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Synthesis of 3-perfluoroalkylpropanals and 3-perfluoroalkylpropionitriles

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Abstract: *Simple method for the preparation of the title fluorous propionaldehydes using silver ion assisted dehydroiodination of 3-perfluoroalkyl-2-iodo-1-propanols (F-iodohydrins) and their effective conversion to the corresponding fluorous nitriles with N,O-bis(trifluoroacetyl)-hydroxylamine is described.*

Keywords: *Fluorous building blocks, F-iodohydrins, dehydroiodination, fluorous Pomeroy reaction.*

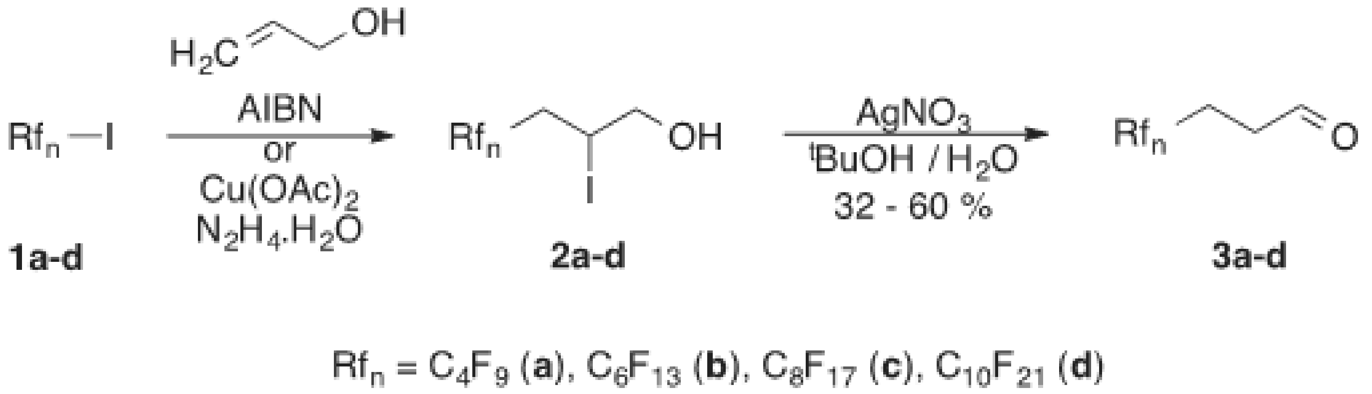
Introduction of some Rf_n-groups into organic molecules is a method to synthesize fluorous compounds. [1]. The fluorous phase affinity of these molecules mostly controlled by the length of the fluorous chain (n in $Rf_n = C_nF_{2n+1}$); however the reactivity of these compounds depend on the number of methylene spacers between the highly electron withdrawing perfluoroalkyl substituent and the functional group. Changing these variables allows the fine tuning of both phase properties and reactivities of such fluorous compounds. [2]Fluorous aldehydes are important building blocks and have been used for the synthesis of recoverable 2° and 3° fluorous amines, [3] and of the fluorous derivatives of racemic and enantiomerically pure 1-phenylethylamine. [4] Recently, fluorous aldehydes were used as analytical reagents for the determination of the concentration of 1° biogen amines in human plasma samples *via* their double reductive *N,N*-fluoroalkylation reaction to form an easy to separate 3° fluorous amine derivative $\{QN[(CH_2)_3R_{f8}]_2\}$ [5]. Fluorinated nitriles are useful raw material for lubricants, fiber-, leather- or paper processing additives, corrosion inhibitors and surfactants [6].

Literature methods for the preparation of the title aldehydes involve either sequential functional group transformations of *F*-carboxylic acids ($Q_FCO_2H \rightarrow Q_FCOCl \rightarrow Q_FCH_2OH \rightarrow Q_FCH{=}O$) [7], or fluorous ethyliodides ($Rf_n(CH_2)_2I \rightarrow Rf_n(CH_2)_2Li \rightarrow Rf_n(CH_2)_2CHO$) [8]; or oxidation of fluorous alcohols ($Q_FCH_2OH \rightarrow Q_FCH{=}O$) [3,9] or the use of convergent synthetic strategies such as hydroformylation reactions of perfluoroalkyl-ethenes ($Rf_nCH{=}CH_2$) using $Co_2(CO)_8$ [10], or Rh/phosphine [11] catalyst.

Preparation of fluorous nitriles based on convergent synthesis strategies, using the reaction of industrial raw materials such as perfluoroalkyl idodides [12], -bromide [12 a-d] or -chloride [13], (Rf_nX, X = I, Br, Cl) with acrylonitrile; perfluoroalkyl-ethenes ($Rf_nCH{=}CH_2$) with HCN or cyanohydrines [6]; and perfluoroalkyl ethyl iodides ($Rf_nCH_2CH_2I$) with alkali cyanides [14].

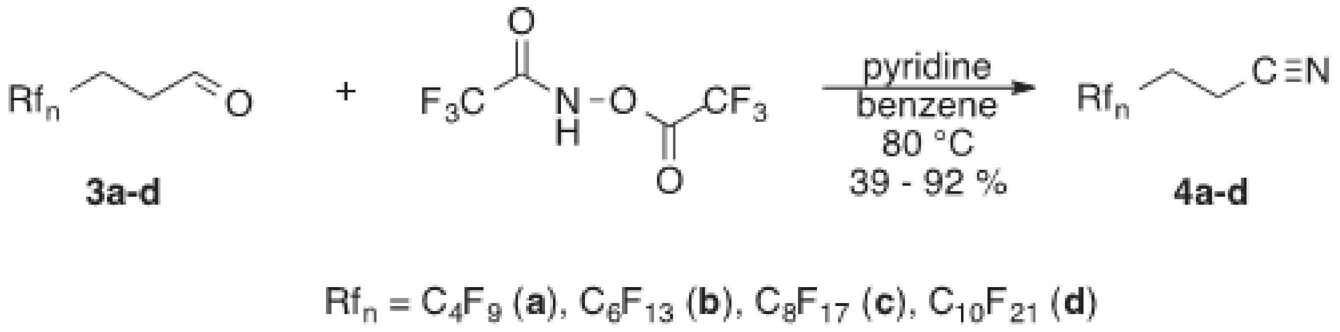
In the present work we describe the synthesis of perfluoroalkylpropanals { $Rf_n(CH_2)_mCH{=}O$ [$Rf_n = C_nF_{2n+1}$, n = 4, 6, 8, 10; m =2]; (*F*-aldehydes)} and perfluoroalkylpropionitriles { $Rf_n(CH_2)_mCN$ [$Rf_n = C_nF_{2n+1}$, n = 4, 6, 8, 10; m =2]; (*F*-nitriles)} using 3-perfluoroalkyl-2-iodo-1-propanols (*F*-iodohydrins; **2a-d**) as starting materials. These presursors can be obtained easily by the radical addition reaction of perfluoroalkyl iodides **1a-d** to allylic alcohols [15] and serve as a platform [16] for the synthesis of *F*-propanols ($Rf_nCH_2CH_2CH_2OH$) [17], *F*-propenols ($Rf_nCH{=}CHCH_2OH$) [18],and *F*-propenes ($Rf_nCH_2CH{=}CH_2$) [19] as well. Following a literature precedent [20] we choose halohydrin to aldehyde transformation as a means for synthesizing valuable fluorous aldehydes **3a-d.**

Our novel procedure involves the silver nitrate assisted dehydroiodination reaction of iodohydrins **2a-d** in a mixture of tert-butanol and water at 60 °C temperature to afford the target aldehydes **3a-d** in acceptable yields (Scheme 1). *However, due to the sensitive nature of these aldehydes - which are prone to form trimers [($Rf_nCH_2CH_2CHO)_3$] [21] on the action of acids, on longer standing, or being heated - great care should be applied during their isolation, purification and storage (see Experimental part).*



Scheme 1. Two step synthesis of *F*-aldehydes starting from perfluoroalkyl iodides.

We also studied the reaction of these fluorous aldehydes with *N,O*-bis(trifluoroacetyl)-hydroxyl amine, which is a reagent that allows the transformation of organic aldehydes to the corresponding nitriles under mild reaction conditions, as first published by Pomeroy and Craig [22]. We found that this reaction could be used for the synthesis of 3-perfluoralkylpropionitriles with good to excellent yields (fluorous Pomeroy reaction) (Scheme 2).



Scheme 2. Synthesis of *F*-propionitriles from their precursor *F*-aldehydes.

Although the above fluorous variant of the Pomeroy reaction is a powerful tool for small scale synthesis of fluorinated nitriles using safe reagents and very mild reaction conditions, on large scale it could not compete with literature methods suitable for production of *F*-propionitriles.

Experimental

F-iodohydrins (**2a-d**) [17,23] and *N,O*-bis(trifluoroacetyl)-hydroxylamine [22] were prepared as reported. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Brucker Avance 250 instrument using a 5 mm ^{1}H/^{13}C/^{31}P/^{19}F quad probe head at room temperature (298 K). Chemical shifts (δ) are given in parts per million (ppm) units relatively to the internal standard 1% TMS (δ = 0.00 for ^{1}H, δ = 0.00 for ^{13}C) and to 0.5% $CFCl_3$ as internal standard (δ = 0.00 for ^{19}F). Melting points were determined on a Boetius micro-melting point apparatus and are not corrected. The reactions were monitored and the product analyzed by gas chromatography (Hewlett-Packard 5890 Series II, PONA [crosslinked methylsilicone gum] 50 m × 0.2 mm × 0.5 µm column, H_2 carrier gas, FID detection; Program: 120 °C, 5 min, 10 °C/min, 250 °C, 5 min; Injector temperature: 250 °C, Detector temperature: 280 °C). The IR spectra were recorded on Bruker Alpha fourier transformation IR spectrometer, solid sample in KBr pastille, liquid sample film between KBr windows.

General procedure for synthesis of 3-perfluoroalkylpropanals (3a-d)

To the mixture of *F*-iodohydrine **2a-d** (10 mmol) in *tert*-butanol (10 ml) the solution of $AgNO_3$ (2.04 g, 12 mmol) in water (5 ml) was added. The reaction mixture was heated to 60 °C (internal temperature, oil temperature: 75 °C) and was stirred for 3 hours. Then the reaction mixture was cooled to room temperature, filtered and the solid material was washed with ether (10 ml). The phases of the two-phase filtrate was separated, the organic phase was washed with water (3 × 10 ml) and dried over Na_2SO_4. The solvent was removed under *vacuo*, and the crude product was purified by column chromatography (10 × 3 cm silicagel, eluent: pentane-dichloromethane = 1:1) or by vacuum distillation.

*4,4,5,5,6,6,7,7,7-Nonafluoroheptanal (**3a**)*

The mixture of **2a** (5.00 g; 12.4 mmol) in ^{t}BuOH (10 ml) and $AgNO_3$ (2.52 g; 15 mmol) in water (5 ml) were reacted to yield 1.1 g (32 %) colorless oil with GC purity of 99.1 %; showing agreable NMR data to that reported in [11b]. ^{1}H NMR ($CDCl_3$) δ: 2.47 (m, 2H, $CF_2C\mathbf{H}_2$); 2.83 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, $C\mathbf{H}_2CHO$), 9.84 (s, 1H, $C\mathbf{H}O$). ^{19}F NMR ($CDCl_3$) δ: -81.57 (m, 3F, CF_3); -115.03 (m, 2F); -125.03 (m, 2F); -126.59 (m, 2F).

*4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononanal (**3b**)*

The mixture of **2b** (5.00 g; 10.0 mmol) in ^{t}BuOH (10 ml) and $AgNO_3$ (2.02 g; 12 mmol) in water (5 ml) were reacted to yield 1.77 g (48 %) colorless oil with GC purity of 94.8 %. ^{1}H NMR ($CDCl_3$) δ: 2.46 (m, 2H, $CF_2C\mathbf{H}_2$); 2.83 (t, 2H,$^{3}J_{HH}$ = 7.5 Hz, $C\mathbf{H}_2CHO$), 9.84 (s, 1H, $C\mathbf{H}O$). ^{13}C NMR ($CDCl_3$, partial) δ: 24.0 (t, $^{3}J_{CF}$ = 22.0 Hz, $CF_2\mathbf{C}H_2$); 35.1 ($\mathbf{C}H_2CHO$); 198.3 (CHO).^{19}F NMR ($CDCl_3$) δ: -81.42 (tt, 3F, $^{3}J_{FF}$ = 10.0 Hz, $^{5}J_{FF}$ = 2.2 Hz, CF_3); -114.94 (m, 2F); -122.47 (m, 2F); -123.49 (m, 2F); -124.10 (m, 2F); -126.77 (m, 2F).

*4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecanal (**3c**)*

The mixture of **2c** (10.0 g; 16.6 mmol) in ^{t}BuOH (20 ml) and $AgNO_3$ (3.10 g; 18.2 mmol) in water (10 ml) were reacted to yield 3.8 g (48 %) white waxy solid, with GC purity of 95.9 %; showing agreable NMR data to that reported in [11b]. ^{1}H NMR ($CDCl_3$) δ: 2.47 (m, 2H, $CF_2C\mathbf{H}_2$); 2.82 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, $C\mathbf{H}_2CHO$), 9.83 (s, 1H, $C\mathbf{H}O$). ^{13}C NMR ($CDCl_3$, partial) δ: 24.0 (t, $^{3}J_{CF}$ = 23.4 Hz, $CF_2\mathbf{C}H_2$); 35.1 ($\mathbf{C}H_2CHO$); 198.3 (CHO). ^{19}F NMR ($CDCl_3$) δ:

-81.48 (t, 3F, $^3J_{FF}$ = 9.9 Hz, CF_3); -115.00 (m, 2F); -122.71 (m, 6F); -123.49 (m, 2F); -124.18 (m, 2F); -126.93 (m, 2F).

*4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heneicosafluorotridecanal (**3d**)*

The mixture of **2d** (10.00 g; 14.2 mmol) in ^{t}BuOH (20 ml) and $AgNO_3$ (2.89 g; 17.0 mmol) in water (10 ml) were reacted to yield 3.5 g (43 %) white waxy solid, with GC purity of 91.6 %. ^{1}H NMR ($CDCl_3$) δ: 2.47 (m, 2H, $CF_2C\mathbf{H}_2$); 2.83 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $C\mathbf{H}_2CHO$), 9.84 (s, 1H, $C\mathbf{H}O$). ^{13}C NMR ($CDCl_3$, partial) δ: 24.2 (t, $^3J_{CF}$ = 24.1 Hz, $CF_2\mathbf{C}H_2$); 34.9 ($\mathbf{C}H_2CHO$); 198.2 (CHO). ^{19}F NMR ($CDCl_3$) δ: -81.51 (t, 3F, $^3J_{FF}$ = 10.0 Hz, CF_3); -112.52 (m, 2F); -115.00 (m, 2F); -122.71 (m, 8F); -123.49 (m, 2F); -124.18 (m, 2F); -126.93 (m, 2F).

Upscaled procedure for the synthesis of 3-perfluorooctylpropanal (3c)

To the mixture of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-iodopropan-1-ol (**2c**, 300 g, 0.50 mol) in *tert*-butanol (600 ml) the solution of $AgNO_3$ (93 g, 0.55 mol) in water (300 ml) was added. The reaction mixture was heated to 60 °C (internal temperature, oil temperature: 75 °C) and was stirred for 3 hours. Then the reaction mixture was cooled to room temperature, filtered and the solid material was washed with ether (300 ml). The phases of the two-phase filtrate was separated, the organic phase was washed with water (3 × 300 ml) and dried over Na_2SO_4. The solvent was removed under *vacuo*, and the crude product was purified by vacuum distillation (bp = 78-84 °C/1 mmHg). Yield: 141.2 g (60 %). **Note:** *Bath temperature should not exceed 100 °C and the whole preparation must be executed on the same day, since overnight standing or higher bath temperature results in the drop of yield and purity.*

General procedure for the synthesis of 3-perfluoroalkylpropionitriles (4a-d)

The solution of 3-perfluoroalkylpropanal **3a-d** (2.5 mmol), *N,O*-bis(trifluoroacetyl)-hydroxylamine (0.56 g; 2.5 mmol) and pyridine (0.40 g; 5.0 mmol) in benzene (4 ml) was heated for 1 h at 80 °C. The solvent was removed under *vacuo*, the solid residue was dissolved in ether (10 ml) and washed with 1M HCl (5 ml) and water (3 × 10 ml). After drying over Na_2SO_4 the solvent was removed in *vacuo*. The crude product was purified by column chromatography (8 × 1.5 cm silicagel, eluent: pentane-dichloromethane = 1:1) or by recrystallization from 2,2,4-trimethylpentane (isooctane).

*4,4,5,5,6,6,7,7,7-Nonafluoroheptanenitrile (**4a**)*

The mixture of **3a** (0.9 g; 3.3 mmol) *N,O*-bis(trifluoroacetyl)-hydroxylamine (0.73 g; 3.3 mmol) and pyridine (0.52 g; 6.5 mmol) in benzene (4 ml) was reacted to yield 0.35 g (39 %) colorless oil with GC purity of 90.1 %. (Lit. bp = 64 °C/5 mmHg [24].) ^{1}H NMR ($CDCl_3$) δ: 2.52 (m, 2H, $C\mathbf{H}_2CN$); 2.70 (m, 2H, $CF_2C\mathbf{H}_2$).^{19}F NMR ($CDCl_3$) δ: -81.58 (tt, 3F, $C\mathbf{F}_3$,$^3J_{FF}$ = 9.5 Hz, $^5J_{FF}$ = 3.0 Hz); -116.13 (m, 2F); -124.95 (m, 2F); -126.58 (m, 2F). IR (film): 3145, 1665, 1401, 1359, 1230, 1135, 1052, 1015, 981, 881, 881, 853, 749, 735, 713, 599.

*4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononanenitrile (**4b**)*

The mixture of **3b** (1.0 g; 2.7 mmol), *N,O*-bis(trifluoroacetyl)-hydroxylamine (0.60 g; 2.7 mmol) and pyridine (0.42 g; 5.4 mmol) in benzene (4 ml) was reacted to yield 0.90 g (91 %) colorless oil, with GC purity of 90.9 %.(Lit. bp = 79 °C/5 mmHg [25].) ^{1}H NMR ($CDCl_3$) δ: 2.51 (m,2H, $C\mathbf{H}_2CN$); 2.69 (m, 2H, $CF_2C\mathbf{H}_2$). ^{19}F NMR ($CDCl_3$) δ: -81.45 (tt, 3F, $C\mathbf{F}_3$,$^3J_{FF}$ =

9.8 Hz, $^5J_{FF}$ = 2.7 Hz); -115.96 (m, 2F); -122.46 (m, 2F); -123.46 (m, 2F); -124.05 (m, 2F); -126.77 (m, 2F). IR (film): 2983, 2258, 1691, 1446, 1390, 1367, 1319, 1240, 1146, 1122, 1075, 1020, 981, 926, 846, 812, 780, 746, 732, 709, 697, 653, 568, 533.

*4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecanenitrile (**4c**)*

The mixture of **3c** (1.0 g; 2.1 mmol), *N,O*-bis(trifluoroacetyl)-hydroxylamine (0.47 g; 2.1 mmol) and pyridine (0.33 g; 4.2 mmol) in benzene (4 ml) was reacted to yield 0.91 g (92 %) white solid of mp = 70-72 °C with GC purity of 95.6 %. (Lit. mp = 64 - 66 °C [26] and Lit. bp = 106 °C/5 mmHg [24].) ^{1}H NMR ($CDCl_3$) δ: 2.52 (m, 2H, C**H**$_2$CN); 2.70 (m, 2H, CF_2C**H**$_2$). ^{19}F NMR ($CDCl_3$) δ: -81.18 (t, 3F, C**F**$_3$,$^3J_{FF}$ = 10.0 Hz); -115.77 (m, 2F); -122.11 (m, 2F); -122.33 (m, 4F); -123.15 (m, 2F); -123.82 (m, 2F); -126.56 (m, 2F). IR (KBr): 2257, 1374, 1335, 1203, 1147, 11115, 1078, 1037, 980, 921, 873, 705, 662, 606, 560, 531.

*4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heneicosafluorotridecanenitrile (**4d**)*

The mixture of **3d** (1.0 g; 1.74 mmol), *N,O*-bis(trifluoroacetyl)-hydroxylamine (0.39 g; 1.74 mmol) and pyridine (0.28 g; 3.5 mmol) in benzene (4 ml) was reacted to yield 0.91 g (92 %) white solid of mp = 102-104 °C, with GC purity of 95.6 %. ^{1}H NMR ($CDCl_3$) δ: 2.52 (m, 2H, C**H**$_2$CN); 2.70 (m, 2H, CF_2C**H**$_2$). ^{19}F-NMR ($CDCl_3$) δ: -81.19 (t, 3F, C**F**$_3$,$^3J_{FF}$ = 9.7 Hz); -115.77 (m, 2F); -122.18 (m, 10F); -123.14 (m, 2F); -123.81 (m, 2F); -126.56 (m, 2F). IR (KBr): 3424, 2258, 1641, 1445, 1376, 1345, 1211, 1151, 1112, 1080, 982, 884, 751,712, 665,647, 556, 530.

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