Journal of Fluorine Chemistry, 49 (1990) 433–437

Received March 6, 1990, accepted May 28, 1990

PRELIMINARY NOTE

Reaction Of Perhalofluoroalkyl Sulfinates With One-Electron Transfer Oxidants. A Facile Method For the Synthesis Of Perhalofluorocarboxylic Acids

CHANG-MING HU , ZE-QI XU AND WEI-YUAN HUANG

Shanghai Institute of Organic Chemistry, Shanghai 200032 (China)

SUMMARY

Reaction of perhalofluoroalkyl sulfinates with one-electron transfer oxidants, such as $(NH_4)_2S_2O_8$, $Ce(SO_4)_2$ or H_2O_2/Fe^{2+} afforded perhalofluorocarboxylic acids R_FCO_2H [R_F= $Cl(CF_2)_8OCF_2$, $F(CF_2)_8OCF_2$, C_7F_{15}, $Cl(CF_2)_5$] in good yield.

In recent years, fluorine chemists are interested in the conversion of perfluoroalkylsulfonyl fluorides ($R_FCF_2SO_2F$) into the corresponding perfluorocarboxylic acids[1]. For example, on hydrolysis with dilute H_2SO_4, varying amounts of both perfluorocarboxylic acid and perfluorosulfonic acid were formed from the corresponding perfluorosulfinate. Behr suggested that such a reaction was merely a kind of hydrolysis.

In previous paper[2], we reported that photooxidation of perhalofluoroalkyl sulfinates ($R_FCF_2SO_2Na$) afforded under mild conditions a simple and effective synthesis of perhalofluorocarboxylic acids and their esters in good yields. Mechanistic study showed that in these reactions a photochemical electron transfer from the sulfinates to oxygen took place and $R_FCF_2\cdot$ was formed. Such radicals can be trapped by t-BuNO and detected by ESR [3].

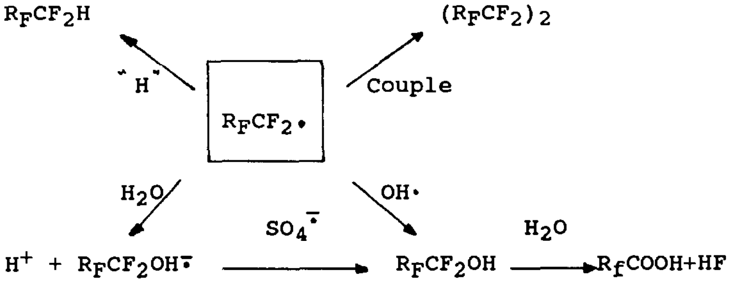
$$\underset{X,Y=F,Cl}{R_FCXYSO_2^-} \xrightarrow{UV} R_FCXYSO_2\cdot \longrightarrow R_FCXY\cdot \text{------} \xrightarrow{O_2 \text{ or } O_2^-} \underset{R=H,\ Me}{R_FCO_2R}$$

0022-1139/90/$3 50

The above facts seemed to suggest that perfluorocarboxylic acids could be synthesized via radical intermediates $R_FCF_2\bullet$. In order to verify such a hypothesis further, the reaction of perhalofluoroalkyl sulfinates with various one-electron transfer oxidizing agents like $(NH_4)_2S_2O_8$, $Ce(SO_4)_2$, H_2O_2/Fe^{2+} was examined. An alternative method for the synthesis of perfluorocarboxylic acids from the corresponding perfluorosulfinates was found.

The results shown in Table 1 indicated that oxidation of perhalofluoroalkyl sulfinates by $(NH_4)_2S_2O_8$ afforded the corresponding perhalofluorocarboxylic acids in good yields. The best molar ratio of R_FSO_2Na / oxidant was 1/(0.5-1). If the ratio was larger than that stated in Table 1, hydrogen abstraction products (R_FCF_2H) or coupled products $(R_FCF_2)_2$ could be isolated. The reaction rate was lowered if the ratio was less than the amount mentioned. The perfluo vinyl ether group ($CF_2{=}CFO{-}$) was totally destroyed under these conditions. A tentative mechanism of such reactions was postulated as follows.

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{\overline{\bullet}} \qquad \text{(ref. 4)}$$
$$R_FCF_2SO_2^- + SO_4^{\overline{\bullet}} \longrightarrow R_FCF_2SO_2\bullet + SO_4^{2-}$$
$$R_FCF_2SO_2\bullet \longrightarrow R_FCF_2\bullet + SO_2$$
$$H_2O + SO_4^{\overline{\bullet}} \longrightarrow HO\bullet + H^+ + SO_4^{2-}$$



Treatment of $R_FCF_2SO_2Na$ with aq. H_2O_2 gave the corresponding sulfonic acid as the major product.

$$\underset{}{C_8F_{17}SO_2Na} \xrightarrow[8h]{H_2O_2} \underset{68\%}{C_8F_{17}SO_3H} + \underset{24\%}{C_7F_{15}CO_2H}$$

In the presence of Fe^{2+}, however, oxidation of $R_FCF_2SO_2Na$ with H_2O_2 gave R_FCO_2H in good yields (Table 1). Apparently, Fe^{2+} relayed the electron transfer as depicted in the following.

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO\bullet + HO^- \qquad \text{(ref. 5)}$$

$$R_FCF_2SO_2^- + Fe^{3+} \longrightarrow R_FCF_2SO_2\bullet + Fe^{2+}$$

$$R_FCF_2SO_2\bullet \longrightarrow R_FCF_2\bullet + SO_2$$

$$R_FCF_2\bullet + HO\bullet \longrightarrow R_FCF_2OH \xrightarrow{-HF} R_FCFO \xrightarrow{H_2O} R_FCO_2H + HF$$

TABLE 1

Oxidation Of Sulfinates With One-Electron Transfer Oxidants

$$\underset{\textbf{1a--1d}}{R_FCF_2SO_2F} \xrightarrow{Na_2SO_3} \underset{\textbf{2a--2d}}{R_FCF_2SO_2Na} \xrightarrow[H_2O]{Oxidant} \underset{\textbf{3a--3d}}{R_FCO_2H}$$

a, $R_F=Cl(CF_2)_8OCF_2$; b, $R_F=F(CF_2)_8OCF_2$; c, $R_F=C_7F_{15}$; d, $R_F=Cl(CF_2)_5$

Starting Material	g(mmol)	Method[a]	Time (h)	Product	Yield[b] (%)
1a	5.0(7.90)	A	6	**3a**	87
1b	4.8(7.90)	A	8	**3b**	81
1c	5.0(9.96)	A	8	**3c**	79
2a	1.0(1.57)	B	3	**3a**	82
2b	1.0(1.60)	B	4	**3b**	88
2c	1.5(3.00)	B	6	**3c**	69
2a	1.0(1.57)	C	8	**3a**	59
2b	1.0(1.60)	C	8	**3b**	60
2c	0.8(1.60)	C	8	**3c**	53
2a	2.0(3.14)	D	5	**3a**	81
2c	2.5(4.98)	D	6	**3c**	85
2d	2.0(2.27)	D	5	**3d**	87

[a] See experimental.

[b] Isolated yield.

Method A

R_fSO_2F was reduced with Na_2SO_3 under N_2 in the usual way[6]. The sulfinate thus formed was dissolved in 60 ml H_2O and an equivalent molar quantity of $(NH_4)_2S_2O_8$ was added.The solution was then kept at 60-65°C for several hours. After that the solution was acidified and extracted with ether. Pure acid was obtained after distillation under reduced pressure or converted directly into the corresponding ester. The acid or ester thus obtained was characterized by IR, ^{1}H NMR and ^{19}F NMR.

3a. $Cl(CF_2)_8OCF_2COOH$ mp 160-161.5°C. δ_F (in CCl_4): -7.5(2F, S, CF_2Cl), 2.3(2F, S, OCF_2COOH), 7.2(2F, S, CF_2O), 44.3(2F, S, CF_2), 45.3(8F,broad S, 4XCF_2), 49.3(2F, S, CF_2)ppm.

3b. $F(CF_2)_8OCF_2COOCH_3$ bp 55°C(2mmHg). ν_{max} 1790 (vs, $COOCH_3$)cm. δ_H (neat): 3.92(S, OCH_3)ppm. δ_F (neat): 5.7(3F, S, CF_3), 7.0(2F, S, CF_2O), 45.5(8F, broad S, 4XCF_2), 49.3(2F, S, CF_2), 50.0(2F, S, CF_2)ppm.

3c. $C_7F_{15}COOCH_3$ bp 39-40°C(2.5mmHg). ν_{max} 1790(vs, $COOCH_3$). δ_H (neat): 3.98(S, OCH_3)ppm. δ_F (neat): 5.7(3F, S, CF_3), 42.7(2F, S, CF_2COOMe), 45.8-46.5(8F, broad S, 4XCF_2), 50.2(2F, S, CF_2)ppm.

Method B

Same as method A, except the molar ratio of sulfinate to $(NH_4)_2S_2O_8$ was changed from 1:1 to 2:1.

Method C

Same as method A, except an equivalent mole of $Ce(SO_4)_2 \cdot 5H_2O$ was used instead of $(NH_4)_2S_2O_8$.

Method D

$R_FCF_2SO_2Na$ and $FeSO_4 \cdot 7H_2O$ (3:1, molar ratio) were dissolved in 25ml H_2O and cooled to 0°C. 5ml H_2O_2 (ca.30%) was added dropwise with stirring within 30 min. Then the temperature was allowed to come to 25°C and the solution was stirred at that temperature for several hours. Perfluorocarboxylic acid was then isolated in the usual way.

3d $Cl(CF_2)_5COOH$ bp 94°C(30mmHg).δ_H (neat): 11.39(S)ppm. δ_F (neat): -9.3(2F, S, CF_2Cl), 40.4(2F, S, CF_2COOH), 43.0(2F, S, CF_2), 44.9(2F, S, CF_2), 52.2(2F, S, CF_2)ppm.

1 (a) F.E. Behr and G.G.I. Moore, J. Fluorine Chem., 29 (1985) 122.
(b) W.G. Grot, C.J. Molnar and P.R. Resnick, Ger. Offen, 2 817 315 (1978) and Pat. Specif. (Aust.), AU 544 027 (1985).
(c) K. Kimoto, H. Miyauchi, J. Ohmura, M. Ebisawa and T. Hane, Laid Open Jap. Pat. Appl., 55-160 029 (1980).
(d) M.Seko, Y.Yamakoshi, H.Miyauchi, M.Fukumoto, K.Kimoto, I.Watanabe, T.Hane and S.Tsushima, Ger. Offen, 2 630 584 (1975).

2 C.M. Hu, Z.Q. Xu and W.Y. Huang, J. Fluorine Chem., 42 (1989) 145.

3 C.M. Hu, Z.Q. Xu and F.L. Qing, Tetrahedron Lett., in press.

4 (a) M.K. Kberhardt, J. Am. Chem. Soc., 103 (1981) 3876.
(b) A. Ledwith, P.J. Russell and L.H. Sutcliffe, J. Chem. Soc., Chem. Comm., (1971) 964.

5 F. Fontana, F. Minisci and E. Vicmara, Tetrahedron Lett., 28 (1987) 6373.

6 F.J.Pavlik, U.S. Pat. 3 420 877; Chem. Abstr. 70 (1969) 67609.