

# Studies on sulfinatodehalogenation. XXIX. The sulfinatodehalogenation of primary polyfluoroalkyl iodides and bromides by sodium disulfite

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## Abstract

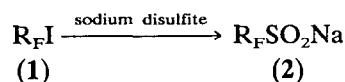
Using DMF, acetonitrile and alcohols as cosolvents, both polyfluoroalkyl iodides, such as  $\text{Cl}(\text{CF}_2)_n\text{I}$  ( $n=4, 6, 8$ ; **1a–c**) and  $\text{F}(\text{CF}_2)_n\text{I}$  ( $n=6, 8$ ; **1d, e**), and polyfluoroalkyl bromides, such as  $\text{Cl}(\text{CF}_2)_6\text{Br}$  (**3b**) and  $\text{F}(\text{CF}_2)_8\text{Br}$  (**3e**), react with sodium disulfite in neutral aqueous solution to give the corresponding sulfinates  $\text{Cl}(\text{CF}_2)_n\text{SO}_2\text{Na}$  ( $n=4, 6, 8$ ; **2a–c**) and  $\text{F}(\text{CF}_2)_n\text{SO}_2\text{Na}$  ( $n=6, 8$ ; **2d, e**) in good yield. In a similar manner,  $\text{CF}_3\text{CCl}_3$  (**4a**) reacted with sodium disulfite to give  $\text{CF}_3\text{CCl}_2\text{SO}_2\text{Na}$  (**5a**).

## Introduction

Since we discovered the first sulfinatodehalogenation reaction using sodium sulfite in aqueous dioxan solution [1], several new sulfinatodehalogenation reagents have been found such as dithionite [2], thiourea dioxide [3] and Rongalite [4]. To study the reaction and expand the range of reaction reagents, we have continued searching for new sulfinatodehalogenation reagents.

Sodium disulfite is a weak reductant, usually used in redox catalyst systems with persulfate for polymerization [5]. In the presence of an initiator, sodium disulfite can add to C=C bonds [6]. It was also been reported that sodium disulfite can react with propargyl chloride to give propargyl sulfonate [7]. Here we wish to report a new application of sodium disulfite in sulfinatodehalogenation reactions.

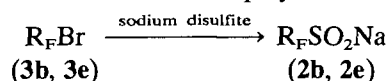
In neutral aqueous dimethylformamide (DMF) solution, sodium disulfite reacted with polyfluoroalkyl iodides (**1a–e**) to form the corresponding polyfluoroalkanesulfinates (**2a–e**).



[**(a)**  $\text{R}_F = \text{Cl}(\text{CF}_2)_4$ ; **(b)**  $\text{R}_F = \text{Cl}(\text{CF}_2)_6$ ; **(c)**  $\text{R}_F = \text{Cl}(\text{CF}_2)_8$ ; **(d)**  $\text{R}_F = \text{F}(\text{CF}_2)_6$ ; **(e)**  $\text{R}_F = \text{F}(\text{CF}_2)_8$ ]

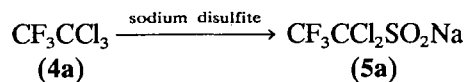
Although the C–Br bond is much stronger than the C–I bond, polyfluoroalkyl bromides also react with

sodium disulfite in a similar manner if an extended reaction time is employed.



The optimal reaction temperature range was 70–80 °C. Alcohols and acetonitrile could be used as cosolvents, but the ratio of the solvents had a considerable effect upon the reaction. When the volume ratio of water to alcohols or acetonitrile was less than 1:1, the sulfinatodehalogenation reaction of sodium disulfite proceeded well. Under other circumstances, the polyfluoroalkyl halides were recovered. Further results are listed in Table 1.

$\text{CF}_3\text{CCl}_3$  reacted with sodium disulfite to give 1,1-dichlorotrifluoromethane sulfinates, but the yield was low.



We suggest that the sodium disulfite forms the anion radicals of  $\text{SO}_2$  and/or  $\text{SO}_3$  and that the reaction is initiated by these anion radicals and proceeds through a single-electron-transfer process. Polar solvents, such as DMF,  $\text{CH}_3\text{CN}$  and alcohols, may favor homolysis of the S–S bond.

## Experimental

Temperatures were uncorrected. IR spectra were recorded on Perkin–Elmer 983 and IR-440 spectro-

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TABLE 1. The effect of solvent and temperature on the reaction of sodium disulfite with **1a** (conversion and yield of sulfinate determined by  $^{19}\text{F}$  NMR spectroscopy)

Entry No.	Solvent <sup>a</sup>	Volume ratio	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)
1	a/b	3:1	85	12	0	—
2	a/b/d	3:1:1	85	24	100	90
3	a/b/d	3:1:1	85	11	83	60
4	a/d	1:3	85	24	0	—
5	a/d	3:1	80	11	50	50
6	c/d	3:1	80	16	100	50
7	c/d	3:1	10	13	0	—
8	b/d	2:1	80	10	80	80
9	c/d	2:1	80	2	100	90
10 <sup>b</sup>	e/d	3:1	30	12	75	75
11	e	—	80	3	0	—
12 <sup>c</sup>	d	—	25	0.5	0	—
13	c/d	2:1	50	12	100	86

<sup>a</sup>a, acetonitrile; b, methanol; c, ethanol; d, water; e, DMF.

<sup>b</sup>R<sub>F</sub>I was Cl(CF<sub>2</sub>)<sub>2</sub>I.

<sup>c</sup>With ultrasonic radiation.

meters with KBr pellets.  $^{19}\text{F}$  NMR spectra were recorded on a Varian EM-360L spectrometer at 60 MHz. Chemical shifts were positive upfield using TFA as external standard. The values reported are  $\delta_{\text{F}} = \delta_{\text{TFA}} + 76.8$  ppm. All materials were of commercial grade and were used without further purification.

#### Typical procedure

A mixture consisting of **1b** (2.3 g, 5.0 mmol), sodium disulfite (1.90 g, 10 mmol), DMF (10 ml) and water (5 ml) was stirred vigorously at 80 °C for 2 h. The solvent was removed under reduced pressure and the dry solid left in the flask was extracted with hot ethyl acetate (3 × 20 ml). The ester solution was evaporated to dryness and the solid remaining recrystallized from isopropanol to yield **2b** (1.71 g, 81%). IR  $\nu_{\text{max}}$  cm<sup>-1</sup>: 1020 (SO<sub>2</sub>Na).  $^{19}\text{F}$  NMR (EtOAc)  $\delta$ : 67.2 (2F, s, CF<sub>2</sub>Cl); 119.0 (2F, m, CF<sub>2</sub>CF<sub>2</sub>Cl); 130.0 (2F, s, CF<sub>2</sub>SO<sub>2</sub>Na); 121.0 (6F, m, other fluorine atoms) ppm.

Compounds **1a** and **1c–1e** were converted to **2a** (85%), **2c** (79%), **2d** (80%) and **2e** (77%), respectively [4], in a similar manner.

Compound **2a**: IR  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 1020 (SO<sub>2</sub>Na).  $^{19}\text{F}$  NMR (EtOAc)  $\delta$ : 68.8 (2F, s, CF<sub>2</sub>Cl); 120.1 (2F, m, CF<sub>2</sub>CF<sub>2</sub>Cl); 122.3 (2F, m, CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>Na); 131.0 (2F, s, CF<sub>2</sub>SO<sub>2</sub>Na) ppm.

Compound **2e**: Colorless needles. IR  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 1020 (SO<sub>2</sub>Na).  $^{19}\text{F}$  NMR (EtOAc)  $\delta$ : 81.5 (3F, s, CF<sub>3</sub>); 127.0 (2F, m, CF<sub>2</sub>CF<sub>3</sub>); 131.0 (2F, s, CF<sub>2</sub>SO<sub>2</sub>Na); 122.7 (10F, m, other fluorine atoms) ppm.

The other products were characterized by comparison of their IR and  $^{19}\text{F}$  NMR spectra with those of the corresponding authentic compounds [4].

#### Reaction of polyfluoroalkyl bromides with sodium disulfite

In a typical process, a mixture of **3e** (2.49 g, 5 mmol), sodium disulfite (1.90 g, 10 mmol), DMF (10 ml) and water (5 ml) was stirred at 80 °C for 6 h. Treatment as above gave **2e** (1.97 g, 78%). Compound **3b** was converted to **2b** (79%) in a similar manner [4].

#### Reaction of **4a** with sodium disulfite

A mixture of **4a** (3.70 g, 20 mmol), sodium disulfite (7.60 g, 40 mmol), DMF (20 ml) and water (10 ml) was stirred at 60 °C for 9 h. Treatment as above gave **5a** (0.88 g, 19%), colorless crystals. IR  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 1020 (SO<sub>2</sub>Na).  $^{19}\text{F}$  NMR (EtOAc)  $\delta$ : 71.8 ppm. These IR and  $^{19}\text{F}$  NMR spectra are in agreement with those of an authentic specimen [8].

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