Journal of Fluorine Chemistry, 67 (1994) 233–234

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

Wu Fan-Hong and Huang Bing-Nan*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032 (China)

(Received March 12, 1993; accepted June 9, 1993)

Abstract

Using DMF, acetonitrile and alcohols as cosolvents, both polyfluoroalkyl iodides, such as $Cl(CF_2)_nI$ ($n=4$, 6, 8; **1a–c**) and $F(CF_2)_nI$ ($n=6$, 8; **1d**, **e**), and polyfluoroalkyl bromides, such as $Cl(CF_2)_6Br$ (**3b**) and $F(CF_2)_8Br$ (**3e**), react with sodium disulfite in neutral aqueous solution to give the corresponding sulfinates $Cl(CF_2)_nSO_2Na$ ($n=4$, 6, 8; **2a–c**) and $F(CF_2)_nSO_2Na$ ($n=6$, 8; **2d**, **e**) in good yield. In a similar manner, CF_3CCl_3 (**4a**) reacted with sodium disulfite to give $CF_3CCl_2SO_2Na$ (**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**).

$$\underset{(\mathbf{1})}{R_FI} \xrightarrow{\text{sodium disulfite}} \underset{(\mathbf{2})}{R_FSO_2Na}$$

[(**a**) $R_F=Cl(CF_2)_4$; (**b**) $R_F=Cl(CF_2)_6$; (**c**) $R_F=Cl(CF_2)_8$; (**d**) $R_F=F(CF_2)_6$; (**e**) $R_F=F(CF_2)_8$]

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.

$$\underset{(\mathbf{3b},\ \mathbf{3e})}{R_FBr} \xrightarrow{\text{sodium disulfite}} \underset{(\mathbf{2b},\ \mathbf{2e})}{R_FSO_2Na}$$

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.

$$\underset{(\mathbf{4a})}{CF_3CCl_3} \xrightarrow{\text{sodium disulfite}} \underset{(\mathbf{5a})}{CF_3CCl_2SO_2Na}$$

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 S−S bond.

Experimental

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

---

*Author to whom correspondence should be addressed.

SSDI 0022-1139(93)02964-G

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	e/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	e/d	2:1	50	12	100	86

[a] a, acetonitrile; b, methanol; c, ethanol; d, water; e, DMF.
[b] R_FI was $Cl(CF_2)_2I$.
[c] With 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 $\delta_F = \delta_{TFA} + 76.8$ 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 (SO_2Na). ^{19}F NMR (EtOAc) δ: 67.2 (2F, s, CF_2Cl); 119.0 (2F, m, CF_2CF_2Cl); 130.0 (2F, s, CF_2SO_2Na); 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 (SO_2Na). ^{19}F NMR (EtOAc) δ: 68.8 (2F, s, CF_2Cl); 120.1 (2F, m, CF_2CF_2Cl); 122.3 (2F, m, $CF_2CF_2SO_2Na$); 131.0 (2F, s, CF_2SO_2Na) ppm.

Compound **2e**: Colorless needles. IR ν_{max} (cm^{-1}): 1020 (SO_2Na). ^{19}F NMR (EtOAc) δ: 81.5 (3F, s, CF_3); 127.0 (2F, m, CF_2CF_3); 131.0 (2F, s, CF_2SO_2Na); 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 **3c** (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 (SO_2Na). ^{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].

References

1 W.-Y. Huang, B.-N. Huang and C.-M. Hu, *J. Fluorine Chem.*, *23* (1983) 193.
2 W.-Y. Huang, B.-N. Huang and W. Wang, *Acta Chim. Sinica*, *43* (1985) 252.
3 W.-Y. Huang and J.-L. Zhuang, *Chin. Chem. Lett.*, *1* (1990) 191.
4 B.-N. Huang and J.-T. Liu, *Chin. J. Chem.*, *8* (1990) 355.
5 N. Hiroshi, *Jpn. Kokai Tokkyo, Koho, 78 106 721* (1978); [*Chem. Abs.*, *90* (1978) 39587e].
6 P. Emilio and N. Carlo, *Ger. Offen. 2 460 246* (1975); [*Chem. Abs.*, *83* (1975) 163 638s].
7 B. Dung, J. Houben and A. Oftring, *Ger. Offen. DE 3 830 696* (1990); [*Chem. Abs.*, *112* (1990) P237 202].
8 W.-Y. Huang, B.-N. Huang and J.-L. Chen, *Acta Chim. Sinica*, *44* (1986) 45.