

Easy Preparation of [*Bis*(trifluoroacetoxy)iodo]arenes from Iodoarenes, with Sodium Percarbonate as the Oxidant[†]

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Abstract: Easy and effective preparations of the nearly pure [*bis*(trifluoroacetoxy)-iodo]arenes, ArI(OCOFCF₃)₂, from some iodoarenes, ArI, are reported, using an anhydrous sodium percarbonate/(CF₃CO)₂O/CH₂Cl₂ system. The colorless, freshly prepared ArI(OCOFCF₃)₂ thus obtained were 98-99% pure (by iodometry).

Keywords: [*Bis*(trifluoroacetoxy)iodo]arenes from iodoarenes, sodium percarbonate as oxidant

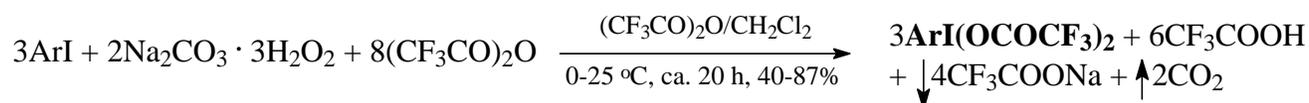
Introduction

[*Bis*(trifluoroacetoxy)iodo]arenes, ArI(OCOFCF₃)₂, are potent and selective oxidants, widely used in modern organic synthesis. So far, they have been synthesized from either ArI, or ArIO, or ArICl₂, or directly from ArH, but the most common method depends on their preparation (in moderate yields) from the corresponding (diacetoxyiodo)arenes, ArI(OAc)₂, by their recrystallization from CF₃COOH [1, 2].

Results and Discussion

Recently, in our laboratory we have devised a simple, easy, and efficient method for the direct preparation of $\text{ArI}(\text{OCOCF}_3)_2$ from the respective iodoarenes, ArI , in a binary *anhydrous* solvent system, $(\text{CF}_3\text{CO})_2\text{O}/\text{CH}_2\text{Cl}_2$, using commercially available **sodium percarbonate**, $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, as the oxidant (Scheme 1 and Table 1):

Scheme 1



In practice, only the *fairly stable* parent compound, $\text{PhI}(\text{OCOCF}_3)_2$ has found widespread use in organic synthesis [1-3], although it should be noted that *p*-Cl- and *p*-F- $\text{C}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$ are even more stable. A limited number of other ring-substituted $\text{ArI}(\text{OCOCF}_3)_2$ have been reported in the literature [4-6]. We have *unexpectedly* found that several other $\text{ArI}(\text{OCOCF}_3)_2$ compounds are less stable, particularly *p*-Me $\text{C}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$, and they usually deteriorate within several days to finally form oily residues with a strong acidic odor – even when stored in a dark cooler. As far as limitations of the reported method are concerned, we have found that it is not suitable for the preparation of the three $\text{O}_2\text{N-C}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$ isomers, as well as *p*-MeOC $_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$. It is also seen from the data in Table 1 that 3-F $_3\text{CC}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$ was obtained in only 40% yield by our new method, cf. [6].

Experimental

General

Chemical structures of the compounds in Table 1 were confirmed by satisfactory microanalyses of the crude, freshly prepared products ($\text{C} \pm 0.2$, $\text{H} \pm 0.1$, $\text{I} \pm 0.2\%$) obtained at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

Optimized Procedure for Preparing [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes:

A solution of an appropriate *iodoarene* (5 mmol) in a mixture of $(\text{CF}_3\text{CO})_2\text{O}$ (12 mL) and CH_2Cl_2 (40 mL) was cooled with stirring to 0-2 °C. Next, sodium percarbonate (2.1 g; 13.4 mmol; 300% excess) was added portionwise, and the stirring was continued for 2 h at 0-2 °C, and further at room temperature for ca. 18 h. The *precipitated* CF_3COONa was collected by filtration under reduced pressure, washed with CH_2Cl_2 (2 x 20 mL), and discarded. The filtrates were evaporated under vacuum. The solid residues were triturated with hexane (10 mL), collected by filtration, washed with hexane on the filter, and quickly air-dried by the suction, leaving the **colourless** title products,

$\text{ArI}(\text{OCOCF}_3)_2$ (40-87% yields). Their yields and melting points are given in Table 1 below. In practice these products need not to be recrystallized. They should be stored in the dark, preferably in a cooler, avoiding any moisture [3]. The freshly prepared products were **98-99%** pure (by iodometry [7]).

Table 1. Yields and melting points (uncorrected) for the prepared [*bis*(trifluoroacetoxy)iodo]arenes, $\text{ArI}(\text{OCOCF}_3)_2$

Ar	Yield [%]	Mp [°C]	Lit. Mp [°C]
phenyl	87	122-124	120-122 [4]
2-methylphenyl	81	89-92	88-90 [4]
3-methylphenyl	86	93-96	87-90 [5]
4-methylphenyl	76	112-115	114-116 [4]
4-fluorophenyl	77	103-105	88-90 [4]
4-chlorophenyl	74	129-132	131-133 [5]
3-(trifluoromethyl)phenyl	40	97-100	99-100 [6]

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- [3] *Aldrich Handbook of Fine Chemicals and Laboratory Equipment 2003-2004*, p. 241; a m.p. of 121-125 °C is reported for 97% $\text{PhI}(\text{OCOCF}_3)_2$, with a note: MOISTURE-SENSITIVE.
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Sample Availability: Available from the authors.