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CESIUM FLUOROXYSULFATE ADDITION TO ALKENES LEADING TO VICINAL FLUOROALKYLSULFATES

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Abstract - The addition of cesium fluoroxysulfate (1) to a variety of alkenes (1-hexene, styrene, E-stilbene, cyclohexene, diene 14) proceeds under mild conditions giving the previously unknown vicinal fluoro alkyl sulfates. The structures of these products were rigorously established by thorough ^{1}H, ^{19}F and ^{13}C NMR data analyses. The studied reactions exhibit low regio- and stereoselectivities with a preference for anti-Markovnikov- and syn-addition. The predominance of cis-product formation is consistent with a concerted mechanism for the addition.

Introduction

Hypohalogenites, which contain strong electron-withdrawing groups such as perchlorate and sulfonate, are of considerable interest as powerful halogenating reagents[1-3]. Electrophilic properties of halogen atoms are most pronounced in perchlorates X-$OClO_3$[1], sulfates X-OSO_2F[2], and triflates X-OSO_2CF_3[3], which are able to undergo low-temperature addition reactions with alkenes, even when double bond is inactivated by electronegative substituents. The most extensively studied reagents are those with X = Cl, Br and I. The usual products of their reactions with alkenes are vicinal halogen alkyl perchlorates[1a] or -sulfonates[2,3a]. All known fluoro derivatives of this type (X = F) are violently aggressive towards organic substrates, and their addition products could be isolated only in the reactions with perfluoroalkenes[1a].

Recently a formal analog of the hypohalogenites, cesium fluoroxysulfate (1), has attracted substantial attention as a convenient and mild ionic fluorinating reagent[5-9]. The main result of its reactions with various organic substrates, such as aromatic carbo- and heterocyclic compounds[5,6], organotin derivatives[7], β-diketones[6], alkylhalogenides[6], enolacetates, and alkenes[8,9], is electrophilic fluorination by the hypofluorite moiety in the anionic fragment F-O-SO_3^- of this reagent. The main result of its reaction with alkenes is the formation of vinyl fluorides[8] or products of fluorine addition with the participation of external

nucleophiles[9]. For instance, M. Zupan et al. have shown that reagent 1 reacts with substituted alkenes in CH_2Cl_2 at room temperature to give fluoroalkenes. The same reaction in CH_3OH gave β-methoxyalkylfluorides, and in a CH_2Cl_2/AcOH or CH_2Cl_2/HF mixture produced vicinal fluoroacetates and difluorides, respectively. These products are, according to the authors[4b,9], products of addition of electrophilic fluorine and an external nucleophile to the double bond in accordance with Markovnikov's rule. The addition of 1 in CH_3OH or CH_2Cl_2/HF to E- and Z-stilbenes, acenaphthalene, and substituted indenes proceeds nonstereoselectively, but with preferential formation of products of syn-addition[9].

From the above data it is clear that cesium fluoroxysulfate (1) as well as covalent hypochlorites possess high electrophilic reactivity towards alkenes, but the composition of their products is quite different. The main difference is that reagent 1 never gives β-fluoroalkylsulfates, the products of normal 1,2-addition. This unusual fact is in contradiction with data on addition of other hypofluorites[1a,c] and our results on binding of different nucleofugic anions[10,11] including substituted sulfonate anions[11] in Ad_E processes. These observations prompted us to make an investigation of cesium fluoroxysulfate reactions with different alkenes with the aim of preparing 1,2-addition products and examining the regio- and stereochemistry of these reactions (preliminary communication see[12]).

RESULTS

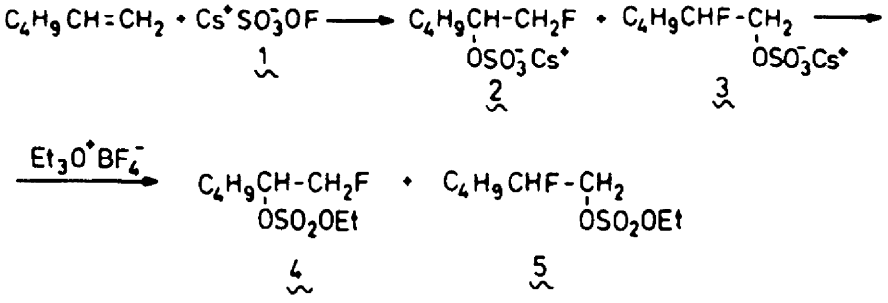
We have studied the reactions of cesium fluoroxysulfate (1) with a variety of alkenes: acyclic (1-hexene, styrene, E-stilbene), cyclic (cyclohexene), and the polycyclic (trioxolo[4.2.2.$0^{2,5}$]decane derivative 14). Reactions have been performed by the careful addition of alkene (2-4 fold excess) to a suspension of 1 in the appropriate solvent, with stirring and at ambient temperature or under mild cooling (0- -10°C). The reactions were monitored by a potassium iodide - starch indicator. The β-fluoroalkylsulfate cesium salts formed were separated by precipitation by the addition of ether and analysed by NMR. Mother liquors were not analysed in detail, but their NMR spectra indicates an insignificant quantity of fluoroalkenes in the complex mixture. Reaction conditions and yields of the β-fluoroalkylsulfate cesium salts are listed in Table 1. In some cases the structures of the cesium salts were additionally proven by the transformation into covalent ethoxysulfates by treatment with triethyloxonium tetrafluoroborate. Microanalysis data for Cs and F were obtained for all products.

Table 1. Reactions of Cesium Fluoroxysulfate with Alkenes.

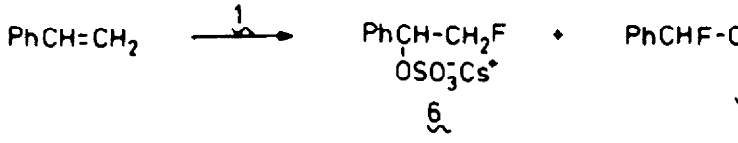
Alkene	Solvent	Temperature °C	Time h	Product (yield, %)
1-hexene	CH_2Cl_2	20	20	2(31), 3(31)
	EtOAc	20	15	2(24), 3(48)
	CH_3CN	0	2	2(11), 3(63)
styrene	CH_3CN	-10	10	6(20), 7(51)
E-stilbene	CH_3CN	0	20	8(42), 9(22)
cyclo-	CH_2Cl_2	20	20	10(20), 11(20)
hexene	EtOAc	20	15	10(30), 11(20)
	CH_3CN	0	2	10(52), 11(30)
14	EtOAc	20	40	15(27), 17(20)
	CH_3CN	20	10	15(40), 16(20)

The regiochemistry of the addition of cesium fluorosulfate to 1-hexene and styrene has been examined. The reactions of 1-hexene were performed in three different solvents: methylene chloride, ethyl acetate, and acetonitrile. In all cases a mixture of the two regioisomeric adducts 2 and 3 were obtained. The structures and yields were determined using ^1H, ^{19}F and

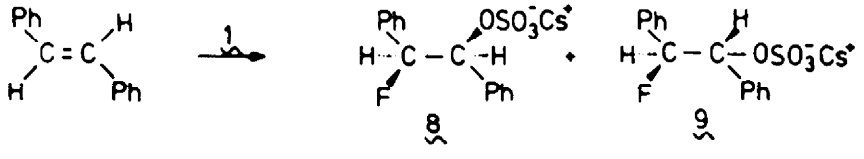
^{13}C NMR data. The ^{1}H NMR spectrum contained signals for the aliphatic protons and a complex pattern for the α-protons. In the ^{19}F NMR spectrum there appeared two separate signals with chemical shifts of -230 ppm (td, J_{F-H} = 47.0 and 20.0 Hz) and -187 ppm (m), which were attributed to fluorine atoms of the CH_2F and CHF groups, respectively. ^{13}C NMR spectra were in agreement with the proposed structures with corresponding signals for all the carbon atoms and anticipated C-F couplings. For an additional identification the salts 2 and 3 were transformed into the ethoxysulfates (4 and 5), which in addition to ^{1}H and ^{19}F NMR spectra, were identified by a mass-spectral analysis and microanalysis. The mass spectrum of isomers 4 and 5 contained a molecular peak m/e 228 and fragments corresponding to $[M - F]^+$, $[M - CH_2F]^+$, $[M - C_4H_9CHF]^+$, etc.



The reaction of reagent 1 with styrene in acetonitrile proceeded exothermally and led to a mixture of the regioisomers 6 and 7 in a ratio of 2:5 (determined from ^{1}H and ^{19}F NMR spectra). There were two different fluorine signals in the ^{19}F NMR spectrum at -226 and -180 ppm with the F-H coupling constants corresponding to CH_2F and CHF groups. The ^{1}H NMR spectrum exhibited a signal for the CHF-proton at 5.7 ppm (ddd, J = 49.0, 7.2 and 3.6 Hz) and two signals for the diastereotopic CH_2F -protons with very similar chemical shifts near 4.6 ppm with couplings of 47 and 5 Hz. The ^{13}C NMR spectrum supported these assignments, exhibiting signals for four different carbons (besides the phenyl group) with $^{1}J_{C-F}$ = 172-173 Hz and $^{2}J_{C-F}$ = 20-25 Hz.

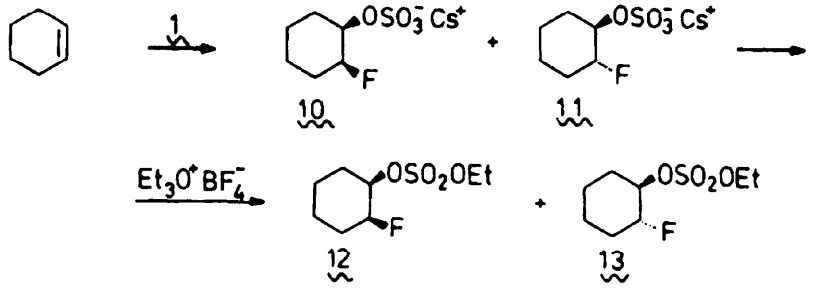


We then investigated the stereochemistry of the reactions of cesium fluoroxysulfate 1 with E-stilbene, cyclohexene, and the diene 14. E-stilbene reacted readily at 0°C giving threo-(8) and erythro-(9) isomers in a 2:1 ratio in a high yield. The structures for 8 and 9 were elucidated by NMR by comparison with spectral data for similar β-fluoroethanes[9].

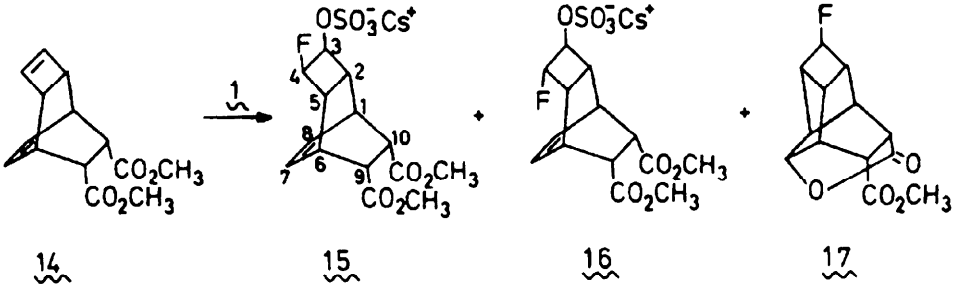


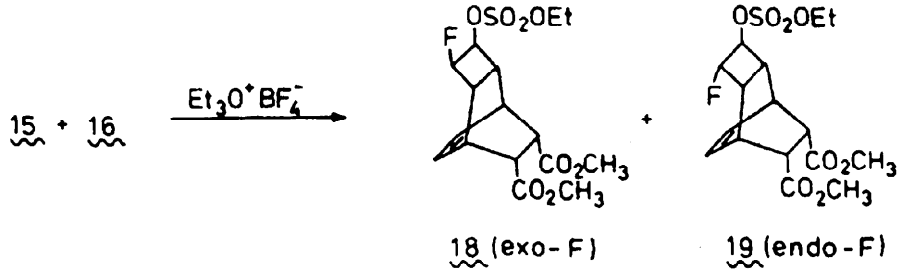
The reaction of cyclohexene was studied in three different solvents: acetonitrile, ethyl acetate, and methylene chloride. The reaction in acetonitrile required cooling to 0°C because of its vigorous nature. A mixture of the cis- and trans-isomers, 10 and 11, was obtained in all cases with the ratio of products depending on the nature of the solvent. Structures of these adducts (10,11) were elucidated from ^{1}H, ^{19}F and ^{13}C NMR spectra. The configuration of the substituents in these compounds was determined from vicinal proton couplings[13]: 5.4, 2.2, 2.2 Hz

- for the cis-adduct 10, and 8.1, 7.2, 3.9 Hz for the trans-isomer 11. The ratio of the isomers 10 and 11 was determined by ^{19}F NMR spectroscopy, where a broad signal appeared at δ -180 ppm for the cis-adduct and a narrow signal at -198 ppm appeared for the trans-adduct, which were in accordance with previously published data on β-fluorocyclohexanes[14]. An additional identification of these products (10 and 11) was performed by their transformation into the ethoxysulfates 12 and 13. In the chemical ionization mass spectrum of the sulfate esters (12,13) there appeared a molecular ion with m/e 227 $[M+H]^+$, corresponding to cluster-ions $[M+39]^+$ and $[M+56]^+$, and fragments $[M+H - HF]^+$, and $[M+H - HOSO_2OEt]^+$.



The caged alkene 14 reacted with cesium fluoroxysulfate in acetonitrile to give the products 15 and 16 in which the cyclobutene double bond was functionalized. The same reaction in ethyl acetate led to a complex mixture where the cis-isomer 15 was identified. In this case the fluorolactone 17 (yield 20%) was also isolated from the mother liquor and identified by its NMR and mass spectra. Adducts 15 and 16 were transformed into the ethoxysulfates 18 and 19, and their structures were confirmed by ^1H, ^{19}F and ^{13}C NMR analyses. In the ^1H NMR spectrum of the trans-isomer 18 the HCF hydrogen atom had coupling constants 52.0, 9.0, 4.1 and 1.5 Hz, and the HCO proton - 16.0, 4.3, 4.3 and 2.0 Hz. Coupling constants for the HCF hydrogen in the cis-isomer 19 were 52.0, 5.9 and 2.6 Hz. The configurational assignment in the four-membered ring was based on values for the vicinal H-H coupling constants as previously reported[15]. The exo-configuration of fluorine was confirmed by the presence of a coupling constant of 9.0 Hz with the proton at C-2. Additional proof of this configuration was based on a positive Overhauser effect with the olefinic protons.





DISCUSSION

The main results of the present investigation are the following: (i) the reactions of cesium fluoroxysulfate 1 with alkenes give 1,2-addition products, which implies that 1 is not only a fluorinating agent, but also an oxygenating reagent; (ii) the addition to unsymmetric alkenes gives products in which the major product has fluorine located at the most substituted carbon; (iii) in contrast with published results[9] we have never isolated products of nucleophilic binding of external nucleophiles, even in nucleophilic solvents such as acetonitrile; (iv) the main stereochemical result of these particular reactions is a predominance of syn-addition.

These data enable us to make some conclusions about the mechanism for addition of cesium fluoroxysulfate to a double bond. First of all, data from the literature and our results permit us to exclude from consideration a free radical mechanism. Our data could be rationalized in terms of two other alternative mechanisms, one being heterolytic, the second involving a concerted molecular process.

It has been proposed in the majority of previous papers[4-9] (but see [5a]) that in cesium fluoroxysulfate the fluorine atom is the electrophilic center. In general our results are in accordance with this point of view since all of the reaction products contained fluorine. Moreover, compound 17 doesn't contain the sulfate moiety, and its lactone structure with an exo-fluorine in the cyclobutane fragment is in accordance with numerous literature data on electrophilic additions to diene 14[10a,15,16]. The important argument for the electrophilic fluorine atom in reagent 1 is Zupan's data[9] on the Markovnikov type regioselectivity and the incorporation of external nucleophiles in its reactions with indene.

In contrast to this data[9], however, our results show another regioselectivity. The preferential formation of compounds 3 and 7, in which the oxygen atom is linked to the less substituted carbon atom, lead to the conclusion that, in agreement with Markovnikov's rule, the electrophilic center in cesium fluoroxysulfate is not the fluorine atom, but the hypofluorite oxygen. This suggestion is supported by the structure of compound 16, the significant feature of which is the exo-configuration of the sulfate group in the cyclobutane moiety. It is well known that exo-attack is the main direction of electrophilic approach to the cyclobutenic double bond in 14[10a,15,16]. Although the possibility of electrophilic attack by oxygen atom of reagent 1 was previously proposed[5a], our experimental results are the first which confirm this hypothesis. However, the suggested heterolytic mechanism does not clarify all of our results. First of all, none of studied reactions gave products of participation by external nucleophiles, such as solvent (acetonitrile) or specially added anions of strong acids (lithium perchlorate or tetrabutylammonium tosylate). Furthermore, in the reactions of E-stilbene, cyclohexene, and diene 14 the main products are compounds 8, 10 and 15 with cis- configuration of the addends. All of this indicates that the addition does not include intermediate formation of carbocations or "onium" ions. The high yield of syn-adducts may be explained by suggesting a concerted molecular mechanism for this reaction. This suggestion does not contradict with literature data on the mechanism of addition of another hypofluorites[1a,c]. Although our results throw some light upon cesium fluoroxysulfate reactivity, we are not able to explain yet all of these data in the limits of a single mechanism.

In conclusion we should emphasize the synthetic importance of the reported reactions. We have found a convenient method for the one-step introduction of both fluorine and sulfate moieties. This reaction opens a broader synthetic outlook because the sulfate moiety can be easily substituted with other groups. Although the first products of these reactions are salt-like sulfates, they can be conveniently transformed into covalent ethoxysulfates by treatment with triethyloxonium tetrafluoroborate.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were recorded in the pulse Fourier transform mode on a Bruker WM-250 spectrometer (250.13 and 235.34 MHz respectively) with Me_4Si or CCl_3F as an internal reference. Upfield shifts in ^{19}F are indicated as negative. Errors in chemical shifts: in ^1H NMR

spectra - ±0.003, ^{13}C NMR - ±0.01, ^{19}F NMR - ±0.03 ppm; and in coupling constants: 0.1 Hz (^{1}H), 0.3 Hz (^{19}F) and 0.4 Hz (^{13}C NMR). All NMR spectra of cesium salts were obtained in DMSO-d_6 and ethoxysulfates in $CDCl_3$ solutions.

Mass spectra were obtained on a Varian MAT 44S and MAT CH-6 (electron impact, 75 eV; chemical ionization: isobutane plasma).

All the materials used in this work were commercially available. Cesium fluoroxysulfate[17] and 9,10-dimethoxycarbonyltricyclo[4.2.2.$0^{2,5}$] deca-3,7-diene 1a[16a] were prepared by known procedures.

Caution: Working with cesium fluoroxysulfate can be dangerous. Avoid sharp strikes and heating. A protective shield always should be used.

Reactions of cesium fluoroxysulfate (1) with alkenes (general procedure).

An alkene (4-8 mmol) solution in 1 mL of the appropriate solvent was added slowly to a stirred mixture of cesium fluoroxysulfate (0.5 g, 2 mmol) in the same solvent (5 mL) at -10 - +20°C (for reaction conditions see Table 1). The reaction mixture was stirred at room temperature until reagent 1 completely disappeared (according to the KI-starch indicator). Then dry ether (5 mL) was added and the resulting white solid was filtered, washed with ether, and dried under vacuum.

1-Fluoro-2-hexylsulfate-(2) and 2-fluoro-1-hexylsulfate-(3) cesium salts. Yield 62-74%. Found: F, 5.56; Cs, 40.41. $C_6H_{12}O_4CsFS$ requires F, 5.72; Cs, 40.02. For 2: ^{1}H NMR: δ4.42 (m, 2H, CH_2F), 4.65 (m, 1H, $CHOSO_3Cs$), 1.9-1.3 (m, 6H, $3CH_2$), 0.9 (t, 3H, $^{3}J_{H-H}$ = 7.0 Hz, CH_3). ^{19}F NMR: δ-230.24 (td, $^{2}J_{F-H}$ = 47.0 Hz, $^{3}J_{F-H}$ = 20.0 Hz, FCH_2). ^{13}C NMR: δ84.26 (td, $^{1}J_{C-H}$ = 152.6 Hz, $^{1}J_{C-F}$ = 167.8 Hz, C^1), 78.41 (dd, $^{1}J_{C-H}$ = 153.1 Hz, $^{2}J_{C-F}$ = 19.8 Hz, C^2), 30.19 (td, $^{1}J_{C-H}$ = 130.0 Hz, $^{3}J_{C-F}$ = 4.8 Hz, C^3), 26.91 (t, $^{1}J_{C-H}$ = 128.0 Hz, C^4), 22.21 (t, $^{1}J_{C-H}$ = 125.2 Hz, C^5), 14.02 (q, $^{1}J_{C-H}$ = 123.9 Hz, C^6). For 3: ^{1}H NMR: δ4.72 (m, 1H, CHF), 3.95 (m, 2H, CH_2OSO_3Cs), 1.9-1.3 (m, 6H, $3CH_2$), 0.9 (t, 3H, $^{3}J_{H-H}$ = 7.0 Hz, CH_3). ^{19}F NMR: δ-187.61 (dm, $^{2}J_{F-H}$ = 49.0 Hz, CHF). ^{13}C NMR: δ92.18 (dd, $^{1}J_{C-H}$ = 152.1 Hz, $^{1}J_{C-F}$ = 169.3 Hz, C^2), 67.68 (dd, $^{1}J_{C-H}$ = 144.1 Hz, $^{2}J_{C-F}$ = 22.1 Hz, C^1), 30.58 (td, $^{1}J_{C-H}$ = 123.0 Hz, $^{2}J_{C-F}$ = 20.4 Hz, C^3), 26.62 (td, $^{1}J_{C-H}$ = 130.2 Hz, $^{3}J_{C-F}$ = 4.5 Hz, C^4), 22.04 (t, $^{1}J_{C-H}$ = 125.6 Hz, C^5), 13.94 (q, $^{1}J_{C-H}$ = 124.0, C^6).

2-Fluoro-1-phenyl-1-ethylsulfate-(6) and 1-fluoro-2-phenyl-2-ethylsulfate-(7) cesium salts. Yield 71%. Found: F, 5.03; Cs, 37.21. $C_8H_8O_4CsFS$ requires F, 5.39; Cs, 37.74.

For 6: ^{1}H NMR: δ7.6-7.2 (m, 5H, C_6H_5), 5.26 (dt, 1H, $^{3}J_{H-F}$ = 20.8 Hz, $^{3}J_{H-H}$ = 4.5 Hz, $CHOSO_3Cs$), 4.62 (ddd, $1H_A$, $^{2}J_{H-F}$ = 47.0 Hz, $^{2}J_{H-F}$ = 10.0 Hz, $^{3}J_{H-H}$ = 4.5 Hz, CH_AH_BF), 4.59 (dddm $1H_B$, $^{2}J_{H-F}$ = 47.0 Hz, $^{2}J_{H-H}$ = 10.0 Hz, $^{3}J_{H-H}$ = 4.5 Hz, CH_AH_BF). ^{19}F NMR: δ-225.72 (td, $^{2}J_{F-H}$ = 47.0 Hz, $^{3}J_{F-H}$ = 20.8 Hz, CH_2F). ^{13}C NMR: δ138.32 (d, $^{3}J_{C-F}$ = 4.0 Hz, C_{ipso}), 129.0-125.5 (m, $5C_{Ar}$), 84.67 (tdd, $^{1}J_{C-H}$ = 153.9 Hz, CH_2F), 75.38 (dd, $^{1}J_{C-H}$ = 144.0 Hz, $^{2}J_{C-F}$ = 20.2 Hz, $CHOSO_3Cs$).

For 7: ^{1}H NMR: δ7.6-7.2 (m, 5H, C_6H_5), 5.72 (ddd, 1H, $^{2}J_{H-F}$ = 49.3 Hz, $^{3}J_{H-H}$ = 7.2 Hz, $^{3}J_{H-H}$ = 3.5 Hz, CHF), 4.02 (ddd, $1H_A$, $^{2}J_{H-H}$ = 11.9 Hz, $^{3}J_{H-F}$ = 20.4 Hz, $^{3}J_{H-H}$ = 7.2 Hz, $CH_AH_BOSO_3Cs$), 3.92 (ddd, $1H_B$, $^{2}J_{H-H}$ = 11.9 Hz, $^{3}J_{H-F}$ = 29.4 Hz, $^{3}J_{H-H}$ = 3.5 Hz, $CH_AH_BOSO_3Cs$). ^{19}F NMR: δ-180.47 (ddd, $^{2}J_{F-H}$ = 49.3 Hz, $^{3}J_{F-H}$ = 29.4, $^{3}J_{F-H}$ = 20.4). ^{13}C NMR: δ136.81 (d, $^{2}J_{C-F}$ = 18.0 Hz, C_{ipso}), 129.0-125.5 (m, $5C_{Ar}$), 92.07 (ddt, $^{1}J_{C-H}$ = 156.2 Hz, $^{1}J_{C-F}$ = 171.9 Hz, $^{2}J_{C-H}$ = 3.5 Hz, CHF), 68.77 (tdd, $^{1}J_{C-H}$ = 146.0, $^{2}J_{C-F}$ = 24.8 Hz, $^{2}J_{C-H}$ = 3.8 Hz, CH_2O).

Threo-(8) and erythro-(9) 1,2-diphenyl-1-fluoro-2-ethylsulfate cesium salts. Yield 64%. Found: F, 4.24; Cs, 31.58. $C_{14}H_{10}O_4CsFS$ requires F, 4.45; Cs, 31.18. For 8: ^{1}H NMR: δ 7.6-7.2 (m, 10H, C_6H_5), 5.77 (dd, 1H, $^{2}J_{H-F}$ = 45.5 Hz, $^{3}J_{H-H}$ = 6.0 Hz, HCF), 5.43 (dd, 1H, $^{3}J_{H-H}$ = 6.0 Hz, $^{3}J_{H-F}$ = 12.3 Hz, $HCOSO_3Cs$). ^{19}F NMR: δ-180.38 (dd, $^{2}J_{F-H}$ =

45.5 Hz, $^3J_{F-H}$ = 12.3 Hz, FCH). ^{13}C NMR: δ138.0-125.7 (m, C_6H_5), 93.85 (dd, $^1J_{C-F}$ = 176.6 Hz, CHF), 78.43 (dd, $^2J_{C-F}$ = 26.7 Hz, $CHOSO_3Cs$).

For 9: ^1H NMR: δ7.6-7.2 (m, 10H, C_6H_5), 6.01 (dd, 1H, $^1J_{H-F}$ = 47.2 Hz, $^3J_{H-H}$ = 3.0 Hz, HCF), 5.29 (dd, 1H, $^3J_{H-F}$ = 24.3 Hz, $^3J_{H-H}$ = 3.0 Hz, $HCOSO_3Cs$). ^{19}F NMR: δ -192.45 (dd, $^2J_{F-H}$ = 47.2 Hz, $^3J_{F-H}$ = 24.3 Hz, FCH). ^{13}C NMR: δ138.0-125.7 (m, C_6H_5), 94.55 (dd, $^1J_{C-F}$ = 178.8 Hz, CHF), 80.07 (dd, $^2J_{C-F}$ = 22.3 Hz, $CHOSO_3Cs$).

Cis-(10) and trans-(11)-2-fluoro-1-cyclohexylsulfate cesium salts. Yield 82%. Found: F, 5.32; Cs, 40.76. $C_6H_{10}O_4CsFS$ requires F, 5.76; Cs, 40.26. For 10: ^1H NMR: δ4.95 (dddd, 1H, $^2J_{H-F}$ = 51.0 Hz, J_{H-H} = 5.4, 2.4 and 2.4 Hz, CHF), 4.18 (m, 1H, CHO), 2.5-1.0 (m, 8H). ^{19}F NMR: δ -197.5 (br.s).

For 11: ^1H NMR: δ4.45 (dddd, 1H, $^2J_{H-F}$ = 48.0 Hz, J_{H-H} = 8.1, 7.2 and 3.8 Hz, CHF), 4.25 (m, 1H, CHO). ^{19}F NMR: δ-179.8 (dm, $^2J_{F-H}$ = 48.0 Hz).

Cis-(15) and trans-(16)-(4-fluoro-9,10-cis-endo-dimethoxycarbonyltricyclo[4.2.2.$0^{2,5}$]-dec-7-en-3-yl-sulfate cesium salts. Yield 60%. Found: F, 3.76; Cs, 27.15. $C_{14}H_{16}O_8CsFS$ requires F, 3.83; Cs, 26.78. For 15: ^{19}F NMR: δ-192.24 (ddd, $^2J_{F-H}$ = 53.8, $^3J_{F-H}$ = 11.6, $^3J_{F-H}$ = 27.7 Hz, FCH).

For 16: ^{19}F NMR: δ-188.53 (ddd, $^2J_{F-H}$ = 53.4 Hz, $^3J_{F-H}$ = 11.2 Hz, $^3J_{F-H}$ = 18.0 Hz, FCH).

Reactions of 2-fluoroalkylsulfate cesium salts with triethyloxonium tetrafluoroborate (general procedure)

Triethyloxonium tetrafluoroborate (0.32 g, 2 mmol) was added to a stirred mixture of the corresponding cesium salt (1 mmol) in 1 mL ethylacetate at 20°C. The reaction mixture was stirred at room temperature for 4 hours, then 3 mL hexane was added and the mixture was filtered through a thin layer of silica gel, which was then washed with 20 mL ethylacetate-hexane 1:1 mixture. Additional purification can be performed by column chromatography on silica gel.

1-Fluoro-2-hexyl(ethyl)- (4) and 2-fluoro-1-hexyl(ethyl)- (5) sulfates. Yield 90%. Found: F, 8.58; S, 13.62. $C_8H_{17}O_4FS$ requires F, 8.32; S, 14.04. Mass-spectrum (m/e): 228 (M^+), 209 (M^+ - F), 195 (M^+ - CH_2F), 139 ($CH_2OSO_2OC_2H_5$).

For 4: ^1H NMR: δ4.60 (m, 1H, CHO), 4.46 (m, 2H, CH_2F), 4.35 (q, 2H, $^3J_{H-H}$ = 7.0 Hz, CH_2O, 2.09 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH_3), 1.9-1.3 (m, 6H, $3CH_2$), 0.90 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH_3). ^{19}F NMR: δ-229.67 (td, $^2J_{F-H}$ = 48.0 Hz, $^3J_{F-H}$ = 20.0 Hz).

For 5: ^1H NMR: δ4.69 (m, 1H, CHF), 4.25 (m, 4H, $2CH_2O$), 2.08 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH_3), 1.9-1.3 (m, 6H, $3CH_2$), 0.9 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH_3). ^{19}F NMR: δ -187.31 (dm, $^2J_{F-H}$ = 49.0 Hz).

Cis-(12) and trans-(13) 2-fluoro-1-cyclohexyl(ethyl) sulfates. Yield 85%. Found: F, 8.02; S, 13.86. $C_8H_{15}O_4FS$ requires F, 8.40; S, 14.17. Mass-spectrum (chemical ionization, m/e); 227 (M^+ + H), 207 (M^+ + H - HF), 101 (M^+ + H - $HOSO_2OC_2H_5$).

For 12: ^1H NMR: δ 4.85 (dddd, 1H, $^2J_{H-F}$ = 51.0 Hz, J_{H-H} = 5.7, 2.2 and 2.2 Hz, CHF), 4.70 (m, 1H, CHO), 4.39 (q, 2H, OCH_2), 2.5-1.3 (m, 11H). ^{19}F NMR: δ-194.27 (br.s, CHF).

For 13: ^1H NMR: δ4.65 (dddd, 1H, $^2J_{H-F}$ = 49.0 Hz, J_{H-H} = 8.1, 7.2 and 3.9 Hz, CHF), 4.48 (m, 1H, CHO), 4.38 (q, 2H, OCH_2), 2.5-1.3 (m, 11H). ^{19}F NMR: δ-180.7 (dm, $^2J_{F-H}$ = 49.0 Hz, CHF).

Cis-(18) and trans-(19)-3-(4-fluoro-9,10-cis-endo-dimethoxycarbonyltricyclo[4.2.2.$0^{2,5}$]-dec-7-ene)(ethyl) sulfates. Yield 91%. Found: F, 4.96; S, 7.88. $C_{16}H_{21}O_8FS$ requires F, 4.84; S, 8.17.

For 18: ^1H NMR: δ6.48 (m, 2H, $H^{7,8}$), 4.55 (ddd, 1H, $^2J_{H-F}$ = 53.0 Hz, J_{H-H} = 6.0 and 3.0 Hz, H^4), 4.45 (m, 1H, H^3), 4.40 (q, 2H, OCH_2), 3.60 (s, 6H, OCH_3), 3.5-1.3 (m, 9H). ^{19}F NMR: δ-194.24 (ddd, $^2J_{F-H}$ = 53.0 Hz, $^3J_{F-H}$ = 27.7 and 11.6 Hz). ^{13}C NMR: δ 172.28 (s, COO), 133.25 (d, $C^{7(8)}$), 133.05 (d, $C^{8(7)}$), 87.80 (dd, $^1J_{C-F}$ = 218 Hz, C^4), 76.05 (dd, $^2J_{C-F}$ = 16.4 Hz, C^3), 70.45 (t, OCH_2), 51.88 (q, CH_3O), 45.55 (d, $C^{1(6)}$),

45.30 (d, $C^{6(1)}$), 44.11 (dd, $^2J_{C-F}$ = 23.7 Hz, C^5), 34.21 (d, C^9C^{10}), 33.82 (dd, $^3J_{C-F}$ = 4.8 Hz, C^2), 14.61 (q, CH_3).

For 19: ^{1}H NMR: 66.48 (m, 2H, $H^{7,8}$), 5.04 (dddd, 1H, $^2J_{H-F}$ = 52.0 Hz, J_{H-H} = 9.0, 4.5 and 1.8 Hz, H^4), 4.75 (dtd, 1H, $^3J_{H-F}$ = 16.0 Hz, J_{H-H} = 4.5 and 1.5 Hz, H^3), 4.40 (q, 2H, OCH_2), 3.5-1.3 (m, 9H). ^{19}F NMR: 6-191.10 (ddd, $^2J_{F-H}$ = 52.0 Hz, $^3J_{F-H}$ = 18.0 and 11.0 Hz). ^{13}C NMR: 6172.28 (s, COO), 133.85 (d, C^7), 131.53 (d, C^8), 90.11 (dd, $^1J_{C-F}$ = 226.0 Hz, C^4), 82.82 (dd, $^2J_{C-F}$ = 25.3 Hz, C^3), 70.23 (t, CH_2O), 51.88 (q, CH_3O), 45.55 (d, $C^{1(6)}$), 45.30 (d, $C^{6(1)}$), 39.65 (dd, $^2J_{C-F}$ = 22.0 Hz, C^5), 34.21 (d, C^9,C^{10}), 32.65 (dd, $^3J_{C-F}$ = 3.8 Hz, C^2), 14.61 (q, CH_3).

6-Endo-hydroxy-4-methoxycarbonyl-9-exo-fluoro-tetracyclo[6.1.1.$0^{2,7}0^{5,10}$]deca-3-carboxylic acid lactone (17). Yield 20%. Found: F, 7.59. $C_{13}H_{13}O_4F$ requires F, 7.53. Mass-spectrum (chemical ionization, m/e): 253 (M^+ + H). ^{1}H NMR: 6 4.82 (d, 1H, $^1J_{H-F}$ = 62.6 Hz, CHF), 4.80 (ddt, 1H, J = 7.0, 2.5 and 0.8 Hz, CHO), 3.70 (s, 3H, CH_3O), 3.6-2.0 (m, 8H). ^{19}F NMR: 6-207.33 (dt, $^2J_{F-H}$ = 62.6 Hz, $^3J_{F-H}$ = 4.6 Hz).

References

1. (a) C.J. Sohack, D. Pilipovich, J. Fon, Inorg. Chem., 12, 897 (1973). (b) C.J. Sohack, D. Pilipovich, K.O. Christe, Inorg. Chem., 14, 145 (1975). (c) R.S. Porter, G.H. Cady, J. Am. Chem. Soc., 79, 5626 (1957). J.A.C. Allison, G.H. Cady, J. Am. Chem. Soc., 81, 1089 (1959).
2. N.S. Zefirov, A.S. Koz'min, V.D. Sorokin, V.V. Zhdankin, Z. Org. Khim., 22, 898 (1986). N.S. Zefirov, A.S. Koz'min, V.D. Sorokin, J. Org. Chem., 49, 4086 (1984). A.V. Fokin, Yu.N. Studnev, L.D. Kuznetsova, I.N. Krotovitch, Chem. Rev. USSR, 51, 1258 (1982). A.V. Fokin, Yu.N. Studnev, L.D. Kuznetsova, Izv. AN SSSR, ser. khim., 1839 (1982). A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, J. Fluor. Chem., 18, 553 (1981). D.D. DesMarteau, Inorg. Chem., 7, 434 (1968). A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, L.D. Kuznetsova, Izv. AN SSSR, ser. khim., 1892 (1974). F. Aubke, G.H. Kady, Inorg. Chem., 4, 269 (1965). F. Aubke, P.J. Gillespie, Inorg. Chem., 7, 599 (1968).
3. (a) Y. Katsuhara, D.D. DesMarteau, J. Org. Chem., 45, 2441 (1980). (b) Y. Katsuhara, D.D. DesMarteau, J. Am. Chem. Soc., 102, 2681 (1980). Y. Katsuhara, D.D. DesMarteau, J. Fluor. Chem., 16, 257 (1980).
4. For recent reviews see: (a) S.T. Purrington, B.S. Kagen, Chem. Rev., 86, 997 (1986). (b) M. Zupan, Vestn. Slov. Kem. Drus., Suppl., 31, 151 (1984).
5. (a) E.H. Appelman, L.J. Basile, R. Hayatsu, Tetrahedron, 40, 189 (1984). (b) D.P. Ip, C.D. Arthur, R.F. Winans, E.H. Appelman, J. Am. Chem. Soc., 103, 1964 (1981). S. Stavber, M. Zupan, J. Org. Chem., 50, 3609 (1985). S. Stavber, M. Zupan, J. Chem. Soc., Chem. Comm., 148 (1981).
6. S. Stavber, M. Zupan, J. Chem. Soc., Chem. Comm., 563 (1983).
7. M.F. Bryce, R.D. Chambers, S.T. Mullins, A. Parkin, J. Chem. Soc., Chem. Comm., 1623 (1986).
8. S. Stavber, M. Zupan, J. Chem. Soc., Chem. Comm., 795 (1981).
9. S. Stavber, M. Supan, J. Org. Chem., 919 (1987).
10. (a) N.S. Zefirov, A.S. Koz'min, V.N. Kirin, V.V. Zhdankin, R. Caple, J. Org. Chem., 46, 5264 (1981). N.S. Zefirov, A.S. Koz'min, V.V. Zhdankin, Tetrahedron, 38, 291 (1982). (b) N.S. Zefirov, A.S. Koz'min, V.V. Zhdankin, V.N. Kirin, G.B. Sergeev, Z. Org. Khim., 16, 1085 (1980). N.S. Zefirov, A.S. Koz'min, V.V. Zhdankin, A.V. Nikulin, N.V. Zyk, J. Org. Chem., 47, 3679 (1982).
11. N.S. Zefirov, A.S. Koz'min, Yu.V. Dan'kov, V.V. Zhdankin, V.N. Kirin, Z. Org. Chem., 18, 1993 (1982). N.S. Zefirov, A.S. Koz'min, V.D. Sorokin, V.V. Zhdankin, Z. Org. Khim., 18, 1768 1982). N.S. Zefirov, A.S. Koz'min, Yu.V. Dan'kov, V.V. Zhdankin, V.N. Kirin, Z. Org. Khim., 20, 233 (1984). N.S. Zefirov, A.S. Koz'min, V.D. Sorokin, V.V. Zhdankin, Yu.N. Studnev, A.V. Fokin, Izv. AN SSSR, ser. khim., 389 (1985).
12. N.S. Zefirov, V.V. Zhdankin, A.A. Gakh, B.I. Ugrak, S.V. Romaniko, A.S. Koz'min, A.A. Fainzilberg, Izv. AN SSSR, ser. khim., 2636 (1987).

13. N.S. Zefirov, V.V. Samoshin, O.A. Subbotin, I.V. Baranenkov, S. Wolf, Tetrahedron, 34, 2953 (1978).

14. J. Levisalles, M. Rudler-Charivin, J. Martin, Bull. Soc. Chim. France, 167 (1980).

15. N.S. Zefirov, A.S. Kos'min, V.N. Kirin, V.V. Zhdankin, O.V. Lagodzinskaya, K.A. Potekhin, E.N. Kurkutova, Zhur. J. Chim., 4, 475 (1980).

16. (a) G. Mehta, P.N. Pandey, J. Org. Chem., 40, 3631 (1975). (b) A. Kondo, T. Yamane, T. Ashida, T. Sasaki, K. Kanematsu, J. Org. Chem., 43, 1180 (1978). T. Sasaki, K. Kanematsu, A. Kondo, Y. Nishitani, J. Org. Chem., 39, 3569 (1974). T. Sasaki, K. Kanematsu, A. Kondo, J. Chem. Soc., Perkin Trans., 1, 2516 (1976).

17. E.H. Appelman, L.J. Basile, R.C. Thompson, J. Am. Chem. Soc., 101, 3384 (1979).