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TEMPO mediated oxidation of fluorinated alcohols to carboxylic acids

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ABSTRACT

Fluorinated carboxylic acids (**3a–f**) have been prepared in good yield by oxidizing the corresponding alcohols (**2a–f**) in the presence of TEMPO (**1**) as catalyst, using oxidants like bleach and oxygen.

1. Introduction

The synthesis of fluorinated carboxylic acids and derivatives thereof has attracted much attention due to their manifold industrial applications for instance as emulsifying agents [1]. These compounds can be prepared by electrolytic fluorination of the parent hydrocarbon compounds [2], oxidative cleavage of perfluorinated olefins [3], by ring-opening addition of hexafluorooxetane to fluorine containing acyl fluorides [4] or in reactions of perfluoroalkyl iodides with carbon dioxide [5].

Oxidation of fluorinated alcohols is also well known. The most commonly applied methods included such oxidants as potassium permanganate [6], chromium (VI) oxide [7], RuO_4 or OsO_4 in the presence of NaOCl [8], chlorine [9], nitric acid in the presence of an iron based catalyst [10], dinitrogen tetroxide [11], periodic acid [12], the Dess–Martin reagent [13], CuCl/o-phenanthroline complex in the presence of oxygen [14], or vanadium pentaoxide/oxygen [15]. In addition, electrochemical oxidation [16] can be applied. Many of these methods have drawbacks concerning the heavy metal residues, harsh reaction conditions or high costs of reagents. Therefore, new methods including easily accessible catalysts in the combination with, clean oxidants" [17] such as hydrogen peroxide or molecular oxygen are still sought. Non-metal oxidation catalysts seem to be a good alternative, particularly nitroxyl radicals especially 2,2,6,6-tetramethylpiperidin-1-oxyl known as TEMPO (**1**), which is widely used in the oxidation of secondary and primary alcohols [18]. The active species in these processes is the oxoammonium ion generated by oxidation of 1 or its disproportion under acidic conditions.

TEMPO is a rather expensive reagent, therefore its efficient recycling and reuse is an important task. Different approaches were applied, mainly devoted to preparation and use of polymer or silica supported TEMPO derivatives [19], applications of perfluoroalkyl substituted TEMPO in fluorous biphasic conditions [20] and use of TEMPO in ionic liquids [21].

It was also reported that TEMPO effectively mediates oxidation of fluorinated alcohols $CF_3(CF_2)_m(CH_2)_nCH_2OH$ ($m = 5–9$, $n = 2–4$) to the corresponding aldehydes (60–83%) in the presence of iodobenzene diacetate or trichloroisocyanuric acid (TCCA) as oxidants [22]. However, these processes were claimed to be sluggish when $KHSO_5$ and NaOCl were applied.

In this paper, we report results of our studies on the TEMPO (**1**) mediated oxidation of fluorinated alcohols **2a–f** to the corresponding carboxylic acids **3a–f**.

2. Results and discussion

In the course of this study, we decided to apply very effective combination TEMPO (**1**)/sodium hypochlorite [18] in the oxidation of our model substrate 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**). The commonly accepted mechanism of this reaction assumes the formation of the N-oxoammonium ion, which oxidizes the alcohol to the respective carbonyl compound and simultaneously is reduced to N-hydroxyl TEMPO. Regeneration of the oxoammonium ion is the result of

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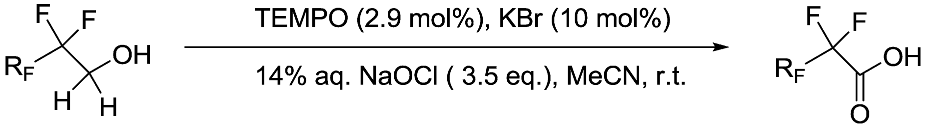
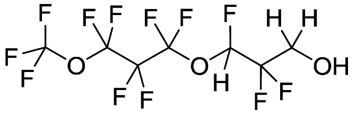
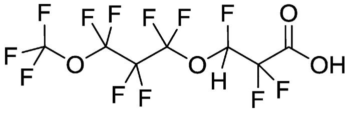
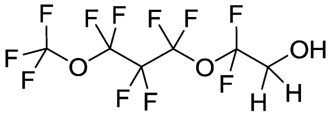
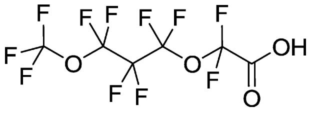
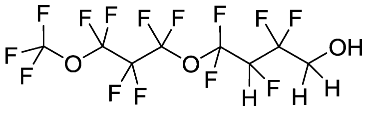
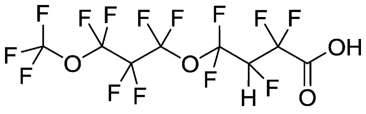
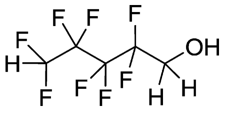
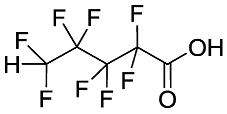
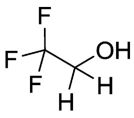
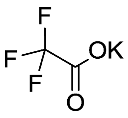
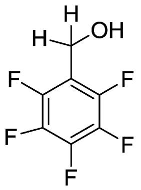
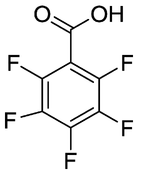
Table 1
Oxidation of fluorinated alcohols **2a–f** by TEMPO in MeCN: 14% aq. NaOCl.



(**2**) (**3**)

Entry	Substrate[a]		Product		Yield [%][b]
1		**2a**		**3a**	82
2		**2b**		**3b**	87
3		**2c**		**3c**	81
4		**2d**		**3d**	80
5		**2e**		**3e**[c]	86
6[d]		**2f**		**3f**	82

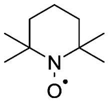
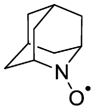
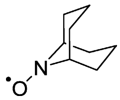
[a] Conditions as described in Section 3.
[b] Isolated yields.
[c] The solution of crude product in acetonitrile was treated with MeOK.
[d] 4-Methoxy-TEMPO was used as catalyst.

oxidizing *N*-hydroxyl TEMPO by sodium hypochlorite. The oxidation of **2a** was initially carried out in a biphasic system (14% aq. NaOCl (1.25 eq.): CH_2Cl_2) in the presence of 5 mol% of TEMPO, 10 mol% of KBr and 7 mol% of phase transfer catalyst TEBAC (benzyltriethylammonium chloride). In the ^{19}F NMR spectrum of the reaction mixture recorded after 24 h of stirring, the expected acid **3a** was observed in traces. Further efforts were then focused on optimizing the reaction conditions. It has been proved that the addition of 3.5 eq. of 14% aq. NaOCl during two days of stirring is required to complete the reaction. Later it also turned out that the reaction time can be limited to 7 h. When dichloromethane was replaced by acetonitrile, the presence of phase transfer catalyst was no longer necessary. Under such conditions 2.5–4 mol% of TEMPO was employed, what is desirable taking into account the cost of this reagent. Once the reaction was completed, the product was isolated by phase separation *via* addition of sulphuric acid followed by addition of water or by acidification and extraction. The crude fluorinated carboxylic acids were then purified by distillation or crystallization. Only in the case of trifluoroacetic acid (**3e**) due to the similar boiling points of solvent and product, the latter one was identified as potassium salt. Since instability of fluoroaldehydrols and fluoroaldehydes to concentrated 50% aq. KOH is a known fact [23], formation of potassium salt of **3a** under treatment of KOH confirms decisively the presence of carboxylic group. To illustrate the generality of this oxidation procedure, the following fluorinated carboxylic acids **3a–f** were prepared (Table 1).

The presence of TEMPO as an oxidant is essential. In the absence of 1 the conversion of 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**) did not exceed 10% after 18 h of stirring with 3.5 eq. of NaOCl. The comparison of the reactivity of TEMPO (**1**) with AZADO (2-azaadamantane *N*-oxyl (4)) and ABNO (9-aza-bicyclo[3.3.1]nonane *N*-oxyl (**5**)) confirmed the higher reactivity of **4** and **5**. After 25 min of stirring the conversion in the case of AZADO and ABNO was 43% while using TEMPO it was 30%. As a consequence only 2.7 eq. of NaOCl was required to complete the reaction in the time of 2–3.5 h. In the case of TEMPO the same result was achieved using 3.5 eq. of NaOCl during 7 h (Table 2).

The application of supported TEMPO derivatives simplifies the work up and enables their recovery. Under reaction conditions

Table 2
Oxidation of **2a** in a presence of TEMPO (**1**), AZADO (**4**) and ABNO (**5**) in MeCN: 14% aq. NaOCl.

Entry	Substrate[a]	TEMPO[b]		NaOCl	Time (h)	Product	Yield [%][c]
1	**2a**		**1**	3.5 eq.	7	**3a**	61
2	**2a**		**4**	2.7 eq.	2	**3a**	72
3	**2a**		**5**	2.7 eq.	3.5	**3a**	77

[a] 0.00137 mol of substrate was used in each run.
[b] 2.9 mol% of catalyst was used in each run.
[c] Isolated yields

Table 3
Oxidation of **2a** in a presence of supported TEMPO in MeCN: 14% aq. NaOCl.

Entry	Substrate	TEMPO[c]	Product	Yield [%][d]
1	**2a**[a]	**6**	**3a**	74
2	**2a**[b]	**7**	**3a**	91

[a] 0.0055 mol of substrate was used in 1 run.
[b] 1.37 mol of substrate was used in 2 run.
[c] 2.9 mol% of catalyst was used in each run.
[d] Isolated yields.

described above we employed with success 2.9 mol% of TEMPO supported on polyethylene glycol (loading 0.25–0.75 mmol/g) (**6**) and 2.9 mol% of TEMPO supported on polystyrene (loading 2.5 mmol/g) (**7**) (Table 3).

It was claimed that the presence of bromide ion in Montanari conditions [24] has an accelerating effect due to formation of HOBr, however in the reaction conditions described above the oxidation of **2a** undergoes equally fast without potassium bromide. The acid **3a** was isolated in 79% yield.

TEMPO in combination with $NaNO_2$ and HCl or HBr as cocatalyst was effectively applied in the oxidation of various primary and secondary alcohols [25]. It is assumed that the HCl or HBr reacts with $NaNO_2$ to give a NO/NO_2 mixture and NOX (X = Cl, Br). Then in the reaction between NOX and TEMPO or *N*-hydroxyl TEMPO, oxoammonium ion is generated.

Continuing our investigations in the field of TEMPO mediated oxidations of fluorinated alcohols, we applied the TEMPO/$NaNO_2$/O_2/$Bu_4N^+Br^-$ system [26] in the oxidation of **2a**. We have chosen the following conditions for this reaction: 8 mol% of TEMPO, 24 mol% of $NaNO_2$ and 22 mol% of Aliquat 336 (methyltrioctylammonium chloride). After 24 h of heating at 60 °C in acetic acid under oxygen at atmospheric pressure the conversion of **2a–3a** was determinated as 60%. Further 48 h of heating with additional amounts of TEMPO (8 mol%) and $NaNO_2$ (24 mol%) allowed to complete the reaction and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionic acid (**3a**) was isolated in 54% yield. If only $NaNO_2$ was added without TEMPO, the conversion remained unchanged. The oxidation was not completed until the second portion of TEMPO was added, what led us to conclusion that the removal of the catalyst or its precursor from the catalytic cycle occurred. Since disproportion of TEMPO is pH dependent, we decided to conduct the reaction in the presence of buffer, namely sodium acetate. The addition of 0.8–3 eq. of CH_3CO_2Na in the combination with 8 mol% of TEMPO and 24 mol% of $NaNO_2$ allowed to complete the reaction during 16 h of heating at 60 °C under oxygen at atmospheric pressure. The expected carboxylic acid **3a** was obtained in 68% yield. This procedure was applied in the oxidation of fluorinated alcohols **2a–f** (Table 4).

The fluorinated carboxylic acids **3a–f** were purified by distillation or crystallization. In the case of compound **3a** the crude product was estrificated and methyl ester of 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionic acid (**8a**) was obtained in 75% yield (Scheme 1).

In the oxidation of various primary and secondary alcohols similar reaction conditions were applied, in which catalytic amounts of manganese and cobalt nitrates were used instead of sodium nitrite [27]. It was reported that oxygen in the presence of Mn (II)–Co (II) or Mn (II)–Cu (II) nitrates oxidizes *N*-hydroxyl TEMPO to TEMPO, which next undergoes disproportion in acidic medium to *N*-oxoammonium ion.

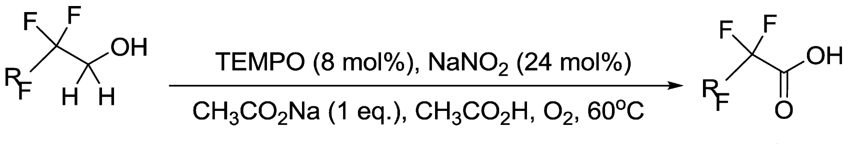
We employed these conditions in the oxidation of **2a**. The initial experiment was run with 10 mol% of TEMPO, 2 mol% of $Mn(NO_3)_2{\cdot}4H_2O$, 2 mol% of $Co(NO_3)_2{\cdot}6H_2O$ at 60 °C in acetic acid under oxygen at atmospheric pressure. After 24 h of heating, the conversion of only 30% was observed. The expected acid **3a** was isolated in 13% yield. As previously, the addition of 1 eq. of sodium acetate enabled to complete the reaction during 16 h of heating at 60 °C under oxygen at atmospheric pressure. The acid **3a** was isolated in 70% yield (Scheme 2).

In conclusion, TEMPO mediated oxidations of fluoroalkyl substituted alcohols to the corresponding carboxylic acids were performed under mild conditions using sodium hypochlorite and oxygen as oxidants. Comparing these both procedures it is seen that oxidation of alcohols **2a–f** by TEMPO/NaOCl occurs faster (7 h) in a room temperature, requires lower amounts of catalyst (2.9 mol%) and gives corresponding acids **3a–f** with better yields (80–87%). The oxidation of the same alcohols by TEMPO/$NaNO_2$/O_2 system, not only requires larger amount of TEMPO (10 mol%), longer reaction time (16 h) and the higher reaction temperature (60 °C) but also gives the acids **3a–f** with lower yields (55–80%). In the above mentioned reactions the primary oxidant seems to be the *N*-oxoammonium ion generated from TEMPO. Some of above results were patented [28].

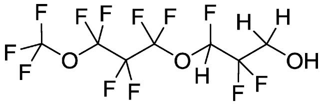
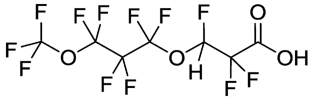
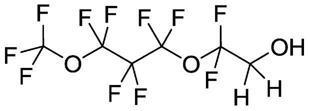
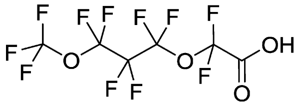
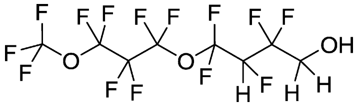
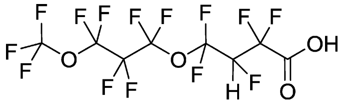
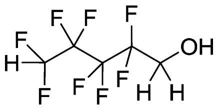
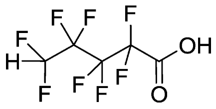
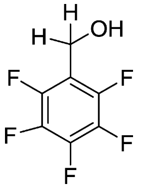
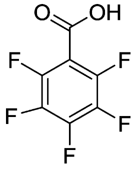
3. Experimental

Melting points were determined in capillaries and boiling points were measured during distillation; both are uncorrected. ^1H NMR and ^{19}F NMR spectra were recorded with Bruker DPX-200 spectrometer and JEOL ECX 400 spectrometer, both in $CDCl_3$ or D_2O (compound **3e**) or CD_3CN (compound **3f**) solutions. Chemical shifts are quoted in ppm from internal TMS for ^1H and from internal $CFCl_3$

Table 4
Oxidation of fluorinated alcohols **2a–f** by TEMPO/$NaNO_2/O_2$ in CH_3CO_2H.



(**2**) (**3**)

Entry	Substrate[a]		Product		Yield [%][b]
1		2a		3a	68
2		2b		3b	78
3		2c		3c	71
4		2d		3d	55
5[c]		2f		3f	80

[a] Conditions as described in Section 3.

[b] Isolated yields.

[c] 4-Methoxy-TEMPO was used as catalyst.

for ^{19}F nuclei. Mass spectra (ESI) of pure compounds were obtained with HCT Ultra spectrometer.

TEMPO (**1**), AZADO (**4**), TEMPO supported on polyethylene glycol (loading 0.25–0.75 mmol/g) (**6**), TEMPO supported on polystyrene (loading 2.5 mmol/g) (**7**), 2,2,3,3,4,4,5,5-octafluoro-pentan-1-ol (**2d**), and 2,2,2-trifluoroethanol (**2e**) were commercial reagents. ABNO (5) was prepared according to known procedure [29]. 2,2,3-Trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**) was kindly donated us by Dyneon Company. 2,2-Difluoro-2-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-ethanol (**2b**) was prepared in 51% yield according to known procedure [30] by reduction of difluoro-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-acetic acid (**3b**), which was a gift from Dyneon 3 M. 2,2,3,4,4-Pentafluoro-4-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-butan-1-ol (**2c**) was prepared in 75% yield by radical addition of methanol [31] to 1,1,2,3,3-pentafluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propene, which was also donated to us by Dyneon Company.

3.1. *Representative procedure for the oxidation of alcohols (**2a–e**) by TEMPO in MeCN: 14% aq. NaOCl*

5.5 ml of aq. solutions of KBr (0.55 mol/dm^3), 20 ml MeCN, TEMPO (0.12 g, 0.00077 mol), and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**) (10 g, 0.0275 mol) were placed in the flask. 14% aq. NaOCl (48 ml) buffered by $NaHCO_3$ (5.2 g) were added *via* the dropping funnel in 3 portions during two days of stirring in a room temperature (slight exothermic effect). The progress of reaction was monitored by ^{19}F NMR spectroscopy. Then concentrated sulfuric acid followed by water was added. After extraction with diethyl ether, the organic phases were dried over magnesium sulfate. The solvent was evaporated to give a colorless liquid, which was distilled.

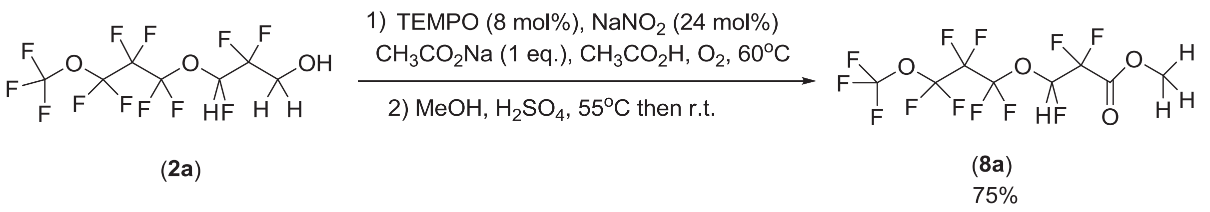
2,2,3-Trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionic acid (**3a**): Colorless liquid (b.p. 92 °C/20 mm). Yield: 82%. ^1H NMR δ: 6.20 (dm, J_{HF} = 54.6 Hz, 1H); 9.10 (s, 1H); ^{19}F NMR δ: −56.3 (t, J = 9 Hz, 3F); −85.2 (AB system, J = 142 Hz, 1F); −86.9 (m, 2F); −87.8 (AB system, J = 142 Hz, 1F); −123.6 (m, 2F); −130.4 (m, 2F); −146.5 (dm, J_{HF} = 54 Hz, 1F);

HRMS (ESI, negative): m/z: Found: 376.9687 [M−H]$^-$; Calc. for $C_7HF_{15}O_4$: 376.9689;

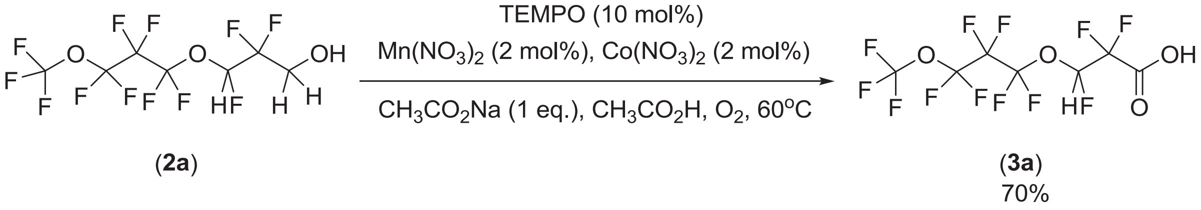
Difluoro-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-acetic acid (**3b**): Colorless liquid (b.p. 70 °C/20 mm).Yield: 87%. ^1H NMR δ: 9.39 (s, 1H); ^{19}F NMR δ: −56.3 (t, J = 8.7 Hz, 3F); −79.2 (t, J = 11.9 Hz, 2F); −84.6 (m, 2F); −86.9 (m, 2F); −130.4 (m, 2F);

HRMS (ESI, negative): m/z: Found: 344.9628 [M−H]; Calc. for $C_6F_{14}O_4$: 344.9626;

2,2,3,4,4-Pentafluoro-4-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-butyric acid (**3c**): Colorless liquid (b.p. 104 °C/20 mm). Yield: 81%. ^1H NMR δ: 5.20 (dm, J_{HF} = 43 Hz, 1H); 10.20 (s, 1H); ^{19}F NMR δ: −56.3(t, J = 8.3 Hz, 3F); −78.5 (m, 2F); −84.7 (m, 2F); −86.9 (m, 2F); −117.9 (AB system, J = 277 Hz, 1F); −121.6 (AB



Scheme 1.



Scheme 2.

system, $J = 277$ Hz, 1F); −130.5 (m, 2F); −214.1 (dm, $J_{HF} = 43$ Hz, $J = 11$ Hz, 1F);

HRMS (ESI, negative): *m/z*: Found: 426.9656 $[M-H]^-$; Calc. for $C_8HF_{14}O_4$: 426.9657;

2,2,3,3,4,4,5,5-Octafluoro-pentanoic acid (**3d**): Colorless liquid (b.p. 73 °C/20 mm). Yield: 80%. ^1H NMR δ: 6.08 (tt, $J_{HF} = 52$ Hz, $J_{FF} = 5.3$ Hz, 1H); 8.6 (s, 1H); ^{19}F NMR δ: −120.6 (t, $J = 9.2$ Hz, 2F); −125.8 (m, 2F); −130.6 (m, 2F); −138.4 (dm, $J_{HF} = 52$ Hz, 2F);

HRMS (ESI, negative): *m/z*: Found: 244.9908 $[M-H]^-$; Calc. for $C_5HF_8O_2$: 244.9915;

Potassium trifluoroacetate (**3e**): Yield: 86%. ^{19}F NMR (D_2O) δ: −76.82 (s, 3F);

2,3,4,5,6-Pentafluorobenzoic acid (**3f**): White solid (m.p. 99–101 °C). Yield: 82%. ^{19}F NMR (CD_3 CN) δ: −140.47 (m, 2F); −151.55 (m, 1F); −163.05 (m, 2F);

HRMS (ESI, negative): *m/z*: Found: 210.9823 $[M-H]^-$; Calc. for $C_7F_5O_2$: 210.9824;

3.2. Potassium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionate (3a)

The sample of crude 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionic acid (**3a**) (5.34 g, 0.014 mol) was treated with KOH (0.88 g, 0.015 mol). After evaporation of solvent the white solid of potassium salt of (**3a**) was identified by ^{19}F NMR. Yield: 85%

^1H NMR (D_2O) δ: 6.44 (dt, $J = 54$ Hz, $J = ca.$ 5.5 Hz, 1H); ^{19}F NMR (D_2O) δ: −54.8 (m, 3F); −84.0 (AB system, $J = ca.$ 144 Hz, 1F); −85.5 (m, 2F); −86.1 (AB system, $J = ca.$ 144 Hz, 1F); −119.5 (AB system, $J = ca.$ 260 Hz, 1F); −122.7 (AB system, $J = ca.$ 260 Hz, 1F); −129.1 (m, 2F); −146.6 (dm, $J_{HF} = 54$ Hz, 1F);

3.3. General procedure for the oxidation of alcohol (2a) by TEMPO-PS in MeCN: 14% aq. NaOCl

275 ml of aq. solution of KBr (0.54 mol/dm^3), 1000 ml MeCN, TEMPO on polystyrene 2.5 mmol/g loading (15.9 g, 2.9 mol%), and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**) (500 g, 1.37 mol) were placed in the flask. 14% aq. NaOCl (2400 ml) buffered by $NaHCO_3$ to pH 9 were added *via* the dropping funnel in 3 portions during two days of stirring in a room temperature. Then the catalyst was filtered off and the concentrated sulfuric acid following by water was added. After separation, the organic phase was evaporated to give a colorless liquid (615 g), which was distilled at 20 mm (b.p. 92 °C) to give 471 g of pure acid (**3a**). Yield: 91%.

3.4. General procedure for the oxidation of alcohols (2a–d) by TEMPO/NaNO$_2$/O$_2$ in CH$_3$CO$_2$H

In a 500 ml glass flask equipped with a balloon with oxygen, reflux condenser and stirrer 150 ml of CH_3CO_2H, $NaNO_2$ (0.91 g, 0.013 mol), TEMPO (0.68 g, 0.004 mol), CH_3CO_2Na (3.78 g, 0.046 mol) and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (2a) (20 g, 0.054 mol) were placed. The mixture was stirred 16 h at 60 °C under oxygen at atmospheric pressure (flow). The progress of reaction was monitored by ^{19}F NMR spectroscopy. After acidification and extraction with diethyl ether, the combined organic phases were washed by water and dried over magnesium sulfate. The solvent was removed and the residue was distilled to give 14.2 g of acid (**3a**) (58 °C/1.6 mmHg). Yield: 68%.

3.5. Methyl 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionate (8a)

In a 1000 ml glass flask equipped with a balloon with oxygen, reflux condenser and stirrer 200 ml of CH_3CO_2H, $NaNO_2$ (8.71 g, 0.12 mol), TEMPO (6.85 g, 0.04 mol), CH_3CO_2Na (45.1 g, 0.55 mol) and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (2a) (200 g, 0.55 mol) were placed in the flask. The mixture was stirred 16 h at 60 °C under oxygen at atmospheric pressure. The progress of reaction was monitored by ^{19}F NMR spectroscopy. Then the mixture was acidified and water was added till the bottom phase of perfluorinated compound appeared. The phases were separated. To the crude acid (**3a**) (262.3 g) sulfuric acid (130 g, 1.32 mol) and methanol (30 g, 0.93 mol) were added, the whole mixture was stirred one day at 55 °C and then two days at room temperature. After dilution with water the bottom phase of perfluorinated compound was separated. This product was distilled to give 162 g of (8a). Yield: 75%.

2,2,3-Trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propionic acid (8a): Colorless liquid (b.p. 52 °C/water pump).^1H NMR δ: 3.94 (s, 3H); 6.19 (dt, $J_{HF} = 53$ Hz, $J_{FF} = 5.5$ Hz, 1H); ^{19}F NMR δ: −55.0 (m, 3F); −84.1 (AB system $J_{FF} = 147$ Hz, 1F); −85.7 (m, 2F); −86.5 (AB system $J_{FF} = 147$ Hz, 1F); −122.3 (m, 2F); −129.1 (m, 2F); −145.7 (d, $J_{HF} = 53$ Hz, 1F);

3.6. Representative procedure for the oxidation of alcohol (**2a**) by TEMPO/$Co(NO_3)_2$/$Mn(NO_3)_2$/O_2 in CH_3CO_2H

In a 100 ml glass flask equipped with a balloon with oxygen, reflux condenser and stirrer 50 ml of CH_3CO_2H, $Mn(NO_3)_2 \cdot 4H_2O$ (0.137 g, 0.00054 mol), $Co(NO_3)_2 \cdot 6H_2O$ (0.159 g, 0.00054 mol), TEMPO (0.42 g, 0.0027 mol), CH_3CO_2Na (2.24 g, 0.027 mol) and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxy-propoxy)-propan-1-ol (**2a**) (10 g, 0.027 mol) were placed. The mixture was stirred 16 h at 60 °C under oxygen at atmospheric pressure (flow). The progress of reaction was monitored by ^{19}F NMR spectroscopy. After acidification and extraction by diethyl ether, the combined organic phases were washed with water and dried over magnesium sulfate. The solvent was removed and the residue was distilled to give 7.3 g of acid (**3a**) (b.p. 58 °C/1.6 mmHg). Yield: 70%.

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References

[1] (a) R. Renner, Environmental Science and Technology 35 (2001) 154A;
(b) J.P. Giesy, K. Kannan, Environmental Science and Technology 36 (2002) 146A;
(c) M.M. Schutz, D.F. Barofsky, J.A. Field, Environmental Engineering Science 20 (2003) 487.
[2] T. Abe, H. Baba, K. Okuhara, H. Fukaya, Journal of Fluorine Chemistry 111 (2001) 115.
[3] A. Hirokazu, Ch. Yasumichi, US 5945562.
[4] M. Shigeru, T. Yoshiki, W. Keiko, T. Nobuhiko, K. Mitsuru, WO2005003075.
[5] S. Benefice-Malouet, H. Blancou, J. Itier, A. Commeyras, Synthesis 8 (1991) 647.
[6] W. Dmowski, H. Plenkiewicz, K. Piasecka-Maciejewska, Journal of Fluorine Chemistry 48 (1990) 77.
[7] S. Achilefu, L. Mansuy, C. Selve, S. Thiebaut, Journal of Fluorine Chemistry 70 (1995) 19.
[8] A. Hirokazu, Ch. Yasumichi, JP 10279517A.
[9] E.T. McBee, O.R. Pierce, W.F. Marzluff, Journal of the American Chemical Society 75 (1953) 1609.
[10] K. Ichihara, S. Yodogawa, WO 9962859A1.
[11] R.M. Scribner, Journal of Organic Chemistry 29 (1964) 279.
[12] G. Olah, A. Pavlath, Acta Chimica Academiae Scientarium Hungaricae 3 (1953) 431.
[13] (a) R.J. Linderman, D.M. Graves, Journal of Organic Chemistry 54 (1989) 661;
(b) R.J. Linderman, D.M. Graves, Tetrahedron Letters 28 (1987) 4259.
[14] (a) I.P. Skibida, A.M. Sakharov, J.L. Bakhmutov, V.F. Denisenkov, N.P. Martynova, EP 0635468 A1.
(b) I.P. Skibida, A.M. Sakharov, Catalysis Today 27 (1996) 187.
[15] M. Braid, US Pat. 3,038,936 (1962).
[16] A.R. Diesslin, E.A. Kauck, J.H. Simons, S.P. Minn, DE 836796.
[17] A. Dijksman, G.J. Brink, I.W.C.E. Arends, R.A. Sheldon, Accounts of Chemical Research 35 (2002) 774.
[18] (a) A.E.J. Nooy, A.C. Besemer, H. Bekkum, Synthesis 10 (1996) 1153;
(b) T. Vogler, A. Studer, Synthesis 13 (2008) 1979.
[19] (a) C. Bolm, A.S. Magnus, J.P. Hildebrand, Organic Letters 2 (2000) 1173;
(b) P. Ferreira, E. Phillips, D. Rippon, S.C. Tsang, W. Hayes, Journal of Organic Chemistry 69 (2004) 6851;
(c) M. Gilhespy, M. Lok, X. Baucherel, Catalysis Today 117 (2006) 114;
(d) M. Benaglia, A. Puglisi, O. Holczknecht, S. Quici, G. Pozzi, Tetrahedron 61 (2005) 12058;
(e) A. Dijksman, I.W.C.E. Arends, R.A. Sheldon, Chemical Communications 4 (2000) 271;
(f) T. Fey, H. Fischer, S. Bachmann, K. Albert, C. Bolm, Journal of Organic Chemistry 61 (2001) 8154;
(g) A. Michaud, G. Gingras, M. Morin, F. Bland, R. Ciriminna, D. Avnir, M. Pagliaro, Organic Process Research and Development 11 (2007) 766.
[20] (a) B. Betzemeier, M. Cavazzini, S. Quici, P. Knochel, Tetrahedron Letters 41 (2000) 4343;
(b) O. Holczknecht, G. Pozzi, S. Quici, Quantitative Structure–Activity Relationship in Combustion Science 25 (2006) 736;
(c) O. Holczknecht, M. Cavazzini, S. Quici, I. Shepperson, G. Pozzi, Advanced Synthesis and Catalysis 347 (2005) 677;
(d) A.P. Dobbs, M.J. Penny, P. Jonem, Tetrahedron Letters 49 (2008) 6955.
[21] (a) N. Jiang, J.A. Ragauskas, Organic Letters 7 (2005) 3689;
(b) I.A. Ansari, R. Gree, Organic Letters 4 (2002) 1507;
(c) N. Jiang, J.A. Ragauskas, Tetrahedron Letters 46 (2005) 3323;
(d) X.E. Wu, L. Ma, M.X. Ding, L.X. Gao, Synlett 4 (2005) 607;
(e) W. Qian, E. Jin, W. Bao, Y. Zhang, Tetrahedron 62 (2006) 556.
[22] G. Pozzi, S. Quici, I. Shepperson, Tetrahedron Letters 43 (2002) 6141.
[23] (a) D.R. Husted, A.H. Ahlbrecht, Journal of the American Chemical Society 74 (1952) 5422;
(b) N.O. Brace, Journal of Organic Chemistry 26 (1961) 4005.
[24] (a) P.L. Anelli, C. Biffi, F. Montanari, S. Quici, Journal of Organic Chemistry 52 (1987) 2559;
(b) P.L. Anelli, C. Biffi, F. Montanari, Journal of Organic Chemistry 54 (1989) 2970.
[25] X. Wang, R. Liu, Y. Jin, X. Liang, Chemistry: A European Journal 14 (2008) 2679.
[26] B. Karimi, A. Biglari, J.H. Clark, V. Budarin, Angewandte Chemie 119 (2007) 7348.
[27] A. Cecchetto, F. Fontana, F. Minisci, F. Recupero, Tetrahedron Letters 42 (2001) 6651.
[28] K. Hintzer, D.E. Vogel, M.A. Guerra, J. Ignatowska, G.-V. Röschenthaler, O. Shyshkov, K.M. Vogel, T.C. Zipplies, WO2011/050131A2.
[29] M. Shibuya, M. Tomizawa, Y. Sasano, Y. Iwabuchi, Journal of Organic Chemistry 74 (2009) 4619.
[30] A. Battais, Y. Boutevin, Y. Pietrasanta, P. Sierra, Journal of Fluorine Chemistry 19 (1981) 35.
[31] J.D. Lazerte, R.J. Koshar, Journal of the American Chemical Society 77 (1955) 910.