

An Efficient Method for the Preparation of Pentafluoroiodoethane from Chloropentafluoroethane[†]

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An efficient method was developed for the synthesis of pentafluoroiodoethane from chloropentafluoroethane. Sulfinatodechlorination of $\text{CF}_3\text{CF}_2\text{Cl}$ was carefully investigated. Subsequent iodination can be conducted in one pot without further purification, giving the corresponding $\text{CF}_3\text{CF}_2\text{I}$ in practically acceptable yield.

Keywords pentafluoroiodoethane, chloropentafluoroethane, sulfinatodechlorination, perfluoroalkyl iodide

Introduction

The introduction of perfluoroalkyl groups into organic compounds often brings about dramatic changes in their properties such as excellent low surface energy, small reflective value, high thermal stability, high electronegativity, *etc.*^{1–5} Thus, perfluoroalkyl iodides (R_fI) are valuable intermediates for the synthesis of the corresponding perfluoroalkyl carboxylic acids or alcohols, which can be used as oil-proofing, water-proofing, soil-release agents or as hydraulic fluids.^{6–9} For example, perfluoroalkyl iodides with a chain length more than 6 carbon atoms are particularly suitable for the production of materials for the finishing of textiles.⁹ To obtain R_fI having such a chain length, telomerization is usually employed for chain length elongation by the addition of tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) as a taxogen while using short chain R_fI as a telogen. Pentafluoroiodoethane ($\text{CF}_3\text{CF}_2\text{I}$) is a well known, valuable telogen which can be reacted with $\text{CF}_2=\text{CF}_2$ to form long chain R_fI . Therefore, considerable effort has been devoted to developing methods for the preparation of $\text{CF}_3\text{CF}_2\text{I}$. Banks *et al.*¹⁰ first described the preparation of pentafluoroiodoethane from the reaction of tetraiodoethylene with iodine pentafluoride. Many methods have been reported since then.^{11–15} However, most of the processes suffer from the disadvantages of requiring the use of iodine pentafluoride which is very toxic, highly expensive and difficult to handle.

Chloropentafluoroethane ($\text{CF}_3\text{CF}_2\text{Cl}$), the counterpart of $\text{CF}_3\text{CF}_2\text{I}$, was easily obtained from the fluorination of 1,2-dichloro-tetrafluoroethane or 1-chloro-2-iodo-tetrafluoroethane.¹⁶ Its low price and ready availability once made it a widely used refrigerant, yet its

production and use is seriously regulated because of its ozone depletion potential. However, it is still a side product in the preparation of substitutes for ozone depleting substances (ODS) such as R-134a ($\text{CF}_3\text{CH}_2\text{F}$). To convert chloropentafluoroethane to the environmental benign chemicals will be a good solution. Chemical transformations from $\text{CF}_3\text{CF}_2\text{Cl}$ to $\text{CF}_3\text{CF}_2\text{I}$ might be expected due to their high structural similarities.

Different from fluoroalkyl iodides or bromides, the C—Cl bond in fluoroalkyl chlorides is very strong and always remains intact under most reaction conditions.^{17,18} Recently, Chen and co-workers¹⁹ found that the inert C—Cl bond could be activated under the modified sulfinatodehalogenation conditions. Perfluoroalkyl chlorides were found to be converted to the corresponding iodides by this method.^{20–22} In view of the importance of pentafluoroiodoethane in fluorochemical industry and the necessity of removing $\text{CF}_3\text{CF}_2\text{Cl}$, we investigated the conversion from $\text{CF}_3\text{CF}_2\text{Cl}$ to $\text{CF}_3\text{CF}_2\text{I}$ and found that the modified sulfinatodehalogenation reaction can also be used in the synthesis of telogen ($\text{CF}_3\text{CF}_2\text{I}$) for R_fI from the byproduct ($\text{CF}_3\text{CF}_2\text{Cl}$). Herein we report the results.

Experimental

$\text{Na}_2\text{S}_2\text{O}_4$ (0.28 mol, 90%, 55 g), NaHCO_3 (0.29 mol, 24 g) and DMSO (200 mL) were added into a 500 mL autoclave equipped with mechanical stirrer. Then the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$. At this temperature, $\text{CF}_3\text{CF}_2\text{Cl}$ (0.39 mol, 60 g) was transferred into the autoclave. After being warmed to room temperature, the autoclave was heated to $80\text{ }^\circ\text{C}$ and kept at

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this temperature for 5 h. Then the reaction mixture was filtered and a DMSO (250 mL) solution of I₂ (0.65 mol, 166 g) was added to the filtrate at room temperature with vigorous stirring. After 5 h reaction, the pentafluoroiodoethane was separated from the reaction mixture by vaporization and collected in a cold trap at -196 °C. The desired CF₃CF₂I could be obtained in 25% yield based on Na₂S₂O₄. ¹⁹F NMR (DMSO-*d*₆, 282 MHz) δ: -83.8 (t, 3F), -73.4 (m, 2F).

Results and discussion

The traditional sulfinatodehalogenation reaction discovered by Huang can be effectively applied to the reaction of fluoroalkyl halides with alkenes, dienes, alkynes or aromatics.¹⁷ But this reaction is limited to fluoroalkyl iodides or bromides and not applicable for fluoroalkyl chlorides.^{17,18} Chen^{23,24} found that solvent played a pivotal role in this reaction. Using dimethyl sulfoxide (DMSO) as a solvent instead of CH₃CN/H₂O (in Na₂S₂O₄/NaHCO₃), fluoroalkyl chlorides, even non-fluorinated chlorides such as chloroform can either be converted to the corresponding sulfinate salts or alkylate alkenes and alkynes.

Treatment of chloropentafluoroethane under this modified sulfinatodehalogenation condition in autoclave resulted in the formation of the corresponding sulfinatodechlorinated product **1** (Table 1). The signals at δ -77.7 (3F, CF₃) and -131.2 (2F, CF₂SO₂Na) in the ¹⁹F NMR spectrum confirmed the formation of **1**. CF₃CF₂Cl was used in large excess over Na₂S₂O₄ for the convenience of operation. Therefore, the yield of **1** was determined by ¹⁹F NMR based on Na₂S₂O₄, using hexafluorobenzene as an internal standard.

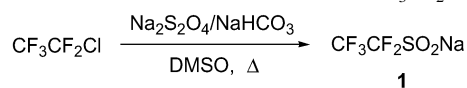
As indicated in Table 1, the formation of **1** was strongly influenced by the reaction conditions including the temperature, the concentration of Na₂S₂O₄ and the base. Heating is necessary for efficient cleavage of the C—Cl bond in R_fCl. While at room temperature no reaction happened (Entry 1), high temperature had a deleterious effect on the formation of the corresponding

sulfinate. Almost no desired pentafluoroethanesulfinate **1** could be obtained after heating the reaction mixture at 100 °C for 5 h (Entry 2). The optimum reaction temperature range should be 80 to 90 °C (Entries 3—6). It is presumed that pentafluoroethanesulfinate might be decomposed readily in DMSO at temperature above 100 °C. Furthermore, the sulfinatodechlorination of CF₃CF₂Cl could be promoted by decreasing the concentration of radical initiator (Na₂S₂O₄) in DMSO. Thus slightly higher yield of **1** can be achieved when less Na₂S₂O₄ was used (Entries 3, 4). In addition, the yield could also be improved with the prolonging of reaction time (Entries 5, 6). However, longer reaction time might lead to the decomposition of **1** and only trace amount of **1** was determined after 12 h (Entry 7). It is noteworthy that base played an important role in the reaction. In the absence of NaHCO₃, no pentafluoroethanesulfinate **1** could be obtained under otherwise the same reaction conditions (Entry 8).

Under the optimized reaction condition, pentafluoroethanesulfinate **1** could be produced in practically acceptable yield. However, attempts to isolate **1** from the reaction mixture failed, which might result from the instability of **1** in DMSO at high temperature. Nevertheless, it is not necessary to use pure sulfinate salt for the next iodination. The sulfinatodechlorination reaction mixture of CF₃CF₂Cl can be directly used for the next reaction.

The iodination of pentafluoroethanesulfinate **1** was performed at room temperature (Scheme 1). According to the literature, the pentafluoroethanesulfonyl iodide **2** was supposed to be the intermediate which would be extremely unstable and could decompose even at low temperature to give the corresponding iodides after evolution of SO₂.²⁵ This is indeed the case for the iodination of pentafluoroethanesulfinate **1**. Addition of the DMSO solution of I₂ to the above sulfinatodechlorination reaction mixture did give pentafluoroiodoethane **3**. Oxidants were not necessary to be added to facilitate the reaction. Iodine itself could act as the oxidant to generate pentafluoroethyl radical in this reaction system.

Table 1 Sulfinatodechlorination of CF₃CF₂Cl



Entry	Na ₂ S ₂ O ₄ : DMSO ^a /(g•mL ⁻¹)	CF ₃ CF ₂ Cl : Na ₂ S ₂ O ₄ : NaHCO ₃ ^b	Temperature/°C	Time/h	Yield ^c /%
1	1 : 100	0.65 : 1 : 1	r.t.	17	0
2	1 : 4	1.6 : 1 : 1	100	5	Trace
3	1 : 5	0.86 : 1 : 1	80	5	26
4	1 : 13	0.86 : 1 : 1	80	5	30
5	1 : 4	1.4 : 1 : 1	85	6	30
6	1 : 2	1.5 : 1 : 1	85	3	0.5
7	1 : 4	1.4 : 1 : 1	85	12	Trace
8	1 : 4	2.3 : 1 : 0	85	6	0

^a The mass-volume rate of Na₂S₂O₄ to DMSO; ^b the molar ratio of CF₃CF₂Cl, Na₂S₂O₄ and NaHCO₃; ^c Determined by ¹⁹F NMR based on Na₂S₂O₄.

