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α-Fluorocarbonyl Compounds by Isomerization of 2-Fluorooxiranes

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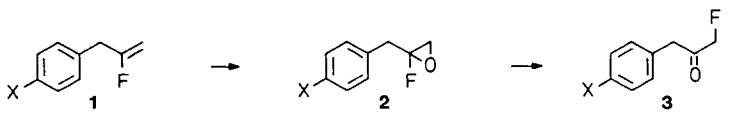
Abstract: 2-Fluorooxiranes **2** can be isolated after peracid oxidation of fluoroalkenes **1**. When treated with the triethylamine hydrogen fluoride adduct, the intermediates **2** isomerize to afford α-fluorinated carbonyl compounds **3**.

As reported in a preceding article [1], a 1-fluoro-4-arylbutan-2-one has been prepared from the corresponding 2-fluoro-2-(2-arylethyl)oxirane in high yield by simple treatment with triethylamine-tris(hydrofluoride). A few related reactions can be found in literature. Hexafluoroacetone is virtually quantitatively obtained when 1,2-epoxyperfluoropropene is carried by a nitrogen stream over fluorine and oxygen doped alumina heated to 180 °C [2]. However, in the presence of good nucleophiles and at moderate temperatures, the same starting material gives products which have formally originated from pentafluoropropanoyl fluoride [3]. Most remarkably, Elkik *et al.* [4] have observed the thermal or boron trifluoride promoted decomposition of 2-fluorooxiranes leading to α-fluorocarbonyl compounds. Unfortunately, neither yields nor product compositions nor reaction conditions were mentioned. Therefore, we wanted to explore the scope and possible limitations of the isomerization reaction by applying it to a number of representative examples.

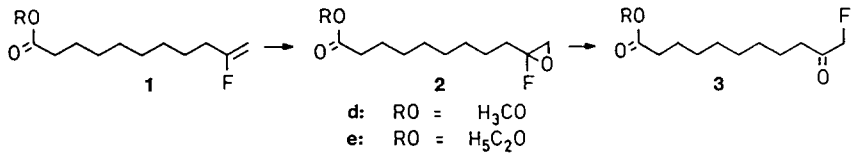
The first set of substrates was obtained by epoxidation of 2-fluoroallylbenzene **1a** and its *para*-substituted derivatives **1b** and **1c**. In the presence of triethylamine-tris(hydrofluoride) at 125 °C, the oxiranes **2a** - **2c** underwent smooth isomerization to give the 3-aryl-1-fluoroalkan-2-ones **3a** (65%), **3b** (48%) and **3c** (65%).



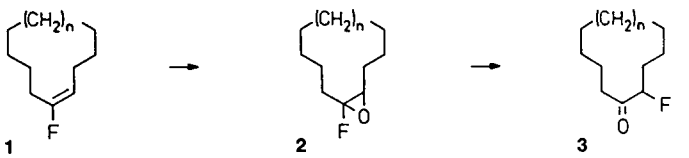
a: X = H
b: X = H_3CO
c: X = H_3CCOO

The tolerance of ester functions by the reagent was confirmed in another series of experiments. When methyl and ethyl 10-fluoroundec-10-enoate (**1d** and **1e**) were consecutively submitted to the action of *meta*-

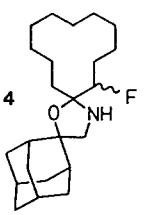
chloroperbenzoic acid and hydrogen fluoride, the corresponding fluorooxiranes (**2d** and **2e**) and fluoroketones (**3d**, 43%, and **3e**, 80%) were readily formed.



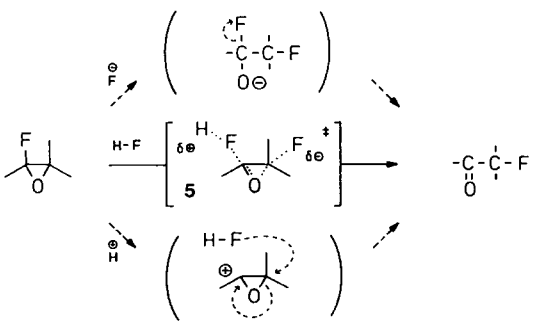
Finally, our study was extented to cyclic substrates. We have been able to convert 1-fluorocyclododec-1-ene (**1f**) and 1-fluorocyclopentadec-1-ene (**1g**), both (*Z*/*E*) mixtures, into the epoxides (**2f** and **2g**) and the latter into 2-fluorocyclododecanone (**3f**, 69%) and, respectively, 2-fluorocyclopentadecanone (**3g**, 61%) without encountering any problems.



2-Fluorocyclododecanone (**3f**) was condensed with 2-(aminomethyl)adamant-2-ol to provide the spiro compound **4**. The halogen-free analogue [5] is known for its antiinflammatory properties.



No mechanistically oriented investigations have been carried out. Nevertheless we consider anionic or cationic intermediates to be less probable. Under conditions as employed by us, a concerted *push-pull* reaction (transition state **5**) involving simultaneous attack of a proton and a fluoride ion appears to offer the most plausible explanation of the results.



α-Fluorinated aldehydes and ketones [6] are accessible in many ways, in particular by oxidation of β-fluoroalkanols [7], treatment of diazoketones with hydrogen fluoride [8] or reaction of enolates, enethers or other enol derivatives with hypofluorides such as fluorooxytrifluoromethane [9] or acetyl hypofluorite [10]. The 2-fluorooxirane isomerization method described above is useful because of its complementarity and attractive because of its simplicity.

EXPERIMENTAL

Starting materials have been purchased from Fluka AG (Buchs), Aldrich-Chemie (Steinheim), or Merck-Schuchardt (Hohenbrunn), unless literature references or details of the preparation are given. Potassium *tert*-butoxide was supplied by Hüls (Troisdorf). All commercial reagents were used without further purification.

Tetrahydrofuran was obtained anhydrous by distillation from sodium wire after the characteristic blue color of *in situ* generated sodium diphenyl ketyl [11] was found to persist. *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.

"Room temperature" (22 - 26 °C) is consistently indicated as 25 °C. *Melting ranges* (mp) are reproducible after resolidification, unless stated otherwise ("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. If reduced pressure is not specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg).

Silica gel (Merck Kieselgel 60) of 70 - 230 mesh (0.06 - 0.20 mm) particle size was used for *column chromatography*. The solid support was suspended in hexane and, when all air bubbles had excaped, was sluiced into the column. When the level of the liquid was still some 3 - 5 cm above the silica layer, the dry powder obtained by absorption of the crude product mixture on 5 g silica gel and subsequent evaporation of the solvent was poured on top of the column.

^{1}H-NMR spectra were recorded at 250 MHz in deuterochloroform solution and ^{19}F-NMR spectra in the same solvent at 376 MHz. Chemical shifts δ refer to the signal of tetramethylsilane in the case of ^{1}H spectra and to α,α,α-trifluorotoluene in the case of ^{19}F-NMR. Coupling constants (*J*) are measured in Hz. Abbreviations of coupling patterns : s (singlet), d (doublet), t (triplet), q (quadruplet), td (triplet of doublets) and [symm.] m ([symmetrical] multiplet). High resolution nuclear magnetic resonance spectroscopy commonly produces signals showing fine structure due to long-range coupling. Except in very special cases, coupling constants smaller than 1 Hz have little informative value and hence are neglected.

Elementary analyses were made by the laboratory of I. Beetz, D-96'302 Kronach, Germany.

1. Fluoroolefins

(2-Fluoroprop-2-enyl)benzene (**1a**) [12], 1-(2-fluoroprop-2-enyl)-4-methoxybenzene (**1b**) [13] and 1-fluorocyclodedecene (**1f**) [14] (*cis/trans* = 30 - 70) were prepared according to literature procedures.

4-(2-Fluoroprop-2-enyl)phenyl acetate (1c) : 4-(2-Fluoro-3-iodopropyl)phenyl acetate (32 g, 0.10 mmol; by treating 4-allylphenyl acetate [15, 16] during 10 h with a slight excess of *N*-iodosuccinimide and triethylamine tri(hydrofluoride) in dichloromethane; purification by elution with a 1 : 10 (v/v) mixture of diethyl ether and pentane from silica gel; 65%; mp 15 - 18 °C; n_D^{20} 1.5555 [17]), 1,8-diazabicyclo[5.4.0]undec-7-ene ("DBU"; 29 mL, 30 g, 0.20 mol) and benzene (0.25 L) were heated to reflux for 24 h. When cold, the mixture was washed with 2 N hydrochloric acid (3 × 50 mL). Distillation afforded product **1c** as a colorless liquid; 58%; bp 109 - 110 °C/4 mmHg; n_D^{20} 1.5020. - ^{1}H-NMR : δ 7.2 (2 H, dm, *J* 8.5), 7.0 (2 H, dm, *J* 8.5), 4.61 (1 H, dd, *J* 16.8, 2.9), 4.3 (1 H, dm, *J* 49.2), 3.49 (2 H, d, *J* 15.5), 2.29 (3 H, s). - ^{19}F-NMR : δ -31.7 (1 F, dq, *J* 48, 16). - Analysis : calc. for $C_{11}H_{11}FO_2$ (194.20) C 68.03, H 5.71; found C 68.02, H 5.82%.

Methyl 10-fluoroundec-10-enoate (1d) : A solution of 10-fluoroundec-10-enoic acid [14] (20 g, 0.10 mol), *N,N'*-carbonyldiimidazole (13 g, 0.10 mol) in anhydrous tetrahydrofuran (0.10 L) was kept 15 min at 25 °C before methanol (10 mL, 8.0 g, 0.25 mol) and a spatula tip of potassium hydride were added. After 1 h at 25 °C, the mixture was absorbed on silica gel. The dry powder was eluted with a 1 : 10 (v/v) mixture of diethyl ether and pentane to give, after distillation, analytically pure ester **1d**; 72%, mp -38 to -37 °C; bp 93 - 95 °C/ 0.7 mmHg; n_D^{20} 1.4340. - ^{1}H-NMR : δ 4.47 (1 H, dd, *J* 17.5, 2.5), 4.19 (1 H, dd, *J* 50.5, 2.5), 3.66 (3 H, s), 2.30 (2 H, t, *J* 7.5), 2.16 (2 H, dt, *J* 16.0, 7.5), 1.4 (12 H, m). - ^{19}F-NMR : δ -31.9 (1 F, dq, *J* 51, 18). - Analysis : calc. for $C_{12}H_{21}FO_2$ (260.13) C 66.64, H 9.79; found C 66.78, H 9.80%.

Ethyl 10-fluoroundec-10-enoate (1e) was obtained analogously; 76%; mp -53 to -50 °C; bp 130 - 132 °C/12 mmHg; n_D^{20} 1.4337. - ^{1}H-NMR : δ 4.49 (1 H, dd, *J* 18.0, 2.8), 4.19 (1 H, ddt, *J* 50.8, 2.8, 1.0), 4.13 (2 H, q, *J* 7.2), 2.29 (2 H, t, *J* 7.5), 2.17 (2 H, symm. m), 1.6 (2 H, m), 1.5 (2 H, m), 1.3 (8 H, m), 1.26 (3 H, t, *J* 7.2). - ^{19}F-NMR : δ -32.0 (1 F, dq, *J* 50, 18). - Analysis : calc. for $C_{13}H_{23}FO_2$ (230.33) C 67.79, H 10.06; found C 67.81, H 9.98%.

1-Fluorocyclopentadec-1-ene (1g) : 1-Bromo-2-fluorocyclopentadecane (31 g, 0.10 mol; by treating cyclopentadecene [18] during 10 h with a slight excess of *N*-bromosuccinimide and triethylamine-tris[hydrofluoride] in dichloromethane; purification by elution with a 1 : 10 mixture of diethyl ether and pentane from silica gel; 79%; n_D^{20} 1.4968) and potassium *tert*-butoxide (22 g, 0.20 mol) were dissolved in anhydrous tetrahydrofuran (0.25 L). After 6 h the mixture was directly distilled to give the fluoroolefine **1g**; 86%; mp 21 - 22 °C; bp 103 - 106 °C/3 mmHg. - ^{1}H-NMR : δ 4.99 (0.6 × 1 H, dt, *J* 22.5, 7.9), 4.45 (0.4 × 1 H, dt, *J* 38.4, 7.3), 2.1 (4 H, m), 1.3 (22 H, m). - ^{19}F-NMR : δ -42.3 (0.6 × 1 F, q, *J* 23), -48.5 (0.4 × 1 F, dm, *J* 38). Analysis : calc. for $C_{15}H_{27}F$ (226.38) C 79.59, H 12.02; found C 79.78, H 12.12%.

2. Fluorooxiranes

2-Benzyl-2-fluorooxirane (2a) : 3-Chloroperbenzoic acid (12 g of 55% technical quality, approx. 38 mmol pure product) was extracted under stirring into chloroform (0.10 L). This solution was dried and filtred before (2-fluoroprop-2-enyl)benzene [9] (2.7 g, 20 mmol) was dissolved in it. After 24 h at 25 °C, potassium fluoride (5.8 g, 0.10 mol) was added and the suspension was vigorously stirred for 5 h. The mixture was filtered and the solvent evaporated. The residue was distilled in a Hickmann flask to afford a colorless liquid; 50%; bp 111 - 112 °C/20 mmHg; n_D^{20} 1.4949. - ^{1}H-NMR : δ 7.3 (5 H, m), 3.33 (2 H, symm. m), 3.09 (1 H, dm, *J* 4.0), 2.60 (1 H, dd, *J* 4.0, 1.1). - ^{19}F-NMR : δ -70.5 (1 F, t, *J* 13). - Analysis : calc. for C_9H_9FO (152.17) C 71.04, H 5.96; found C 71.03, H 6.14%.

The other fluorooxiranes were prepared in the same way. Most of them decompose spontaneously in the course of a few hours; in such cases it was impossible to obtain correct combustion analyses.

2-Fluoro-2-([4-methoxyphenyl]methyl)oxirane (2b) : 61% (with respect to **1b**); bp 115 - 117 °C/5 mmHg; n_D^{20} 1.5110. - ^{1}H-NMR : δ 7.19 (2 H, dm sym., *J* 8.7), 6.86 (2 H, dt, *J* 8.7, 2.5), 3.79 (3 H, s), 3.26 (2 H, symm. m), 3.07 (1 H, dm, *J* 4.0), 2.58 (1 H, dd, *J* 4.0, 1.2). - ^{19}F-NMR : δ -70.6 (1 F, t. *J* 12.5).

4-(2,3-Epoxy-2-fluoropropyl)phenyl acetate (2c) : 73 % (with respect to **1c**); mp 16 - 19 °C; bp 121 - 123 °C/4 mmHg. - ^{1}H-NMR : δ 7.3 (2 H, dm, *J* 8.5), 7.05 (2 H, dt, *J* 8.5, 2.2), 3.30 (2 H, symm. m), 3.09 (1 H, dm, *J* 4.0), 2.61 (1 H, dd, *J* 4.0, 1.1), 2.30 (3 H, s). - ^{19}F-NMR : δ -70.5 (1 F, t, *J* 13).

Methyl 10,11-epoxy-10-fluoroundecanoate (2d) : 80% (with respect to **1d**); mp 17 - 20 °C; bp 90 - 91 °C/0.5 mmHg. - ^{1}H-NMR : δ 3.67 (3 H, s), 3.08 (1 H, d, *J* 4.0), 2.67 (1 H, dd, *J* 4.0, 1.1), 2.30 (2 H, t, *J* 7.5), 1.9 (2 H, m), 1.4 (12 H, m). - ^{19}F-NMR : δ -72.0 (1 F, t, *J* 15).

Ethyl 10,11-epoxy-10-fluoroundecanoate (2e) : 89% (with respect to **1e**); bp 139 - 140 °C/3 mmHg; n_D^{20} 1.4384. - ^{1}H-NMR : δ 4.13 (2 H, q, *J* 7.1), 3.1 (1 H, m), 2.68 (1 H, dd, *J* 4.2, 1.3), 2.29 (2 H, t, *J* 7.6), 2.0 (2 H, m), 1.6 (2 H, m), 1.5 (2 H, m), 1.3 (8 H, m), 1.26 (3 H, t, *J* 7.1). - ^{19}F-NMR : δ -71.5 (1 F, t, *J* 15).

1,2-Epoxy-1-fluorocyclododecane (2f) : 78% (with respect to **1f**); mp -17 to -14 °C; bp 110 - 112 °C/5 mmHg; n_D^{20} 1.4702. - ^{1}H-NMR : δ 3.2 (0.7 × 1 H, m), 2.9 (0.3 × 1 H, m), 2.5 (0.3 × 2 H, m), 2.2 (0.7 × 2 H,

m), 1.4 (18 H, m). - ^{19}F-NMR : δ -66.8 (0.7 × 1 F, symm. m), -79.7 (0.3 × 1 F, symm. m). - Analysis : calc. for $C_{12}H_{21}FO$ (200.30) C 71 96, H 10.57; found C 71.56, H 10.82%.

1,2-Epoxy-1-fluorocyclopentadecane (2g) : 84% (with respect to **1g**); mp 42 - 43 °C; bp 132 - 133 °C/1 mmHg. - ^{1}H-NMR : δ 3.21 (0.6 × 1 H, ddd, *J* 8.1, 5.0, 1.0), 2.89 (0.4 × 1 H, ddd, *J* 8.9, 3.6, 1.6), 2.2 (2 H, m), 1.3 (24 H, m). - ^{19}F-NMR : δ -65.5 (0.6 × 1 F, m), -81.0 (0.4 × 1 F, m). - Analysis : calc. for $C_{15}H_{27}FO$ (242.38) C 74.33, H 11.23; found C 74.10, H 10.98%.

3. α-Fluoroketones

1-Fluoro-3-phenylpropan-2-one [19] **(3a)** : A mixture of the fluorooxirane **2a** (1.5 g, 10 mmol) and triethylamine tri(hydrofluoride) (0.32 mL, 0.32 g, 2.0 mmol) was heated for 2 h to 125 °C. The product was isolated by chromatography using silica gel as the support and a 1 : 10 (v/v) mixture of diethyl ether and pentane as the eluent; 65%; bp 62 - 63 °C/1 mmHg; n_D^{20} 1.5148. - ^{1}H-NMR : δ 7.3 (5 H, m), 4.86 (2 H, d, *J* 47.3), 3.84 (2 H, d, *J* 3.4). - ^{19}F-NMR : δ -164.4 (1 F, tt, *J* 47, 3).

1-Fluoro-3-(4-methoxyphenyl)propan-2-one (3b) : As described above; 48% (with respect to **1b**); bp 100 - 101 °C/3 mmHg; n_D^{20} 1.5258. - ^{1}H-NMR : δ 7.1 (2 H, dm, *J* 8.5), 6.9 (2 H, dm, *J* 8.5), 4.85 (2 H, d, *J* 47.5), 3.80 (3 H, s), 3.79 (2 H, d, *J* 3.5). - ^{19}F-NMR : δ -164.4 (1 F, tt, *J* 47, 3). - Analysis : calc. for $C_{10}H_{11}FO_2$ (182.19) C 65.92, H 6.09; found C 65.81, H 5.98%.

4-(3-Fluoro-2-oxopropyl)phenyl acetate (3c) : As described above, except that the reaction mixture was only heated 5 min rather than 2 h to 125 °C; 65% (with respect to **2c**); mp 58 - 59 °C (sublimed). - ^{1}H-NMR : δ 7.23 (2 H, dt, *J* 8.5, 2.3), 7.06 (2 H, dt, *J* 8.5, 2.3), 4.85 (2 H, d, *J* 47.5), 3.82 (2 H, d, *J* 3.3), 2.28 (3 H, s). - ^{19}F-NMR : δ -164.1 (1 F, tt, *J* 48, 3). - Analysis : calc. for $C_{11}H_{11}FO_3$ (210.20) C 62.85, H 5.27; found C 62.67, H 5.38%.

Methyl 11-fluoro-10-oxoundecanoate (3d) : As described above; 43% (with respect to **2d**); mp 16 - 18 °C. - ^{1}H-NMR : δ 4.79 (2 H, d, *J* 47.8), 3.66 (3 H, s), 2.53 (2 H, td, *J* 7.4, 2.8), 2.30 (2 H, t, *J* 7.5), 1.6 (4 H, m), 1.3 (8 H, m). - ^{19}F-NMR : δ -164.6 (1 F, t, *J* 48). - Analysis : calc. for $C_{12}H_{21}FO_3$ (232.30) C 62.05, H 9.11; found C 62.23, H 9.16%.

Ethyl 11-fluoro-10-oxoundecanoate (3e) : As described above; 80% (with respect to **2e**); mp 26 - 28 °C; bp 125 - 126 °C/3 mmHg. - ^{1}H-NMR : δ 4.80 (2 H, d, *J* 47.9), 4.12 (2 H, q, *J* 7.0), 2.54 (2 H, td, *J* 7.2, 2.8), 2.28 (2 H, t, *J* 7.5), 1.61 (4 H, symm. m), 1.3 (8 H, m), 1.25 (3 H, t, *J* 7.0). - ^{19}F-NMR : δ -164.8 (1 F, tt, *J* 48, 3). - Analysis : calc. for $C_{13}H_{23}FO_3$ (246.33) C 63.39, H 9.41; found C 62.89, H 9.05%.

2-Fluorocyclododecan-1-one [20] **(3f)** : As described above; 80%; mp 53 - 54 °C; bp 149 - 150 °C/8 mmHg. - ^{1}H-NMR : δ 4.86 (1 H, ddd, *J* 49.3, 7.0, 4.2), 2.8 (1 H, dm, *J* 18.5), 2.5 (1 H, dm, *J* 18.0), 2.0 (2 H, m), 1.8 (2 H, m), 1.4 (14 H, m). - ^{19}F-NMR : δ -126.7 (1 F, symm. m). - Product **3f** (5.0 mmol) was heated for 100 h with an equivalent amount of 2-(aminomethyl)adamantan-2-ol [5] in refluxing xylene (10 mL). After evaporation of the solvent, the residue was crystallized from acetone to give **dispiro(2-fluorocyclododecane-1,2'-oxazolidine-5',2''-tricyclo[3.3.1.1^{3,7}]decane) (4)**; 69% (with respect to **3f**); mp 99 - 100 °C. - ^{1}H-NMR : δ 4.8 (0.4 × 1 H, dm, *J* 49.0), 4.7 (0.6 × 1 H, dm, *J* 50.0), 3.2 (1 H, m), 2.9 (1 H, m), 2.2 (2 H, m), 1.5 (32 H, m). - ^{19}F-NMR : δ -136.7 (0.4 × 1 F, m), -137.3 (0.6 × 1 F, m). - Analysis : calc. for $C_{23}H_{38}FNO$ (363.56) C 75.99, H 10.54; found C 75.91, H 10.96%.

2-Fluorocyclopentadecan-1-one (3g) : As described above; 61% (with respect to **2g**); mp 54 - 55 °C. - ^{1}H-NMR : δ 4.8 (1 H, dm, *J* 49.7), 2.8 (1 H, m), 2.42 (1 H, dtd, *J* 17.5, 6.1, 2.7), 1.9 (2 H, m), 1.3 (22 H, m). - ^{19}F-NMR : δ -128.2 (1 F, m sym.). - Analysis : calc. for $C_{15}H_{27}FO$ (242.38) C 74.33, H 11.23; found C 74.15, H 11.03%.

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