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REGIOSELECTIVE FORMATION OF FLUOROHYDRINS AND THEIR STEREOSELECTIVE CONVERSION TO FLUOROOLEFINS

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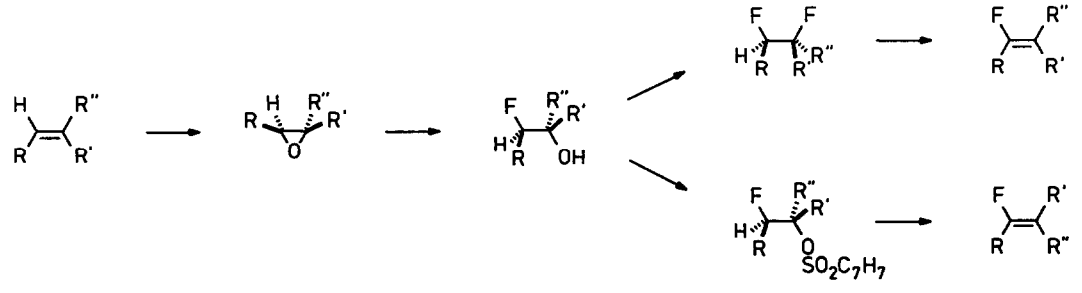
Summary : When treated with potassium *tert*-butoxide in tetrahydrofuran, *p*-toluenesulfonates derived from fluorohydrins afford fluoroolefins (*e.g.*, *Z*- or *E*-3) with high yields. Fluorohydrins are readily and stereoselectively accessible by *anti*-periplanar addition of hydrogen fluoride to oxiranes. Terminal epoxides give preferentially 2-fluoro-1-alkanols (*e.g.*, 4) if an hydrogen fluoride/pyridine mixture is used in toluene medium while mainly 1-fluoro-2-alkanols (*e.g.*, 5) result from the reaction with "Hünig's hydrofluoride" (*i.e.*, the adduct of hydrogen fluoride an *N*-ethyldiisopropylamine). With 2-hydroxymethyl substituted oxiranes, predominantly if not exclusively, 3-fluoro-1,2-alkanediols (*e.g.*, 11) are obtained.

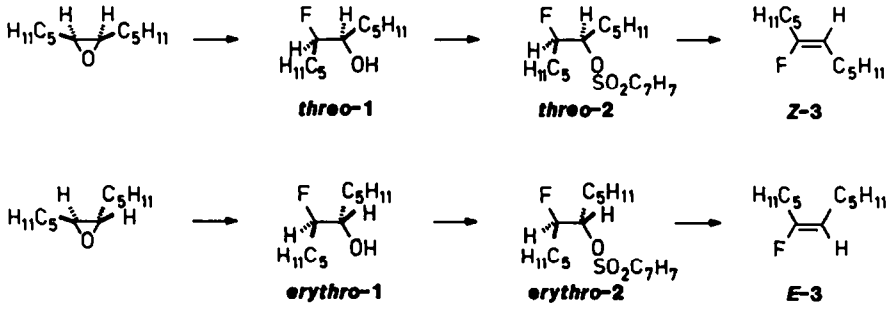
Recently we have disclosed a general access to fluoroolefins by base promoted 1,2-elimination of hydrogen fluoride from *vic*-difluoroalkanes [1]. The latter are readily prepared from alkenes by consecutive epoxydation, opening of the oxiranes to fluorohydrines and, finally, substitution of the hydroxy group by fluorine [2]. The last step, however, requires long reaction times and gives only moderate yields (typically 50 - 60%), even under optimized conditions.



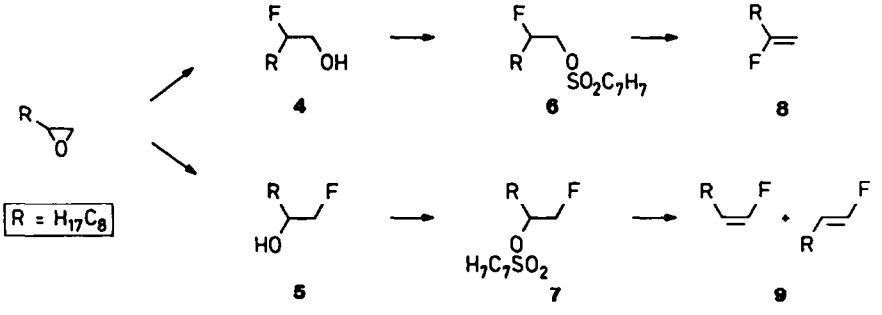
If the fluorohydrines were converted to β-fluoroalkyl *p*-toluenesulfonates rather than to *vic*-difluoroalkanes, three major advantages should immediately result from this modification : the *p*-toluenesulfonates could be formed rapidly and almost quantitatively, the isolation of such intermediates would no longer be necessary and the ultimate sulfonate elimination would occur smoothly, under much milder conditions than any dehydrofluo-

rination. On the other hand, the envisaged modification should affect the stereochemical outcome. Since the new reaction sequence involves only two, rather than three, configurational inversions, (*Z*)-fluoroalkenes should be produced where previously the (*E*)-isomers were obtained and *vice versa*.

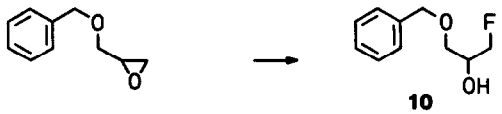
These expectations proved to be entirely correct. Both *cis*- and *trans*-6,7-epoxydodecane gave the *threo*- and *erythro*-fluorohydrins **1** and the corresponding *p*-toluenesulfonates **2** with high yields. The sulfonate elimination was brought about with potassium *tert*-butoxide already at 25 °C and afforded (*Z*)- or (*E*)-6-fluoro-6-dodecene (**3**) (87% and 83%, respectively).



Next, we wanted to apply the method to typical terminal epoxides. All efforts [3] to achieve a regioselective addition of hydrogen fluoride to such substrates have met only unsatisfactory success so far. Therefore, we started a systematic investigation of all variable parameters and finally were able to identify conditions for the formation of either 2-fluoro-1-alkanols or 1-fluoro-2-alkanols, both with quite acceptable selectivities. When 1,2-epoxydecane was treated with poly(hydrogen fluoride)/pyridine in toluene, an almost quantitative yield of 2-fluoro-1-decanol (**4**) of 92% regioisomeric purity was obtained. Conversely, 1-fluoro-2-decanol (**5**) of 90% regioisomeric purity was isolated as the main product after heating the oxirane with a 1 : 1 adduct of hydrogen fluoride and *N*-ethyldiisopropylamine ("Hünig's base") to 150 °C. Reaction of the corresponding tosylates **6** and **7** with potassium *tert*-butoxide gave 2-fluoro-1-decene (**8**) and 1-fluoro-1-decene (**9**, *cis* : *trans* = 1 : 3), respectively.



Donor functional groups appear to increase the regioselectivity of the reaction between a terminal epoxide and "Hünig's hydrofluoride", the hydrogen fluoride/*N*-ethyldiisopropylamine adduct. Thus, 2-(benzyloxymethyl)-oxirane gave 3-benzyloxy-1-fluoro-2-propanol (**10**) with 97% regioisomeric purity. So far, less than 94% were achieved as the best regioselectivity with this substrate when a hydrogen fluoride/diisopropylamine adduct [4] was employed. [5] The addition became completely regiorandom when poly(hydrogen fluoride)/pyridine in toluene was employed.



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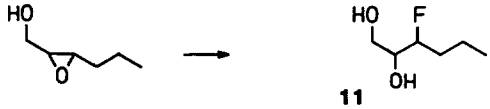
The orienting effect of free hydroxy groups was found to be particularly powerful. When treated with "Hünig's hydrofluoride", *trans*-2,3-epoxy-1-hexanol afforded 3-fluoro-1,2-hexandiol (**11**) exclusively.



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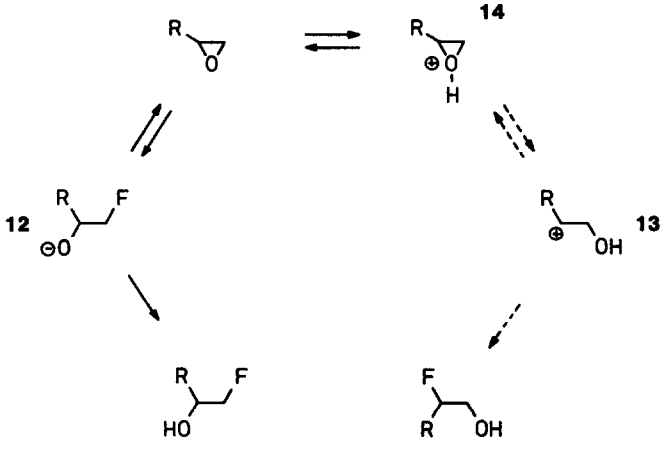
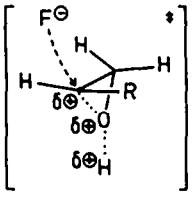
We now wish to consider a few mechanistic hypotheses in an attempt to rationalize how the regiochemical outcome of the hydrogen fluoride addition to oxiranes depends on the medium and the reagents. As a crude estimate on the basis of homolytic bond dissociation energies $D°$ (C-C : 85, C-F : 110 kcal/mol) [6], ring tension (oxirane : 25 kcal/mol) [7] and electron affinities (RO : 40, F: 80 kcal/mol) [6] reveals, addition of "naked" fluoride to an epoxide should be a slightly exothermal process. Solution or complexation of the halide ion would shift the equilibrium in favor of the dissociated components. Nevertheless, the 1-fluoro-2-alkanolate **12** would remain thermodynamically accessible as long as the fluoride is not trapped by protic solvents nor strongly binding counterions such as lithium. In other words, the conversion of terminal epoxides to 1-fluoro-2-alkanols may well pass through anions **12** which either reversibly decompose to the components or, competitively, are stabilized by protonation.



In contrast, the formation of 2-fluoro-1-alkanols under relatively acidic conditions can hardly be explained by the intermediacy of secondary (hydroxymethyl)carbenium ions **13**. An active participation of such cations can be ruled out on the basis of experimental evidence. As already mentioned, *cis*- and *trans*-6,7-epoxydodecanes are converted by hydrogen fluoride in toluene to the *threo*- and *erythro*-fluorohydrines **1** without any stereochemical contamination. Furthermore, a thermochemical comparison between these carbocations (*e.g.*, propanol : -61 [8]; hydride abstraction at 2-position : ΔH°_f estim. +256 [9]; dihydrogen formation from $H^{\oplus}$ and $H^{\ominus}$: ΔH°_f -400 kcal/mol [10]) and the isomeric protonated oxiranes **14** (2-methyloxirane : -23 [8]; heat of protonation : ΔH°_f estim. -198 [11]) shows the latter to be 10 or even 15 kcal/mol more stable.

Nucleophilic attack of fluoride at a protonated oxirane **14** should, however, produce a mixture of regioisomeric fluorohydrines. Hence, the observed selectivity can be understood only if a new transient species is taken into account. This might be a hybrid between the open cation **13** and the protonated oxirane **14**, a bridged 2-hydroxycarbenium ion **15** carrying a substantial fraction of positive charge at both, the oxygen and a carbon center. Since the addition of hydrogen fluoride to oxiranes is an *anti*-periplanar process, such a bimolecular reaction would imply, however, extensive charge separation at the transition state. Therefore, we prefer rather to postulate a "conveyer belt mechanism", as previously established [12] for elimination reactions in solvents of low polarity, now also for an addition reaction. At the transition state **16** a trimeric chain of hydrogen fluoride molecules spans from the oxygen atom to the rear of the carbon atom which undergoes substitution. This picture is in agreement with the generally accepted view [13] that hydrogen fluoride maintains its oligomeric structure even in the presence of pyridine.



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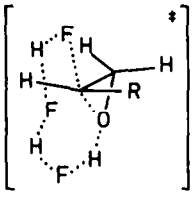

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EXPERIMENTAL PART

1. General remarks

Starting materials have been purchased from Fluka AG (Buchs), Aldrich-Chemie (Steinheim), or Merck-Schuchardt (Darmstadt), unless literature sources or details for the preparation are given. All commercial reagents were used without further purification.

Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure nitrogen.

Anhydrous diethyl ether and *tetrahydrofuran* were obtained by distillation as soon as the characteristic blue color of in situ generated sodium diphenylketyl [14] was found to persist. *Hexane* and *toluene* were dried by careful azeotropic distillation.

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75 °C, "room temperature" (22 - 26 °C) as 25 °C. If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg). *Melting ranges* (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as -75 °C.

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by calibration factors. The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were chosen as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). All packed columns were made of glass, while quartz was chosen as the material for coated, GROB-type capillary columns (≥ 10 m long). A stationary phase of the silicon rubber type (OV-1701) was most frequently used.

Infrared spectra were recorded of films if the sample was liquid at room temperature, while solid substances were embedded in potassium bromide pellets. The intensities of absorption bands are abbreviated : s (strong), m (moderate) and w (weak).

In general, *nuclear magnetic resonance spectra* of hydrogen-1 nuclei were recorded at 360 MHz and of fluorine-19 nuclei at 188 MHz. ^{1}H-NMR spectra marked with an asterisk, however, were taken at 250 MHz. Chemical shifts refer to the signal of tetramethylsilane (δ = 0 ppm), which served as an internal standard in the case of ^{1}H and ^{13}C spectra, and of α,α,α-trifluorotoluene for ^{19}F spectra. Coupling constants (J) are measured in Hz. Coupling patterns are described by abbreviations : s (singulet), d (doublet), t (triplet), q (quadruplet), pent (pentuplet), *hex* (hexuplet), td (triplet of a doublet) and *m* (multiplet).

In general, *mass spectra* were obtained at a 70 eV ionisation potential. M^+ means the peak of the intact molecule in form of its radical-cation.

2. Hydrogen Fluoride/Amine Mixtures

Adducts of anhydrous hydrogen fluoride and pyridine (~ 9 : 1), collidine (~ 3 : 2) and triethylamine (~ 3 : 1) are commercially available. Alternatively, they can be readily prepared according to literature procedures [4, 16 - 18], for example by distilling gaseous hydrogen fluoride (Merck, Fluka) into an ethereal solution of the amine.

***N*-Ethyldiisopropylamine tris(hydrofluoride) ["Hünig's hydrofluoride"]** : Using polyethylene equipment and under strict exclusion of moisture, liquid hydrogen fluoride (0.16 L, 0.12 kg, 6.0 mol) was syphoned into anhydrous diethyl ether (0.30 L) cooled to 0 °C. *N*-Ethyldiisopropylamine (0.34 L, 0.26 kg, 2.0 mol), dried beforehand by storage over molecular sieves (4 Å pore width), was slowly added to the well stirred solution. Of the two layers formed, the lighter ether containing phase was decanted and the remainder distilled under reduced pressure; 0.32 kg, bp 93 - 95 °C/4 mmHg.

3. Fluorohydrines

The *threo*- and the *erythro*-diastereoisomer of **6-fluoro-5-dodecanol** (*threo*- and *erythro*-**1**) were prepared from *cis*- and, respectively, *trans*-5,6-epoxydodecane using triethylamine tris(hydrofluoride), as described [1]. With the hydrogen fluoride/pyridine complex (5.0 mmol) in toluene (20 mL) the reaction was fast already at -20 °C. After 2 h, 50% of 99% pure *cis* oxirane had been consumed to give *threo*-**1**, while the other half of the starting material was recovered in form of a *cis/trans* mixture (84 : 16). With the *trans* epoxide the reaction went only to 40% completion after 2 h; besides *erythro*-**1** configurationally unchanged starting material (approximately 60%) was recovered.

2-Fluoro-1-decanol (4) : A solution of 1,2-epoxydecane (9.3 mL, 7.8 g, 50 mmol) and hydrogen fluoride/pyridine adduct (4.4 mL, 5.0 g, 50 mmol) in toluene (10 mL) was stirred 2 h at 0 °C. The mixture was absorbed on silica gel (10 g). After evaporation of the volatile components the dry powder was poured on top of a chromatography column filled with a hexane slurry of fresh silica gel (50 g). Elution with a 8 : 1 (v/v) hexane/ethyl acetate mixture and distillation gave a colorless liquid which was composed of **4** and its regioisomer **5** (see below) in the ratio of 92 : 8 (50 m OV-1701, 125 °C; 3 m 5% SE-30, 130 °C); 7.2 g (82%); mp 30 - 32 °C (after crystallization from pentane); bp 76 - 78 °C/5 mmHg. - ^{1}H-NMR ($CDCl_3$) : 5.58 (1 H, ddddd, *J* 50.3, 7.2, 6.2, 4.5, 3.8), 3.7 (2 H, m), 2.31 (1 H, t, *J* ~ 5), 1.7 (2 H, m), 1.6 (2 H, m), 1.28 (10 H, m, s-like), 0.88 (3 H, t, *J* 6.9). - Analysis : calc. for $C_{10}H_{21}FO$ (176.28) C 68.14, H 12.01; found C 67.94, H 12.01%.

1-Fluoro-2-decanol (5) : A mixture of 1,2-epoxydecane (18.6 mL, 15.6 g, 100 mmol), *N*-ethyldiisopropylamine tris(hydrofluoride) (18.9 g, 100 mmol) and *N*-ethyldiisopropylamine (34.7 mL, 25.9 g, 200 mmol) was heated 5 h at 150 °C. After dilution with diethyl ether (100 mL), the organic layer was washed with 10% hydrochloric acid (2 x 25 mL), saturated aqueous solution (50 mL) and brine (50 mL). After drying and evaporation of the solvent, the residue was distilled under reduced pressure; 14.1 g (80%) of **4** and **5** in the ratio of 10 : 90 (by gas chromatography : 50 m OV-1701, 125 °C); bp 73 - 78 °C/5 mmHg. - Pure **5** was obtained by treating a solution of this product mixture in dichloromethane (50 mL) 5 h at -40 °C with pivaloyl chloride (2.5 mL, 2.4 g, 20 mmol) and pyridine (1.6 mL, 1.6 g, 20 mmol). Extraction and distillation afforded **5** as a colorless liquid; 11.1 g (63%); mp -11 to -10 °C; bp 72 - 73 °C/5 mmHg; n_D^{20} 1.4258. - ^{1}H-NMR ($CDCl_3$) : 4.45 (1 H, ddd, *J* 47.5, 9.6, 3.0), 4.29 (1 H, ddd, *J* 48.0, 9.6, 6.9), 3.9 (1 H, m), 2.2 (1 H, s, broad), 1.47 (2 H, m, s-like), 1.3 (12 H, m), 0.89 (3 H, t, *J* 7.0). - Analysis : calc. for $C_{10}H_{21}FO$ (176.28) C 68.14, H 12.01; found C 67.94, H 12.01%.

2-Fluoro-1- and **1-fluoro-2-octanol** were prepared in strictly the same manner.

3-Benzyloxy-1-fluoro-2-propanol (10) : A mixture of 2-(benzyloxymethyl)oxirane [19] (3.3 g, 20 mmol), *N*-ethyldiisopropylamine tris(hydrofluoride) (3.8 g, 20 mmol) and *N*-ethyldiisopropylamine (6.8 mL, 5.2 g, 40 mmol) was heated 3 h to 150 °C. After washing, column chromatography and distillation, 3.2 g (87%) of **10** were isolated; bp 171 - 174 °C/5 mmHg; n_D^{20} 1.5042. According to gas chromatography (50 m OV-1701, 175 °C) ≤ 3% of 3-benzyloxy-2-fluoro-1-propanol (see below) were present. - ^{1}H-NMR ($CDCl_3$) : 7.3 (5 H, m), 4.55 (2 H, s), 4.45 (1 H, 333, *J* 47.6, 9.6, 4.4), 4.43 (1 H, ddd, *J* 47.3, 9.6, 5.3), 4.02 (1 H, dtt, *J* 18.5, ~ 5.5, ~ 4.5), 3.55 (2 H, symm. m, like 2 x ddd), 2.62 (1 H, s). - Analysis : calc. for $C_{10}H_{13}FO_2$ (184.21) C 65.20, H 7.11; found C 65.14, H 7.22%.

3-Benzyloxy-2-fluoro-1-propanol : Reaction between 2-(benzyloxymethyl)oxirane [19] and the hydrogen fluoride/pyridine adduct in toluene, as described for 2-fluoro-1-decanol (**4**, see above), produced a 55 : 45 mixture of **10** and 3-benzyloxy-2-fluoro-1-propanol. The spectral data of the latter component were listed after deduction of the signals attributed to the regioisomer **10**. - ^{1}H-NMR ($CDCl_3$) : 7.3 (5 H, m), 4.71 (1 H, dpent, *J* 48.5, 4.6), 4.53 (2 H, s), 3.80 (2 H, dd, *J* 23.5, 4.5), 3.69 (2 H, dd, *J* 22.0, 4.8), 2.52 (1 H, s).

erythro-**3-Fluoro-1,2-hexandiol (11)** : A mixture of *trans*-2,3-epoxy-1-hexanol [20] (2.3 g, 20 mmol), *N*-ethyldiisopropylamine tris(hydrofluoride) (3.8 g, 20 mmol) and diisopropylamine (6.8 mL, 5.2 g, 40 mmol) were heated 5 h to 150 °C. Diethyl ether (50 mL) was added and the solution was washed with 10% hydrochloric acid (20 mL), a saturated aqueous solution (20 mL) of sodium hydrogen carbonate and brine (20 mL). After drying and evaporation of the solvent 2.0 g (75%) of **11** were obtained as a colorless crystalline mass; mp 23 - 25 °C. - ^{1}H-NMR ($CDCl_3$) : 4.46 (1 H, dm, J_{HF} 48.5), 3.7 (3 H, m), 3.46 (2 H, s), 1.5 (4 H, m), 0.96 (3 H, t, *J* 6.9).

The crude product was converted to *erythro*-**(1-fluoropropyl)ethylidene diacetate** (79%) by treatment with excess acetic anhydride in the presence of catalytic amounts of 4-dimethylaminopyridine. ^{1}H-NMR ($CDCl_3$) : 5.10 (1 H, symm. m), 4.59 (1 H, d of symm. m, J_{HF} 48.0), 4.44 (1 H, ddd, *J* 12.3, 3.0, 1.3), 4.14 (1 H, ddd, *J* 12.3, 6.7, 1.3), 2.11 (3 H, s), 2.07 (3 H, s), 1.6 (4 H, m), 0.96 (3 H, t, *J* 6.9).

4. α-Fluoroalkyl *p*-Toluenesulfonates

General working procedure : The fluorohydrine (50 mmol) was added to a solution of *p*-toluenesulfonyl chloride (10.5 g, 55 mmol) in pyridine (50 mL). After 12 h at 25 °C, the mixture was diluted with diethyl ether (100 mL) and extracted with 10% hydrochloric acid (2 × 25 mL). The organic layer was evaporated and eluted from silica gel (200 g) with a 8 : 1 (v/v) mixture of hexane and ethyl acetate. - Alternatively, tosylates were prepared by consecutive treatment of the fluorohydrine with potassium hydride and catalytic amounts of 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6") in tetrahydrofuran at -25 °C (until the hydrogen evolution had ceased) and then with *p*-toluenesulfonyl chloride.

threo-**1-(1-Fluorohexyl)hexyl *p*-toluenesulfonate** (*threo*-**2**) : 93%. - ^{1}H-NMR (C_6D_6) : 7.81 (2 H, d, *J* 8.5), 7.33 (2 H, d, *J* 8.5), 2.59 (1 H, symm. m), 4.47 (1 H, dddd, *J* 47.2, 8.5, 3.9, 3.0), 2.45 (3 H, s), 1.6 (4 H, m), 1.3 (12 H, m), 0.88 (3 H, t, *J* 7.1), 0.85 (3 H, t, *J* 7.1).

erythro-**1-(1-Fluorohexyl)hexyl *p*-toluenesulfonate** (*erythro*-**2**) : 86%. - ^{1}H-NMR (C_6D_6) : 7.81 (2 H, d, *J* 8.4), 7.35 (2 H, d, *J* 8.4), 4.60 (1 H, symm. m), 4.53 (1 H, ddt, *J* ~ 48, 9.0, 3.0), 2.46 (3 H, s), 1.6 (4 H, m), 1.3 (12 H, m), 0.89 (3 H, t, *J* 7.1), 0.85 (3 H, t, J 7.1).

1-(Fluoromethyl)nonyl *p*-toluenesulfonate (**7**) : 91%; n_D^{20} 1.4874. - ^{1}H-NMR ($CDCl_3$) : 7.86 (2 H, d, *J* 8.4), 7.39 (2 H, d, *J* 8.4), 4.70 (1 H, d of symm. m, J_{HF} ~ 20), 4.46 (2 H, d of symm. m, like dddd, J_{HF}47.3), 2.51 (3 H, s), 1.7 (2 H, m), 1.3 (12 H, m), 0.93 (3 H, t, *J* 7.1).

5. Fluoroolefins

General working procedure : Potassium *tert*-butoxide (5.6 g, 50 mmol) and α-fluoroalkyl *p*-toluenesulfonate (25 mmol) were dissolved in tetrahydrofuran (50 mL) and kept 6 h at 25 °C. Then, the mixture was poured into hexane (150 mL) and, after addition of some diatomite ("Celite", kieselguhr), centrifuged. The fluoroolefin was isolated by distillation of the supernatant liquid.

(*Z*)-**6-Fluoro-6-dodecene** [1] (*Z*-**3**) : 87%; n_D^{20} 1.4263. - ^{1}H-NMR (C_6D_6) : 4.45 (1 H, dt, *J* 38.0, 7.5), 2.11 (2 H, dt, *J* 17.5, 7.5), 2.04 (2 H, q, *J* 7.6), 1.45 (2 H, pent-like m, *J* ~ 7), 1.3 (10 H, m), 0.92 (3 H, t, *J* 7.2), 0.90 (3 H, t, *J* 7.2). - By mistake, previously [1] a coupling constant of J_{HF} 48.5 was reported with respect to the δ 4.45 signal.

(*E*)-**6-Fluoro-6-dodecene** [1] (*E*-**3**) : 94%; n_D^{20} 1.4248. - ^{1}H-NMR : ref. [1].

2-Fluoro-1-decene (**8**) : 83%; mp -74 to -72 °C; bp 86 - 88 °C/21 mmHg; n_D^{20} 1.4142. - ^{1}H-NMR ($CDCl_3$) : 4.48 (1 H, dd, *J* 17.5, 2.7), 4.19 (1 H, dd, *J* 50.5, 2.7), 2.17 (2 H, pent, *J* 7.8), 1.51 (2 H, pent, broad, *J* 7.5), 1.3 (10 H, m, narrow), 0.89 (3 H, t, *J* 6.9). - MS : 109 (8%), 96 (35%), 82 (43%), 70 (59%), 56 (100%). - Analysis : calc. for $C_{10}H_{19}F$ (158.26) C 75.89, H 12.10; found C 75.79, H 12.03%.

1-Fluoro-1-decene (**9**, *cis/trans* = 1 : 3) : 83%; mp -73 to -67 °C; bp 96 - 97 °C/38 mmHg; n_D^{20} 1.4159. The nmr spectra were recorded of the stereoisomeric mixture, but the peak assignment was straightforward. - *cis*-**9** : 6.44 (1 H, ddt, *J* 86.2, 4.8, 1.5), 4.73 (1 H, dtd, *J* 43.8, 7.7, 4.9), 2.12 (2 H, qt, *J* 6.8, 1.5), 1.3 (12 H, m), 0.88 (3 H, t, *J* 6.8). - *trans*-**9** : 6.49 (1 H, ddt, *J* 86.5, 11.0, 1.5), 5.35 (1 H, dtd, *J* 19.2, 11.2, 7.7), 1.90 (2 H, qt, *J* 6.7, 1.6), 1.3 (12 H, m), 0.88 (3 H, t, *J* 6.8). - Analysis : calc. for $C_{10}H_{19}F$ (158.26) C 75.89, H 12.10; found C 76.14, H 12.04%.

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