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The Reaction of XeF_2 with Trialkylvinylstannanes: Scope and Some Mechanistic Observations

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Abstract: The combination of a vinylstannane with xenon difluoride in the presence of silver(I) triflate results in a very rapid process leading to the corresponding vinyl fluoride. The reaction is regio- and stereospecific and does not require stoichiometric Ag(I). No evidence could be obtained of radical intermediates on the reaction pathway leading to the vinyl fluorides. A symmetrical dimer derived from the vinylstannane, which was obtained as a reaction byproduct, was shown to arise from oxidative coupling by the silver salt. The results are consistent with an electrophilic mechanism following an initial interaction of the vinylstannane with Ag(I).

Introduction

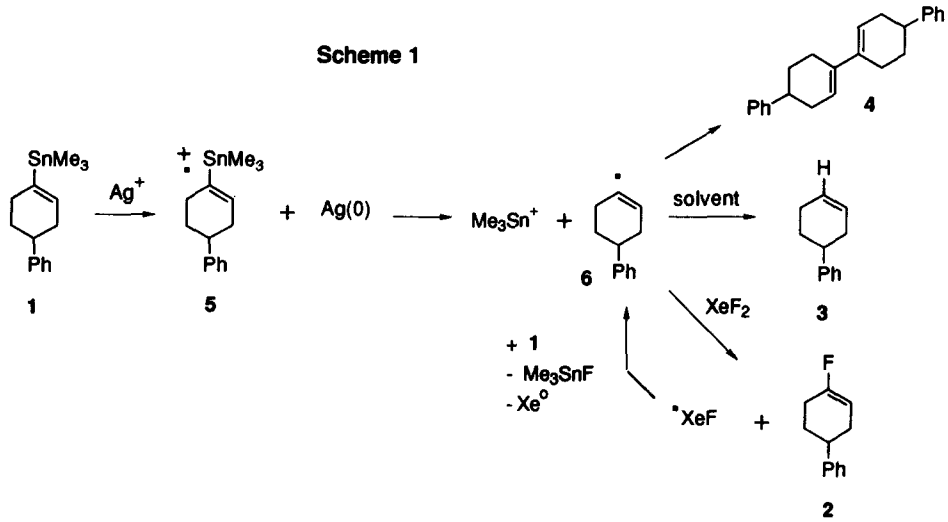
An ongoing research problem in our group required the development of a convenient and general method for the introduction of fluorine into vinylstannanes. A rapid reaction was preferred, because an ancillary goal of the research was the development of methodology for labelling organic molecules with ^{18}F ($t_{1/2}$ = 110 min). This short-lived fluorine isotope is a positron emitter, and is useful for *in vivo* metabolic studies and receptor mapping.[1] Vinyl stannanes are easily prepared through a variety of chemical pathways,[2] and are known to react with carbon- and heteroatomic electrophiles in high yield.[3] Consequently, the combination of a vinylstannane with an *electrophilic* source of fluorine might reasonably be expected to produce a vinyl fluoride.[4] Analogous reactions with iodine, bromine or chlorine are certainly well-known.[3] Two preliminary accounts of our efforts in this area have been disclosed. In the first,[5] the reaction of vinylstannanes, xenon difluoride (XeF_2) and silver(I) hexafluorophosphate was described. The second account[6] disclosed a much faster process which utilizes silver(I) trifluoromethanesulfonate (AgOTf, silver(I) triflate), XeF_2 and silver(I) carbonate. The work herein describes further refinements of the method, its scope and limitations, and provides some insight into the mechanism(s) of the reaction.

Discussion

Trimethylvinylstannane **1** was prepared from 4-phenylcyclohexanone via the trisylhydrazone in 50% overall yield from the ketone.[7] Exposure of **1** to XeF_2 in dichloromethane in the presence of stoichiometric $AgPF_6$ produced a mixture of vinyl fluoride **2** and alkene **3** in 51% and 34% yield, respectively (Scheme 1). The reaction was complete within 3 h at 25 °C. A much faster reaction took place with AgOTf: within 5 min the reaction was complete and **2** was formed in 79% yield. Fluorination also proceeds in the absence of Ag(I), but in lower yield, and in a much slower reaction: only 10-20% of **2** could be isolated after 2-3 d at 25 °C, the

balance of the material being present as alkene **3**.[8] This trend appears to be general: slow reactions produce vinyl fluorides in poor yield, whereas the most rapid reactions proceed in the highest yields. Related to this observation is the fact that the slow reactions are accompanied by larger amounts of the alkene. In some reactions a byproduct was observed: in the case of **1**, the structure of this byproduct was shown to correspond to dimer **4**, which was present as a mixture of diastereoisomers.

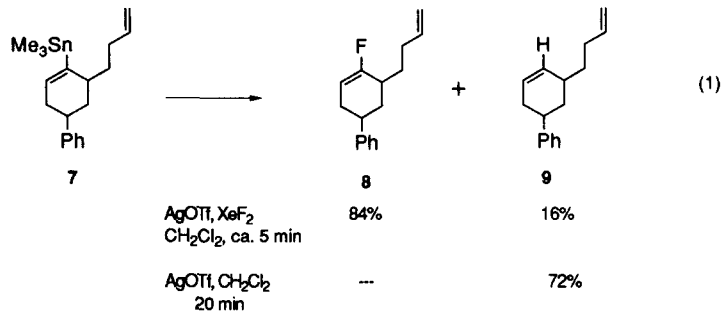
Scheme 1



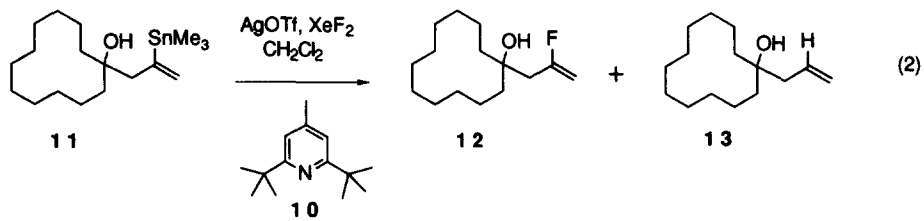
A mechanism which might explain the observed distribution of products is summarized in Scheme 1. Single electron transfer from stannane **1** to silver(I) would lead to radical cation **5** and elemental silver.[9] Fragmentation of **5** would lead to a trimethylstannyl cation and vinyl radical **6**, which could react with XeF_2 to produce **2** and a fluoroxenon radical.[10] The fluoroxenon radical could react with stannane **1** to generate trimethyl tin fluoride and vinyl radical **6** in a chain process. Alkene **3** presumably could arise from a hydrogen atom abstraction process, whereas radical coupling would lead to **4**. Thus the occurrence of **4** would not require XeF_2. Indeed, treatment of **1** with 1.1 equiv of AgOTf in the absence of XeF_2 led to **4** in 79% yield; the deposition of a silver mirror was observed during this reaction. The mechanism of Scheme 1 also suggests that silver may be acting as an initiator for a radical chain process, in which case the reaction leading to **2** would be expected to take place in the presence of substoichiometric quantities of the silver salt. This was also found to be the case: the reaction of **1** with 1.0 equiv of XeF_2 and 0.4 equiv of AgOTf produced vinyl fluoride **2** in 66% yield along with 24% of alkene **3**. The reaction with 0.3 or 0.5 equiv of AgOTf was no different. The reaction with 0.1 equiv of $AgBF_4$ afforded **2** in 48% yield, along with 37% of **3**.

Scheme 1 was plausible, but if vinyl radical **6** was indeed an intermediate, then one might expect to be able to intercept this species. All attempts to do this failed. Substituting dideuteriodichloromethane for dichloromethane led to the same ratio and isolated yields of fluoride **2**, alkene **3** and dimer **4** (8/1.5/0.5) No incorporation of deuterium was detected. No difference in reaction products could be observed when hexafluorobenzene or 1,1,2-trichloro-1,2,2,-trifluoroethane was used as the reaction solvent, or in the presence of 5 equiv of acrylonitrile or 10 equiv of 1,1-dichloroethylene which were added as radical traps.[11]

The fluorination proceeded smoothly even in neat 1,1-dichloroethylene, and gave **2** in 76% isolated yield. In the absence of XeF_2, the reaction of **1** with 1.1 equiv of AgOTf in neat 1,1-dichloroethylene led to a mixture consisting of dimer **4** as the major product, along with lesser amounts of alkene **3**. There was no indication of any products derived from radical **6**.



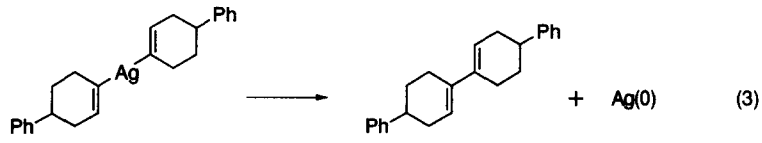
Additional evidence against the intermediacy of a radical came from the reactions of **7** (eq 1).[12] Exposure of **7** to 1.1 equiv of XeF_2 and 1.1 equiv AgOTf in dichloromethane led to vinyl fluoride **8** in 84% isolated yield, along with ca. 16% of alkene **9**. The reaction was complete within 5 min at 25 °C. In the absence of XeF_2, alkene **9** was the sole isolated product in 72% yield. It has been shown that oxidative decarboxylation of 6-heptenoic acid with XeF_2, a process which proceeds via hex-5-enyl radical, leads to a 1:3 mixture of (fluoromethyl)cyclopentane and 6-fluoro-1-hexene.[13] Furthermore, Beckwith has shown that the rate for the 5-*exo* ring closure of vinyl radicals is even greater (ca. 10 X) than for ring closure of hex-5-enyl radical.[14] Therefore if a vinyl radical had been generated from **7**, the cyclic product would have been observed.



Radicals are not implicated in the formation of **3** and **4**, neither are they required in order to rationalize the observed products. Protiodestannylation of **1** by HF, which is produced by the slow decomposition of XeF_2 in dichloromethane, would lead to **3**. The observation that the slower fluorination reactions were accompanied by greater amounts of alkene is consistent with this hypothesis. Heterogeneous bases had no effect on the fluorination reaction, or on the proportion of **3** in the product. The addition of 2,6-di-*tert*-butyl-4-methylpyridine **10** to the fluorination reaction as a soluble proton scavenger was an effective way to improve the yields of the slower fluorinations. For example, in the absence of a proton scavenger, stannane **11** led to fluoride **12** in 55% yield, along with ca. 45% of alkene **13** (eq 2). In the presence of 1 equiv of **10**, the molar ratio of **12** to **13** was 4:1 (74% yield of **12**). Increasing to four the number of equivalents of **10** did not

improve the product ratio. As little as 0.1 equiv of **10** effectively suppressed the formation of alkene, probably by inhibiting the HF-catalyzed decomposition of XeF_2.

Assuming that the mechanism which led from **1** to **4** in the presence of XeF_2 was the same as in the absence of the fluorinating agent, **2** and **4** need not have a common intermediate. The appearance of metallic silver in the reaction suggests that **4** is formed from the reductive elimination of an organosilver intermediate,[9] perhaps as represented by **14** in eq 3. The failure of **7** to undergo dimerization (**9** is the sole product of reaction with AgOTf) may be the consequence of steric inhibition due to the butenyl appendage. No effort was made to determine the scope of the dimerization.



14 **4**

$$AgF + FXeOSO_2CF_3 \longleftarrow AgOSO_2CF_3 + XeF_2 \longrightarrow AgF + Xe^{\circ} + FOSO_2CF_3 \quad (4)$$

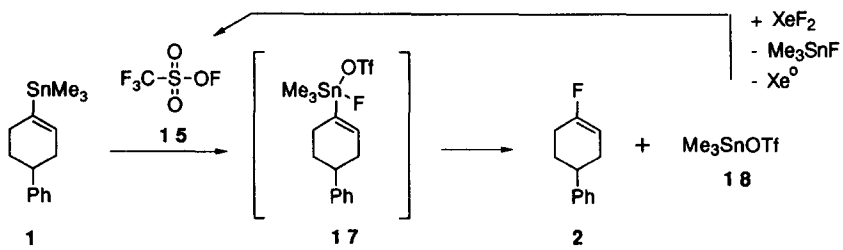
16 **15**

Since no evidence to support a radical mechanism could be obtained, an ionic process appeared likely. The dramatic accelerating effect of silver ion suggested that it might be combining with XeF_2 to form a more reactive source of fluorine. Silver triflate might undergo a reaction with XeF_2 to produce solid AgF and either xenon gas and trifluoromethanesulfonyl hypofluorite **15**,[15] or the fluoroxenon triflate **16** (eq 4). Both **15** and **16** would be expected to be extremely reactive sources of F^+ and XeF^+, respectively. Any mechanism which is postulated must account for the fact that the reaction proceeds with sub-stoichiometric AgOTf. The proposed mechanism of Scheme 2 indicates that oxidative addition of **15** to stannane **1** would generate hexacoordinate tin species **17** which would collapse to vinyl fluoride **2** and trimethylstannyl triflate **18**. In the presence of XeF_2, **18** could undergo conversion to hypofluorite **15** with loss of trimethyltin fluoride and xenon gas. This would constitute a chain process which suggested that **18** could be used in place of AgOTf. Accordingly, **18** was prepared from bis(trimethyltin)oxide and triflic anhydride,[16] and the reaction with 1 equiv each of XeF_2, **1** and **18** was carried out. This led to a fast (ca. 5 min) reaction in which 20% of **2** was formed, along with a complex product mixture which contained alkene **3**. The same result was obtained with 0.2 equiv of **18** or when commercially available tri-*n*-butylstannyl triflate was used in place of **18**. These reactions were not appreciably different in the presence of proton scavenger **10**.[17] Since these results were inconclusive, an effort was made to secure some direct evidence for the presence of **15**, **16** or some other source of reactive fluorine which might be generated during the reaction.

The heterogeneous nature of the reaction had discouraged our efforts to use spectroscopy to obtain support for the mechanism. Notwithstanding, a series of experiments was conducted in which AgOTf was added to solutions of XeF_2 in CD_2Cl_2 at temperatures ranging from -80 °C to 25 °C. These experiments were conducted as follows: XeF_2 was dissolved in CD_2Cl_2 in a nmr tube, and cooled to the reaction temperature in a cold bath. The solid AgOTf (25 mg) was added and the heterogeneous mixture was shaken for a few seconds,

then placed in the nmr probe which was equilibrated to the temperature of the reaction. The solutions were monitored by ^{19}F nmr at 283 MHz. Trifluoroacetic acid was used as an external standard (-76.55 ppm, singlet). However, the chemical shifts and the multiplicities of the signals for XeF_2 (-174 ppm, singlet, with ^{129}Xe satellites, $J^{129}_{Xe}{}^{-19}_{F} = 5{,}607$ Hz) and the trifluoromethyl group of silver triflate (-74 ppm, singlet) remained unchanged when compared to samples of each of the individual reagents. At -80 °C, there was no apparent change in the concentration of XeF_2 even after 2 h. As the solutions were allowed to warm to 25 °C, slow decomposition of the XeF_2 was observed, but no peaks corresponding to **15** or **16** could be detected. The sensitivity of these experiments was determined as follows: 25 mg of AgOTf was dissolved in DMSO-d_6 and examined by ^{19}F nmr. The singlet at -77.5 ppm due to the CF_3 group had symmetrical ^{13}C satellites with a 320 Hz coupling constant. That these were, in fact, ^{13}C satellites was confirmed by examining the ^{13}C nmr spectrum of AgOTf in DMSO-d_6 (75 MHz). The quartet at 121 ppm due to the CF_3 group showed coupling of 322 Hz. Since ^{13}C occurs at ca. 1% natural abundance, the detection of the ^{13}C satellites in the ^{19}F nmr suggests that the sensitivity of the nmr experiments was sufficient to detect ca. 0.5% of a soluble species related to **15** or **16**.

Scheme 2

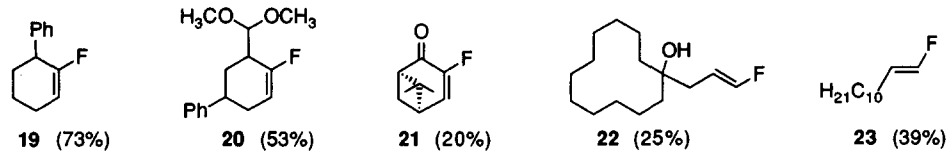


Scope of the Fluorination

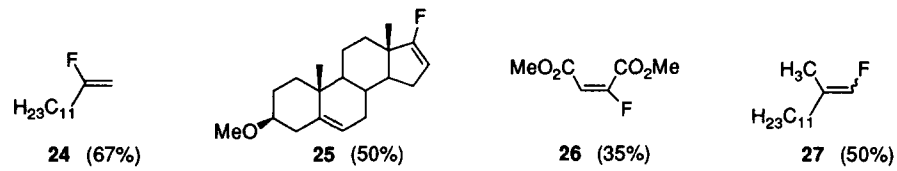
Shown below are some examples of the reaction. The numbers in parentheses correspond to isolated yields of purified products. Volatile products were isolated in lower yields due to evaporative losses (e.g. **21**, **23**, **26**). Vinyl fluorides **19-25** were derived from the corresponding trimethylvinylstannanes, whereas fluorides **26-32** were derived from the tri-*n*-butylvinylstannanes. The reaction appears to be regio- and stereospecific: the carbon bearing the tin in the starting material is bonded to fluorine in the product, and the geometry of the vinylstannane is preserved in the vinyl fluoride.[5, 6, 18] The vinylstannane precursors to **27** and **31** were 1/1 mixtures of geometrical isomers. The ratio of geometric isomers was unchanged in the vinyl fluoride products. The reaction is tolerant of functionality: ketone, ester, ether, tertiary alcohol, carbamate and dimethyl ketal groups are not affected.

The fluorination does not work well for all classes of vinylstannanes. For example, exposure of *N*-phenylsulfonyl-3-trimethylstannylindole to XeF_2 and AgOTf led to the 3-fluoroindole derivative in 30% yield. *N*-Phenylsulfonyl-2-trimethylstannylindole also produced the 3-fluoroindole in 30% yield, along with ca. 7% of the 2-fluoroindole. This was the only non-regiospecific fluorination observed. It is likely that a conventional electrophilic aromatic substitution reaction[10] took place at the reactive C3 of the indole, followed in both cases by destannylation to produce the 3-fluoroindole. The small amount of 2-fluoroindole was

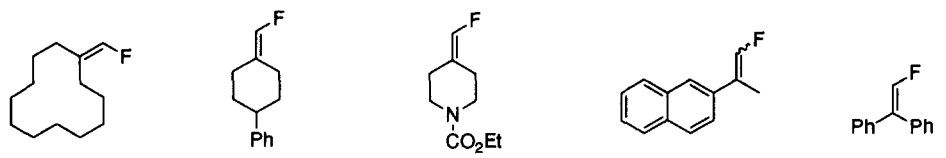
presumably formed through a regiospecific process. Distannane **33** provided only monofluorinated products **12** and **22** (eq 5). Protiodestannylation presumably took place faster than substitution by a second fluorine. The results indicate that fluorination at the most electron-rich carbon atom is favored, and argue strongly against the intermediacy of a carbocationic intermediate. Had such an intermediate been formed from **33**, it would likely have been intercepted by the hydroxyl group to produce a cyclic ether.



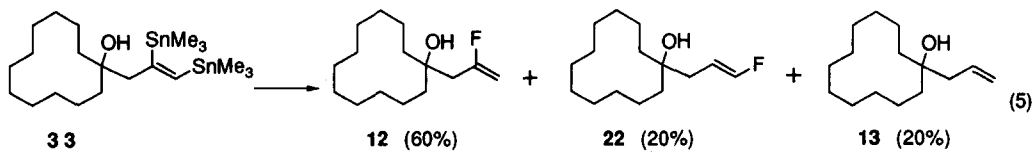
19 (73%) **20** (53%) **21** (20%) **22** (25%) **23** (39%)



24 (67%) **25** (50%) **26** (35%) **27** (50%)

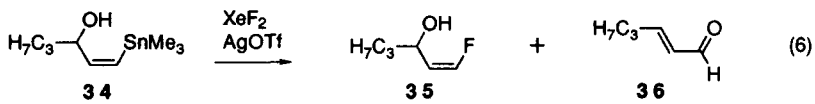


28 (70%) **29** (60%) **30** (57%) **31** (44%) **32** (48%)



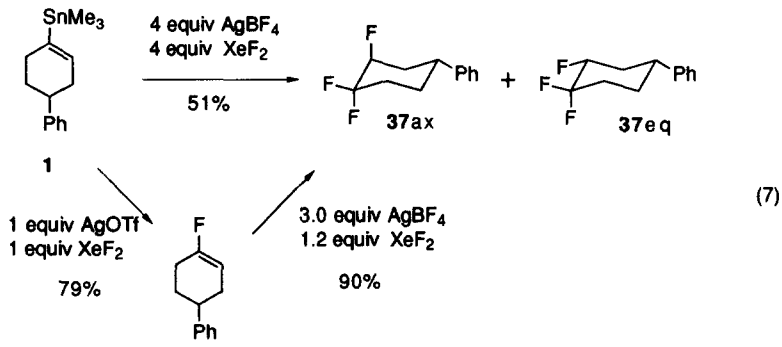
33 **12** (60%) **22** (20%) **13** (20%) (5)

Vinylstannane **34** underwent conversion to fluoride **35** in only ca. 5% yield along with a larger amount (30%) of *trans*-hexenal **36** (eq 6). The aldehyde was probably derived from the acid-catalyzed hydrolysis of **35**. Protonation of the hydroxyl group in **35**, followed by loss of water, would generate a fluoroallyl cation. The destabilizing inductive effect of the fluorine is overwhelmed by resonance stabilization of the positively charged carbon involving the non-bonded electron pairs on the halogen.[19] The fluoroallyl cation undergoes trapping by water to produce a fluorohydrin which collapses to HF and **36**. Similar reactions have been reported by Normant.[20]

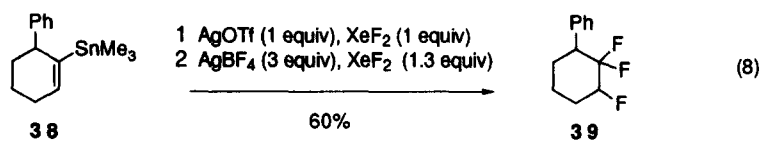


34 **35** **36** (6)

An interesting reaction took place when **1** was exposed to modest excesses of $AgBF_4$ and XeF_2 (eq 7). Diastereomeric trifluorides **37**ax and **37**eq were obtained in a 3:2 ratio. The assignment of structure was made by ^{19}F nmr. The coupling constant in **37**ax of the axial fluorine to the geminal proton is 47 Hz. The vicinal coupling constant of the same fluorine atom to the axial proton is 45 Hz, whereas the coupling to the vicinal equatorial fluorine is 14 Hz. In **37**eq the coupling constant between the equatorial fluorine and the geminal proton is 46 Hz; the coupling constant to each of the two vicinal fluorines is 11 Hz. These values are very similar to the ones reported for fluorine in a six-membered ring.[21] The trifluorides could be prepared in much higher overall yield in two steps, by first converting **1** to vinyl fluoride **2** according to the optimized conditions, followed by exposure of **2** to $AgBF_4/XeF_2$ (eq 7). There is some precedent for this process. The HF-catalyzed addition of XeF_2 to alkenes, leading to vicinal difluorides, is known.[4g, 22] To the best of our knowledge, this reaction has not been reported for vinyl fluorides.[23] The acid which catalyzes the formation of **37**ax and **37**eq is not derived from decomposition of XeF_2, as shown by the fact that exposure of **1** to excesses of AgOTf and XeF_2 led to barely detectable (by ^{19}F and ^1H nmr) amounts of trifluoride. Presumably the HBF_4 which is present in $AgBF_4$ catalyzes the process. This also explains why the two-step process is more efficient: competitive protiodestannylation of **1** by HBF_4 diminishes the yield of trifluorides in the direct process. Furthermore, the addition of 10 equiv of proton scavenger **10** to the reaction of **2** with $AgBF_4$ and XeF_2 completely suppresses the reaction leading to the trifluorides. The reaction appears to be general. Exposure of stannane **38** to excesses of $AgBF_4$ and XeF_2 led to diastereomeric trifluorides **39** in 60% yield (eq 8).



(7)



(8)

Two reagents other than XeF_2/AgOTf for the conversion of vinyl stannanes to vinyl fluorides have been described: cesium fluoroxysulfate[4c] and McCarthy's reagent, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate).[4b] The conversion of **1** to **2** with cesium fluoroxysulfate

takes place at 25 °C overnight in 48% yield. For this particular substrate, the yield is higher in the XeF_2 reaction (79%), and the reaction time is much shorter. Cesium fluoroxysulfate is not an article of commerce and must be prepared from elemental fluorine and cesium sulfate. Moreover, this salt has been reported to be shock-sensitive and also to undergo detonation upon heating.[24] Nevertheless, it is probably the reagent of choice for the electrophilic fluorination of aromatic stannanes.[25] For example, fluorination of 2- and 3-trimethylstannylindole tosylates with cesium fluoroxysulfate in methanol overnight leads regiospecifically to the 2- and 3-fluoroindole derivatives in 61% and 72% yield, respectively.[4c] This is a reaction for which the XeF_2/AgOTf combination of reagents is not effective. McCarthy's reagent is thermally stable and easy to handle. The yield of vinyl fluoride **32** is higher with McCarthy's reagent than with XeF_2/AgOTf (71% vs. 48%). The reaction takes place in 30 min at 80 °C, rather than 5 min at 25 °C for XeF_2/AgOTf.[4b]

Conclusions

A rapid, stereospecific method for converting vinyl stannanes to vinyl fluorides has been described. The reactions typically proceed to completion within 5 to 10 min. Since [^{18}F]XeF_2 has been described,[26] the method is suitable for ^{18}F-labeling. Because the silver counterion is triflate, no dilution of the label is expected to take place, as might be the case with BF_4^- or PF_6^-.[27] The method is best suited for the preparation of non-aromatic trisubstituted alkenes. For other classes of alkenes yields are not always preparatively useful.

There appear to be at least two mechanisms which lead to the vinyl fluorides. A very slow reaction takes place between XeF_2 and vinyl stannanes to produce low yields of the fluorides. A fast reaction takes place in the presence of Ag(I). The rapid fluorination which is catalyzed by Me_3SnOTf **18** (Scheme 2) may represent a third reaction manifold. The AgOTf-catalyzed reaction appears to proceed following initial interaction of the alkene with the silver ion, rather than by production of a more reactive fluorine source from the combination of XeF_2 with silver. The question whether other metals might also catalyze the fluorination was briefly examined. In particular, the reaction with Cu(I) was of interest, since Piers has recently shown that Stille coupling of vinyl stannanes with vinyl iodides can be accomplished with CuCl in the absence of Pd(0), which suggests an interaction between a vinylstannane and Cu(I).[28] The reaction of **1** with XeF_2 in the presence of anhydrous cuprous triflate-benzene complex produced a small amount (ca. 5%) of vinyl fluoride **2**, along with alkene **3** (80%) in a rapid (< 5 min) reaction. This reaction bears further scrutiny.

Acknowledgement is made to NIDA (DA07215 and DA06731) for generous support. We thank Prof. Gordon Gribble for gifts of *N*-phenylsulfonylindole and 3-bromo-*N*-phenylsulfonylindole, and Prof. Andrew Kende for helpful suggestions.

EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectra were recorded at 300 MHz ^{1}H (75 MHz ^{13}C) or 500 MHz ^{1}H (125 MHz ^{13}C) in deuteriochloroform ($CDCl_3$) with chloroform (7.26 ppm ^{1}H, 77.00 ppm ^{13}C) as an internal reference. ^{19}F-NMR spectra were recorded at 283 MHz ($CDCl_3$) with either trifluoroacetic acid (-76.55 ppm ^{19}F) or fluorochloroform (0.00 ppm ^{19}F) as an external standard. Chemical shifts are given in δ; multiplicities are indicated as br (broadened), s (singlet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are reported in hertz (Hz). Infrared spectra were recorded on a Perkin-Elmer IR 1430 spectrometer. Electron impact mass spectra were performed on a VG-70SE mass spectrometer. Mass spectral data are reported in the form of m/e. Thin-layer chromatography (TLC) was performed on EM Reagents precoated silica gel 60 F-254

analytical plates (0.25 mm). Flash column chromatography was performed on Brinkmann silica gel (0.040-0.063 mm) or YMC GEL ODS 120A S-50. Xenon difluoride was purchased from PCR and used as received. The vinylstannane starting materials were prepared in the following ways: (1) The vinyllithium anion derived from the trisylhydrazone[7a] was trapped with trimethyltin chloride[7b] to produce the starting materials for fluorides **2, 19, 20, 24** and **25**. (2) The palladium-catalyzed reaction of the vinyl triflate with hexamethylditin was used to produce the starting materials for fluoride **21**.[2f] (3) Exposure of the vinylsulfones to tri-*n*-butyltin hydride and 1,1'-azobis(cyclohexanecarbonitrile) produced the starting materials for fluorides **27-32**.[29] (4) The palladium-catalyzed reaction of the alkynes with trimethyltin hydride produced the starting materials for fluorides **12, 22, 23** and **26**.[2d] Stannane **33** was prepared in a similar manner by using hexamethylditin in place of trimethyltin hydride. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl, dichloromethane (CH_2Cl_2) from phosphorus pentoxide and hexane from calcium hydride. Other reagents were obtained commercially and used as received unless otherwise specified. All reactions were performed under a static nitrogen or argon atmosphere in flame-dried glassware. The purity and homogeneity of the products on which the high resolution mass spectral data are reported were determined on the basis of 300 MHz ^{1}H-NMR (94%) and multiple elution TLC analysis, respectively. Combustion analyses were performed by Desert Analytics Laboratory.

1-Fluoro-4-phenylcyclohexene (2). (General Procedure)

To a two-neck flask charged with 129 mg (0.47 mmol) of Ag_2CO_3 and 4.5 mL of CH_2Cl_2 was added trifluoromethanesulfonic acid (103 mg, 0.68 mmol).[30] The stirred flask was shielded from light with aluminum foil. After 30 min at 23 °C 200 mg (0.62 mmol) of vinylstannane **1** in 4.5 mL of CH_2Cl_2 containing 13 mg (0.1 equiv) of 2,6-di-*tert*-butyl-4-methylpyridine was transferred by cannula, followed immediately by 116 mg (0.69 mmol) of XeF_2 in 9.0 mL of CH_2Cl_2. After 5 min the solution was transferred to a separatory funnel, and partitioned between sat'd aq $NaHCO_3$ and CH_2Cl_2. The organic phase was dried ($MgSO_4$) and evaporated. The residue was purified by flash column chromatography on silica gel (pentane) to give 87 mg (79% yield) of **2** as a white, crystalline solid:[31] mp 66-68 °C; mass spectrum m/e 176(M^+), 104. Exact mass calculated for $C_{12}H_{13}F$: 176.1001, found: 176.1007. Anal Calcd for $C_{12}H_{13}F$: C, 81.78; H, 7.44. Found: C, 81.70; H, 7.25.

1-Fluoro-4-phenyl-6-(3-butenyl)cyclohexene (8).

Vinyl fluoride **8** (26 mg) was prepared from 51 mg of **7** as an 8/1 mixture of diastereoisomers according to the general procedure described above in 84% yield: colorless oil; (major diastereoisomer) IR (neat) 2920, 1700, 1490, 1450, 1150, 1120, 920 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (br t, J=7.5 Hz, 2H), 7.23 (br d, J=7.5 Hz, 3H), 5.81 (ddt, J=16.9, 10.1, 6.6 Hz, 1H), 5.28 (dm, J=17.6 Hz, 1H), 5.03 (dt, J=17.2, 1.6 Hz, 1H), 4.97 (dd, J=10.1, 1.7 Hz, 1H), 2.85-2.78 (m, 1H), 2.62 (br s, 1H), 2.26-2.21 (m, 2H), 2.21-2.15 (m, 1H), 2.15-2.04 (m, 2H), 1.92-1.85 (m, 1H), 1.61 (dd, J=23.5, 12.7 Hz, 1H), 1.47-1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, J=255.3 Hz), 145.7, 138.4, 128.5, 126.8, 126.4, 114.8, 102.2 (d, J=16.7 Hz), 40.2, 36.7 (d, J=7.4 Hz), 36.3 (d, J=22.2 Hz), 31.1 (d, J=7.4 Hz), 30.7, 30.4; ^{19}F NMR (283 MHz, $CDCl_3$) δ -108.1 (br d, J=10.9 Hz, 1F, minor isomer), -113.4 (br d, J=15.7 Hz, 1F, major isomer); mass spectrum m/e 230(M^+), 204, 188, 173, 146, 129, 115, 105, 91, 77. Exact mass calculated for $C_{16}H_{19}F$: 230.1471, found: 230.1487.

1-(2-Fluoro-2-propenyl)-cyclododecanol (12).

Vinyl fluoride **12** (40 mg) was prepared from 51 mg of **11** according to the general procedure described above in 55% yield. In the presence of 0.1 equiv of **10** the yield of **12** was 74%: colorless oil; IR (neat) 3420, 2920, 2860, 1670, 1470, 1440, 1150, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (dd, J=17.7, 2.7 Hz, 1H), 4.34 (dd, J=50.4, 2.4 Hz, 1H), 2.32 (d, J=22.2 Hz, 2H), 1.70-1.45 (m, 3H), 1.36 (br s, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0 (d, J=257.7 Hz), 93.8 (d, J=20.3 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -88.6 (dtd, J=45.0, 25.0, 20.0 Hz); mass spectrum m/e 242(M^+), 224, 206, 199, 183, 109, 95, 83, 69. Exact mass calculated for $C_{15}H_{27}OF$: 242.2046, found: 242.2043.

1-Fluoro-6-phenylcyclohexene (19).

Vinyl fluoride **19** (121 mg) was prepared from the trimethylvinylstannane (300 mg) according to the general procedure described above in 73% yield: colorless oil; IR (neat) 3080, 3060, 3020, 2930, 2880, 1695, 1600, 1490, 1450, 1440, 1370, 1150, 1130, 885, 870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (br t, J=7.4 Hz, 2H), 7.30-7.20 (m, 3H), 5.49 (dt, J=17.7, 3.9 Hz, 1H), 3.62 (br s, 1H), 2.25-2.00 (m, 3H), 1.85-1.70 (m, 1H), 1.65-1.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5 (d, J=255.0 Hz), 142.0, 127.6, 126.3, 105.5, 104.3 (d, J=21.1 Hz), 42.5 (d, J=24.4 Hz), 32.9 (d, J=6.5 Hz), 23.0 (d, J=7.5 Hz), 19.1; ^{19}F NMR (283 MHz, $CDCl_3$) δ -104.7 (br d, J=12.9 Hz); mass spectrum m/e 176(M^+), 148, 147, 133, 98, 77. Exact mass calculated for $C_{12}H_{13}F$: 176.1001, found: 176.0991.

1-Fluoro-6-(1,1-dimethoxymethyl)-4-phenylcyclohexene (20).

Vinyl fluoride **20** (50 mg) was prepared from the trimethylvinylstannane (148 mg) according to the general procedure described above in 53% yield: colorless oil; IR (neat) 2960, 2940, 2900, 1720, 1600, 1500, 1450, 1240, 1150, 1080, 1020, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 3H), 7.23 (br t, J=3.3 Hz, 2H), 5.46 (br d, J=17.7 Hz, 1H), 4.58 (d, J=5.4 Hz, 1H), 4.32 (heptet, J=6.9 Hz, 1H), 3.44 (s, 6H), 3.25-2.50 (m, 3H), 2.50-1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3 (d, J=256.2 Hz), 104.7 (d, J=16.6 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -107.1 (d, J=12.1 Hz).

3-Fluoroapoverbenone (21).

3-Fluoroapoverbenone **21** (6 mg; volatile!) was prepared from the trimethylstannane (63 mg) according to the general procedure described above in 20% yield: colorless oil; IR (neat) 3050, 2950, 2850, 1700, 1470, 1390, 1370, 1260, 1040, 900, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (br t, J=8.1 Hz, 1H); ^{19}F NMR (283 MHz, $CDCl_3$) δ -141.9 (br t, J=7.0 Hz).

1-(E-3-Fluoro-2-propenyl)-cyclododecanol (22).

Vinyl fluoride **22** (18 mg) was prepared from the trimethylstannane (114 mg) according to the general procedure described above in 25% yield: colorless oil; IR (neat) 3420, 2900, 1720, 1580, 1450, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 (dd, J=85.5, 11.1 Hz, 1H), 5.45 (ddt, J=18.9, 11.1, 8.4 Hz, 1H), 1.99 (d, J=8.4 Hz, 2H), 1.55-1.45 (m, 2H), 1.45-1.25 (br s, 21H); ^{19}F NMR (283 MHz, $CDCl_3$) δ -124.9 (dd, J=84.0, 22.0 Hz); mass spectrum m/e 242(M^+), 224, 204, 190, 163, 149, 95.

E-1-Fluorododecene (23).

Vinyl fluoride **23** (39 mg) was prepared from the trimethylstannane (188 mg) according to the general procedure described above in 39% yield: colorless oil; IR (neat) 2950, 1715, 1600, 1570, 1460, 1410, 1380, 1350, 1250, 1210, 1160, 970, 940, 850, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.51 (dd, J=86.1, 11.1

Hz, 1H), 5.70-5.50 (m, 1H), 2.10-1.90 (m, 2H), 1.37 (br s, 16H), 0.92 (br t, J=7.0 Hz, 3H); ^{19}F NMR (283 MHz, $CDCl_3$) δ -30.8 (dd, J=84.5, 20.7 Hz).

2-Fluorotridecene (24).

Vinyl fluoride **24** (78 mg) was prepared from the trimethylstannane (200 mg) according to the general procedure described above in 67% yield: colorless oil; IR (neat) 2960, 2920, 2850, 1670, 1460, 1380, 1350, 935, 910, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.48 (dd, J=17.7, 2.7 Hz, 1H), 4.19 (dd, J=50.7, 2.7 Hz, 1H), 1.60-1.10 (br s, 20H), 0.89 (br t, J=6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1 (d, J=258.1 Hz), 89.2 (d, J=21.6 Hz), 53.9 (d, J=20.0 Hz), 31.9, 31.7, 29.6, 29.5, 29.3, 28.9, 26.0, 22.7, 14.1; ^{19}F NMR (283 MHz, $CDCl_3$) δ -94.5 (ddt, J=54.3, 17.0, 12.6 Hz). Exact mass calculated for $C_{13}H_{25}F$: 200.1940, found: 200.1938.

Fluorosteroid (25).

Vinyl fluoride **25** (32 mg) was prepared from the trimethylstannane[32] (94 mg) according to the general procedure described above in 50% yield: colorless oil; IR (neat) 2940, 2840, 1720, 1670, 1450, 1380, 1200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.37 (d, J=5.1 Hz, 1H), 4.89 (d, J=1.2 Hz, 1H), 3.36 (s, 3H), 3.15-3.00 (m, 1H), 2.40 (br d, J=10.8 Hz, 1H), 2.30-1.70 (m, 7H), 1.70-1.20 (m, 9H), 1.03 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8 (d, J=289.0 Hz), 143.8, 121.0, 100.6 (d, J=10.8 Hz), 80.2, 55.6, 54.5 (d, J=4.6 Hz), 50.8, 38.7, 37.1, 37.0, 35.9, 32.8, 30.6, 29.9, 27.9, 26.8 (d, J=7.7 Hz), 20.2, 19.2, 15.1; ^{19}F NMR (283 MHz, $CDCl_3$) δ -131.7 (br s).

Dimethyl 2-Fluoromaleate (26).

Vinyl fluoride **26** (65 mg) was prepared from the tri-*n*-butylstannane (500 mg) according to the general procedure described above in 35% yield: colorless oil; IR (neat) 2980, 2850, 2880, 2860, 1740, 1430, 1240, 1170 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (d, J=15.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H); ^{19}F NMR (283 MHz, $CDCl_3$) δ -110.2 (d, J=15.1 Hz).

1-Fluoro-2-methyltridecene (27).

Vinyl fluoride **27** (56 mg) was prepared as a mixture of geometrical isomers from the tri-*n*-butylstannane (255 mg, also a 1/1 mixture of geometrical isomers) according to the general procedure described above in 50% yield: colorless oil; IR (neat) 2960, 2920, 2860, 1690, 1465, 1455, 1380, 1250, 1130, 1095, 890, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, isomeric mixture) δ 6.39 (br d, J=86.7 Hz, 1H), 6.37 (br d, J=86.7 Hz, 1H), 2.10 (br t, J=6.6 Hz, 2H), 2.01 (br t, J=6.9 Hz, 2H), 1.72 (br s, 3H), 1.63 (br s, 3H), 1.50-1.10 (br s, 36H), 0.89 (br t, J=6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, isomeric mixture) δ 143.3 (d, J=250.3 Hz), 142.9 (d, J=250.3 Hz), 118.3 (d, J=6.2 Hz), 118.2 (d, J=4.6 Hz), 31.4 (d, J=7.8 Hz), 29.7, 29.5, 29.45, 29.4, 29.3, 29.1, 27.82, 27.8, 27.7, 27.4, 27.3, 27.0, 22.4, 14.8 (d, J=9.3 Hz), 13.7, 11.8 (d, J=9.3 Hz), 8.7; ^{19}F NMR (283 MHz, $CDCl_3$, isomeric mixture) δ -137.5 (d, J=88.6 Hz), -136.4 (d, J=87.5 Hz). Anal Calcd for $C_{14}H_{27}F$: C, 78.44; H, 12.70. Found: C, 74.24; H, 12.12.

1-Fluoromethylenecyclododecane (28).

Vinyl fluoride **28** (49 mg) was prepared from the tri-*n*-butylstannane (165 mg) according to the general procedure described above in 70% yield: colorless oil; IR (neat) 2960, 2920, 2860, 1460, 1440, 1380, 1370, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.38 (br d, J=87.6 Hz, 1H), 2.87 (br d, J=13.5 Hz, 1H), 2.12 (br dd, J=15.6, 2.1 Hz, 1H), 1.87 (br d, J=9.9 Hz, 2H), 1.63 (br t, J=13.0 Hz, 1H), 1.49-1.40 (m, 1H), 1.35-1.27 (m, 2H), 1.14-0.98 (m, 4H), 0.62 (br s, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1 (d, J=249.7 Hz),

121.6 (d, J=5.6 Hz), 30.1, 29.3, 28.3, 28.1 (d, J=7.4 Hz), 27.6, 27.3, 24.5 (d, J=5.6 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -141.7 (d, J=87.6 Hz).

1-Fluoromethylene-4-phenylcyclohexane (29).

Vinyl fluoride **29** (124 mg) was prepared from the tri-*n*-butylstannane (500 mg) according to the general procedure described above in 60% yield: colorless oil; IR (neat) 3080, 3060, 3030, 2930, 2860, 1690, 1600, 1495, 1450, 1100, 1075, 1060, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (br t, J=7.2 Hz, 2H), 7.21 (br d, J=6.6 Hz, 3H), 6.46 (d, J=87.0 Hz, 1H), 2.97 (br d, J=13.5 Hz, 1H), 2.67 (tt, J=12.3, 3.3 Hz, 1H), 2.22 (br d, J=13.2 Hz, 1H), 2.10-1.90 (m, 3H), 1.84 (br t, J=13.8 Hz, 1H), 1.58-1.50 (m, 1H), 1.49 (tt, J=12.6, 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 140.8 (d, J=250.4 Hz), 128.4, 126.8, 126.1, 120.5 (d, J=6.3 Hz), 44.3, 34.9, 33.8, 27.9 (d, J=7.8 Hz), 24.4 (d, J=6.3 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -140.3 (d, J=85.7 Hz); mass spectrum m/e 190(M^+), 161, 157, 129, 117, 115, 112, 104, 97, 91, 79, 65, 51. Exact mass calculated for $C_{13}H_{15}F$: 190.1112, found: 190.1135.

***N*-Carboethoxy-4-(fluoromethylene)piperidine (30).**

Vinyl fluoride **30** (53 mg) was prepared from the tri-*n*-butylstannane (228 mg) according to the general procedure described above in 57% yield: colorless oil; IR (neat) 2950, 2880, 1710, 1475, 1430, 1280, 1250, 1230, 1210, 1120, 1090, 990 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (d, J=85.5 Hz, 1H), 4.14 (q, J=7.2 Hz, 2H), 3.46 (br t, J=5.4 Hz, 4H), 2.30 (br s, 2H), 2.02 (br s, 2H), 1.26 (t, J=7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 142.0 (d, J=252.4 Hz), 117.6 (d, J=6.9 Hz), 61.4, 45.1, 44.0, 14.6; ^{19}F NMR (283 MHz, $CDCl_3$) δ -138.4 (d, J=85.8 Hz); mass spectrum m/e 187(M^+), 158, 114, 94, 67. Exact mass calculated for $C_9H_{14}FNO_2$: 187.1009, found: 187.1000.

2-(1-Fluoroisopropenyl)naphthalene (31).

Vinyl fluoride **31** (80 mg) was prepared as a mixture of geometrical isomers from the tri-*n*-butylstannane (446 mg, also a mixture of geometrical isomers) according to the general procedure described above in 44% yield: colorless oil; IR (neat) 3060, 2980, 2920, 1660, 1600, 1510, 1140, 1110, 890, 860, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, isomeric mixture) δ 7.93 (br d, J=11.7 Hz, 2H), 7.91-7.82 (m, 4H), 7.78 (br t, J=12.3 Hz, 4H), 7.54-7.46 (m, 4H), 7.11 (dd, J=84.9, 1.5 Hz, 1H), 6.79 (dd, J=84.3, 1.2 Hz, 1H), 2.21 (dd, J=3.9, 1.5 Hz, 3H), 2.05 (dd, J=4.8, 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, isomeric mixture) δ 146.4 (d, J=257.4 Hz), 144.5 (d, J=263.3 Hz), 134.8 (d, J=8.8 Hz), 133.4, 133.2, 132.7, 132.6, 131.0, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 126.5, 126.0, 125.8, 124.5, 123.9, 120.0 (d, J=10.3 Hz), 116.9, 113.0, 108.4 (d, J=28.0 Hz), 16.1 (d, J=7.4 Hz), 12.1 (d, J=5.9 Hz); ^{19}F NMR (283 MHz, $CDCl_3$, isomeric mixture) δ -130.0 (d, J=84.9 Hz), -128.0 (d, J=84.3 Hz).

1-Fluoro-2,2-diphenylethene (32).

Vinyl fluoride **32** (103 mg) was prepared from the tri-*n*-butylstannane (509 mg) according to the general procedure described above in 48% yield: colorless oil; IR (neat) 3120, 3100, 3060, 1650, 1640, 1600, 1500, 1455, 1175, 1090, 1070, 1030, 945, 920, 825 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (br s, 4H), 7.37-7.30 (m, 4H), 7.27-7.20 (m, 2H), 6.97 (d, J=83.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (d, J=268.6 Hz), 129.7 (d, J=3.2 Hz), 128.7, 128.5, 128.2, 127.8 (d, J=4.9 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -128.0 (d, J=79.2 Hz); mass spectrum m/e 198(M^+), 183, 178, 165, 98, 89, 76, 63, 51. Exact mass calculated for $C_{14}H_{11}F$: 198.0829, found: 198.0837.

Trifluorides 37ax and 37eq.

To a two-neck flask charged with 88 mg (0.50 mmol) of vinyl fluoride **2** and 7.1 mL of CH_2Cl_2 was added $AgBF_4$ (292 mg, 1.50 mmol). A solution of 101 mg (0.60 mmol) of XeF_2 in 3.8 mL of CH_2Cl_2 was transferred rapidly by cannula. The flask was covered with aluminum foil and was stirred for 1 d. The reaction mixture was partitioned between sat'd aq $NaHCO_3$ and CH_2Cl_2. The organic phase was dried ($MgSO_4$), filterd through a short pad of silica gel and evaporated. The residue was purified by flash column chromatography on silica gel (hexane) to give 96 mg (90% yield) of **37**ax and **37**eq (2/1) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$, isomeric mixture) δ 7.36-7.28 (m, 2H), 7.24-7.21 (br d, J=8.1 Hz, 2H), 7.19-7.14 (m, 1H), 4.83-4.65 (dm, J=42.6 Hz, 1H), 2.80-2.65 (m, 1H), 2.40-2.08 (m, 3H), 2.08-2.00 (m, 1H), 1.95-1.70 (m, 2H); ^{19}F NMR (283 MHz, $CDCl_3$) [**37**eq] δ -186.7 to -186.5 (dt, J=46.0, 11.0 Hz, 1F), -98.4 to -97.4 (dd, J=235.4, 13.6 Hz, 1F), -97.0 to -96.1 (dd, J=235.4, 6.8 Hz, 1F); [**37**ax] δ -183.5 to -183.0 (dddd, J=47.0, 45.0, 14.0, 12.0 Hz, 1F), -98.4 to -97.4 (dd, J=258.4, 48.1 Hz, 1F), -94.2 to -93.3 (dd, J=258.1, 12.7 Hz, 1F); mass spectrum m/e 214(M^+), 153, 119, 103, 91, 78, 65, 51. Exact mass calculated for $C_{12}H_{13}F_3$: 214.0969, found: 214.0970.

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