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PRELIMINARY NOTE

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# Photooxidation of Perhalofluorosulfinates. A Simple and Effective Method for the Synthesis of Perhalofluorocarboxylic Acids and Their Esters from the Corresponding Sulfonyl Fluorides

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

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai (China)

## SUMMARY

Photooxidation promoted by ultraviolet irradiation of perhalofluorosulfinates afforded a simple and effective method for the synthesis of perhalofluorocarboxylic acids and their esters from the corresponding sulfonyl fluorides.

Nafion type ion-exchange membranes are now used widely as a separator in cells for chloroalkali electrolysis[1]. In order to improve the electrochemical properties of such membranes the conversion of the sulfonic acid group into the carboxylic acid group via sulfinates has been studied extensively in recent years[2]. However such conversions have to be done under rather severe conditions. Thus other vulnerable groups like $CF_2$=CFO- have to be protected[3] or in certain cases, the sulfinates were reconverted to sulfonates in varying amounts together with the

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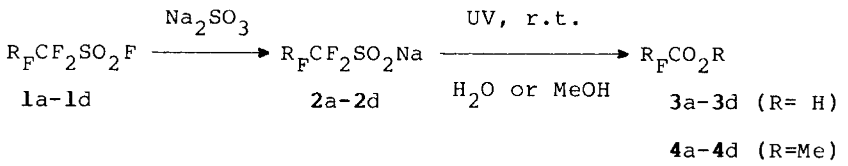
carboxylates[4]. In this paper a simple and effective method for the synthesis of perhalofluorocarboxylic acids and esters is described as the first example of photooxidation of perhalofluorosulfinates. The reaction conditions are mild enough so that even the perfluorovinyl ether group is unaffected.



$$\underset{\textbf{1a-1d}}{R_FCF_2SO_2F} \xrightarrow{Na_2SO_3} \underset{\textbf{2a-2d}}{R_FCF_2SO_2Na} \xrightarrow[H_2O \text{ or } MeOH]{UV,\ r.t.} R_FCO_2R$$

**3a-3d** (R= H)

**4a-4d** (R=Me)

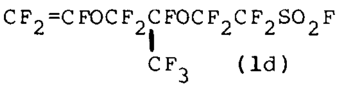
**Typical Procedure:** A mixture of a sulfonyl fluoride(**1a-1d**) and $Na_2SO_3$ in $H_2O$-$CH_3CN$ was heated at 75-80°C for 8h with vigorous stirring under $N_2$. The resultant mixture was then treated by one of the following methods. (A) The mixture was diluted with $H_2O$ to 100ml and irradiated with a 500W high-pressure mercury lamp at ca.15°C. (B) The mixture was evaporated to dryness, extracted with AcOEt and dried. After the removal of solvent, perhalofluorosulfinate (**2a-2d**) was obtained. The sulfinate was then dissolved in 100ml $H_2O$ and irradiated. After the reaction was completed, the aqueous solution was saturated with NaCl, and extracted with $Et_2O$. (C) The dried sulfinate (**2a-2d**) was dissolved in 80ml MeOH, then irradiated under the same conditions. After that the methanolic solution was poured into 200ml $H_2O$ and extracted with $Et_2O$. Table 1 shows some of the results.

As shown in Table 1, except for Runs 2, 3 and 6, the photooxidation of the sulfinate gave the corresponding acid or ester in good yields. Though **1c** and **2b** were oxidized to sulfonates in aqueous solution, their corresponding esters were formed in acceptable yields when methanol was used as solvent(Runs 8 and 9).

Considering that most F-containing salts are good surfactants in aqueous solution, it is reasonable to suppose that such type of reaction is better to be performed in non-aqueous solution where micelles could only be formed with difficulty.

TABLE 1

**The Photooxidation of Sulfinates**

| Run No. | Starting Material | g(mmol) | Method | Time (h) | Product | Yield (%)$^a$ |
|---|---|---|---|---|---|---|
| 1 | $Cl(CF_2)_8OCF_2CF_2SO_2F$(**1a**) | 3.3(5.25) | A | 5 | **3a** | 94 |
| 2 | $F(CF_2)_8OCF_2CF_2SO_2F$(**1b**) | 6.0(9.7) | A | 7 | **3b** | $52^b$ |
| 3 | $C_8F_{17}SO_2F$(**1c**) | 10.0(19.9) | A | 6 | **3c** | $<5^c$ |
| 4 |  $CF_2{=}CFOCF_2\underset{CF_3}{\underset{\mid}{C}}FOCF_2CF_2SO_2F$ (**1d**) | 10.0(22.4) | A | 7 | **4d** | $66^d$ |
| 5 | **2a** | 4.3(6.7) | B | 5 | **3a** | 95 |
| 6 | **2b** | 4.2(6.8) | B | 5 | **3b** | $26^e$ |
| 7 | **2a** | 3.7(5.8) | C | 8 | **4a** | 82 |
| 8 | **2b** | 3.0(4.8) | C | 6 | **4b** | 85 |
| 9 | **2c** | 6.0(11.8) | C | 6 | **4c** | 67 |

[a] isolated yield. [b] some sulfonic acid was formed. [c] only $C_8F_{17}SO_3H$ was formed. [d] the acid was esterified with MeOH. [e] the main product was $F(CF_2)_8OCF_2CF_2SO_3Na$(72%).

In fact, micelle formation could alter the environment of the photochemical reaction and the composition of products [5]. Such a micellar effect was confirmed further by the following two experiments. When an aqueous solution of **2a** and $C_{12}H_{25}SO_4Na$ (mole ratio 1:0.97) was irradiated with UV, **3a** and another product $[Cl(CF_2)_8OCF_2CF_2H]$ were obtained at ratio 59:41. In a mixed solution of $H_2O$-EtOH (60:20), the yield of **3c** was increased from less than 5%(e.g. Run 3) to 53% through the photooxidation of **2c**.

The mechanism of the reaction is now under study.

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