Novel Method for Introduction of the Perfluoroethoxy Group Using Elemental Fluorine. Synthesis and Chemistry of Fluoroxypentafluoroethane

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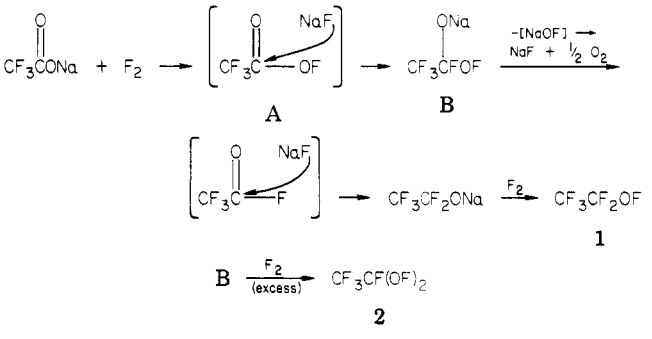
Elemental fluorine reacts with sodium trifluoroacetate to produce several oxidative compounds. When measures are taken to eliminate HF and water from the reaction, the dominant oxidant so formed is CF_3CF_2OF (**1**). Like F_2 and CF_3OF, **1** is an excellent electrophilic reagent, and when it is reacted with some stilbenes, it produces stereospecific (syn addition) and regiospecific adducts. Basic treatment of some adducts causes only an HF elimination, although the choice at this state between anti and syn elimination cannot be clearly made.

Several members of the relatively young family of fluoroxy compounds are known. However, only the first homologue, the commercially available fluoroxytrifluoromethane, CF_3OF, has been widely employed in organic syntheses.[1] Its considerable success has been based mainly on its unusual ability to supply electrophilic fluorine which adds itself in a regiospecific way to various olefins. Unfortunately, its high cost and especially its very limited availability[2] have sharply diminished the volume of work with this promising reagent in the last few years.

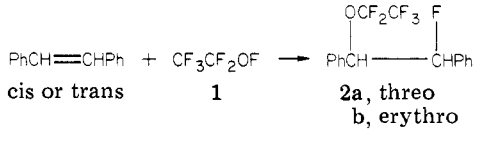
It is some time now since we became involved in developing some new electrophilic fluorination routes. We have shown that elemental fluorine can accomplish in certain cases surprisingly selective fluorinations.[3] It can also act with sodium trifluoroacetate to furnish, under certain conditions, trifluoroacetyl hypofluorite[4] or a mixture of fluoroxy compounds acting as one homogenous reagent.[5] We wish to report here the in situ synthesis of the higher homologue of CF_3OF, fluoroxypentafluoroethane, CF_3CF_2OF (**1**), from elemental fluorine and some of its reactions with olefins.[6] When HF-free fluorine diluted with nitrogen is passed through a suspension of dry CF_3COONa in trichlorofluoromethane (Freon) at −75 °C, an oxidizing solution is obtained in which **1** is the main oxidant.[7] This peculiar reaction is described in Scheme I. The interesting feature of the reaction is the formation of the cage of pair of molecules (A) in which the unsolvated nucleophilic fluorine from the sodium fluoride attacks the carbonyl, thus leading eventually to the fluoroxy compounds.[8] Together with **1**, however, several oxidative fluoroxy compounds like **2** are also formed, although these were not fully identified. It should be noted that the presence of **2** and similar compounds, when both parts of the fluoroxy molecules are needed for the synthesis, leads to the formation of undefined unstable compounds. The amount of the fluoroxy compounds other than **1** can be reduced by using a low concentration of fluorine, but still, the effective highest concentration of **1** did not usually

Scheme I



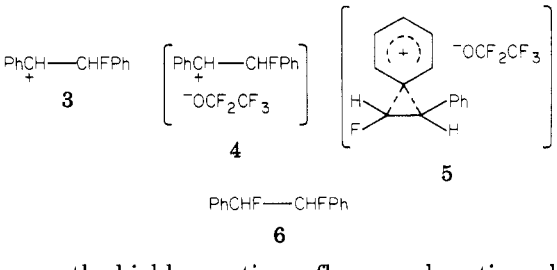
exceed 50% of the overall oxidative mixture.[9]

Resembling CF_3OF and CF_3COOF, **1** is a polarizable compound; its oxygen-bound fluorine has an electrophilic character, and hence it is very reactive toward various olefins. When *trans*-stilbene was added to the oxidizing mixture, we were able to isolate two compounds. The major one proved to be *threo*-1-fluoro-2-(pentafluoroethoxy)-1,2-diphenylethane (**2a**) accompanied by the corre-



sponding erythro isomer **2b** in a ratio of **2a**/**2b** of 5:1. When *cis*-stilbene was similarly treated, again the two isomers **2a** and **2b** were obtained in the same ratio, but this time in favor of the erythro isomer (**2b**/**2a** ratio of 5:1).

The uncommon cis addition of **1** to both stilbenes resembles in some way the addition of CF_3OF to the same olefins.[10a] After the attack of the electrophilic fluorine on the double bond, a tight pair of ions is formed (**4**) which



possesses the highly reactive α-fluoro carbocation which

(1) R. H. Hesse, *Isr. J. Chem.*, **17**, 60 (1978).
(2) The sole supplier of CF_3OF is PCR Research Chemicals Inc. However, they cannot ship it outside the U.S.A.
(3) D. H. R. Barton, R. H. Hesse, R. E. Markwell, M. M. Pechet, and S. Rozen, *J. Am. Chem. Soc.*, **98**, 3036 (1976); S. Rozen, H. Gal, and Y. Faust, *ibid.*, in press.
(4) S. Rozen and O. Lerman, *J. Org. Chem.*, **45**, 672 (1980).
(5) S. Rozen and Y. Menahem, *Tetrahedron Lett.*, 725 (1979); S. Rozen and Y. Menahem, *J. Chem. Soc., Chem. Commun.*, 479 (1980); S. Rozen and Y. Menahem, *J. Fluorine Chem.*, **16**, 19 (1980).
(6) For a preliminary communication see S. Rozen and O. Lerman, *J. Am. Chem. Soc.*, **101**, 2782 (1979).
(7) CF_3CF_2OF was synthesized together with some other fluoroxy compounds. J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965). However, the difficult synthesis and the low yields are responsible for the fact that it was not used as a synthetic tool.
(8) For a full discussion of the mechanism presented in Scheme I see ref 4 and 6.
(9) There are some preliminary indications that use of other salts of the trifluoroacetic acid may give better yields of CF_3CF_2OF. We hope to publish the results of these experiments in the future.
(10) (a) D. H. R. Barton, R. H. Hesse, G. P. Jackman, L. Ogunkoya, and M. M. Pechet, *J. Chem. Soc., Perkin, Trans. 1*, 739 (1974). (b) G. C. Butchard and P. W. Kent, *Tetrahedron*, **35**, 2439 (1979).

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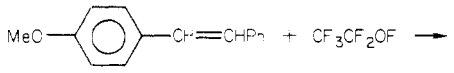
collapses immediately to the corresponding perfluoroethoxy compound **2a** or **2b**. A small leakage to the open ion **3** is responsible, of course, for the observed degree of randomization. Barton and Hesse[10a] also propose a rearrangement to the phenonium ion of type **5** which inevitably leads to the syn adduct.

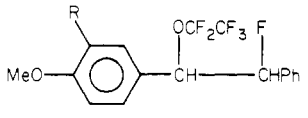
The stereochemistry of the products was determined by their NMR spectra. It is now well established[11] that when a pair of very electronegative atoms such as F and F or F and O are vicinal to each other, a gauche conformation is preferred, and, consequently, one finds that J_{HH}(threo) > J_{HH}(erythro).

When comparing the reactions of 1 and CF_3OF with olefins, one can find two main differences. The first is the higher stereospecificity of the fluoroxypentafluoroethane. This can be explained by the higher nucleophility of the pentafluoroethoxy anion ($CF_3CF_2O^-$) which causes a more rapid collapse of the tight ion pair **4** or **5**. The second difference is the lack of any significant amount of 1,2-difluorobibenzyls of type **6** which are found in substantial amounts in the reaction of CF_3OF with olefins. The source of the difluoro compounds when CF_3OF is used is apparently the decomposition of the CF_3O^- anion to the stable carbonyl fluoride and fluoride anion.[1,10] From our results, it seems that 1 does not decompose significantly in a similar way.

The reaction of the unsymmetrical stilbenes with 1 well demonstrates the electrophilic character of the oxygen-bound fluorine. When *trans*-4-methoxystilbene (**7**) was



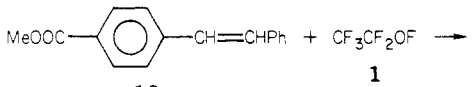
7a, threo
b, erythro



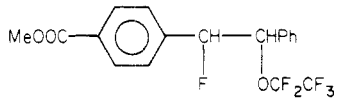
8a,b, R = H
9a,b, R = F

reacted with 1, two main fractions were isolated by high-pressure LC. The mass spectral analysis proved to be of great help in identifying the products. The main fragmentation path in 1-fluoro-2-(pentafluoroethoxy)bibenzyls is always the result of cleavage of the central C–C bond. The peaks of the two resultant benzylic ions are always the most dominant in all the spectra. Thus, the mass spectrum of one of the isolated fractions showed, besides the molecular peak at *m/e* 364, two main peaks at *m/e* 255 [$(p$-$MeOC_6H_4$-CH-$OC_2F_5)^+$] and at *m/e* 109 [$(C_6H_5CHF)^+$], proving that we are dealing with a compound or compounds of type **8**. The ^1H and ^{19}F NMR spectra clearly prove that we have two isomers, namely, *threo*- and *erythro*-1-fluoro-1-phenyl-2-(pentafluoroethoxy)-2-(*p*-methoxyphenyl)ethane **8a** and **8b** in the ratio of about 3:1, respectively. It is worth noting that the relatively high proportion of the erythro isomer **8b** is a direct result of the extra stability which the *p*-methoxy group introduces into the α-fluoro carbocation of type **4**. An additional interesting point arose with respect to the second chromatographic fraction. It proved again to be a nonseparable mixture of the threo and erythro isomers of 1-fluoro-1-phenyl-2-(pentafluoroethoxy)-2-(3-fluoro-4-methoxyphenyl)ethane **9a** and **9b** in the same 3:1 ratio. Mass spectral analysis proved that the extra fluorine lies in the benzylic fragment containing the methoxy group, *m/e* 273 [$[FC_6H_3(OMe)CHOC_2F_5]^+$]. The ^{19}F NMR spectrum showed an aromatic fluorine at 134 ppm which is also quite characteristic for a fluorine atom at a position ortho to the methoxy group.[12] This extra aromatic fluorination stresses again the electrophilic power of the oxygen-bound fluorine in 1 and gives a hint of the additional potential possibilities this reagent may have in aromtic organic chemistry.

When the electron-donor group on the aromatic ring is replaced by an electron-withdrawing one, as in the case of *trans*-4-(carbomethoxy)stilbene (**10**), absolute regio- and

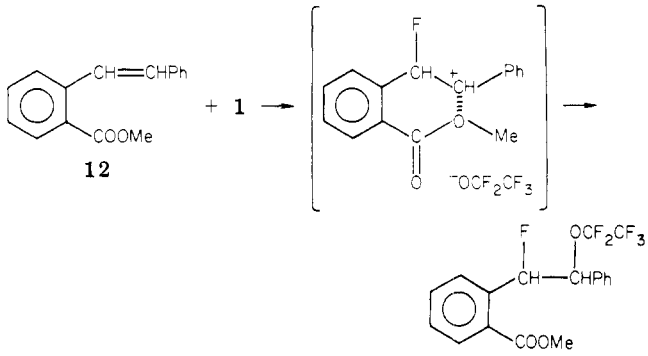


10 1



11a, threo

stereospecifity is observed. Thus, only *threo*-1-fluoro-1-[*p*-(carbomethoxy)phenyl]-2-(pentafluoroethoxy)-2-phenylethane (**11a**) was obtained. The addition of 1 is accomplished in a regiospecific way, establishing once again the electrophilicity of the oxygen-bound fluorine. The somewhat unstabilizing effect of the carbomethoxy group on the α-fluoro carbocation p-$MeOOCC_6H_4CHF$-C^+H-Ph seems to shorten its life time and so to increase the stereoselectivity of the reaction. When, however, *trans*-2-(carbomethoxy)stilbene (**12**) was reacted with 1, the threo



12

13a, threo
b, erythro

and erythro isomers of 1-fluoro-1-[*o*-(carbomethoxy)-phenyl]-2-(pentafluoroethoxy)-2-phenylethane, **13a** and **13b**, were obtained in 1.3:1 ratio, respectively. The methyl ester exerts a considerable steric hindrance upon the cationic center, not allowing an immediate consecutive attack from the pentafluoroethoxy anion. In addition, the oxygen atoms of the carbomethoxy group can be very close to the carbocation, thus permitting an interaction between the positive charge and the oxygen. Such interactions are known in the acetoxyl migration reactions. Consequently, the lifetime of the corresponding unstable α-fluoro cation is sufficiently prolonged, resulting in the randomization of the products.[13]

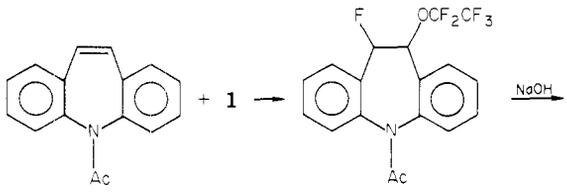
Fluoroxypentafluoroethane also reacts smoothly with olefins containing an amide group. Such a compound is

(11) (a) L. Phillips and V. Wray, *J. Chem. Soc., Chem. Commun.*, 90 (1973); (b) N. S. Zefirov, V. V. Samoshin, O. A. Sabotin, V. I. Baranenkov, and S. Wolfe, *Tetrahedron*, 34, 2953 (1978); (c) ref 4

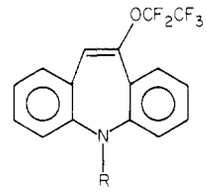
(12) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Eds., "Progress in NMR Spectroscopy", Vol. 7, Pergamon Press, New York, 1971.

(13) The reaction of CF_3CF_2OF with **12** is quite similar to the reaction of CF_3COOF with this stilbene. For a more detailed analysis of the reaction and the identification of the isomers by NMR spectroscopy see ref 4.

N-acetyldibenz[*b*,*f*]azepine (**14**) which was converted to the expected *N*-acetyl-10-fluoro-11-(pentafluoroethoxy)-10,11-dihydrodibenz[*b*,*f*]azepine (**15**).[14]



15



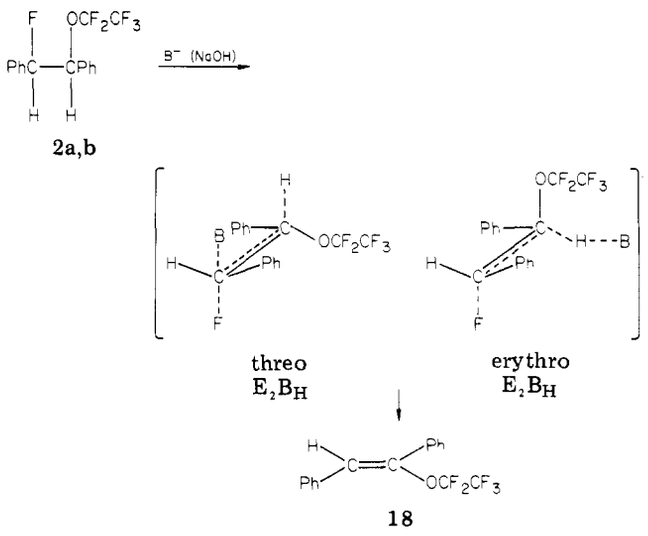
16, R = Ac
17, R = H

The substitution of fluorine or, even better, of a trifluoromethoxy group for hydrogen in order to modify the bioactivity of certain molecules by enhancement of their lipophilicity, which is associated with the corresponding change of both steric and electronic properties, is a well-established practice in medicinal chemistry. Thus the described reactions with 1 open a new route for the preparation of perfluoroalkoxides of biological interest. The dibenzazepine family, for example, has a broad spectrum of antidepressant activity. It was worthwhile, then, to try to eliminate HF from **15** in order to retrieve the 10,11-dehydro skeleton of the dibenzazepine. Indeed, treatment of **15** with NaOH produces the *N*-acetyl-10-(pentafluoroethoxy)dibenz[*b*,*f*]azepine (**16**), while more prolonged reaction also attacks the amide group to produce, in excellent yield, the free amine **17**, which in this state is potentially ready for further biologically interesting chemical transformations.

We have also examined the base-induced elimination in the threo and erythro adducts **2a** and **2b**. These two isomers were treated, separately, with excess ethanolic NaOH at room temperature. Monitoring of the reaction by GC reveals that a very slow elimination process takes place. Raising the temperature to the boiling point speeds up the above elimination, and after 15 h the reaction is complete. Although no kinetic studies were performed, it seems that the rate of the reaction for all three eliminations is practically the same. Only one product was obtained, in high yield, from both isomers **2a** and **2b**. Its spectral properties show clearly that we have obtained *trans*-(α-pentafluoroethoxy)stilbene **18**[15] (Scheme II).

There are two points of interest in the base-induced elimination of the described α-fluoro-β-(pentafluoroethoxy)bibenzyls. Unlike the adducts of CF_3OF which on basic treatment produce mixtures of α-(trifluoromethoxy)stilbene and α-fluorostilbene,[10a] our adducts exclusively eliminate only the elements of HF. This fact may indicate that the pentafluoroethoxy group is somewhat more electronegative than the trifluoromethoxy group, and hence its geminal hydrogen is somewhat more acidic. On the other hand, it may also indicate that $CF_3CF_2O^-$ is a poorer leaving group than the CF_3O^- group, not to mention the fluoride anion. The second point of interest is the elimination mechanism. The conventional anti elimination of the E_2B_C type could take place with the dibenzazepine adduct **15** and the threo isomer **2a**, resulting in **16** and in the *trans*-stilbene derivative **18**, respectively. However, such an anti elimination from the erythro isomer **2b** should inevitably lead to the *cis*-α-(pentafluoroethoxy)stilbene, which was not found in our case, even at the beginning of the reaction at room temperature. It seems that syn elimination of the E_2B_H type is responsible for this reaction. Such a transition state in the elimination of hydrogen fluoride appears to exhibit substantially weaker stereoelectronic interactions and easily becomes degenerate. Thus syn elimination has only been observed to occur from substrates which permit the formation of the relatively unhindered trans olefins.[16] It is not clear at this point whether the two types of mechanism are applicable or if only the syn elimination mechanism is operative. One may argue that the favorable gauche conformation of compounds **15** and **2a** will help the anti elimination mechanism, but on the other hand, the similar rates of reaction for all the eliminations possibly indicates that all of them are of the E_2B_H type.

Scheme II



Experimental Section

Melting points were determined with a Buchi capillary apparatus. ^1H NMR spectra were measured with a Bruker WH-90 spectrometer at 90 MHz and with tetramethylsilane as internal standard. ^{19}F spectra were recorded with the same instrument at 84.67 MHz and were reported in parts per million upfield from $CFCl_3$ as internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. Silica gel 60 (Merck, 70–230 mesh) was used for column chromatography. Final purification was usually obtained by high-pressure LC (Waters Associates) with silica gel (Merck, 10-μm packing).

Fluorination of Stilbenes, General Procedure. Caution: fluorine, CF_3CF_2OF, and other oxidants containing fluoroxy groups are, of course, strong poisons and very corrosive materials. An appropriate vacuum line in a well-ventilated place should be constructed for working with fluorine. Such a vacuum line is described, for example, in Matheson report no. G-115B and can be obtained on request. The reaction itself can be carried out in glass vessels. However, we would like to mention that in more than 4 years of working with F_2 and after hundreds of experiments

(14) This product was also synthesized by S.R. during his work with D. H. R. Barton, R. H. Hesse, and M. M. Pechet in the Research Institute for Medicine and Chemistry, Cambridge, MA. He is very grateful for the opportunity he had to work in their laboratory.

(15) The *trans*- and *cis*-α-trifluoromethoxystilbenes were described by Barton and Hesse.[10a] The UV spectrum of the trans isomer, but not that of the cis one, is practically identical with the UV spectrum of **18**.

(16) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahasi, and S. Winstein, *J. Am. Chem. Soc.*, **93**, 4735 (1971); D. H. Hunter and D. J. Shearing, *ibid.*, **93**, 2348 (1971).

we have not had either an explosion or any accident whatsoever.

An ~0.7% mixture of fluorine (Matheson Gas products) diluted with nitrogen[17] was passed through an HF scavenger trap (NaF pellets) and then bubbled through a suspension of dry CF_3CO-ONa[18] in trichlorofluoromethane (Freon) at −75 °C. A good vibromixer (Chemapec) was used to ensure efficient mixing. Samples of the solution were treated with an acidic solution of KI, and the liberated iodine was titrated with thiosulfate. When the desired concentration of the oxidizing agents was achieved (usually 4–6 mmol), a cold solution of one of the stilbenes (about 2 mmol) in 30 mL of CH_2Cl_2 was added in one portion. After less than 1 min the reaction mixture was poured into dilute thiosulfate solution in order to reduce all the remaining oxidative materials, and the organic layer was separated, washed several times with water, dried over $MgSO_4$, and evaporated. The crude product was subjected to short-column chromatography and then chromatographed by high-pressure LC.

Fluorination of *trans*-Stilbene. To 5 mmol of the oxidizing solution was added 2 mmol of *trans*-stilbene. High-pressure LC with elution with 3% CH_2Cl_2 in cyclohexane yielded 33% of *threo*-1-fluoro-2-(pentafluoroethoxy)-1,2-diphenylethane (**2a**): mp 87 °C (from MeOH); IR ν 1210 cm^{-1} (vs, perfluoro ether group); ^1H NMR δ 7.3 (10 H, m) 5.3–5.9 (2 H, AB portion of ABX, J_{AB} = 7 Hz); ^{19}F NMR ϕ^* 85.6 (3 F, s), 86.7 and 88.7 (2 F, AB spectrum, J_{AB} = 143 Hz[19]), 180.8 (1 F, q, $J_{HF(gem)}$ = 49, $J_{HF(vic)}$ = 12 Hz); mass spectrum, m/e 334 (M^+), 225 [$(PhCHOC_2F_5)^+$, the base peak], 119 [$(C_2F_5)^+$], 109 [$(PhCHF)^+$, very strong]. Anal. Calcd for $C_{16}H_{12}F_6O$: C, 57.48; H, 3.60; F, 34.1. Found: C, 57.39; H, 3.70; F, 33.8. Together with **2a** an additional 6% of **2b** was also found and isolated.

Fluorination of *cis*-stilbene gives *erythro*-1-fluoro-2-(pentafluoroethoxy)-1,2-diphenylethane (**2b**) which was purified by the same procedure: yield 35%; mp 56 °C (from MeOH); the IR and mass spectra and the elemental analysis were practically identical with those of **2a**; ^1H NMR δ 7.25 (10 H, m), 5.35–5.93 (2 H, AB portion of ABX spectra, J_{AB} = 4 Hz); ^{19}F NMR ϕ^* 85.8 (3 F, s), 87.5 and 88.8 (2 F, AB, J_{AB} = 143 Hz), 185.2 (1 F, q, $J_{HF(gem)}$ = 49, $J_{HF(vic)}$ = 12 Hz). Compound **2b** was accompanied by an additional 7% of the threo isomer **2a** which was separated.

Fluorination of *trans*-4-methoxystilbene was carried out as above. To a little more than 6 mmol of oxidative agents was added 2 mmol of **7**. Two main fractions were isolated by high-pressure LC with 12% CH_2Cl_2 in cyclohexane serving as eluent. The first fraction proved to be an inseparable mixture of **8a** and **8b** (ratio 3:1): 38% combined yield; mp (of the mixture) 59–63 °C; IR ν 1210 cm^{-1} (vs, CF_3CF_2O); ^1H NMR δ 6.7–7.3 (9 H, m), 5.3–6.0 (2 H, 2 AB patterns of ABX), 3.8 (OMe, s, threo), 3.72 (OMe, s, erythro); ^{19}F NMR 85.7 (3 F, s), 87.3 and 88.3 (2 F, AB, J_{AB} = 140 Hz for the threo isomer), 179.8 (erythro, q, $J_{HF(gem)}$ = 49 Hz, $J_{HF(vic)}$ = 13 Hz), 185.4 ppm (threo, q, $J_{HF(gem)}$ = 48 Hz, $J_{HF(vic)}$ = 15 Hz); mass spectrum, m/e 364 (M^+), 255 [$(MeOC_6H_4CHOC_2F_5)^+$, base peak], 119 [$(C_2F_5)^+$], 109 [$(PhCHF)^+$, next to the base peak]. Anal. Calcd for $C_{17}H_{14}F_6O_2$: C, 56.04; H, 3.84; F, 31.3. Found: C, 56.46; H, 3.98; F, 31.6. Also the second fraction proved to be an inseparable mixture of **9a** and **9b** (**9a**/**9b** ratio of 3:1): combined yield 12%; oil; IR ν 1210 cm^{-1} (vs, perfluoro ether); NMR δ 6.9–7.7 (8 H, m), 5.15–6.25 (2 H, 2 AB patterns of ABX), 3.9 (OMe, s, threo), 3.85 (OMe, s, erythro); ^{19}F NMR ϕ^* 85.7 (3 F, s), 87.6 and 88.9 (2 F, AB, J_{AB} = 140 Hz, for the threo isomer), 134 (1 F, m, aromatic), 186.4 (erythro, q, $J_{FH(gem)}$ = 50 Hz, $J_{FH(vic)}$ = 14 Hz), 189.6 (threo, q, $J_{FH(gem)}$ = 51 Hz, $J_{FH(vic)}$ = 12 Hz); mass spectrum, m/e 382 (M^+), 273 [$(F(MeO)C_6H_3CHOC_2F_5)^+$, the base peak], 119 [$(C_2F_5)^+$], 109 [$(C_6H_5CHF)^+$]. Anal. Calcd for $C_{17}H_{13}F_7O_2$: C, 53.4; H, 3.44. Found: C, 54.4; H, 3.41.

Fluorination of *trans*-4-(carbomethoxy)stilbene yields *threo*-1-fluoro-1-[4′-(carbomethoxy)phenyl]-2-(pentafluoroethoxy)-2-phenylethane (**11a**): 40% yield; mp 89 °C (from hexane); IR ν 1725 (C=O), 1220 (vs, OCF_2CF_3); ^1H NMR δ 7.07–7.97 (9 aromatic H, m), 5.20–6.00 (2 H, AB part of the ABX system, J = 7 Hz), 3.90 (3 H, s, methyl ester group); ^{19}F NMR ϕ^* 86.5 (3 F, s), 88.8 (2 F, center of the two inner lines), 178.9 (1 F, q, $J_{HF(gem)}$ = 46 Hz, $J_{HF(vic)}$ = 9.2 Hz); mass spectrum, m/e 392 (M^+), 167 [$(MeOOCC_6H_4CHF)^+$], 225 [$(C_6H_5CHOC_2F_5)^+$, the base peak]. Anal. Calcd for $C_{18}H_{14}F_6O_3$: C, 55.10; H, 3.57. Found: C, 55.11; H, 3.58.

Fluorination of *trans*-2-(carbomethoxy)stilbene (12) was carried out as described. High-pressure LC with 7% CH_2Cl_2 in cyclohexane as eluent yielded two fractions. The major one proved to be *threo*-1-fluoro-1-[2′-(carbomethoxy)phenyl]-2-(pentafluoroethoxy)-2-phenylethane (**13a**): yield 22%; mp 66 °C (from MeOH); IR ν 1705 (C=O), 1220 (OCF_2CF_3); ^1H NMR[13] δ 7.32–8.1 (9 H, m), 5.69–6.79 (2 H, AB portion of ABX spectrum, J_{AB} = 1.2 Hz), 3.92 (3 H, s, methyl ester group); ^{19}F NMR ϕ^* 85.6 (3 F, s), 87.8 and 89.5 (2 F, AB pattern, J_{AB} = 143 Hz), 200.0 (1 F, q, $J_{HF(gem)}$ = 48 Hz, $J_{HF(vic)}$ = 24 Hz); mass spectrum, m/e 392 (M^+), 225 [$(C_6H_5CHOC_2F_5)^+$, the base peak], 167 [$(MeOOCC_6H_4CHF)^+$]. Anal. Calcd for $C_{18}H_{14}F_6O_3$: C, 55.10; H, 3.57. Found: C, 55.12; H, 3.64. The minor fraction proved to be the erythro isomer **13b**: yield 17%; oil; IR and mass spectra as for **13a**; ^1H NMR δ 7.0–8.24 (9 H, m), 5.58–7.05 (2 H, AB portion of ABX, J_{AB} = 3 Hz), 3.95 (3 H, s, methyl ester); ^{19}F NMR ϕ^* 86.8 (3 F, s), 87.8 and 89.5 (2 F, AB spectrum, J_{AB} = 143 Hz), 195.8 (1 F, q, $J_{HF(gem)}$ = 48 Hz, $J_{HF(vic)}$ = 23 Hz). Anal. Calcd for $C_{18}H_{14}F_6O_3$: C, 55.10; H, 3.57. Found: C, 55.33; H, 3.51.

Fluorination of *N*-acetyldibenz[*b*,*f*]azepine (14) results in *N*-acetyl-10-fluoro-11-(pentafluoroethoxy)-10,11-dihydrodibenz[*b*,*f*]azepine (**15**): 46% yield; oil; IR ν 1220 cm^{-1} (OCF_2CF_3); ^1H NMR 7.0 (8 H, m), 4.8–6.7 (2 H, AB portion of ABX), 2.0–2.15 (3 H, acetyl group; since room temperature is below the coalescence temperature, one can see two main acetyl peaks for the syn and anti configurations); ^{19}F NMR ϕ^* 84.0 (3 F, s), 86.5 (2 F, center of the AB spectrum), 159 (1 H, q, $J_{HF(gem)}$ = 51 Hz, $J_{HF(vic)}$ = 12 Hz); mass spectrum, m/e 389 (M^+), 346 [$(M - Ac)^+$], 254 [$(M - OCF_2CF_3)^+$]. Anal. Calcd for $C_{18}F_{13}F_6NO_2$: C, 55.53; H, 3.36; F, 29.28. Found: C, 55.12; H, 3.40; F, 29.40.

Dehydrofluorination of 15. A 1-mmol sample of **15** was refluxed under nitrogen with 30 mL of EtOH to which were added 10 mL of 5% NaOH in EtOH and 3 mL of H_2O. It was found that the elimination of HF was complete after 15 h, although only part of the amide group was hydrolyzed. After an additional 48 h the hydrolysis was complete, and **17** was obtained in 92% yield: mp 88 °C (from hexane); IR ν 1240 cm^{-1} (vs, OCF_2CF_3); ^1H NMR δ 6.7–7.4 (8 H, m), 6.6 (1 H, s), 5.15 (1 H, br NH signal); ^{19}F NMR ϕ^* 84 (3 F, s), 86 (2 F, s); UV (EtOH) λ 290 nm (sh, ϵ 6000), 255 (61 000). Anal. Calcd for $C_{16}H_{10}F_5NO$: C, 58.72; H, 3.08; F, 29.03. Found: C, 58.91; H, 3.15; F, 28.5.

Dehydrofluorination of 2a and 2b was carried out as for **15**. After 15 h of reflux, *trans*-α-(pentafluoroethoxy)stilbene (**18**) was obtained in 90% yield from both threo and erythro isomers: mp 52 °C (from hexane); IR ν 1210 cm^{-1} (vs, OCF_2CF_3); ^1H NMR δ 7.25–7.64 (10 H, m), 6.66 (1 H, s, the olefinic proton); ^{19}F NMR ϕ^* 86.3 (all five fluorine atoms resonate as one somewhat broad signal); UV (EtOH) λ 282 nm (ϵ 26 300), 220 (14 600); mass spectrum, m/e 314 (M^+, base peak), 195 [$(M - C_2F_5)^+$], 179 [$(M - OC_2F_5)^+$]. Anal. Calcd for $C_{16}H_{11}F_5O$: C, 61.14; H, 3.50; F, 30.25. Found: C, 61.0; H, 3.77; F, 30.0.

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Registry No. **1**, 3848-94-0; **2a**, 74562-72-4; **2b**, 74562-73-5; **7**, 1694-19-5; **8a**, 74577-80-3; **8b**, 74562-74-6; **9a**, 74562-75-7; **9b**, 74562-76-8; **10**, 1149-18-4; **11a**, 74562-77-9; **12**, 38453-72-4; **13a**, 74562-78-0; **13b**, 74562-79-1; **14**, 19209-60-0; **15**, 74562-80-4; **16**, 74562-81-5; **17**, 74562-82-6; **18**, 74562-83-7; F_2, 7782-41-4; CF_3COONa, 2923-18-4; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8.

(17) While we are making our mixtures of F_2 and N_2 from pure fluorine and nitrogen, it should be mentioned that premixed solutions of F_2/N_2 are commercially available.

(18) Trichlorofluoromethane does not usually require a special purification. The sodium trifluoroacetate was usually dried under a vacuum of 1 mmHg at 120 °C for 24 h prior to being used.

(19) The vicinal fluorines in perfluoro compounds have very small coupling constants. Thus, in this work the J_{FF} between the CF_3 and CF_2 groups is no bigger than 1 Hz and usually cannot be seen. Being prochiralic, the CF_2 group exhibits an AB pattern of which the two central lines are clear and visible while the outer peaks are quite weak.