

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

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Abstract

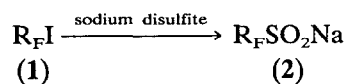
Using DMF, acetonitrile and alcohols as cosolvents, both polyfluoroalkyl iodides, such as $\text{Cl}(\text{CF}_2)_n\text{I}$ ($n=4, 6, 8$; **1a–c**) and $\text{F}(\text{CF}_2)_n\text{I}$ ($n=6, 8$; **1d, e**), and polyfluoroalkyl bromides, such as $\text{Cl}(\text{CF}_2)_6\text{Br}$ (**3b**) and $\text{F}(\text{CF}_2)_8\text{Br}$ (**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, CF_3CCl_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 $\text{C}=\text{C}$ 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.

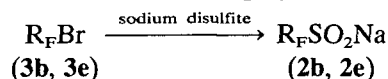
In neutral aqueous dimethylformamide (DMF) solution, sodium disulfite reacted with polyfluoroalkyl iodides (**1a–e**) to form the corresponding polyfluoroalkanesulfinates (**2a–e**).



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

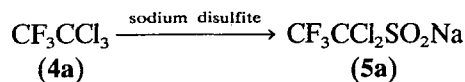
Although the $\text{C}-\text{Br}$ bond is much stronger than the $\text{C}=\text{I}$ bond, polyfluoroalkyl bromides also react with

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.

CF_3CCl_3 reacted with sodium disulfite to give 1,1-dichlorotrifluoromethane sulfinate, but the yield was low.



We suggest that the sodium disulfite forms the anion radicals of SO_2 and/or 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, CH_3CN and alcohols, may favor homolysis of the $\text{S}-\text{S}$ 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}F NMR spectroscopy)

Entry No.	Solvent ^a	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 ^b	e/d	3:1	30	12	75	75
11	e	—	80	3	0	—
12 ^c	d	—	25	0.5	0	—
13	c/d	2:1	50	12	100	86

^aa, acetonitrile; b, methanol; c, ethanol; d, water; e, DMF.

^bR_FI was Cl(CF₂)₂I.

^cWith ultrasonic radiation.

meters with KBr pellets. ^{19}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 ν_{max} cm⁻¹: 1020 (SO₂Na). ^{19}F NMR (EtOAc) δ : 67.2 (2F, s, CF₂Cl); 119.0 (2F, m, CF₂CF₂Cl); 130.0 (2F, s, CF₂SO₂Na); 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 ν_{max} (cm⁻¹): 1020 (SO₂Na). ^{19}F NMR (EtOAc) δ : 68.8 (2F, s, CF₂Cl); 120.1 (2F, m, CF₂CF₂Cl); 122.3 (2F, m, CF₂CF₂SO₂Na); 131.0 (2F, s, CF₂SO₂Na) ppm.

Compound **2e**: Colorless needles. IR ν_{max} (cm⁻¹): 1020 (SO₂Na). ^{19}F NMR (EtOAc) δ : 81.5 (3F, s, CF₃); 127.0 (2F, m, CF₂CF₃); 131.0 (2F, s, CF₂SO₂Na); 122.7 (10F, m, other fluorine atoms) ppm.

The other products were characterized by comparison of their IR and ^{19}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 ν_{max} (cm⁻¹): 1020 (SO₂Na). ^{19}F NMR (EtOAc) δ : 71.8 ppm. These IR and ^{19}F NMR spectra are in agreement with those of an authentic specimen [8].

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