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Fluorination with $CsSO_4F$. Part 21[1]. Effect of the Structure of Alkene and Alcohol on Stereochemistry and Relative Rate of Fluoroalkoxylation

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Abstract: 1-Alkoxy-2-fluoro-1-phenyl benzocycloalkanes are efficiently formed by reactions of 1-phenylbenzocycloalkenes with caesium fluoroxysulphate (CFS) in alcohols (MeOH, EtOH, i-PrOH) at room to moderately elevated temperature. The stereochemistry of the reaction depends on the ring size of the substrate and on the structure of the alcohol, and is *syn* predominant in the case of fluorination of five-, *anti* predominant in six-, and slightly to nearly exclusively *syn* predominant in seven-membered ring benzocycloalkene analogues. The relative rates measured for methoxy-fluorinations of a set of seven phenyl-substituted alkenes with CFS in methanol show a trend to increasing reactivity with decreasing ionisation potential of the named alkenes yielding a linear correlation relationship with a very high correlation factor r=0.945 and slope -1.76, thus indicating that π-bond disruption in the substrate alkene is the rate determinig step of the reaction of the alkenes studied with CFS under the reported reaction parameters.

The family of so-called "electrophilic" fluorinating reagents is a very important group of chemicals useful for the selective introduction of a fluorine atom into organic molecules[2], which covers the fluorofunctionalisation of a comprehensive spectrum of organic compounds, including those that are bioactive[3]. Elemental fluorine[4], XeF_2[5], N-F[6] and fluoroxy reagents[2,4,7] are the main representatives in the group. The high reactivity of elemental fluorine and most of the fluoroxy reagents demand special reaction conditions, equipment and precautions, while caesium fluoroxysulphate ($CsSO_4F$; CFS) is reported to be an easily handled reagent, useful under normal reaction conditions for the selective fluorofunctionalisation or oxidation of a variety of organic molecules[2, 4a, 8].

Phenyl-substituted alkenes have many advantages as model substrates for the study of electrophilic addition reaction in general. When fluorination with "electrophilic" fluorinating reagents is the subject of study, the regiospecificity of the reactions and the stability of the reaction product, in addition to the distinctive possibility of modulation of electronic and steric effects by structural variations, make the phenyl-substituted alkenes decisively advantageous in comparison with other alkenes. Although electrophilic addition to a carbon-carbon double bond is one of the most studied types of reaction in organic chemistry[9], only a few kinetic evaluations of the fluorination of alkenes as a function of their structure are known[1, 6e, 10]. We now report some kinetic and new stereochemical aspects of the fluorination of alkenes with CFS.

RESULTS AND DISCUSSION

It was already demonstrated that the course of reaction of CFS with alkenes is very sensitive to the structure of the alkene and the reaction conditions. The addition-elimination process resulting in fluoroalkenes was found exclusively in the case of reaction of some pheny-substituted alkenes and norbornene with an excess of CFS in methylene chloride medium, while the 1,2-addition process with Markovnikov type incorporation of an external nucleophile (F^-, MeO^- or AcO^-) was established as the result of the reaction when protic species were present in the reaction mixture[1,11], and the stereoselectivity of the addition was slightly to considerably syn prevalent[12]. On the other hand, regio nonselective formation of vicinal fluoro sulphates were observed when a two to four molar excess of various alkenes were treated with CFS in aprotic solvents, the addition being syn predominant[13]. For the present study we chose the 1-phenyl-1-benzocyclene triad (**1a-c**, Scheme 1) as the test compounds in order to evaluate the effect of ring size and the structure of the external nucleophile on the stereoselectivity of the reaction with CFS. The aim was also to investigate the effect of the additional phenyl group in connection with ring magnitude on the kinetic parameters of the reaction, since a phenyl group bonded to the 1-position in benzocyclenes lowered the ionisation potentials (IP) by as much as 0.7 eV in comparison with unsubstituted and by 0.4 eV in comparison with the acyclic analogue (Table 2). In a typical experiment we added a 40-80% molar excess of CFS to a 0.5 M solution of 1-phenyl-1-benzocyclene (**1a-c**) in an appropriate alcohol (R=Me; Et; and iPr; Scheme 1) and after stirring the reaction mixture at room or slightly elevated temperature for one to four hours, the isolation of the reaction products and ^{19}F and ^1H spectra of their crude mixtures revealed the formation of diastereoisomeric pairs of 1-alkoxy-1-phenyl-2-fluorobenzocyclanes (**2-7**; SCHEME 1) in good to excellent yield. After separation of the two components in a particular pair by preparative TLC, we established the structure of each diastereoisomer on the basis of its spectroscopic data. The considerable differences in NMR spectra of *syn* (**2a**, **4a**, **6a**) and *anti* (**3a**, **5a**, **7a**) vicinal alkoxy fluoride adducts, resulting from CFS treatment of 3-phenyl-1H-indene (**1a**), enabled us to establish products having signals in their ^{19}F NMR spectra at higher field (-200 ppm), coupling constants for a fluorine atom with a protons on position 3 with values of 12-14 Hz and 7 Hz, respectively, and two couplings of 7 Hz for a proton at position 2 with protons on position 3, as *syn* 1-alkoxy-2-fluoro adducts, and those with lower field resonance (-183 to -185 ppm), higher $^3J_{FH3}$ (33 to 40 Hz and 22 to 23 Hz), and only one 4 Hz coupling of H_2 and H_3, as *anti* aducts. In the case of the fluorination of 3-phenyl-1H-indene (**1a**) *syn* addition was found to be predominant over *anti* in the range of 2 : 1 when methanol or ethanol were used as the source of the external nucleophile, while only a slight excess of *syn* adduct formation was observed in the i-propyl alcohol mediated reaction (Table 1). We also observed isomerisation of the *cis* 2-fluoro-1-methoxy adduct **2a** to the *trans* isomer **3a** when *cis* or a mixture of both isomers were left in solution. More data concerning this isomerisation, similar to that already observed in the case 5-fluoro-6-alkoxy uracils[14], will be published separately. No isomerisation was observed in the case of fluoro-ethoxy (**4a**, **5a**) and fluoro-i-propoxy (**6a**, **7a**) adducts.

Since the NMR spectra of diastereoisomeric fluoro-alkoxy adducts obtained after fluorination of 4-phenyl-1,2-dihydronaphthalene (**1b**) or 9-phenyl-6,7-dihydro-5H-benzocycloheptene (**1c**) do not show significant differences on the basis of which we could unequivocally define the structures of the isomers, monocrystals of some isolated products had to be grown to established their structures on the

SCHEME 1

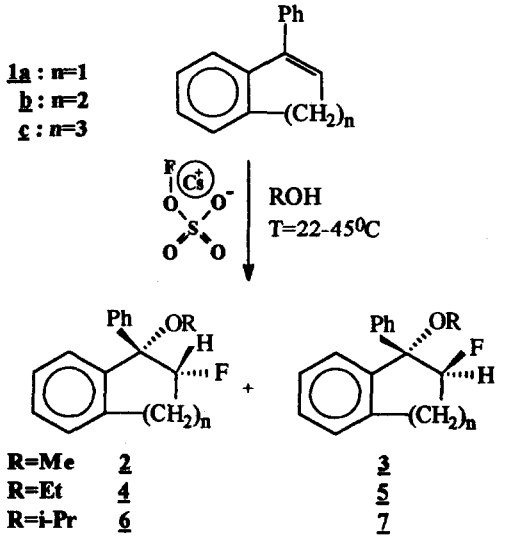


Table 1

Effect of the Structure of Benzocyclene (1a-c) and Alcohol on Stereoselectivity of Formation of Vicinal Fluoro Ethers with $CsSO_4F$.

n	R	Stereoselectivity [a] syn : anti	Yield [b]
1	Me	2.00 : 1	94
	Et	2.03 : 1	91
	i-Pr	1.19 : 1	68
2	Me	0.63 : 1	79
	Et	0.65 : 1	95
	i-Pr	0.31 : 1 [c]	65
3	Me	1.15 : 1	72
	Et	2.94 : 1	72
	i-Pr	9.00 : 1	82

a) Det. from ^{19}F NMR spectra of crude reaction mixtures; b) Det. from ^{19}F NMR spectra of crude reaction mixtures using octafluoro naphthalene as additional standard and calcd. from starting alkene c) Ratio after separation of diastereoisomers.

basis of X-ray diffraction analysis[15]. The structures of the compounds 7b and 4c were thus confirmed, and the structures of others determined on the basis of similarity in the shape of the signals in ^{19}F NMR spectra, with additional comparison of retension factors in their TL chromatograms. It is evident from TABLE 1 that *anti* addition is preferential in the case of the six-membered ring 1-phenyl-1-benzocyclene analogue, while a considerable effect of ring magnitude and the structure of the external nucleophile on the stereoselectivity of the reaction was found in the case of the fluorination of the seven-membered ring derivative 1c. Only a slight excess of *syn* addition process was observed when the reaction was carried out in methanol, while predominantly *syn* and almost diastereospecifically *syn* addition was established after ethanol and i-propyl alcohol mediated reactions, respectively.

In order to evaluate the effect of ring size in benzocyclenes 1 on their reactivity from the kinetic point of view, by applying the known competitive technique[16] we compared the reactivity of analoques 1a-c towards methoxy-fluorination with CFS in methanol and expressed them in terms of relative rates (k_{rel} , Table 2). We found that five and six-membered ring derivatives (1a and 1b) differ in their reactivity insignificantly, but are three fold more reactive than their seven-membered ring analogue 1c. The results are similar in trend, but not in shape, with those observed for the bromination of the same compounds in methanol, where the reaction of 1c was as much as five hundredfold slower than those of 1a and 1b[17]. We further expanded this kinetic evaluation to the phenyl-substituted alkenes for which methoxy-fluorination with CFS was already studied and reported to be selective and giving high yield[11,12a]. As evident from Table 2, the additional phenyl group, bonded to the unsaturated carbon α to the benzene ring in benzocyclene, increases the reactivity of the molecule by more than seventeen times, while the reactivity of 3-phenyl-1H-indene (1a) was found to be nearly three times higher than that of its acyclic analogue 1,1-diphenyl-1-propene.

The correlation of relative reactivity with the ionisation potential of the organic molecule may be used as one of the criteria in assessing mechanistic details of electrophilic addition to alkenes. Some examples of such correlations for a variety of electrophilic addition reactions have been reported and discussed[18,19], but dearth of such data concerning fluorination of the C-C double bond is obvious. It was generally accepted that an increase of electron availibility at the C-C double bond (i.e. a decrease of IP) should increase the rate of electrophilic reaction, and if the disruption of the π sistem in alkenes is the rate determining step of the reaction and given a lack of strong steric effects in the transition-state structure, then a linear correlation between the logarithm of k_{rel} and IP should be obtained[18-20]. The correlation plot of *log* k_{rel} / *IP* for 7 phenyl-substituted alkenes treated in this study indicates a trend of increasing reactivity with decreasing, IP resulting in a linear relationship with a very high correlation constant[21] of r=0.945 and a slope of - 1.76.

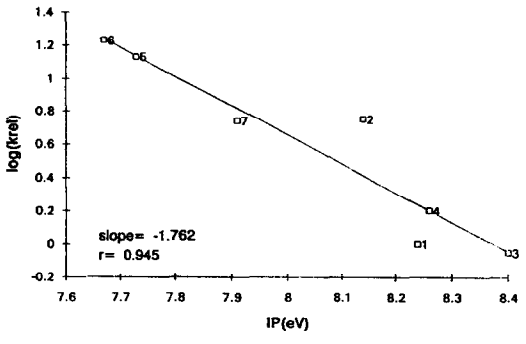
Table 2

Relative rate factors (k_{rel}, relative to 1,1-diphenyl ethene) for the methoxy-fluorination of phenyl substituted alkenes with $CsSO_4F$ in methanol

Entry	Alkene	k_{rel}	IP(eV)
1	1,1-Diphenylethene	1.00	8.24
2	1,1-Diphenyl-1-propene	5.7	8.14
3	Indene	0.9	8.40
4	1,2-Dihydronaphthalene	1.6	8.26
5	3-Phenyl-1H-indene	15.4	7.73
6	4-Phenyl-1,2-dihydro naphthalene	17.1	7.67
7	9-Phenyl-6,7-dihydro-5H-benzocycloheptene	5.5	7.91

Figure 1

Plot of log k_{rel} for methoxy-fluorination of phenyl-substituted alkenes with caesium fluoroxy sulphate in MeOH versus alkene IP

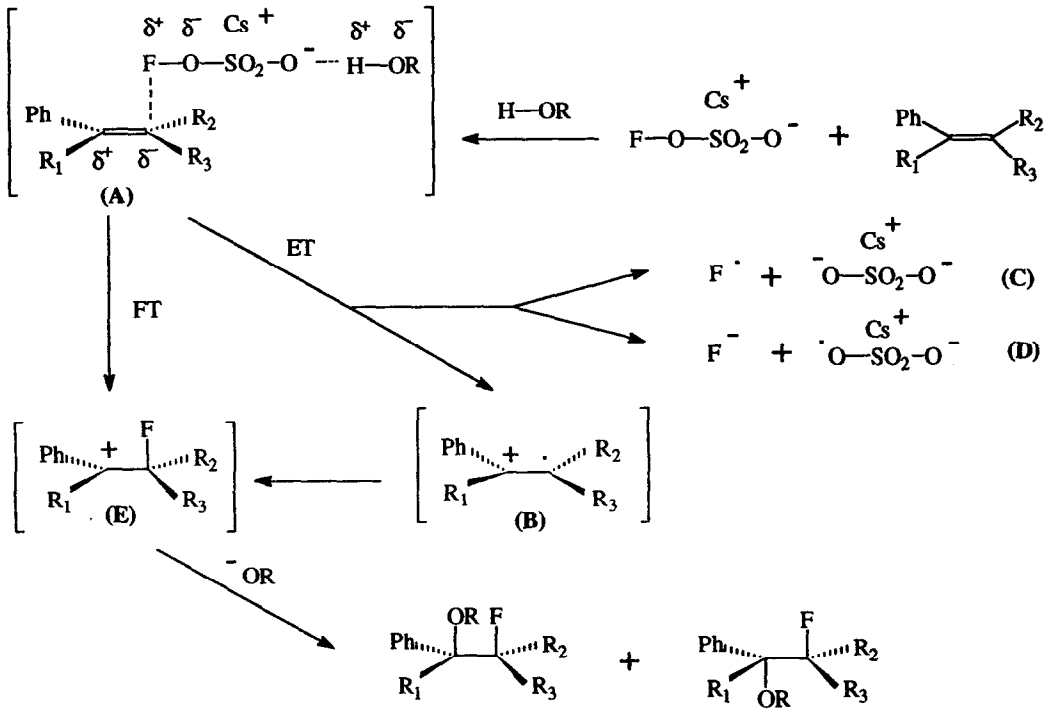


The main subject of debate concerning the posible mechanisms of fluorination of organic compounds with "electrophilic" fluorinating agents is whether the reactions with organic molecules carrying electron-rich centres (C-C double bond, carbanion...) proceed through direct fluorine transfer (FT), or through a two-step process where an electron transfer (ET) precedes a fluorine radical transfer (FRT). Since fluorine is the most electronegative element and has an extremely high ionisation potential[22], electrophilic fluorine transfer was declared unlikely in general[23] and the electron transfer pathway was proposed as a reaction route in fluorination with some N-F[6a,6b] as well as fluoroxy reagents[10,24]. On the basis of use of the radical clock principle as an criterion for distinguishing among FT and ET pathways in reactions of enolates with a group of N-F reagents, the SN_2-type attack of an electron rich centre on the fluorine atom was postulated recently[25]. In our opinion not enough experimental data are so far available in order to enable a nonspeculative general judgement on a matter. Extensive comparative studies concerning the reaction of a selected series of organic molecules which are structural analogues with different "electrophilic" fluorination reagents under comparable reaction conditions would help considerably in clarifying the situation, but so far

the most realistic observation is that the structure of the reagent and the substrate and their relative concentration, the reaction media, temperature, etc., are the variables which crucially influence the selection of a reaction pathway channel.

When discussing the mechanism of reactions of CFS with organic compounds the very pronounced effect of even small variations in reaction parameters on the course of the reactions must be taken into occount, while the fact that the most reported reactions were carried out in heterogenous media represents an additional difficulty in mechanistic generalisation of the reaction pathway. Nevertheless, on the basis of previously reported as well as the present data on the reaction of CFS with alkenes, the reactions with an excess of alkene[13] and these when CFS is in excess[1,11,12] should presumably be discussed separately from the mechanistic point of view, since the results are not comparable because of the considerable differences in the reaction parameters. The proposed pathway for the reaction of CFS with phenyl-substituted alkenes in alcohols is presented on Scheme 2. Normally, the oxygen-fluorine bond in fluoroxy compounds is slightly polar with an excess of electron density on the fluorine[10,26], but in the presence of a phenyl-substituted alkene the electron density can be pushed in the opposite direction forming a π-like complex (A) with electron deficiency on the fluorine atom and at the carbon α to the phenyl group. Such an electron density movement is stimulated not only by possible resonance stabilisation of the positive charge on the carbon α to the phenyl, but also by possible incorporation of an alcohol molecule or molecules in π-like complex

SCHEME 2



coordination. Electron(s) exchange between the electron rich C-C double bond and the electron deficient reagent can proceed through at least two channels: by direct fluorine transfer (FT) to β-fluoro carbocation (E) or by electron transfer (ET) to a cation radical (B). In the latter case the CFS can disproportionate to $F^{\bullet}$ and $SO_4^{=}$ (C), or to F^{-} and $SO_4^{\bullet -}$ (D), while the cation radical (B) can further collapse with $F^{\bullet}$ thus forming a β-fluorocarbonium ion (E). The posibility of converting cation radical (B) with another molecule of CFS to a β-fluorocarbonium ion also cannot be excluded. In this case the $SO_4^{\bullet -}$ species, resulting from this process can interact with an alkene molecule, thus forming once again cation radical (B) and $SO_4^{=}$ and so maintaining the chain reaction. The collapse of the β-fluorocarbonium ion with an alkoxy moiety from the syn or anti side finally results in vicinal fluoroalkoxy products. Markovnikov type regiospecificy and non-stereoselectivity of adduct formation speaks in favour of an open β-fluorocarbonium ion as the intermediate in the reactions of phenyl-substituted alkenes with CFS under reaction parameters reported in the present and previous papers[1,11,12], while slightly to moderate syn prevalent stereochemistry of fluoro-alkoxy addition (except in the case of six-membered ring benzocyclenes 1b) could be explained by ion pairing phenomena as the consequence of the participation of an external nuclephile in the coordination of intermediates. The process which dominates the formation of β-fluoro- carbonium ion (FT or ET-FRT) cannot be unequivocally postulated on the basis results so far, but since the removal of an electron from the C-C double bond, which in this particular situation is a definition of IP, is in linear correlation with the logaritms of the relative reaction rates (FIGURE 1), which means that this step is rate determining at least for the reaction of the studied set of substrates with CFS, the process of formation of a β-fluorocarbonium ion (E) over cation radical intermediate (B) is probable.

EXPERIMENTAL SECTION

^1H and ^{19}F NMR spectra were recorded at 60 and 56.45 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are expressed in ppm from Me_4Si or CCl_3F as internal standards. TLC was carried out on Merck PCS-Fertigplatten Silicagel F-254. CFS was prepared by a literature procedure and handled in compliance with the relevant instructions[27]. 3-Phenyl-1H-indene and 6,7-dihydro-9-phenyl-5H-benzocycloheptene were prepared by known procedures[17], while other alkenes were obtained from commercial sources and purified before use. Since the values for IP obtained from various measuring techniques and literature sources[22] differ considerably, the IP for alkenes (entry 1-7, Table 3) were measured under the same conditions using a mass spectrometric technique, applying electron impact ionisation, and the values obtained from analysis of the ionisation efficiency curves[28]. The purity of all new compounds was verified by combustion elemental analysis.

Fluorination of Phenyl-Substituted Benzocyclenes with CFS. Isolation and Separation of Products. General Procedure.

To a solution of 2 mmols of alkene 1a-c in 4 ml of freshly distilled and dry alcohol (MeOH, EtOH or I-PrOH) 2.8 to 3.6 mmols of CFS were added (in the case of MeOH, CFS was added in several portions in order to avoid to vigorous reaction) and the reaction suspension stirred at room (MeOH) to slightly elevated (45°C, i-PrOH) temperature from 1 to 4 hours and then diluted with 60 ml of CH_2Cl_2. The insoluble residue was filtered off, the filtrate washed with 40 ml of water, dried over anhydrous Na_2SO_4, and the solvent evaporated under reduced pressure. The crude reaction

mixtures were then analysed by ^1H and ^{19}F NMR spectroscopy, and the amounts and the relative ratio of the fluorinated products formed were determined from ^{19}F NMR spectra using octafluoronaphthalene as internal standard and the yield calculated on the basis of the starting alkene (Table 1). The diastereoisomers in a particular pair were separated using preparative TLC (SiO_2, petrol ether/$CHCl_3$ 1:1). In all cases *the syn* adduct had lower a TLC retention factor (0.5) than the *anti* one (0.7). The structures of the products were determined on the basis of the spectroscopic data and in critical cases also by X-ray difraction analysis. In order to obtain satisfactory purity of the products, verified by combustion analysis, we additionally purified them by column chromatography (SiO_2, n-pentane/CH_2Cl_2 2:1) and finally by distillation under reduced pressure or crystallisation from MeOH. The yields listed below refer to satisfactorily pure compouds.

(±)-1-Ethoxy-r-1-phenyl-t-2-fluoroindane (4a): 28%, m_p 66.3-67.7°C (found: C 79.64, H 6.88; calcd. for $C_{17}H_{17}OF$: C 79.65, H 6.70); NMR: δ_H 1.2 (t, J 7 Hz, 3H), δ_H 2.8-3.5 (m, 4H), δ_H 4.9 (ddd, J 52, 7, 7 Hz, 1H), δ_H 7.0-7.6 (m, 9H), δ_F -200.7 (ddd, J 52, 13, 7.5 Hz); MS: m/z: 256(M^+, 70%), 227(28), 212(29), 211(100), 207(33), 179(39), 178(33), 165(20), 151(23), 133(25), 105(17), 77(28).

(±)-1-Ethoxy-r-1-phenyl-c-2-fluoroindane (5a): 19%, m_p 113.7-114.3°C (found: C 79.34, H 6.68); NMR: δ_H 1.1 (t, J 7 Hz, 3H), δ_H 2.6-4.2 (m, 4H), δ_H 5.0 (dd, J 51, 4 Hz, 1H), δ_H 7.0-7.7 (m, 9H), δ_F -184.3 (ddd, J 51, 34, 23 Hz); MS: m/z: 256(M^+, 70%), 227(19), 212(21), 211(100), 209(17), 192(16), 191(24), 179(35), 178(26), 165(13), 151(18), 133(19), 105(16), 77(19).

(±)-r-1-Phenyl-1-i-propoxy-t-2-fluoroindane (6a): 23%, m_p 70.5-72.5°C (found: C 80.16, H 7.44; calcd. for $C_{18}H_{19}OF$: C 79.96, H 7.10); NMR: δ_H 0.7 (d, J 6 Hz, 3H), δ_H 1.2 (d, J 6 Hz, 3H), δ_H 2.9-3.9 (m, 3H), δ_H 4.8 (ddd, J 52, 7, 7 Hz, 1H), δ_H 7.1-7.7 (m, 9H), δ_F -200.5 (ddd, J 52, 12, 7 Hz); MS: m/z: 270(M^+, 85%), 228(15), 227(18), 211(100), 210(70), 209(52), 208(76), 207(56), 191(25), 179(26), 178(28), 165(19), 151(20), 133(29), 119(28), 117(29), 105(2), 91(34), 77(33), 64(32).

(±)-r-1-Phenyl-1-i-propoxy-c-2-fluoroindane (7a): 18%, m_p 56.4-56.8°C; NMR: δ_H 0.5 (d, J 6 Hz, 3H), δ_H 1.1 (d, J 6 Hz, 3H), δ_H 2.6-4.0 (m, 3H), δ_H 4.9 (dd, J 52, 4 Hz, 1H), δ_H 7.0-7.8 (m, 9H), δ_F -185.5 (ddd, J 52, 40, 22 Hz); MS: m/z calcd. for. $C_{18}H_{19}OF$: 270.1420, found m/z: 270.1420; m/z: 270(M^+, 45%), 228(15), 227(15), 211(63), 210(100), 209(74), 208(43), 207(44), 191(15), 133(25), 77(33).

(±)-r-1-Phenyl-1-methoxy-t-2-fluoro-1,2,3,4-tetrahydronaphthalene (2b): 16%, oily product (found: C 79.22, H 7.23; calcd. for $C_{17}H_{17}OF$: C 79.65, H 6.70); NMR: δ_H 1.2-3.1 (m, 4H), δ_H 3.2 (d, J 2 Hz, 3H), δ_H 4.8 (ddd, J 49, 7.5, 3 Hz, 1H), δ_H 6.9-7.5 (m, 9H), δ_F -192.8 (ddd, J 49, 23.5, 7.5 Hz); MS: m/z: 256(M^+, 31%), 225(21), 224(43), 210(43), 209(54), 195(19), 179(100), 178(36), 165(22), 148(30), 147(15), 119(33), 115(22), 109(25), 105(26), 91(40), 77(32).

(±)-r-1-Phenyl-1-methoxy-c-2-fluoro-1,2,3,4-tetrahydronaphthalene (3b): 26%, oily product (found: C 79.62, H 6.93); NMR: δ_H 1.8-3.1 (m, 4H), δ_H 3.1 (s, 3H), δ_H 4.8 (ddd, J 49, 7, 4 Hz, 1H), δ_H 7.0-7.6 (m, 9H), δ_F -194.7 (ddd, J 49, 29, 9 Hz); MS: m/z: 256(M^+, 37%), 225(26), 224(47), 210(51), 209(64), 195(24), 179(100), 178(48), 165(24), 119(13), 117(15), 109(10), 91(14), 77(14).

(±)-1-Ethoxy-r-1-phenyl-t-2-fluoro-1,2,3,4-tetrahydronaphthalene (4b): 19%, m_p 56.1-56.5°C (found: C 79.93, H 7.16; calcd. for $C_{18}H_{19}OF$: C 79.96, H 7.10); NMR: δ_H 1.2 (t, J 7 Hz, 3H), δ_H 1.8-3.7 (m, 6H), δ_H 4.8 (ddd, J 50, 8, 3 Hz, 1H), δ_H 7.0-7.5 (m,9H), δ_F -193.0 (ddd, J 50, 24, 9 Hz); MS: m/z: 270(M^+, 35%), 226(30), 225(38), 224(82), 211(13), 196(19), 195(87), 180(31), 179(100), 178(28),

165(34), 148(46), 147(14), 133(21), 119(32), 117(18), 115(19), 109(25), 105(24), 91(39), 77(30).

(±)-1-Ethoxy-r-1-phenyl-c-2-fluoro-1,2,3,4-tetrahydronaphthalene (5b): 30%, m_p 69.3-71.3°C (found: C 79.40, H 6.97); NMR: δ_H 1.2 (t, J 7 Hz, 3H), δ_H 1.8-3.6 (m, 6H), δ_H 4.8 (ddd, J 50, 6.5, 3 Hz, 1H), δ_H 7.0-7.5 (m, 9H), δ_F -194.8 (ddd, J 50, 30, 9 Hz); MS: m/z: 270(M^+, 40%), 226(38), 225(44), 224(88), 223(38), 196(26), 195(95), 180(42), 179(100), 178(37), 165(42), 152(16), 147(12), 119(14), 117(17), 115(18), 109(31), 105(27), 91(39), 77(30).

(±)-r-1-Phenyl-1-i-propoxy-t-2-fluoro-1,2,3,4-tetrahydronaphthalene (6b): 11%, m_p 58.8-60.7°C (found: C 80.15, H 7.38; calcd. for $C_{19}H_{21}OF$: C 80.24, H 7.46); NMR: δ_H 0.9 (d, J 6 Hz, 3H), δ_H 1.2 (d, J 6Hz, 3H), δ_H 2.0-3.3 (m, 4H), δ_H 3.9 (sept., J 6Hz, 1H), δ_H 4.8 (ddd, J 48.5, 8.5, 3.5 Hz, 1H), δ_H 7.0-7.6 (m, 9H), δ_F -192.3 (ddd, J 48.5, 25, 8 Hz); MS: m/z: 284(M^+, 64%), 226(45), 225(49), 224(32), 196(90), 195(100), 194(29), 180(26), 179(32), 178(38), 165(47), 148(22), 147(21), 119(21), 115(29), 109(43), 105(47), 91(50), 77(43).

(±)-r-1-Phenyl-1-i-propoxy-c-2-fluoro-1,2,3,4-tetrahydronaphthalene (7b): 35%, m_p 105.6-106.0°C (found: C 80.09, H 7.32); NMR: δ_H 0.9 (d, J 6 Hz, 3H), δ_H 1.2 (d, J 6 Hz, 3H), δ_H 1.8-3.2 (m, 4H), δ_H 3.7 (sept., J 6 Hz, 1H), δ_H 4.8 (ddd, J 51, 6, 3 Hz, 1H), δ_H 6.9-7.5 (m, 9H), δ_F -192.3 (ddd, J 51, 23.5, 8.5 Hz); MS: m/z: 284(M^+, 45%), 226(18), 225(33), 224(63), 209(13), 196(74), 195(100), 180(15), 179(19), 178(20), 165(21), 147(12), 109(25), 105(17), 91(22), 77(16).

(±)-r-1-Phenyl-1-methoxy-t-2-fluorobenzocycloheptane (2c): 30%, oily product (found: C 80.03, H 7.15; calcd. for $C_{18}H_{19}OF$: C 79.96, H 7.10); NMR: δ_H 1.0-3.7 (m, 6H), δ_H 3.2 (s, 3H), δ_H 5.3 (ddd, J 46, 7, 4 Hz, 1H), δ_H 6.8-7.5 (m, 9H), δ_F -180.5 (m); MS: m/z: 270(M^+, 100%), 269(38), 239(27), 223(19), 209(22), 193(44), 179(20), 178(22), 165(17), 147(22), 115(21), 105(35), 91(22),77(15).

(±)-r-1-Phenyl-1-methoxy-c-2-fluorobenzocycloheptane (3c): 18%, oily product; NMR: δ_H 0.6-3.0 (m, 6H), δ_H 3.1 (s, 3H), δ_H 4.9 (ddd, J 48, 7, 4 Hz, 1H), δ_H 6.8-7.6 (m, 9H), δ_F -183.9 (m); MS: m/z calcd. for $C_{18}H_{19}OF$: 270.1420; m/z found: 270.1431; m/z 270(M^+, 100%), 269(40), 250(38), 239(30), 223(25), 209(34), 197(24), 193(61), 179(39), 178(42), 165(36), 147(34), 115(38), 105(55), 91(51),77(35).

(±)-1-Ethoxy-r-1-phenyl-t-2-fluorobenzocycloheptane (4c): 25%, m_p 103.4-103,9°C (found: C 79.88, H 7.35; calcd. for $C_{19}H_{21}OF$; C 80.23, H 7.46); NMR: δ_H 1.2 (t, J 6 Hz, 3H), δ_H 1.4-3.0 (m, 6H), δ_H 3.3 (q, J 6 Hz, 2H), δ_H 5.2 (ddd, J 46, 7, 4 Hz, 1H), δ_H 6.8-7.5 (m, 9H), δ_F -178.5 (m); MS: m/z: 284(M^+, 41%), 256(20), 255(11), 203(34), 194(13), 193(18), 179(25), 167(18), 165(17), 149(19), 125(21), 112(56), 111(60), 109(28), 105(31), 97(54), 95(40), 91(24), 85(59), 83(57), 81(42), 57(100).

(±)-1-Ethoxy-r-1-phenyl-c-2-fluorobenzocycloheptane (5c): 18%, m_p 97.5-99.5°C (found: C 79.78, H 7.38); NMR: δ_H 1.2 (t, J 6 Hz, 3H), δ_H 1.5-3.7 (m, 8H), δ_H 4.9 (ddd, J 47, 6.5, 4 Hz, 1H), δ_H 6.8-7.7 (m, 9H), δ_F -180.5 (m); MS: m/z: 284(M^+, 85%), 256(22), 255(22), 207(14), 194(20), 193(34), 179(25), 167(14), 165(23), 129(21), 124(19), 111(38), 109(32), 105(69), 97(54), 95(38), 91(34), 85(48), 83(54), 81(40), 77(26), 69(75), 57(100).

(±)-r-Phenyl-1-i-propoxy-t-2-fluorobenzocycloheptane (6c): 26%, m_p 99.1-99.4°C; NMR: δ_H 0.8 (d, J 6 Hz, 3H), δ_H 1.1 (d, J 6 Hz, 3H), δ_H 1.4-2.8 (m, 6H), δ_H 3.9 (sept., J 6 Hz, 1H), δ_H 5.4 (ddd, J 47, 4, 4 Hz, 1H), δ_H 6.9-8.1 (m, 9H), δ_F -191.3 (m); MS: m/z calcd. for $C_{20}H_{23}OF$: 298.1733; m/z found: 298.1743; m/z: 298(M^+, 95%), 256(56), 255(35), 236(28), 209(34), 208(56), 207(63), 195(62), 194(25), 179(22), 165(20), 133(29), 131(38), 115(17), 109(44), 105(100), 91(48), 77(33), 69(17), 57(15).

(±)-r-Phenyl-1-i-propoxy-c-2-fluorobenzocycloheptane (7c): 7%, m_p 75.5-77.1°C (found: C 80.38, H 7.35; calcd for $C_{20}H_{23}OF$: C 80.49, H 7.78); NMR: δ_H 0.9 (m, 6H), δ_H 1.4-2.9 (m, 6H), δ_H 3.9 (sept., J 6 Hz, 1H), δ_H 5.4 (dm, J 47 Hz, 1H), δ_H 6.9-8.2 (m, 9H), δ_F -175.0 (ddd, J 47, 12, 12 Hz); MS: m/z: 298(M^+, 100%), 274(37), 256(68), 236(40), 209(49), 208(66), 207(69), 195(82), 179(31), 165(30), 133(28), 131(31), 115(16), 109(32), 105(82), 91(36), 77(28), 69(24), 57(22).

Determination of relative rate factors (k_{rel}) for the reaction of phenyl-substituted alkenes with $CsSO_4F$

The relative reactivities of the alkenes (entry 1-7, TABLE 2) were determined by competitive reaction, which was carried out as follows. A total of 1 equiv. (1 mmol) of each alkene to be compared was disolved in dry and freshly distilled MeOH (2 ml), 1 mmol of CFS was added at room temperature and the reaction suspension stirred for one hour at 35°C, then diluted with 40 ml of CH_2Cl_2, the insoluble residue filtered off, and to the filtrate a known amount of OFN added. After washing the solution with water (30 ml) and drying it over Na_2SO_4, the solvent was removed under reduced pressure to a volume of 0.5 ml. The amounts of fluoro-substituted products were determined from ^{19}F NMR spectra of the crude reaction mixtures using OFN as additional standard. Applying this known competitive technique[16,19], relative reactivities expressed by relative rate factors (k_{rel}) were calculated from the equation: $k_{rel}=k_A/k_B=\log((A-X)/A)/\log((B-X)/B)$, derived from the Ingold-Shaw relation[29] where A and B are the amounts (in mmols) of starting material and X and Y the amounts of product derived from them. For optimal precision the competing alkenes were selected so that the relative reactivity of the alkenes in each pair did not differ by more than 7. The relative rate factors thus obtained, collected in Table 2, are the averages of three measurements.

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REFERENCES

1. Part 20: Zupan,M.; Metelko,M.; Stavber,S. *J.Chem.Soc. Perkin Trans. 1* **1993**, 2851.
2. a) German,L.; Zemskov,S. (eds.) *"New Fluorinating Agents in Organic Syntheses"*, Springer-Verlag, Berlin, **1989**; b) Wilkinson,J.A. *Chem.Rev.* **1992**, *92*, 505; c) Olah,G.A.; Surya Prakash,G.K.; Chambers,R.D. "Synthetic Fluorine Chemistry" Wiley, New York, **1992**.
3. a) Filler,R.; Kobayashi,Y. (eds.) "Biomedicinal Aspects of Fluorine Chemistry": Elsevier: Amsterdam, **1982**; b) Welch,J.T. *Tetrahedron* **1987**, *43*, 3123; c) Mann,J. *Chem.Soc.Rev.* **1987**, *16*, 381; d) J.T. Welch and S. Eswarakrishnan, "Fluorine in Biorganic Chemistry", John Wiley, New York, **1991**.
4. a) Purrington,S.T.; Kagen,B.S.; Patrick,T.B. *Chem. Rev.* **1986**, *86*, 997; b) Rosen,S. *Acc.Chem.Res.* **1988**, *21*, 307.
5. Zupan,M. "Xenon Halide Halogenations" in the Chemistry of Functional Groups" Supplement D: "The Chemistry of Halides, Pseudo-Halides and Azides" Part 1 and 2, eds. Patai,S.; Rappoport,Z.

Wiley: Chichester, **1983.**

6. a) Umemoto,T.; Fukami,S.; Tomizawa,G.; Harasawa,K.; Kawada,K.; Tomita,A. *J.Am.Chem.Soc.* **1990**, *112*, 8563; b) DesMarteau,D.D.; Ze-Qi Xu; Witz,M. *J.Org.Chem.* **1992**, *57*, 629; c) Differding,E.; Bersier,P.M. *Tetrahedron* **1992**, *48*, 1595, d) Banks,R.E.; Mohialdin-Khaffaf,S.N.; Lal,G.S.; Sharif,I.; Syvret,R.R. *J.Chem.Soc. Chem. Commun.* **1992**, 595; e) Lal,G.S *J.Org.Chem.* **1993**, *58*, 2791; e) Stavber,S.; Sotler,T.; Zupan,M. *Tetrahedron Lett.* **1994**, *35*, 1105.
7. Hesse,R.H. *Israel J. Chem.* **1978**, *17*, 60.
8. a) Diorazio,L.J.; Widdowson,D.A.; Clough,J.M. *Tetrahedron*, **1992**, *48*, 8073; *J.Chem.Soc. Perkin Trans 1* **1992**, 421; b) Gakh,A.A.; Romaniko,S.V.; Ugrak,B.I.; Fainzilberg,A.A. *Tetrahedron* **1991**, *47*, 7447; c) Stavber,S.; Zupan,M. *J.Org.Chem.* **1991**, *56*, 7347; *Tetrahedron* **1992**, *48*, 5875; c) Stavber,S.; Planinšek,Z.; Košir,I.; Zupan,M. *J. Fluorine Chem.* **1992**, *59*, 409; d) Stavber,S.; Planinšek,Z.; Zupan,M. *J.Org.Chem.* **1992**, *57*, 5334; e) Stavber,S.; Košir,I.; Zupan,M. *J.Chem.Soc. Chem.Commun.* **1992**, 274.
9. a) Patai,S. ed. "*The Chemistry of Functional Groups*" Supplement A "The chemistry of double-bonded functional groups" Vol. 2, Part 1; Willey, Chichester, **1989**; b) Ruasse,M.F. *Acc.Chem.Res.* **1990**, *23*, 87; c) Bethell,D. ed. "*Advances in Physical Organic Chemistry*" Vol. 28; Academic Press, London, **1993.**
10. a) Levy,J.B.; Sterling,D.M. *J.Org.Chem.* **1985**, *50*, 5615. 11.
11. Stavber,S.; Zupan,M. *Tetrahedron* **1986**, *42*, 5035.
12. a) Stavber,S.; Zupan,M. *J.Org.Chem.* **1987**, *52*, 919; b) Stavber,S.; Zupan,M. *Tetrahedron* **1990**, *46*, 3093.
13. Zefirov,N.S.; Zhdankin,V.V.; Kozmin,A.S.; Fainzilberg,A.A.; Gakh,A.A.; Ugrak,R.I.; Romaniko,S.V. *Tetrahedron* **1988**, *44*, 6505.
14. Visser,G.W.M.; Wedzinga,R.; Herscheid,J.D.M. *J. Fluorine Chem.* **1991**, *54*, 190.
15. Leban,I. Abstracts of papers of "*5th Graz-Ljubljana-Trieste Symposium on Organic Chemistry*", Brdo pri Kranju, April 1994, Slovenia. The detailed results and discussion will be published separately.
16. Pearson,R.E.; Martin,J.C. *J.Am.Chem.Soc.* **1963**, *85*, 3142.
17. Dubois,J.E.; Hegarty,A.F. *J.Chem.Soc. (B)* **1969**, 638.
18. Freeman,F. *Chem.Rev.* **1975**, *75*, 439.
19. a) Nelson,D.J.; Soundararajan,R. *Tetrahedron Lett.* **1988**, *29*, 6207; b) Nelson,D.J.; Cooper,P.J.; Soundararajan,R. *J.Am.Chem.Soc.* **1989**, *111*, 1414.
20. a) Fukuzumi,S.; Kochi,J.K. *J.Am.Chem.Soc.* **1981**, *103*, 2783; b) Kochi,J.K. *Angew. Chem.* **1988**, *100*, 1331.
21. Neter,J.; Wasserman,W.; Kutner,M.H. "*Applied Linear Statistical Models*" 2nd ed.; Irwin: Homewood, IL. **1985.**
22. Levin,R.D.; Lias,S.G. "*Ionization Potencial and Appearance Potencial Measurements, 1971-1981*" NSRDS-NBS 71; Washington; **1982.**
23. Christe,K.O. *J. Fluorine Chem.* **1984**, *25*, 269.
24. a) Visser,G.M.B.; Boele,S.; von Halteren;B.W.; Knopes,G.H.J.N.; Hercheid,J.D.; Brinkman,G.A.; Hoekstra,A. *J.Org.Chem.* **1986**, *51*, 1466; b) Stavber,S,; Planinšek,Z.; Zupan,M. *J.Org.Chem.* **1992**, *57*, 5334.
25. a) Differding,E.; Ruegg,G.M. *Tetrahedron Lett.* **1991**, *32*, 3815; b) Differding,E.; Wehrli,M. *Tetrahedron Lett.* **1991**, *32*, 3819.
26. Olsen,J.F. *J. Fluorine Chem.* **1977**, *9*, 471.
27. Appelman,E.H. *Inorg. Synthesis* **1984**, *24*, 22.
28. Bencze,L.; Marsel,J.; Popovič,A.; Lesar,A.; *Org. Mass Spectr.* **1993**, *28*, 1570.
29. Ingold,C.K.; Shaw,F.R. *J.Chem.Soc.* **1927**, *130*, 2918.

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