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Practical and efficient synthesis of perfluoroalkyl iodides from perfluoroalkyl chlorides via modified sulfinatodehalogenation

Hai-Ping Cao, Qing-Yun Chen *

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

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Abstract

A novel two-step one pot synthesis of perfluoroalkyl iodides (α,ω-diiodoperfluoroalkanes) from perfluoroalkyl chlorides (α-chloro-ω-iodoperfluoroalkanes) has been developed by initial conversion to the corresponding sodium perfluoroalkanesulfinates with sodium dithionite and then subsequent oxidation by iodine.

Keywords: Perfluoroalkyl iodides; Perfluoroalkyl chlorides; Sulfinatodehalogenation

1. Introduction

Perfluoroalkyl iodides (R_FI) and α,ω-diiodoperfluoroalkanes[$I(CF_2)_nI$, $n \geqq 1$] are one of the most important, fundamental materials for preparation of other fluorinated compounds or polymers [1–4]. For example, telomerization of fluoroethylenes with R_FI as transfer agents results in the formation of fluorinated telomers. α,ω-Diiodoperfluoroalkanes can be easily converted into other bifunctional groups, such as $–C_2H_4OH$, $–CH_2CO_2H$, $–CH=CH_2\cdots$, from which may further afford fluorinated polymers. All these are involved in many applications (aeronautics, aerospace, engineering, optics, textile finishing, microelectronics) in spite of their high price [4]. Perfluoroalkyl iodides can be prepared by Hunsdiecker's reaction, i.e. pyrolytic reaction of silver salts of perfluorocarboxylic acids in the presence of iodine [5]. The corresponding acids usually come from the electrochemical fluorination of carboxylic acids [6]. Pentafluoroethyl iodide, the most important iodide, may be simply prepared by addition-fluorination of HF/ICl to tetrafluoroethylene (TFE) [7]. However, on an industrial scale it is more effectively manufactured by the reaction TFE with I_2/IF_5 [8,9]. As compared with R_FI, the synthesis of α,ω-diiodoperfluoroalkanes is more difficult and expensive. Fluorinated telechelic diiodides can be derived from the corresponding acid chlorides (KI/200 °C), acid fluoride (KF/I_2 or LiI, >180 °C) or silver salts (I_2/200 °C) [5,10–12]. Both thermally and photochemically induced addition of iodine to TFE leads to ICF_2CF_2I with high yields. However, an excess of TFE under pressure at higher temperature affords higher adducts $[I(CF_2CF_2)_nI$, $n = 1–5]$ due to the known fluorinated radical β-scission [13,14]. On the other hand, per(poly)fluoroalkyl bromides and chlorides, such as R_FX, $RCFX_2$, RCF_2X, $X(CF_2)_nX$, $X(CF_2)_nI$ (X = Cl, Br) are relatively available [15]. Among them, β-chlorotetrafluoroethyl iodide and its telomers with TFE are readily synthesized and telomerized in large scale [16,17]. It would be of interest to convert these α,ω-dihaloperfluoroalkanes into the corresponding diiodides. Based on the modified sulfinatodehalogenation method, we successfully realized this target [18]. Herein, our results are presented.

2. Results and discussion

The sulfinatodehalogenation method discovered by Huang et al. [19] and modified by us [20], has become a widely convenient initiation system not only for perfluoroalkyl iodides, bromides, R_FCCl_3, but also for perfluoroalkyl chlorides and even nonfluorinated compounds such as ethyl dichloroacetate, CCl_3H to give the corresponding sulfinate salts in the presence of $Na_2S_2O_4/NaHCO_3$ in DMSO [20]. According to this method,

* Corresponding author. Fax: +86 21 64166128.
E-mail address: chenqy@mail.sioc.ac.cn (Q.-Y. Chen).

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we envisioned to synthesize perfluoroalkanesulfinates first, which then might be converted into the corresponding iodides. Using $I(CF_2)_4Cl$ (**1a**) as an example, its monosodium sulfinate (**2a**) and disodium sulfinate (**3a**) can be prepared depending on the solvent and reaction temperature used (Scheme 1).

In CH_3CN/H_2O or DMSO at room temperature for 3 h, **2a** was formed nearly quantitatively, as determined by ^{19}F NMR spectra from the reaction of **1a** with $Na_2S_2O_4$ (molar ratio = 1:2). A relatively pure **2a** [only signals of ^{19}F NMR at −68.6 ppm (2F, $ClCF_2$), −120.4 ppm (2F, CF_2), −121.8 ppm (2F, CF_2), −130.0 ppm (2F, CF_2SO_2Na) and no proton signals of ^1H NMR] has been isolated after sequent evaporation, extraction with ethyl acetate and evaporation. When the reaction was carried out in DMSO at higher temperature (e.g. 100 °C), the disodium salt **3a** was quickly (15 min) obtained also quantitatively as determined by its ^{19}F NMR spectrum [with signals of ^{19}F NMR at −122.2 ppm (4F, CF_2), −130.4 ppm (4F, CF_2SO_2Na)]. All attempts to isolate **3a** from the reaction mixture failed because of its instability.

Concerning the chemical conversion of the sulfinates, we are aware that they can react with iodine to form perfluoroalkanesulfonyl iodides which are extremely unstable and decompose even at −30 °C to give the corresponding iodides after evolution of SO_2 [21]. This is the result that we needed.

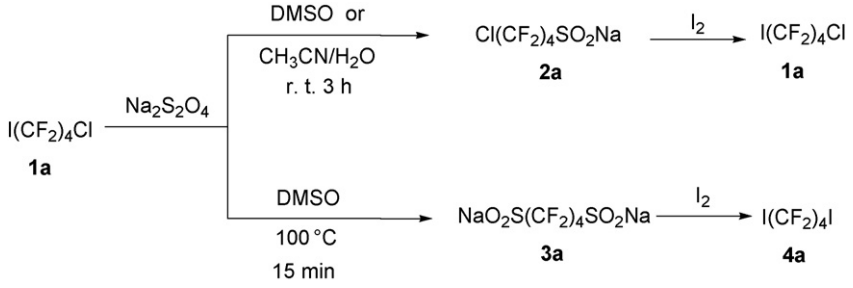
Table 1
The reaction of **2a** with iodine[a]
$Cl(CF_2)_4SO_2Na$ (**2a**) $\longrightarrow^{I_2\ \text{oxidant}}_{\text{solvent}\ (r.t.)}$ $I(CF_2)_4Cl$ (**1a**)

Entry	Oxidant	Solvent	Yield[b]
1	None	DMSO	60
2	None	HOAc	60
3	None	CH_3CN	60
4	None	$DMSO/H_2O$	62
5	$Na_2S_2O_8$	DMSO	61
6	$KMnO_4$	DMSO	55
7	$Na_2S_2O_8$	$DMSO/H_2O$	65

[a] **2a**:I_2 = 1:2, at room temperature for 1 h.
[b] Isolated yield.

Thus, mixing and stirring **2a** and 2 equiv. I_2 in DMSO at room temperature for 1 h gave monoiodide **1a** in 60% yield (entry 1, Table 1). The yields were similar if acetic acid or CH_3CN was used as a solvent instead of DMSO (entries 2–3, Table 1).

Sodium perfluoroalkanesulfinates are known to be oxidized readily with various oxidants to produce perfluoroalkyl radicals [22]. We envisioned that addition of a stronger oxidant might accelerate to generate perfluoroalkyl radicals. However it was found that only a slightly better yield of **1a** (entries 5–7, Table 1) was obtained when adding an oxidant such as $Na_2S_2O_8$



Scheme 1. Sulfinatodehalogenation reaction of **1a**.

Table 2
Synthesis of R_FI via R_FSO_2Na
R_FX (**1**) $\longrightarrow^{Na_2S_2O_4}_{DMSO\ (T)}$ R_FSO_2Na (**3**) $\longrightarrow^{I_2}_{r.t.\ (1\,h)}$ R_FI (**4**)

Entry	Substrate	T (°C)	R_FSO_2Na (%)[a]	R_FI (%)[b]	R_FI (%)[c]
1	$I(CF_2)_4Cl$ (**1a**)	100	$NaO_2S(CF_2)_4SO_2Na$ (**3a**) (100)	$I(CF_2)_4I$ (**4a**) (44)	$I(CF_2)_4I$ (**4a**) (40)
2	$I(CF_2)_4Cl$ (**1a**)	r.t.	$Cl(CF_2)_4SO_2Na$ (**3a′**) (100)	$I(CF_2)_4Cl$ (**1a**) (43)	$I(CF_2)_4Cl$ (**1a**) (42)
3	$I(CF_2)_6Cl$ (**1b**)	100	$NaO_2S(CF_2)_6SO_2Na$ (**3b**) (100)	$I(CF_2)_6I$ (**4b**) (54)	$I(CF_2)_6I$ (**4b**) (49)
4	$I(CF_2)_6Cl$ (**1b**)	r.t.	$Cl(CF_2)_6SO_2Na$ (**3b′**) (100)	$I(CF_2)_6Cl$ (**1b**) (51)	$I(CF_2)_6Cl$ (**1b**) (50)
5	$I(CF_2)_8Cl$ (**1c**)	100	$NaO_2S(CF_2)_8SO_2Na$ (**3c**) (100)	$I(CF_2)_8I$ (**4c**) (61)	$I(CF_2)_8I$ (**4c**) (55)
6	$I(CF_2)_8Cl$ (**1c**)	r.t.	$Cl(CF_2)_8SO_2Na$ (**3c′**) (100)	$I(CF_2)_8Cl$ (**1c**) (55)	$I(CF_2)_8Cl$ (**1c**) (53)
7	$F(CF_2)_6Cl$ (**1d**)	100	$F(CF_2)_6SO_2Na$ (**3d**) (100)	$F(CF_2)_6I$ (**4d**) (40)	$F(CF_2)_6I$ (**4d**) (40)
8	$F(CF_2)_8Cl$ (**1e**)	100	$F(CF_2)_8SO_2Na$ (**3e**) (100)	$F(CF_2)_8I$ (**4e**) (46)	$F(CF_2)_8I$ (**4e**) (42)
9	$Br(CF_2)_6Br$ (**1f**)	r.t.	$NaO_2S(CF_2)_6SO_2Na$ (**3b**) (100)	$I(CF_2)_6I$ (**4b**) (54)	$I(CF_2)_6I$ (**4b**) (50)
10	$I(CF_2)_2O(CF_2)_2SO_2F$ (**1g**)	r.t.	$NaO_2S(CF_2)_2O(CF_2)_2SO_2Na$ (**3g**) (100)	$I(CF_2)_2O(CF_2)_2I$ (**4g**) (65)	$I(CF_2)_2O(CF_2)_2I$ (**4g**) (60)
11	$Cl(CF_2)_8Cl$ (**1h**)	100	$NaO_2S(CF_2)_8SO_2Na$ (**3c**) (20)	$I(CF_2)_8I$ (**4c**) (10)	$I(CF_2)_8I$ (**4c**) (10)
12	$F(CF_2)_6I$ (**4d**)	r.t.	$F(CF_2)_6SO_2Na$ (**3d**) (100)	$F(CF_2)_6I$ (**4d**) (50)	$F(CF_2)_6I$ (**4d**) (50)
13	$F(CF_2)_8I$ (**4e**)	r.t.	$F(CF_2)_8SO_2Na$ (**3e**) (100)	$F(CF_2)_8I$ (**4e**) (57)	$F(CF_2)_8I$ (**4e**) (54)
14	CF_3Cl (**1i**)	80	CF_3SO_2Na (**3i**) (100)	CF_3I (**4i**) (40)[d]	CF_3I (**4i**) (40)[d]

[a] **1**:$Na_2S_2O_4$:I_2 = 1:4:4, the conversion determined by ^{19}F NMR.
[b] **3**:$Na_2S_2O_8$:I_2 = 1:4:4, $DMSO/H_2O$ (v:v = 1:1), the isolated yields based on **1**.
[c] **3**:I_2 = 1:4, $DMSO/H_2O$ (v:v = 1:1), $Na_2S_2O_8$ was absent, the isolated yields based on **1**.
[d] The yield was determined by ^{19}F NMR.

or $KMnO_4$ (2 equiv.) in DMSO or DMSO/H_2O (vol:vol = 1:1). The results are listed in Table 1.

Similarly, treatment of disodium sulfinate **3a** with iodine in DMSO at room temperature for 1 h, gave **4a** in a low yield (20%), but it could be improved to 44% in DMSO/H_2O (vol:vol = 1:1) for 1 h. All the results are listed in Table 2.

It is noted that compared with ICF_2CF_2I, telomerization of ICF_2CF_2Cl with TFE can be carried out more effectively due to the absence of fluorinated radical β-scission [16,17]. Telomers $Cl(CF_2CF_2)_nI$ obtained are the starting materials in this work. They may be first fluorinated with Swartz's reagent ($HF/SbCl_5$) to give $Cl(CF_2CF_2)_nF$, which can be then converted into $F(CF_2CF_2)_nI$ as described above (entries 7 and 8, Table 2). In this case, there is no need of IF_5 for preparing the commercial TFE-telogen CF_3CF_2I [8,9]. On the other hand, the telomers $Cl(CF_2CF_2)_nI$ may be directly transferred to valuable α,ω-diiodoperfluoroalkanes by our method.

3. Conclusion

In summary, we have developed a practical and convenient method for converting $Cl(CF_2CF_2)_nI$ into $F(CF_2CF_2)_nI$ or $I(CF_2CF_2)_nI$ by modified sulfinatodehalogenation method ($Na_2S_2O_4$/DMSO). Further studies on transferring the sulfinates to other functional groups are underway in our laboratory.

4. Experimental

4.1. General

^{19}F NMR spectra were recorded at 282 MHz. Chemical shifts were reported in parts per million relative to $CFCl_3$ as an external standard (positive for up field shifts) for ^{19}F NMR. The solvent for NMR measurement was $CDCl_3$ unless otherwise noted. DMSO were distilled from CaH_2.

4.2. Preparation of 1,4-diiodo-1,1,2,2,3,3,4,4-octafluorobutane from 1-chloro-4-iodo-1,1,2,2,3,3,4,4-octafluorobutane

Under a nitrogen atmosphere, 1-chloro-4-iodo-1,1,2,2,3,3,4,4-octafluorobutane (**1a**) (7.25 g, 20 mmol), $Na_2S_2O_4$ (13.92 g, 80 mmol) and DMSO (100 mL) was added to a 250 mL three-necked round-bottomed flask equipped with stirrer and condenser. The mixture was then heated to 100 °C for 15 min. The conversion of **1a** was 100%, determined by ^{19}F NMR spectra [signals of ^{19}F NMR at −122.2 ppm (4F, CF_2), −130.4 ppm (4F, CF_2SO_2Na)]. After cooling, water (100 mL), $Na_2S_2O_8$ (19.04 g, 80 mmol) and iodine (20.32 g, 80 mmol) was added to the mixture and allowed to react at room temperature for another 1 h. The resultant solution was extracted with ether (3 × 30 mL). The combined extracts were washed with saturated sodium thiosulfate (3 × 30 mL), water (3 × 20 mL) and dried over Na_2SO_4. After removing ether, the residue was distilled to give **4a** (4.0 g, 44%) as a red oil, b.p. 145 °C (lit. [23], 60–63 °C/35 Torr). ^{19}F NMR: $\delta = -58.7$ to −58.8 (m, 4F), −112.1 to −112.2 (m, 4F) (lit. [23], −65.0 (t, $J = 0.2$ Hz, 4F), −114.4 (t, $J = 0.2$ Hz, 4F)).

4b: Colorless oil. b.p. 102 °C/62 Torr (lit. [23], 80–83 °C/15 Torr). ^{19}F NMR: $\delta = -56.9$ (s, 4F), −111.0 (s, 4F), −118.7 (d, $J = 43.4$ Hz, 4F) (lit. [23], −65.0 (t, $J = 0.2$ Hz, 4F), −115.0 (m, 4F), −122.4 (m, 4F)).

4c: White solid. ^{19}F NMR: $\delta = -59.5$ (s, 4F), −113.5 (s, 4F), −121.3 (s, 4F), −122.1 (s, 4F) (lit. [23], −65.0 (t, $J = 0.2$ Hz, 4F), −115.0 (m, 4F), −123.3 (m, 8F)).

4d: Colorless oil. b.p. 115 °C (lit. [24], 117 °C). ^{19}F NMR: $\delta = -59.2$ (d, $J = 16.4$ Hz, 2F), −80.9 (t, $J = 8.0$ Hz, 3F), −113.2 (s, 2F), −121.8 (s, 2F), −122.8 (s, 2F), −126.2 (s, 2F) (lit. [25], −59.9, −82.2, −114.1, −122.2, −123.6, −127.3).

4e: Colorless oil. b.p. 155 °C (lit. [24], 160–161 °C). ^{19}F NMR: $\delta = -59.2$ (t, $J = 15.9$ Hz, 2F), −80.8 (s, 3F), −113.1 (s, 2F), −120.9 (s, 2F), −121.9 (s, 4F), −122.7 (s, 2F), −126.2 (s, 2F) (lit. [26], −58.6, −82.3, −113.5, −122.4, −122.4, −122.4 (4F), −126.6)

4i: ^{19}F NMR: $\delta = -11.5$ (s, 3F) (lit. [27], −3.7 (s, 3F)).

4.3. Preparation of 1,6-diiodo-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane from 1,6-dibromo-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane

A mixture of 1,6-dibromo-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane (**1f**) (9.20 g, 20 mmol), $Na_2S_2O_4$ (13.92 g, 80 mmol) and DMSO (50 mL) was stirred at room temperature for 3 h under nitrogen. The conversion of **1f** was 100%, determined by ^{19}F NMR spectra [signals of ^{19}F NMR at −121.7 ppm (4F, CF_2), −122.2 ppm (4F, CF_2), −130.6 ppm (4F, CF_2SO_2Na)]. To the content was added water (50 mL), $Na_2S_2O_8$ (19.04 g, 80 mmol) and iodine (20.32 g, 80mmol) and allowed to react at room temperature for another 1 h. The resultant solution was extracted with ether (3 × 30 mL). The combined extracts were washed with saturated sodium thiosulfate (3 × 30 mL), water (3 × 20 mL) and dried over Na_2SO_4. After removing ether, the residue was distilled to give **4b** (6.0 g, 54%) as a colorless oil, b.p. 102 °C/62 Torr (lit. [23], 80–83 °C/15 Torr). ^{19}F NMR: $\delta = -56.9$ (s, 4F), −111.0 (s, 4F), −118.7 (d, $J = 43.4$ Hz, 4F) (lit. [23], −65.0 (t, $J = 0.2$ Hz, 4F), −115.0 (m, 4F), −122.4 (m, 4F)).

4g: Yellow oil. b.p. 135 °C (lit. [28], 135–136 °C). ^{19}F NMR: $\delta = -65.0$ (s, 4F), −86.2 (s, 4F) (lit. [28], −65.8 (s, 4F), −88.0 (m, 4F)).

1a: Colorless oil. b.p. 101 °C (lit. [17], 104–105 °C). ^{19}F NMR: $\delta = -59.0$ (s, 2F), −68.2 (s, 2F), −112.5 (s, 2F), −119.2 (s, 2F).

1b: Colorless oil. b.p. 63 °C/48 Torr (lit. [17], 68 °C/45 Torr). ^{19}F NMR: $\delta = -59.1$ (s, 2F), −68.1 (t, $J = 15.2$ Hz, 2F), −113.1 (s, 2F), −120.2 (s, 2F), −121.0 (s, 2F), −121.2 (s, 2F).

1c: White solid. ^{19}F NMR: $\delta = -59.1$ (s, 2F), −68.0 (t, $J = 15.1$ Hz, 2F), −113.1 (s, 2F), −120.1 (s, 2F), −120.9 (s, 2F), −121.1 (s, 2F), −121.7(s, 4F).

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