749 (C=O); ^{1}H NMR for *erythro* isomer[6a] δ 2.06 (3 H, s, CH_3CO), 3.66 (3 H, s, CH_3O), 5.25 (1 H, dd, J = 49.1, 3.7 Hz, CHF), 6.16 (1 H, dd, J = 23.1, 3.8 Hz, CHOAc),

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7.26–7.39 (5 H, m, phenyl H); for *threo* isomer δ 2.09 (3 H, s, CH_3CO), 3.71 (3 H, s, CH_3O), 5.06 (1 H, dd, J = 47.0, 3.3 Hz, CHF), 6.18 (1 H, dd, J = 24.7, 3.4 Hz, CHOAc), 7.26–7.39 (5 H, m, phenyl H); ^{19}F NMR for *erythro* isomer[6a] δ −202.67 (dd, J = 48.8, 22.7 Hz, CFH); for *threo* isomer δ −202.99 (dd, J = 47.4, 24.7 Hz, CFH); MS m/e (CI) 241 (67.0, M + 1), 220 (10.8, M − HF), 181 (78.8, M − AcO), 179 (100, M − F − CH_3CO).

1,1-Diphenyl-2-fluoroethylene (5). A 0.27-g (1.5-mmol) portion of 1,1-diphenylethylene (4) reacted with 0.48 g (1.6 mmol) of 1 in 4 mL of CH_2Cl_2 and 2 mL of AcOH at rt for 3 h, and then the temperature was allowed to warm to rt. Separation using petroleum ether–CH_2Cl_2 (3:1) as eluent gave 0.18 g (61%) of 5, colorless liquid: IR (cm^{-1}) (neat) 1631 (C=C); ^1H NMR δ 6.94 (1 H, d, J = 83.4 Hz, CHF), 7.15–7.34 (10 H, m phenyl H); ^{19}F NMR δ −128.48 (d, J = 83.6 Hz, CFH); MS m/e (EI) 199 (21.1, M + 1), 198 (87.8, M), 165 (46.3, M − CFH − 1), 51 (100, C_4H_2), 50 (96.7, C_4H_3).

2,2-Difluoro-1,1-diphenylethanol (27). A 70-mg (0.35-mmol) portion of 5 reacted with 0.11 g (0.35 mmol) of 1 in 2 mL of CH_2Cl_2 and 1 mL of AcOH at rt for 18 h. Purification using CH_2Cl_2 as eluent gave 70 mg (85%) of 27, colorless heavy liquid: IR (cm^{-1}) (neat) 3455 and 3541 (broad, OH); ^1H NMR δ 2.84 (1 H, broad OH), 6.19 (1 H, t, J = 55.1 Hz, CF_2H), 7.29–7.37 (6 H, m, phenyl H), 7.43–7.48 (4 H, m, phenyl H); ^{19}F NMR δ − 128.13 (d, J = 55.2 Hz, CF_2H); MS m/e (EI) 183 (100, Ph_2COH), 105 (87.8, PhCO), 77 (32.1, Ph); m/e (CI) 217 (100, M − OH), 183 (78.8, Ph_2COH), 157 (27.2, M − C_6H_5), 105 (21.0, M − PhCO).

1-Fluoro-1,2,2-triphenylethylene (28). A 0.20-g (0.78-mmol) portion of triphenylethylene (12) reacted with 0.24 g (0.78 mmol) of 1 in 4 mL of CH_2Cl_2 and 2 mL of AcOH at 0 °C for 1.5 h and then at rt for 4 h. Separation using petroleum ether–CH_2Cl_2 (2:1) as eluent gave 0.15 g (70%) of 28, mp 101–103 °C: IR (cm^{-1}) (neat) 1632 (C=C); ^1H NMR δ 7.17–7.36 (m, phenyl H); ^{19}F NMR δ −103.44 (s, CF); MS m/e (EI) 274 (100, M), 253 (19.1, M − F), 196 (32.8, M − Ph + 1); m/e (CI) 275 (85.9, M + 1), 274 (100, M), 255 (72.3, M − F). These data are not in agreement with those reported in ref. 31.

2,2-Difluoro-1,1,2-triphenylethanol (29). A 0.20-g (0.78-mmol) portion of 12 reacted with 0.48 g (1.6 mmol) of 1 in 4 mL of CH_2Cl_2 and 2 mL of AcOH as rt for 24 h. Separation using petroleum ether–CH_2Cl_2 (1:1) as eluent gave 0.15 g (61%) of 29, wax-like, mp 91–96 °C: IR (cm^{-1}) (Nujol mull) 3582 (sharp, OH); ^1H NMR δ 2.85 (1 H, s, OH), 7.02–7.82 (15 H, m, phenyl); ^{19}F NMR δ −101.75 (s, CF_2); MS m/e (EI) 183 (100, Ph_2COH), 105 (80.5, PhCO), 77 (42.5, Ph); m/e (CI) 293 (100, M − OH), 213 (33.5, M − HF − C_6H_5), 183 (24.5, Ph_2COH), 105 (33.8, PhCO).

2,2,2-Triphenylacetophenone (34). A 0.25-g (0.75-mmol) portion of tetraphenylethylene (14) reacted with 0.25 g (0.84 mmol) of 1 in 4 mL of CH_2Cl_2 and 2 mL of AcOH at 0 °C for 1.5 h and then at rt for 4.5 h. Purification using petroleum ether–CH_2Cl_2 (1:2) as eluent gave 0.23 g (88%) of 36, mp 185–187 °C (lit.[33] mp 175–177 °C, 181–183 °C). ^1H NMR and IR are consistent with that reported in ref 33.

1,3-Dimethyl-5,5-difluoro-5,6-dihydro-6-acetoxyuracil (43). A 0.21-g (1.5-mmol) portion of 40 was stirred with 1.0 g (3.3 mmol) of 1 in 4 mL of AcOH at rt for 48 h. Reaction mixture was diluted with 10 mL of CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O, aqueous $NaHCO_3$, and saturated brine and dried over Na_2SO_4. Purification by column chromatography using CH_2Cl_2–AcOEt (5:3) as eluent gave 0.30 g of 43 (85%): IR (cm^{-1}) (neat) 1760, 1748, 1739 (C=O); ^1H NMR δ 2.16 (3 H, s, CH_3CO), 3.18 (3 H, s, CH_3), 3.29 (3 H, s, CH_3), 6.20 (1 H, dd, J = 6.8, 2.4 Hz, CH); ^{19}F NMR δ −111.9, 126.9 (AB type, J_{AB} = 282.6 Hz, J_{HA} = 6.6 Hz, CF_2); ^{13}C NMR δ 20.20 (s, CH_3), 28.18 (s, CH_3), 35.40 (s, CH_3), 78.09 (dd, J = 39.5, 30.0 Hz, CHOAc), 105.62 (dd, J = 255.7 Hz, J = 244.2 Hz, CF_2), 150.88 (s, CO), 159.01 (t, J = 29.5 Hz), 188.91 (s, CO); MS m/e (EI) 177 (12.6, M − OAc), 120 (7.8, $C_3F_2NO_2$), 92 (10.3, C_2F_2NO), 43 (100, CH_3CO), 42 (39.8, CH_2CO); m/e (CI) 177 (100, M − OAc).

1,2-Difluoro-1,1,2-triphenylethane (50). A 0.30-g (1.0-mmol) portion of 1 in 1 mL of CH_2Cl_2 was cooled at 0 °C in a 50-mL fluoropolymer plastic vessel. A 0.20-g (0.78-mmol) portion of 12 and 0.68 g of $(HF)_nPy$ (70%) were added in one portion. The resultant mixture turned to blue and was stirred at 0 °C for 2 h, and then quenched with iced H_2O and extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O, aqueous $NaHCO_3$, and saturated brine and dried over Na_2SO_4. After partial removal of solvent, purification by chromatography using petroleum ether as eluent gave 0.22g white crystals of 50 (96%), mp 94–96 °C: ^1H NMR δ 6.21 (1 H, dd, J = 44.0, 17.9 Hz, CHF), 7.19–7.46 (15 H, m, phenyl H); ^{19}F NMR δ −160.26 (1 F, t, J = 16.6 Hz), CF), −182.12 (1 F, dd, J = 44.2, 15.6 Hz, CFH); ^{13}C NMR δ 94.45 (dd, J = 185.6, 26.6 Hz, CFH), 98.30 (dd, J = 183.8, 24.3 Hz, CF), 122.68–139.95 (phenyl C); MS m/e (EI) 185 (100, Ph_2CF), 167 (69.9, Ph_2C + 1), 165 (43.4, Ph_2C − 1); m/e (CI) 275 (49.5, M − F), 256 (10.2, M − 2F), 217 (59.5, M − Ph), 185 (100, Ph_2CF), 165 (31.7, Ph_2C − 1), 109 (17.3, PhCFH). These data are not in agreement with a previous report of this compound.[11c]

1,2-Difluoro-1,1,2,2-tetraphenylethane (51). The reaction conditions were similar to those reported in the previous section. From 0.25 g (0.75 mmol) of 14, 0.25 g (0.85 mmol) of 1, and 0.68 g $(HF)_nPy$ in 1.5 mL of CH_2Cl_2 was obtained 0.28 g of white crystals of 51 (100%), mp 235–37 °C dec, after column chromatography using petroleum ether as eluent: ^1H NMR δ 7.02–7.27 (m, phenyl H); ^{19}F NMR δ −148.63 (s); ^{13}C NMR δ 99.73 (dd, J = 183.0, 29.9 Hz, CF), 126.38, 127.50, 127.62, 128.23, 131.30, 140.44 (d, J = 22.3 Hz), 143.70; MS m/e (EI) 185 (100, Ph_2CF), 165 (29.1, Ph_2C − 1); m/e (CI) 185 (63.2, Ph_2CF), 183 (64.7, Ph_2CF − 2), 165 (100, Ph_2C − 1).

Reaction of 1,1-Diphenylethylene (4) in CH_2Cl_2–$(HF)_nPy$. The reaction conditions were similar to those reported in the previous section. From 0.27 g (1.5 mmol) of 4, 0.50 g (1.7 mmol) of 7 and 0.68 g of $(HF)_nPy$ in 2 mL of CH_2Cl_2 was obtained 0.29 g of slightly yellow heavy liquid after chromatography using petroleum ether–CH_2Cl_2 (1:1) as eluent. It was a mixture of 52, 53, and 6 at a ratio of 49:47:6.

1,2,2-Trifluoro-1,1-diphenylethane (52):[34] ^1H NMR δ 6.19 (td, J = 54.5, 5.5 Hz, CF_2H), 6.79–7.42 (m, phenyl H); ^{19}F NMR δ −128.35 (dd, J = 54.7, 10.6 Hz, CF_2H), −156.46 (td, J = 10.6, 5.5 Hz, CF).

1-(Fluoromethyl)-1,3,3-triphenylindan (53): ^1H NMR δ 3.28, 3.38 (AB type, J_{AB} = 13.3 Hz, J_{FA} = 1.9 Hz, CH_2), 4.56 (d, J = 47.7 Hz, CFH_2), 6.79–7.42 (m, phenyl H); ^{19}F NMR δ −214.46 (t, J = 47.7 Hz, CFH_2).

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Supplementary Material Available: ^1H NMR spectra of all new compounds, known compounds where NMR data were not available, and known compounds where erythro and threo isomers were not assigned and full X-ray structural data (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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