participation must remain elusive. The MM approach allows to quantify rate enhancements and to predict in most cases (Scheme I) rate reductions, which obviously can be due to steric hindrance of solvation and/or hindrance of elimination. As elimination dominates in the weakly nucleophilic solvents and as there is evidence of very stringent E_2-type steric requirements for the abstraction of the β-proton[11,34] a detailed study of solvolysis products and particularly of kinetic isotope effects is of obvious need.

(34) The available evidence points toward E_2-type and to a lesser degree to E_1-type mechanism even in weakly nucleophilic solvents; cf. ref 11 and 18 and: Shiner, V. J.; Jewett, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 1383. Saunders, W. H.; Finley, K. T. *Ibid.* **1965**, *87*, 1384. See also the discussion of a large β-deuterium isotope effect in ref 10a.

(35) For a related recent publication, see: Bentley, T. W., Roberts, K. *J. Org. Chem.* **1985**, *50*, 5852.

Experimental and computational details are described in earlier papers;[1,9,30] for reaction conditions see Table I.

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Supplementary Material Available: Rate constants at different temperatures in HFIP and in part in trifluoroethanol (TFE), k_s/k_c ratios and steric hindrance model numbers SH, and strain energies with different functional groups X for **1a–29** (7 pages). Ordering information is given on any current masthead page.

Direct Addition of Elemental Fluorine to Double Bonds

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The addition of elemental fluorine to the carbon–carbon double bond in a variety of olefinic substrates proceeds in a stereoselective syn manner. The addition of a proton donor to the conventional $CHCl_3$–$CFCl_3$ solvent system suppresses radical processes usually resulting in tar formation so the slower ionic type of addition of F_2 to the double bond takes place. Rapid collapse of the ion pair involving the α-fluoro carbocation ion is believed to account for the stereospecificity. This ion is also an intermediate in the formation of the 1,1,2-trifluoroalkanes which are also formed in the fluorination of terminal alkenes. Fluorination of enones which are generally deactivated also proceeds without complications. In such cases dehydrofluorination is an easy optional process resulting in α-fluoro enones.

Addition of most of the halogens to double bonds is a standard procedure since the beginning of modern organic chemistry. It is therefore of note that the first member of the halogen family—F_2—does not share the same popularity when reactions with alkenes are considered. It seems that the major obstacle for generalizing this reaction is the fact that the F–F bond is weak and can be readily cleaved to the very reactive and indiscriminating fluorine radicals. In fact a number of indirect methods have been developed for constructing vicinal difluoro compounds in order to circumvent the direct use of the element itself.[1] Some early success in adding F_2 to unsaturated centers was achieved by using perfluoroalkenes, resulting in formation of the corresponding perfluoroalkanes. In many cases, however, the dominant products are dimers which obviously originate from radical reactions.[2] This has been used very successfully by Scherer for preparing some of the most stable radicals known to organic chemistry.[3]

Working with unfluorinated alkenes, however, is another matter. The expected highly exothermic nature of the reaction of F_2 with olefins discouraged many from experimenting with this halogen. The pioneering work of Merritt[4] showed that it is not impossible to add fluorine to centain simple olefins. His technique was, however, quite unusual and rather inconvenient. As a result, 15 years passed before an additional paper dealing with this subject appeared.[5] We present here a general way for preparing the uncommon 1,2-difluoro compounds directly from F_2 and alkenes.

During our work with elemental fluorine in a direct[6] or indirect[7] mode, we have noticed that low temperature and especially polar solvents can suppress fluorine radical formation and encourage polar processes. We found that the latter are much more gentle and able to perform surprisingly selective reactions.[8] Thus working with a very dilute stream of fluorine in nitrogen in the presence of the highly polar ethanol which also serves as an acceptor for

(1) See, for example: Bornstein, J.; Borden, M. R.; Nunes, F.; Tarlin, H. I., *J. Am. Chem. Soc.* **1963**, *85*, 1609. Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 2169. Shellhamer, D. F.; Conner, R. J.; Richardson, R. E.; Heasley, V. L. *J. Org. Chem.* **1984**, *49*, 5015.

(2) Miller, W. T.; Staffer, J. O.; Fuller, J.; Currie, A. C. *J. Am. Chem. Soc.* **1964**, *86*, 51.

(3) Scherer, K. V., Jr.; Ono, T.; Yamanouchi, K.; Fernandez, R.; Henderson, P. *J. Am. Chem. Soc.* **1985**, *107*, 718.

(4) (a) Merritt, R. F.; Johnson, F. A. *J. Org. Chem.* **1966**, *31*, 1859. (b) Merritt, R. F.; Steven, T. E. *J. Am. Chem. Soc.* **1966**, *88*, 1822. (c) Merritt, R. F. *J. Org. Chem.* **1966**, *31*, 3871. (d) Merritt, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 609.

(5) Barton, D. H. R.; James, J. L.; Hesse, R. H.; Pechet, M. M.; Rozen, S. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1105.

(6) See, for example: Gal, C.; Rozen, S. *Tetrahedron Lett.* **1985**, *26*, 2793.

(7) (a) Rozen, S.; Lerman, O.; Kol, M.; Hebel, D. *J. Org. Chem.* **1985**, *50*, 4753. (b) Rozen, S.; Brand, M. *Ibid.* **1985**, *50*, 3342.

(8) See, for example: Gal, C.; Rozen, S. *Tetrahedron Lett.* **1985**, *26*, 2793. Rozen, S.; Gal, C.; Faust, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6861.

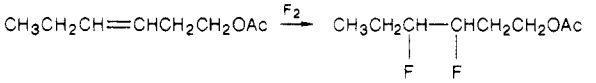
0022-3263/86/1951-3607$01.50/0

the F^- through a hydrogen bonding slows down the rate of the reaction by at least a factor of 2 when compared to reactions carried out in $CFCl_3$–$CHCl_3$ alone.[9] One of the beneficial results is the facilitation of the absorption of the evolved heat, which could encourage fluorine radical formation. When indeed the alcohol was omitted, the reaction produced, in addition, many unidentified products as evidenced by the ^{19}F NMR spectra which show many fluorine signals, a characteristic of the nondiscriminating fluorine radical attack.

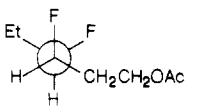
When fluorine at a concentration of about 1% in nitrogen was bubbled slowly through a cold solution (−78 °C) of *trans*-3-hexen-1-ol acetate (**1**) in a mixture of trichlorofluoromethane, chloroform, and ethanol, only one difluoro adduct was isolated in 55% yield. This product, which was identified as *threo*-3,4-difluorohexan-1-ol acetate (**2**), results from syn addition of the fluorine molecule to

A

X = OCF_3[10a] OCF_2CF_3[10c] $OCOCF_3$[10a] $OCOCH_3$[7a] F

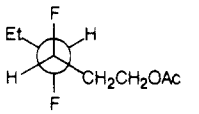


1 (trans) 2 (threo)



B

3 (cis) 4 (erythro)

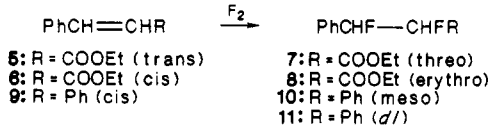


C

the olefin. The same mode of addition was observed when *cis*-3-hexen-1-ol acetate (**3**) was reacted. In this case only the erythro difluoro derivative **4** was obtained in similar yield. In both cases the adducts were not contaminated by each other, excluding the possibility of any anti addition process. The exclusive syn addition, which is opposite to the reaction mode of the other halogens, is very characteristic of all electrophilic fluorination processes[7a,10] and can be considered as a good criterion for their existence. This mode of addition originates from the initial nucleophilic attack of the double bond on the fluorine atom either when it is a part of some fluoroxy reagent or as in the present case, in the form of the fluorine molecule itself. The resulting α-fluoro carbocation is of course highly unstable and the tight ion pair A collapses before any rotation around the carbon–carbon bond in question can take place. The fact that no fluoro ethers were detected supports the argument that no open linear or cyclic carbonium ion, which could have been attacked by the nucleophilic EtOH,[7b] is formed in substantial amounts.

The distinction between the threo and the erythro isomers (**2** and **4**) is based mainly on their ^1H NMR spectra. The most stable conformer of **2** should be the one where the two bulky alkyl groups are anti and the two fluorine atoms gauche to each other (conformation B). In **4**, the dominating conformation C would also be the one with the two bulky alkyl groups anti to each other, this time outweighting the gauche effect (0.5–1 kcal/mol) which attracts the two fluorine atoms to mutually gauche position.[11] Reflection of these conformations is found in the $^3J_{HF}$ coupling constants for **2** and **4**: 23 and 17 Hz, respectively, as well as in the corresponding $^3J_{HH}$ couplings of 3.0 and 4.0 Hz. It should also be noted that in all the pairs we have examined the fluorine atoms in the threo isomers always resonate at a higher field than in the corresponding erythro ones.

Similar results were obtained when *trans*- and *cis*-ethyl cinnamate (**5** and **6**, respectively) were reacted. Again, only one isomer was obtained from each cinnamate (the two isomers have different GC retention times) and it proved to be the one resulting from syn addition. Thus the trans olefin **5** produced *threo*-ethyl 2,3-difluoro-3-phenylpropionate (**7**) while the cis isomer was converted to the erythro difluoro adduct **8**, both in good yields. As in the previous case the identification of the products was based on the ^1H and ^{19}F NMR spectra.

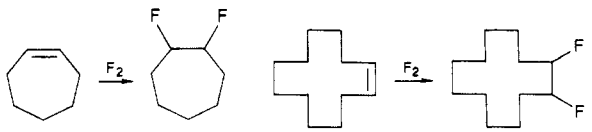


5: R = COOEt (trans)
6: R = COOEt (cis)
9: R = Ph (cis)

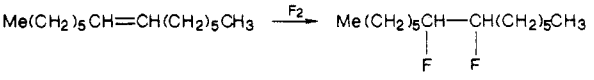
7: R = COOEt (threo)
8: R = COOEt (erythro)
10: R = Ph (meso)
11: R = Ph (*dl*)

It was argued[4a-d] that the syn addition can originate from a concerted four-center reaction between the olefin and the fluorine molecule. Apart from theoretical considerations involving the geometry of the fluorine molecule and the lack of low energy empty orbitals which do not favor such a mechanism, it can be demonstrated that when an extra stabilization to the α-fluoro carbocation is provided, one can find a higher proportion of leakage to the open ion which then can be randomly recombined with the nucleophilic F^-. *cis*-Stilbene (**9**) provides such an example. Its charged intermediate [PhCHF–$^+$CHPh] is appreciably more stable than the others mentioned in this work, and, indeed, lower stereospecificity is observed compared to the other cases. Thus, while syn addition produces in this case *meso*-1,2-difluoro-1,2-diphenylethane (**10**) as the major product, we were able to isolate also the *dl* isomer **11**, which obviously originates from the attack of the F^- on the open α-fluoro carbocation.[4d,10]

Cyclic or straight-chained olefins with no functional groups can also be easily and selectively fluorinated. Cycloheptene (**12**) was fluorinated in 40% yield to 1,2-difluorocycloheptane (**13**). Larger rings react efficiently and stereoselectively as well. A mixture of *trans*- and *cis*-



12 **13** **14** (trans:cis = 2:1) **15** (*dl*) **16** (meso)



17 (trans:cis = 2.5) **18** (*dl*) **19** (meso)

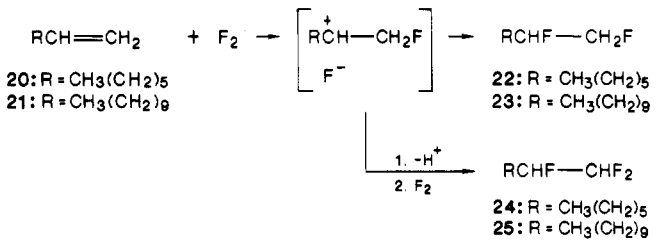
(9) Relative rates were determined from the amount of fluorine passed through two different reactions carried in otherwise identical conditions. While EtOH was serving as a proton donor to most of the reactions described, other alcohols such as MeOH and *i*-PrOH were also used with similar results.

(10) (a) Barton, D. H. R.; Hesse, R. H.; Jackmann, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 739. (b) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. (c) Lerman, O.; Rozen, S. *J. Org. Chem.* **1980**, *45*, 4122. (d) Rozen, S.; Brand, M. *J. Org. Chem.* **1985**, *50*, 3342.

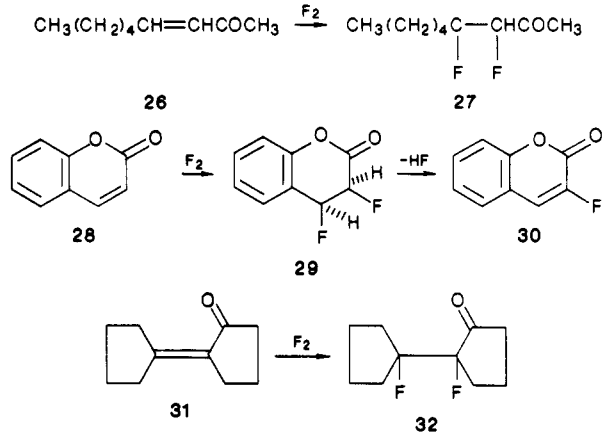
(11) Zefirov, N. S.; Samoshin, V. V.; Sabotin, O. A.; Baranenkov, V. I.; Wolfe, S. *Tetrahedron* **1978**, *34*, 2953.

cyclododecene (14) in a ratio of trans:cis = 2 was fluorinated to produce two isomers which were separated and identified as *dl*- and *meso*-difluorocyclododecane (15 and 16) in yields of 40% and 20%, respectively. The ratio similarity of the reactant and the products combined with the results from the other experiments in this work support again the notion that where no extra stabilization for the α-fluoro carbocation is available the fluorine addition to a double bond proceeds in an exclusively syn mode. Parallel results were obtained with the straight-chain hydrocarbon 7-tetradecene (17), in which the ratio of the trans to cis isomers was 2.5. Again two difluoro adducts were obtained, separated and identified as *dl*-7,8-difluorotetradecane (18), 50% yield, and *meso*-7,8-difluorotetradecane (19), 20% yield, once more in agreement with a syn mode of addition.

Terminal olefins such as 1-octene (20) and 1-dodecene (21) behaved in a somewhat different manner from their internal double bonded counterparts. In addition to the expected major vicinal difluoro adducts 22 and 23, minor amounts of the 1,1,2-trifluoro derivatives 24 and 25 were also isolated. The latter products did not result from over-fluorination, since an attempt to force additional fluorination of the difluoro derivatives 22 and 23 resulted in indiscriminate fluorine substitution and C–C cleavage. Nor is it likely that they resulted from HF elimination from the difluoro derivatives, followed by a subsequent F_2 addition, since it is not easy to dehydrofluorinate the adducts 22 and 23 using the reaction conditions (HF-promoted elimination). It seems that some fluoroolefin is produced immediately after the formation of the α-fluoro carbocation by ejection of a proton, since it is likely that the protons of the primary $^+CCH_2F$ carbocation are more acidic than any ^+CCHFR hydrogen in the internal olefins. Such an olefin will react immediately with an additional molecule of fluorine to produce the trifluoro derivatives 24 and 25. These products are an additional evidence against any concerted four-center reaction mechanism.



Fluorine addition to deactivated α,β-unsaturated carbonyls could also be achieved, although at a considerably slower rate. This was evidenced by the large excess of fluorine gas (about three times more than that for isolated double bonds) required to complete the reaction. The nonrigid, aliphatic α,β-unsaturated carbonyl compound *trans*-3-nonen-2-one (26) afforded *threo*-3,4-difluoro-2-nonanone (27) in 50% yield without any detectable amount of the corresponding erythro isomer. In the case of a rigid cyclic conjugated enone, like coumarine (28), the difluoro adduct 29 was obtained in 55% yield along with an additional minor elimination product 30[12] which apparently was formed during the workup of the reaction. It should be noted that 29 could be quantitatively dehydrofluorinated to 30, simply by adsorbing it on a silica gel column. The easy elimination of HF is due to the anti configuration of the H and F atoms resulting from the syn fluorine addition. This configuration is also supported by the $^3J_{HF}$ coupling constants, 30 and 6 Hz, in accordance with two H–C–C–F dihedral angles of about 85° and 170°.



The wide scope of this reaction was demonstrated by the extreme case of a tetrasubstituted enone which would not normally react with halogens in an ionic mode. Fluorine, however, reacts with such a compound even at −75 °C. Thus, 2-cyclopentylidenecyclopentanone (31) when treated with F_2 produced the difluoro adduct 32 in moderate yield.

In conclusion, we have shown that low temperature fluorination of ionic character can be applied to a variety of olefinic systems to give vicinal difluoro adducts with very good stereoselectivity and satisfactory yields.

Experimental Section

^1H NMR spectra were recorded with a Bruker WH-90 and a Bruker WH-360 spectrometer at 90 and 360 MHz, respectively, with $CDCl_3$ as solvent and Me_4Si as an internal standard. The ^{19}F spectra were measured at 84.67 and 338.8 MHz, respectively, and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. The proton broad band decoupled ^{13}C NMR spectra were recorded on Bruker WH-90 and WH-360 spectrometers at 22.63 and 90.52 MHz, respectively. $CDCl_3$ served as a solvent and Me_4Si as internal standard. Mass spectra were measured with a DuPont 21-491B spectrometer. IR spectra were recorded as neat films in $CHCl_3$ solution or in KBr pellets on a Perkin-Elmer 177 spectrophotometer.

General Fluorination Procedure. A description of the set-up and the procedure for working with elemental fluorine has previously been described.[10b,c] Although mentioned in previous works, it is worth stressing again that F_2 should be treated with care since it is a strong oxidizer. The work should be conducted in an efficient hood or in a well ventilated area. If elementary precautions are taken, work with fluorine is relatively simple. In the past we have had no bad experiences working with this element. The reactions were usually carried out on scales of 7–15 mmol, monitored by GC on a 3% SE-30 column, and usually stopped when the conversion reached about 95%. Fluorine, at a concentration of 1% in N_2, was passed as a slow stream through a cold (−75 °C) and vigorously stirred solution of the substrate dissolved in 250 mL of $CFCl_3$, 200 mL of $CHCl_3$, and 50 mL of EtOH. The term "worked up as usual" means stopping the reaction by pouring it into 500 mL of water, washing the organic layer with $NaHCO_3$ solution followed by water until neutral, drying the organic layer over $MgSO_4$, and finally evaporating the solvent. The crude product was usually purified by vacuum flash chromatography using silica gel 60-H (Merck) and if needed also by HPLC (Waters) on Merck's LiChrosorb Si-100.

Fluorination of *trans*-3-hexen-1-ol acetate (1) was carried out on 750 mg (5.3 mmol). After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The threo adduct 2 was thus obtained in 55% yield as an oil: IR 1720 cm^{-1}; ^1H NMR δ 4.60 (1 H at C-3, four dt, $^2J_{HF}$ = 48 Hz, $^3J_{HF}$ = 23 Hz, J_{HH} = 3.0 and 9.5 Hz), 4.44–4.16 (3 H at C-1 and C-4, m), 2.07 (3 H, s), 1.04 (3 H, t, J_{HH} = 7.5 Hz), 1.95–1.25 (4 H, m); ^{19}F NMR −201.3

(12) Bergmann, E. D.; Shahak, I. *J. Chem. Soc.* **1961**, 4033. See also ref 7a.

(1 F, m, $W_{h/2}$ = 99 Hz), -198.3 (1 F, m, $W_{h/2}$ = 100 Hz); ^{13}C NMR 170.8 (CO), 94.42 (C-3, dd, $^1J_{CF}$ = 190 Hz, $^2J_{CF}$ = 20 Hz), 89.93 (C-4, dd, $^1J_{CF}$ = 190 Hz, $^2J_{CF}$ = 22 Hz), 60.33 (C-1), 30.01 (C-2, dd, $^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 5 Hz), 23.58 (C-5, dd, $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 4 Hz), 20.79 (*C*OC), 9.27 (C-6); MS, m/e 160 [(M - HF)$^+$], 121 [(M - OAc)$^+$]. Anal. Calcd for $C_8H_{14}F_2O_2$: C, 53.33; H, 7.78. Found: C, 53.25; H, 7.70.

Fluorination of *cis*-3-hexen-1-ol acetate (3) was carried on 750 mg (5.3 mmol). After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The erythro adduct **4** was thus obtained in 50% yield as an oil: IR 1720 cm^{-1}; ^{1}H NMR δ 4.59 (1 H at C-3, two wings of m, $^2J_{HF}$ = 48 Hz, from which one can clearly extract a coupling constant of J_{HH} = 4.0 Hz), 4.43–4.17 (3 H at C-1 and C-4, m), 2.07 (3 H, s), 1.05 (3 H, t, J_{HH} = 7.5 Hz), 2.00–1.20 (4 H, m); ^{19}F NMR -196.1(1 F, m, $W_{h/2}$ = 105 Hz), -194.7 (1 F, m, $W_{h/2}$ = 103 Hz); ^{13}C NMR 170.8 (CO), 94.67 (C-3, dd, $^1J_{CF}$ = 206 Hz, $^2J_{CF}$ = 25 Hz), 90.54 (C-4, dd, $^1J_{CF}$ = 186 Hz, $^2J_{CF}$ = 27 Hz), 60.29 (C-1), 30.07 (C-2, dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 4 Hz), 23.82 (C-5, dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 4 Hz), 20.70 (*C*OC), 9.19 (C-6); MS, *m/e* 121 [(M - OAc)$^+$]. Anal. Calcd for $C_8H_{14}F_2O_2$: C, 53.33; H, 7.78. Found: C, 53.20; H, 7.75.

Fluorination of *trans*-ethyl cinnamate (5) was performed on 1.5 g (8.5 mmol). After the usual workup the crude reaction mixture was purified by vacuum flash chromatography as above. The threo adduct **7** was thus obtained in 55% yield as an oil: IR 1750 cm^{-1}; ^{1}H NMR δ 7.40 (5 H br s), 5.84 (1 H, three d, $^2J_{HF}$ = 44 Hz, $^3J_{HF}$ = 23 Hz, J_{HH} = 3.1 Hz), 5.06 (1 H, three d, $^2J_{HF}$ = 47 Hz, $^3J_{HF}$ = 26 Hz, J_{HH} = 3.0 Hz), 4.26 (2 H, q, J = 7 Hz), 1.25 (3 H, t, J = 7 Hz); ^{19}F NMR -192.5 (1 F, three d, $^2J_{HF}$ = 44 Hz, $^3J_{HF}$ = 26 Hz, $^3J_{FF}$ = 11 Hz), -205.0 (1 F, three d, $^2J_{HF}$ = 47 Hz, $^3J_{HF}$ = 23 Hz, $^3J_{FF}$ = 11 Hz); ^{13}C NMR 166.5 (CO), 126–134 (C-arom), 92.13 (CF, dd, $^1J_{CF}$ = 200 Hz, $^2J_{CF}$ = 20 Hz), 89.96 (CF, dd, $^1J_{CF}$ = 197 Hz, $^2J_{CF}$ = 20 Hz), 62.15 (CH_2O), 14.02 (CH_3); MS, *m/e* 214 (M)$^+$, 194 [(M - HF)$^+$]. Anal. Calcd for $C_{11}H_{12}F_2O_2$: C, 61.68; H, 5.61. Found: C, 61.68; H, 5.56.

Fluorination of *cis*-ethyl cinnamate (6) was carried on 1.5 g (8.5 mmol) as described previously. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The *erythro*-ethyl 2,3-difluoro-3-phenylpropionate (**8**) was thus obtained in 50% yield as an oil: IR 1750 cm^{-1}; ^{1}H NMR δ 7.38 (5 H, br s), 5.83 (1 H, three d, $^2J_{HF}$ = 44 Hz, $^3J_{HF}$ = 20 Hz, J_{HH} = 3.6 Hz), 5.30 (1 H, three d, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = 13 Hz, J_{HH} = 3.6 Hz), 4.22 (2 H, q, J = Hz), 1.25 (3 H, t, J = 7 Hz); ^{19}F NMR -187.2 (1 F, three d, $^2J_{HF}$ = 44 Hz, $^3J_{HF}$ = 13 Hz, $^3J_{FF}$ = 30 Hz), -202.8 (1 F, three d, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = 20 Hz, $^3J_{FF}$ = 30 Hz); ^{13}C NMR 165.0 (CO), 126–129 (C_{arom}), 91.79 (CF, dd, $^1J_{CF}$ = 181 Hz, $^2J_{CF}$ = 22 Hz), 89.41 (CF, dd, $^1J_{CF}$ = 195 Hz, $^2J_{CF}$ = 27 Hz), 62.04 (CH_2O), 14.00 (CH_3); MS, *m/e* 214 (M)$^+$, 194 [(M - HF)$^+$]. Anal. Calcd for $C_{11}H_{12}F_2O_2$: C, 61.68; H, 5.61. Found: C, 61.22; H, 5.76.

Fluorination of *cis*-stilbene (9)[10] was as described above. After the usual workup the crude reaction mixture was found to consist of a 47% yield of the meso adduct **10** and 13% yield of the *dl* derivative **11**. Both isomers were identical in all respects with the ones already described in the literature.[10]

Fluorination of cycloheptene (12) was carried out as described above on 1.25 g (13 mmol). After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using petroleum ether as eluent. The difluoro adduct **13** was thus obtained in 40% yield as an oil: ^{1}H NMR δ 5.24–4.35 (2 H, CHF, m), 1.25–1.99 (10 H, m); ^{19}F NMR -185.0 (m, $W_{h/2}$ = 93 Hz); MS, *m/e* 134 (M)$^+$, 114 [(M - HF)$^+$]. Anal. Calcd for $C_7H_{12}F_2$: C, 62.69; H, 8.96. Found: C, 62.50; H, 8.90.

Fluorination of Cyclododecene (14). A mixture of the cis and trans isomers (1.66 g, 10 mmol) in a respective ratio of 1:2 was reacted with F_2 according to the general procedure to provide a mixture of the *dl* (**15**) and meso (**16**) isomers, separated by HPLC using cyclohexane as eluent. The more polar **15** was obtained in 40% yield: mp 60 °C (*i*-PrOH–H_2O); ^{1}H NMR δ 4.80–4.62 (2 H, two wings of m, $^2J_{HF}$ = 50 Hz out of which a coupling constant of J_{HH} = 4.0 can clearly be seen), 2.17–1.25 (20 H, m); ^{19}F NMR -193.5 (m, $W_{h/2}$ = 84 Hz); ^{13}C NMR 92.50 (CF, dd, $^1J_{CF}$ = 175 Hz, $^2J_{CF}$ = 19.5 Hz), 28.12 and 27.96 (2 C, d, $^2J_{CF}$ = 14 Hz), 24.26, 23.97, 22.86, 20.62 (the rest of the signals); MS, *m/e* 204 (M)$^+$, 184 [(M - HF)$^+$]. Anal. Calcd for $C_{12}H_{22}F_2$: C, 70.59; H, 10.78. Found: C, 70.35; H, 10.65. The less polar **16** was obtained in 20% yield: mp 54 °C (*i*-PrOH/H_2O); ^{1}H NMR δ 4.65 (2 H, four t, $^2J_{HF}$ = 48 Hz, $^3J_{HF}$ = 24 Hz, J_{HH} = 6.5 Hz), 1.99–1.25 (20 H, m); ^{19}F NMR -191.2 (m, $W_{h/2}$ = 100 Hz); ^{13}C NMR 92.63 (CF, dd, $^1J_{CF}$ = 176 Hz, $^2J_{CF}$ = 20.0 Hz), 25.81 and 25.50 (2 C, d, $^2J_{CF}$ = 22 Hz), 24.26, 22.70, 21.91, 21.14 (the rest of the signals); MS, *m/e* 204 (M)$^+$, 184 [(M - HF)$^+$].

Fluorination of 7-Tetradecene (17). A mixture of the trans and cis isomers (1.50 g, 7.65 mmol) in a respective ratio of 2.5:1 was fluorinated according to the general procedure to provide a mixture of the *dl* (**18**) and meso (**19**) isomers, separated by HPLC using cyclohexane as eluent. The more polar **18** was obtained in 50% yield: mp 40 °C (*i*-PrOH/H_2O); ^{1}H NMR δ 4.41 (2 H, four m, $^2J_{HF}$ = 47 Hz, $^3J_{HF}$ = 23 Hz), 1.80–1.30 (20 H, m), 0.89 (6 H, t, J = 7 Hz); ^{19}F NMR -196.8 (m, $W_{h/2}$ = 94 Hz); ^{13}C NMR 93.46 (CF, dd, $^1J_{CF}$ = 176 Hz, $^2J_{CF}$ = 22.0 Hz), 30.60 (2 C, d, $^2J_{CF}$ = 26 Hz), 31.76, 29.14, 25.07, 22.63, 14.04 (the rest of the signals); MS, *m/e* 234 (M)$^+$, 214 [(M - HF)$^+$]. Anal. Calcd for $C_{14}H_{28}F_2$: C, 71.79; H, 11.97. Found: C, 71.56; H, 11.71. The less polar **19** was obtained in 18% yield, oil: ^{1}H NMR δ 4.46 (2 H, two m, $^2J_{HF}$ = 48 Hz, $^3J_{HF}$ = 15 Hz), 1.70–1.30 (20 H, m); ^{19}F NMR -193.1 (m, $W_{h/2}$ = 100 Hz); ^{13}C NMR 93.85 (CF, dd, $^1J_{CF}$ = 173 Hz, $^2J_{CF}$ = 26 Hz), 30.37 (2 C, d, $^2J_{CF}$ = 22 Hz), 31.70, 29.09, 25.04, 22.57, 14.00 (the rest of the signals); MS, *m/e* 234 (M)$^+$, 214 [(M - HF)$^+$], 194 [(M - 2 HF)$^+$]. Anal. Calcd for $C_{14}H_{28}F_2$: C, 71.79; H, 11.97. Found: C, 71.67; H, 12.14.

Fluorination of 1-octene (20) was carried out as described above on 1.12 g (10 mmol). After the usual workup two compounds were obtained and separated by HPLC using cyclohexane as eluent. The more polar compound was identified as the difluoro adduct **22** obtained in 40% yield as an oil: ^{1}H NMR δ 4.05–4.89 (3 H, C*H*FCH_2F, m), 1.33 (10 H, narrow m), 0.89 (3 H, t, J = 8 Hz); ^{19}F NMR -230.0 (1 F, tt, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = $^3J_{FF}$ = 21 Hz), -189.0 (1 F, m, $W_{h/2}$ = 96 Hz); MS, *m/e* 150 (M)$^+$, 130 [(M - HF)$^+$]. Anal. Calcd for $C_8H_{16}F_2$: C, 64.00; H, 10.67. Found: C, 63.76; H, 10.60. The less polar derivative was identified as the trifluoride **24**, 22% yield, oil: ^{1}H NMR δ 5.65 (1 H, CHF_2, three dd, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 6 Hz, J_{HH} = 4 Hz), 4.35 (1 H, CHF, dm, $^2J_{HF}$ = 46 Hz, $W_{h/2}$ of each m = 15 Hz), 0.86 (3 H, t, J = 5 Hz); ^{19}F NMR -132.5 (1 F, dt, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = $^3J_{FF}$ = 12 Hz), -131.0 (1 F, br d, $^2J_{HF}$ = 55 Hz), -202.3 (1 F, m, $W_{h/2}$ = 89 Hz); MS, *m/e* 168 (M)$^+$, 117 [(M - CHF_2)$^+$], 97 [(M - CHF_2 - HF)$^+$]. Anal. Calcd for $C_8H_{15}F_3$: C, 57.14; H, 8.93. Found: C, 57.20; H, 8.88.

Fluorination of 1-dodecene (21), as described above on 1.68 g (10 mmol), afforded two compounds which were separated by HPLC using cyclohexane as eluent. The more polar compound was identified as the difluoro adduct **23** obtained in 40% yield as an oil: ^{1}H NMR δ 4.03–4.89 (3 H, C*H*FCH_2F, m), 1.27 (18 H, narrow m), 0.87 (3 H, t, J = 8 Hz); ^{19}F NMR -230.0 (1 F, tt, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = $^3J_{FF}$ = 22 Hz), -189.0 (1 F, m, $W_{h/2}$ = 98 Hz); MS, *m/e* 206 (M)$^+$, 186 [(M - HF)$^+$]. Anal. Calcd for $C_{12}H_{24}F_2$: C, 69.90; H, 11.65. Found: C, 69.74; H, 11.55. The less polar derivative was identified as the trifluoride **25**, 25% yield, oil: ^{1}H NMR δ 5.76 (1 H, CHF_2, three dd, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 6 Hz, J_{HH} = 4 Hz), 4.42 (1 H, CHF, dm, $^2J_{HF}$ = 46 Hz, $W_{h/2}$ of each m = 12 Hz), 0.88 (3 H, t, J = 5 Hz); ^{19}F NMR -132.0 (1 F, dt, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = $^3J_{FF}$ = 12 Hz), -130.9 (1 F, br d, $^2J_{HF}$ = 55 Hz), -202.0 (1 F, m, $W_{h/2}$ = 89 Hz); MS, *m/e* 224 (M)$^+$, 173 [(M - CHF_2)$^+$], 153 [(M - CHF_2 - HF)$^+$]. Anal. Calcd for $C_{12}H_{23}F_3$: C, 64.28; H, 10.27. Found: C, 65.00; H, 9.99.

Fluorination of *trans*-3-nonen-2-one (26) was carried out, using 750 mg (5.4 mmol), followed by the usual workup and vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The threo adduct **27** was thus obtained in 50% yield as an oil: IR 1730 cm^{-1}; ^{1}H NMR δ 4.82 (1 H at C-4, four ddd, $^2J_{HF}$ = 46 Hz, $^3J_{HF}$ = 27 Hz, J_{HH} = 1.4, 5.4 and 8.5 Hz), 4.65 (1 H at C-3, four d, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = 31 Hz, J_{HH} = 1.4 Hz), 2.33 (3 H, CH_3CO, d, $^4J_{HF}$ = 5 Hz), 1.5–1.1 (8 H, m), 0.92 (3 H, t, J_{HH} = 7.0 Hz); ^{19}F NMR -197.1 (1 F, m, $W_{h/2}$ = 72 Hz), -208.4 (1 F, m, $W_{h/2}$ = 102 Hz); ^{13}C NMR 95.14 (C-3, dd, $^1J_{CF}$ = 195 Hz, $^2J_{CF}$ = 21 Hz), 92.47 (C-4, dd, $^1J_{CF}$ = 176 Hz, $^2J_{CF}$ = 20 Hz), 30.16 (C-5, d, $^2J_{CF}$ = 18 Hz), 24.51 (C-1, d, $^3J_{CF}$ = 4 Hz), 31.43 (C-6), 29.40 (C-7), 22.45 (C-8); MS, *m/e* 178 (M)$^+$, 158 [(M - HF)$^+$]. Anal. Calcd for $C_9H_{16}F_2O$: C, 60.67; H, 8.99. Found: C, 59.70; H, 8.91.

Fluorination of coumarin (28) was carried out on 1.0 g (6.8 mmol) as described previously. After the usual workup two compounds were obtained and eluted by HPLC using 15% EtOAc in cyclohexane. The major fraction was identified as 3,4-dihydro-3,4-difluorocoumarin (**29**) obtained in 55% yield as an oily solid which failed attempted crystallization: IR 1725 cm^{-1}; ^1H NMR δ 7.60–7.10 (4 H, m), 5.41 (1 H, three d, $^2J_{HF}$ = 46 Hz, $^3J_{HF}$ = 30 Hz, J_{HH} = 3.0 Hz), 5.76 (1 H, ddd, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 6 Hz, J_{HH} = 3.0 Hz); ^{19}F NMR -176.5 (1 F, three d, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 30 Hz, $^3J_{FF}$ = 15 Hz), -206.0 (1 F, three d, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = 6 Hz, $^3J_{FF}$ = 15 Hz); MS, *m/e* 184 $(M)^+$, 164 $[(M - HF)^+]$, 136 $[(M - HF - CO)^+]$. Anal. Calcd for $C_9H_6F_2O_2$: C, 58.69; H, 3.26. Found: C, 57.90; H, 3.95. The minor fraction proved to be the known dehydrofluorinated product **30**,[12] 15% yield: mp 150 °C (from MeOH); IR 1710 cm^{-1}; ^1H NMR δ 7.60–7.26 (m); ^{19}F NMR -130.5 (d, $^3J_{HF}$ = 9 Hz). The transformation **29** → **30** could be quantitatively achieved by absorbing the difluoro adduct on a silica gel column for a period of 24 h.

Fluorination of 2-cyclopentylidenecyclopentanone (31) was carried as described previously. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The difluoro adduct (**32**) was thus obtained in 35% yield as an oil: IR 1760 cm^{-1}; ^1H NMR δ 2.6–1.8 (m); ^{19}F NMR -159.6 (1 F, t, $^3J_{HF}$ = 26 Hz), -150.7 (1 F, quintet, $^3J_{HF}$ = 30 Hz); MS, *m/e* 188 $(M)^+$, 168 $[(M - HF)^+]$. Anal. Calcd for $C_{10}H_{14}F_2O$: C, 63.83; H, 7.45. Found: C, 63.21; H, 7.22.

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Registry No. 1, 3681-82-1; (±)-**2**, 103225-29-2; **3**, 3681-71-8; (±)-**4**, 103239-64-1; **5**, 4192-77-2; **6**, 4610-69-9; (±)-**7**, 103225-30-5; (±)-**8**, 103225-31-6; **9**, 645-49-8; *meso*-**10**, 14090-31-4; (±)-**11**, 52795-54-7; **12**, 628-92-2; **13**, 103225-32-7; (*E*)-**14**, 1486-75-5; (*Z*)-**14**, 1129-89-1; (±)-**15**, 103225-33-8; *meso*-**16**, 103302-88-1; (*E*)-**17**, 41446-63-3; (*Z*)-**17**, 41446-60-0; (±)-**18**, 103225-34-9; *meso*-**19**, 103225-35-0; **20**, 111-66-0; **21**, 112-41-4; (±)-**22**, 103225-36-1; (±)-**23**, 103225-37-2; (±)-**24**, 103225-38-3; (±)-**25**, 103225-39-4; **26**, 18402-83-0; (±)-**27**, 103225-40-7; **28**, 91-64-5; (±)-**29**, 103225-41-8; **30**, 704-60-9; **31**, 825-25-2; **32**, 103225-42-9; F_2, 7782-41-4.

Cycloaddition of Chloro-, Cyano-, Methoxy-, and (Phenylthio)allene with 1,1-Dichloro-2,2-difluoroethene (1122). Competitive Cyclodimerization and Trapping of the Cyclodimers with 1122

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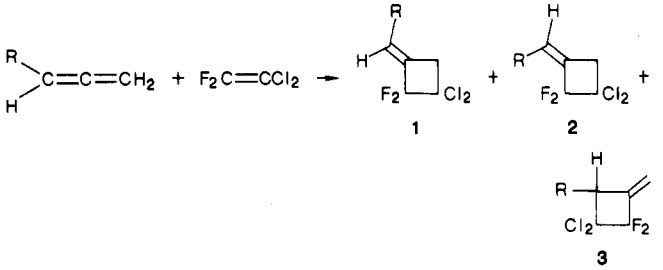
The cycloaddition reactions of chloro- (ClA), cyano- (CNA), methoxy- (MEOA), and (phenylthio)allene (PHSA) with 1,1-dichloro-2,2-difluoroethene (1122) have been investigated. Cycloadducts are derived by initial attack of 1122 at both C_2 and C_3 in ClA, CNA, and MEOA, and only at C_2 of PHSA. Competitive cyclodimerization of the substituted allenes occurs extensively with ClA and CNA and to lesser extents with MEOA and PHSA. The cyclodimerization of ClA produces a mixture of tail-to-tail (T–T), head-to-tail (H–T), and head-to-head (H–H) cyclodimers, while CNA forms only T–T and H–T cyclodimers, PHSA forms only H–T and H–H cyclodimers, and MEOA apparently forms only the H–H cyclodimer. Only the T–T cyclodimerization of ClA and CNA has been previously detected. The H–T and H–H cyclodimers react further with 1122 to produce 2:1 adducts. The T–T cyclodimers do not react with 1122.

Recent studies in our laboratories have focused on gaining an understanding of the mechanistic details of the free-radical[1,2] and cycloaddition reactions of substituted allenes with dienophiles.[3-5] The results of these studies have shown that the cycloaddition reactions proceed via two-step, diradical-intermediate pathways and have provided valuable information concerning the structures of the diradical intermediates and the factors affecting the relative rates of cleavage, internal rotation, and ring closure.[3-5] One of our objectives has been to determine the effect of substituents on the rates of formation of the diradical intermediates and to measure activation parameters for their formation. Our early observations indicated that all substituents, regardless of their electron-donating or electron-withrawing properties, accelerated the rate of formation of the diradical intermediate relative to hydrogen,[3,4] suggesting a rather late transition state. Two criteria must be met in order to accurately measure relative and/or specific rate constants for diradical intermediate formation: (1) the formation of the intermediate must be irreversible and (2) the reactions should occur cleanly involving attack only at the central carbon atom of the allene to produce the normal cycloaddition products. Our previous studies suggested that 1,1-dichloro-2,2-difluoroethene (1122) might be an excellent choice as the substituted alkene, the reactions of 1122 with monoalkylallenes occurring in a clean manner to produce the cycloadducts **1–3**,[3] and the formation of the diradical intermediate in



the reaction with phenylallene appearing to be irreversible.[6]

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