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Easy Preparation of (Diacetoxyiodo)arenes from Iodoarenes with Sodium Percarbonate as the Oxidant†

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Abstract: Easy and effective preparations of nearly pure (diacetoxyiodo)arenes, $ArI(OAc)_2$, from iodoarenes, ArI, are reported. In most cases the crude colorless products thus obtained need not be further purified, i.e., by recrystallization. As an example, the $PhI(OAc)_2$ thus prepared was 99% pure (by iodometry).

Keywords: (Diacetoxyiodo)arenes from iodoarenes, sodium percarbonate as oxidant

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Introduction

(Diacetoxyiodo)arenes, $ArI(OAc)_2$, and particularly the parent compound (diacetoxyiodo)benzene, $PhI(OAc)_2$, have been known for a long time [1]. The well - pronounced electrophilic character of organic hypervalent iodine compounds is utilized in many organic syntheses, while (diacetoxyiodo)arenes are used as potent, often chemoselective, oxidizing agents. They are also used for the facile syntheses of, for example, [*bis*(trifluoroacetoxy)iodo]arenes, [hydroxy(tosyloxy)iodo]arenes (*selective oxidants*), and aromatic iodonium salts (*arylating reagents*).

Several methods are available for the preparation of (diacetoxyiodo)arenes [2, 3]. Historically, the first member – (diacetoxyiodo)benzene (DIB) – was synthesized by Willgerodt in 1892, by dissolving iodosylbenzene in hot acetic acid [4]. So far, the *substrates* used have generally been:

- *iodosylarenes* dissolved in glacial acetic acid;
- *(dichloroiodo)arenes* in which the chlorine atoms are exchanged by acetoxy groups coming either from silver, lead(II) or sodium acetate, or from acetic acid in the presence of mercury(II) oxide in chlorinated solvents;
- *iodoarenes* are oxidized in *warm* glacial acetic acid by either peracetic acid, sodium perborate tetrahydrate, or electrolytically [5].

The standard, and most general, method for the synthesis of $ArI(OAc)_2$ (oxidative diacetoxylation of ArI by warm peracetic acid solutions) is, in fact, a very prolonged reaction (12-16 hours), and the utmost care should be taken to maintain the exact temperature, 40˚C. Better methods were published in references [2] and [3].

Results and Discussion

In our laboratory, we have recently devised a simple and efficient method for preparing $ArI(OAc)_2$ from the respective iodoarenes in an *anhydrous* ternary solvent system: $Ac_2O/AcOH/CH_2Cl_2$, using commercial **sodium percarbonate**, $2Na_2CO_3{\cdot}3H_2O_2$, as the oxidant (Scheme 1). Our results are summarized in Table 1.

Scheme 1

$$3ArI + 2Na_2CO_3{\cdot}3H_2O_2 + 8Ac_2O \xrightarrow[25\text{-}40^{\circ}C,\ ca.\ 6.5h,\ 18\text{-}84\%]{AcOH/Ac_2O/CH_2Cl_2} \mathbf{3ArI(OAc)_2} + 6AcOH + \downarrow 4AcONa + \uparrow 2CO_2$$

Table 1. Yields and melting points (uncorrected) of the (diacetoxyiodo)arenas prepared

Substrate	**Product**	**Yield (%)**	**Mp (^{o}C)**	**Lit. [3] mp (^{o}C)**
C_6H_5-I	C_6H_5-I$(OAc)_2$	79	159-161	161.1-162.2
4-FC_6H_4-I	4-FC_6H_4-I$(OAc)_2$	80	179-181	177.0-179.8
2-MeC_6H_4-I	2-MeC_6H_4-I$(OAc)_2$	84	139-140	140.0-142.0
3-MeC_6H_4-I	3-MeC_6H_4-I$(OAc)_2$	76	150-152	154
4-MeC_6H_4-I	4-MeC_6H_4-IO_2	28	230 (expl.)	229 (dec.)
2-$MeOC_6H_4$-I	2-$MeOC_6H_4$-I$(OAc)_2$	76	146-148	146.9-150.1
3-$MeOC_6H_4$-I	3-$MeOC_6H_4$-I$(OAc)_2$	74	129-131	133-135
2-ClC_6H_4-I	2-ClC_6H_4-I$(OAc)_2$	20	140-142	140-142
3-ClC_6H_4-I	3-ClC_6H_4-I$(OAc)_2$	18	148-151	153.1-154.7
4-ClC_6H_4-I	4-ClC_6H_4-IO_2	70	240 (expl.)	243 (expl.)

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Experimental

General

Chemical structures of the compounds in Table 1 were confirmed by microanalyses at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

Optimized Procedure for Preparing (Diacetoxyiodo)arenes from Iodoarenes

Sodium percarbonate (18.4 mmol, 330% excess) was slowly added portionwise to a stirred mixture of Ac_2O (7.0 mL), AcOH (5.8 mL), and CH_2Cl_2 (40 mL). The stirring was continued for 1.5 h at $\leq$ 30˚C. An appropriate *iodoarene* was then added (6.4 mmol), and the reaction mixture was then stirred at 40˚C for 5 h. After cooling, the *precipitated* CH_3COONa was collected by filtration under reduced pressure, washed with CH_2Cl_2 (2 x 15 mL) and discarded. The filtrates were evaporated under vacuum, and cold (0-5 ˚C) 10% aq. CH_3COOH (15 mL) was rapidly added. The flask was left in a cooler for a few hours. The *colorless* crystals formed were collected by filtration, washed with hexane and air-dried in the dark. Most of those crude products thus obtained need not be further purified, as they were 96-99% pure, according to iodometric analysis [6]. When necessary, the crude products were recrystallized from AcOEt/Ac_2O (9:1, v/v) [2]. They should be stored in the dark, preferably in a cooler. See Table 1 for more details. Under these conditions 4-iodotoluene and 4-chloroiodobenzene were unexpectedly oxidized to the corresponding iodylarenes (recrystallized from boiling water).

References

1. Willgerodt, C. *Die organischen Verbindungen mit mehrwertigem Jod*; Enke Verlag: Stuttgart, 1914.
2. Kazmierczak, P.; Skulski, L. A Simple, Two-Step Conversion of Various Iodoarenes to (Diacetoxyiodo)arenes with Chromium(VI) Oxide as the Oxidant. *Synthesis* **1998**, 1721-1723, and references therein.
3. Kazmierczak, P.; Skulski, L.; Kraszkiewicz, L. Syntheses of (Diacetoxyiodo)arenes or Iodylarenes from Iodoarenes, with Sodium Periodate as the Oxidant. *Molecules* **2001**, *6*, 881-891; Avail. at URL: http://www.mdpi.org/molecules/papers/61100881.pdf
4. Willgerodt, C. Zur Kenntniss aromatischer Jodidchloride, des Jodoso- und Jodobenzols. *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 3494-3502, p3498.

5. Skulski, L. Organic Iodine(I, III, and V) Chemistry: 10 Years of Development at the Medical University of Warsaw, Poland. *Molecules* **2000**, *5*, 1331-1371; Avail. at URL: http://www.mdpi.org/molecules/papers.51201331.pdf
6. Lucas, H. J.; Kennedy, E. R.; Formo, M. W. *Org. Synth.* **1942**, *22*, 70.

Sample Availability: Available from the authors.