

# Synthesis of $\alpha$ , $\omega$ perfluoropolyether iodides

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## Abstract

Perfluoropolyether (PFPE) diacyl halides of formula  $XCOCF_2O[(CF_2O)_n(CF_2CF_2O)_m]_pCF_2COX$ , with  $X = Cl, F$  and molecular weight (MW) 400–4000  $g\ mol^{-1}$  are smoothly converted in high yields to the corresponding  $\alpha$ ,  $\omega$  diiodides in the absence of solvent, employing KI or LiI at 210 °C with extrusion of CO. During the reactions,  $\beta$ -elimination of  $COF_2$  from the terminal difluoromethylene oxide units ( $-CF_2O-$ ,  $C_1$  unit) occurs to some extent until a tetrafluoroethylene oxide unit ( $-OCF_2CF_2-$ ,  $C_2$  unit) is encountered yielding a  $-OCF_2CF_2I$  terminus. This considerably alters the MW distribution of the final diiodide especially for low MW PFPEs. Operating in supercritical conditions of CO (scCO) or both scCO and  $CO_2$  (scCO<sub>2</sub>) on low ( $<600\ g\ mol^{-1}$ ) MW diacyl halides, lowers  $\beta$ -elimination from 95 to 52 mol% if KI is used or from 43 to 30 mol% if LiI is used. With higher MW ( $>600\ g\ mol^{-1}$ )  $\beta$ -elimination is lowered from 15 to  $<1$  mol% in scCO conditions employing KI.

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## 1. Introduction

Photooxidation of tetrafluoroethylene at low temperature leads to the formation of PFPE polyperoxide mixtures [1]. Subsequent peroxide removal and end group stabilization afford chemically inert, neutral mixtures of oxytetrafluoroethylene ( $OCF_2CF_2$ )/oxydifluoromethylene ( $OCF_2$ ) random perfluoropolyethers commercialized under the tradename of Fomblin® Z fluids [2]. In reductive conditions [3] the PFPE (poly)peroxides can be cleaved yielding acyl fluorides with functionalities approaching to two; these are starting materials for a wide variety of telechelic derivatives which have found various and innovative applications, for example, in the fields of high performance polymeric materials, lubrication of magnetic recording media, antirust and antiwear additives for lubricants [4].

Perfluoroalkyl  $\alpha$ ,  $\omega$  diiodides are usually made directly by the radical telomerization of iodine and tetrafluoroethylene

[5]. However, PFPE  $\alpha$ ,  $\omega$  diiodides have been made in several ways always starting from a suitable PFPE derivative [6,7]. The known synthetic methodologies depend strongly on the structure of the PFPE backbone and hence on the different end groups. They can be divided into three classes depending on the reaction mechanism:

- Reactions involving radical intermediates:* Decompositions of PFPE (poly)diacyl peroxides in the presence of  $I_2$  which proceeds with high yields and selectivities [8]; this synthetic route is critical for the synthesis of the PFPE polydiacyl peroxide precursor. Thermal decomposition of a peroxidic perfluoropolyether in the absence of UV radiation and at temperatures above 180 °C in the presence of iodo-containing compounds as described by Marchionni and Guarda [9].
- Single electron transfer (SET) reactions:* These reactions take advantage of the reactivity of PFPE carboxylic functionalities towards benzoyl peroxide, BPO, in the presence of  $I_2$  as described by Silbert for similar compounds [10]. The reaction proceeds

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smoothly and in good yield; the main drawback is the purification of the PFPE diiodides from the main side-product, iodobenzene.

- (c) *Elimination reactions via a carbanion intermediate:* The starting material for these reactions is a PFPE dicarboxylic acid derivative. Performing either the Hunsdieker reaction [7] on the  $\text{Ag}^+$  carboxylate salt or decarboxylating the  $\text{K}^+$  salts in the presence of  $\text{I}_2$  or  $\text{ICl}$  gives moderate PFPE diiodide yields only on PFPE structures characterized by terminal  $-\text{OCF}_2\text{CF}_2\text{COF}$  or  $-\text{OCF}(\text{CF}_3)\text{COF}$  groups. This is due primarily to the very fast kinetics of the  $\text{COF}_2$   $\beta$ -elimination reaction. The ionic synthetic approaches to diiodides failed on all those PFPE acyl halides, which do have terminal  $-\text{OCF}_2\text{COF}$ . This is the case of PFPE type structures [1]. A particularly interesting synthesis of diiodides involves the transformation of acyl halides (fluorides, chlorides and bromides) in acyl iodides employing  $\text{KI}$  or  $\text{LiI}$  in aprotic solvents followed by a thermal or photolytic extrusion of  $\text{CO}$  in the presence of  $\text{I}_2$ . This reaction has been reported starting either from perfluoroalkyl halides [11,12–14] or from PFPEs with  $-\text{OCF}_2\text{CF}_2\text{COF}$  or  $-\text{OCF}(\text{CF}_3)\text{COF}$  end groups [15] but never from terminal  $-\text{OCF}_2\text{COX}$  ( $\text{X} = \text{F}, \text{Cl}$ ). It has been postulated that the fundamental step of the reaction, the extrusion of  $\text{CO}$ , has radical character [12,13].

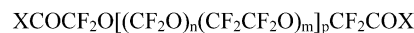
We have used this synthetic route on PFPE acyl halides with the aim of providing an effective synthesis to PFPE diiodides, limiting or eliminating the side reaction of  $\text{COF}_2$  elimination [16,17].

## 2. Results and discussion

### 2.1. Synthesis of Z-PFPE diiodides versus $\beta$ -elimination

Both iodination methods, acyl chloride +  $\text{KI}$  or acyl fluoride +  $\text{LiI}$ , have been fully described in the literature [7,10–15].

$\beta$ -Elimination is responsible for the loss of  $-\text{CF}_2\text{O}-$  units, called  $\text{C}_1$  units, from the linear Z-PFPE structure shown in Scheme 1, generating carbonyl fluoride,  $\text{COF}_2$ ;  $\beta$ -elimination stops once a  $-\text{OCF}_2\text{CF}_2-$  unit, called a  $\text{C}_2$  unit, is



Where:  
 $m/n = 0,5 - 1.0$   
 $p = 0-20$   
 $\text{X} = \text{F}, \text{Cl}$

Scheme 1.

encountered along the Z-PFPE backbone. As a consequence,  $-\text{OCF}_2\text{CF}_2\text{I}$  termini are generated together with  $-\text{OCF}_2\text{I}$  termini.

$\beta$ -Elimination is responsible for mass loss from the starting general structure shown in Scheme 1. This side reaction does not necessarily alter conversions or yields but rather the MW distribution of the final Z-PFPE diiodide mixture with respect to the initial MW of the starting PFPE diacyl halide.  $\beta$ -Elimination is therefore a particularly undesired side-reaction when the MW starting distribution is low ( $< 600$ ) [8]. Its maximum extent is reached with Z-PFPE structures having  $P = 0$  and  $\text{X} = \text{F}$  (see Scheme 1).

The thermally induced iodination reaction of Z-PFPE diacyl halides in the presence of either  $\text{KI}$  or  $\text{LiI}$  is shown in Fig. 1.

This proceeds via an isolatable acyl iodide intermediate [13], which is formed at relatively low ( $120^\circ\text{C}$ ) temperatures. Both our experiments and literature data [12,18] do not distinguish between a mechanism where the homolysis of the  $\text{sp}^2$  hybridized  $\text{CO}\cdots\text{I}$  bond is concerted with  $\text{CO}$  elimination and formation of the  $\text{sp}^3$  hybridized  $\text{CF}\cdots\text{I}$  bond and a radical mechanism with an  $\text{R}_f\text{-OCF}_2^\bullet$  intermediate.

Fig. 1 shows that  $\beta$ -elimination is in competition with the iodide entrapment of the intermediate. Once the first  $\beta$ -elimination event occurs, the scission reaction can proceed until a  $\text{C}_2$  unit is encountered along the Z-PFPE backbone.

### 2.2. $\text{Li}^+$ effect

It is known [13,14] that the  $-\text{COX} \rightarrow -\text{COI}$  halogen exchange reaction works well with acyl chlorides and  $\text{KI}$  and  $\text{LiI}$ , while with acyl fluorides only  $\text{LiI}$  is a suitable reagent. The bond energy for a  $\text{F}-\text{CO}-$  bond is greater than that for a  $\text{Cl}-\text{CO}-$  bond ( $498 \text{ kJ mol}^{-1}$  versus  $349 \text{ kJ mol}^{-1}$ , respectively) [19]; therefore, the iodination of an acyl fluoride is

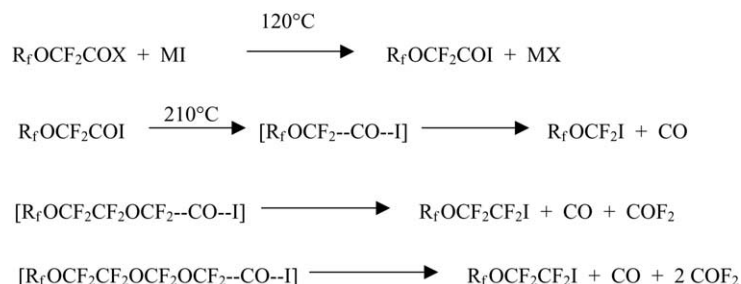


Fig. 1. Thermal iodination reaction mechanism of Z-PFPE acyl halides ( $\text{X} = \text{Cl}, \text{F}$ ) in the presence of  $\text{MI}$  ( $\text{M} = \text{K}$  and  $\text{Li}$ ).

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