

# Easy and Safe Preparations of (Diacetoxyiodo)arenes from Iodoarenes, with Urea-Hydrogen Peroxide Adduct (UHP) as the Oxidant and the Fully Interpreted $^1\text{H}$ - and $^{13}\text{C}$ -NMR Spectra of the Products<sup>†</sup>

Agnieszka Zielinska and Lech Skulski \*

Chair and Laboratory of Organic Chemistry, Faculty of Pharmacy, Medical University, 1 Banacha Street, PL 02-097 Warsaw, Poland

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\* To whom correspondence should be addressed; E-mail: [lechskulski@yahoo.com](mailto:lechskulski@yahoo.com); Tel./Fax: (+48) 22 5720643;

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**Abstract:** An easy and safe, though only moderately effective method is presented for preparing (diacetoxyiodo)arenes,  $\text{ArI}(\text{OAc})_2$ , from iodoarenes,  $\text{ArI}$ , using the commercially available and easily handled urea-hydrogen peroxide adduct (UHP) as the oxidant. The reactions take place in *anhydrous*  $\text{AcOH}/\text{Ac}_2\text{O}/\text{AcONa}$  (a catalyst) mixtures, at 40 °C for 3.5 h to afford the purified  $\text{ArI}(\text{OAc})_2$  in 37-78% yields. The *fully interpreted*  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the  $\text{ArI}(\text{OAc})_2$  products are reported.

**Keywords:** (Diacetoxyiodo)arenes, iodoarenes, urea-hydrogen peroxide adduct as oxidant,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra

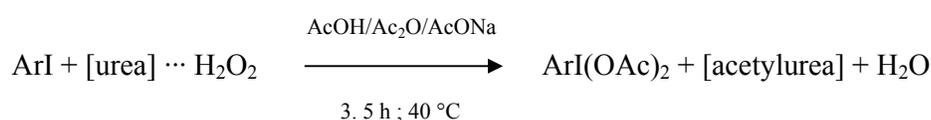
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## Introduction

(Diacetoxyiodo)arenes,  $\text{ArI}(\text{OAc})_2$ , and particularly the parent compound (diacetoxyiodo)benzene,  $\text{PhI}(\text{OAc})_2$ , have been known for a long time [1,2]. They are used in organic synthesis as potent, often chemoselective, oxidizing agents. They are also used for facile syntheses of several classes of aromatic

hypervalent iodine compounds, e.g. [bis(trifluoroacetoxy)iodo]arenes, [hydroxy(tosyloxy)iodo]arenes, aromatic iodonium salts [3], etc. In our two latest reviews [4,5] we relate and explain our previous novel syntheses of ArI(OAc)<sub>2</sub> from corresponding ArI, as well our novel aromatic iodination methods, and preparations of several classes of aromatic hypervalent iodine compounds, easily attainable from aromatic iodides; particularly see ref. 4, pp. 1343-1345 and 1352-1354.

During the course of our systematic studies on effective and easy preparations of ArI(OAc)<sub>2</sub> from the corresponding ArI [4, 5], we have devised several methods for their syntheses. In this work we have oxidized seven iodoarenes (Table 1) in *anhydrous* AcOH/Ac<sub>2</sub>O mixtures; the reactions did *not* proceed in the *absence* of sodium acetate, AcONa (used in a stoichiometric quantity) – cf. our former work [6], where its presence in the reaction mixtures was also indispensable. The reactions took place as follows:



In our opinion, the novel method presented in this paper is easy and safe, albeit only moderately effective (yields are in the 37-78% range). For the first time, we have used UHP as the oxidant. This compound, which is now *commercially available*, may be considered a “dry carrier” of the unstable and hazardous hydrogen peroxide. The UHP solid is easy to handle, safe and stable at room temperature. Its ability to release oxidative species in water and organic media has made it a useful reagent in organic synthesis [7].

## Experimental

### General

Melting points submitted in the Table 1 are uncorrected. All the reagents were purchased from Aldrich or Lancaster and were used without further purification. The NMR spectra were run in CDCl<sub>3</sub> solutions at room temperature, with TMS as an internal standard; the spectra were recorded on a Bruker AVANCE DMX 400 spectrometer. To obtain better assignments, also <sup>1</sup>H – <sup>13</sup>C NMR correlation spectra were recorded.

### Optimized Procedure for Preparing (Diacetoxyiodo)arenes from Iodoarenes:

Urea-Hydrogen Peroxide adduct, 98% (3.02 g, 31.5 mmol, 350% excess) was added portionwise to a stirred mixture of glacial AcOH (24 mL) with Ac<sub>2</sub>O (9 mL). An appropriate *iodoarene* (7 mmol) was slowly added, the solution was cooled to 10-15 °C, and powdered AcONa (1.26 g, 15 mmol) was suspended. Stirring at 40 °C was continued for 3.5 h. After cooling, water (35 mL) was slowly added with stirring. The precipitated ArI(OAc)<sub>2</sub> were collected by filtration, washed on the filter with a cold (5-10 °C) 10% aq. AcOH, and air-dried in the dark; if necessary, they were recrystallized from AcOEt/Ac<sub>2</sub>O (9:1, v/v). The oily or semisolid products were extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined

extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered, the solvent was distilled off under vacuum, and the solidified residues were recrystallized from  $\text{AcOEt}/\text{Ac}_2\text{O}$  (9:1). The purities and homogeneities of the purified  $\text{ArI}(\text{OAc})_2$  were firstly checked by TLC, and next confirmed by their melting points, all close to those reported in the literature (Table 1). Their chemical structures were fully supported by the  $^1\text{H}$ -NMR (Table 2) and  $^{13}\text{C}$ -NMR (Table 3) spectra (in  $\text{CDCl}_3$ ).

**Table 1.** Final yields and melting points (uncorrected) of the purified (diacetoxyiodo)-arenes obtained from the corresponding iodoarenes.

Substrate	Product	Yield (%)	Mp (°C)	Lit. Mp (°C)
$\text{C}_6\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{I}(\text{OAc})_2$	44	161-162	161-163 [6]
3- $\text{FC}_6\text{H}_4\text{I}$	3- $\text{FC}_6\text{H}_4\text{I}(\text{OAc})_2$	37	143-145	144-145 [8]
4- $\text{FC}_6\text{H}_4\text{I}$	4- $\text{FC}_6\text{H}_4\text{I}(\text{OAc})_2$	78	177-180	179 [8]
2- $\text{MeC}_6\text{H}_4\text{I}$	2- $\text{MeC}_6\text{H}_4\text{I}(\text{OAc})_2$	64	142-147	140-142 [6]
2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{I}$	2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{I}(\text{OAc})_2$	69	126-128	128 [9]
2- $\text{MeOC}_6\text{H}_4\text{I}$	2- $\text{MeOC}_6\text{H}_4\text{I}(\text{OAc})_2$	48	145-147	147-149 [6]
3- $\text{MeOC}_6\text{H}_4\text{I}$	3- $\text{MeOC}_6\text{H}_4\text{I}(\text{OAc})_2$	57	130-132	133-135 [6]

**Table 2.**  $^1\text{H}$ -NMR chemical shifts for pure (diacetoxyiodo)arenes. Cf. our present experimental values with those previously reported [11].

Product	Chemical shifts $\delta$ (ppm)								
	$\text{H}_2$	$\text{H}_3$	$\text{H}_4$	$\text{H}_5$	$\text{H}_6$	$\text{OCH}_3$	$\text{CH}_3$ ( <i>o</i> )	$\text{CH}_3$ ( <i>p</i> )	$\text{CH}_3$ in OAc
$\text{C}_6\text{H}_5\text{I}(\text{OAc})_2$	8.10 d	7.50 t	7.60 t	7.50 t	8.10 d	-	-	-	2.01 s
3- $\text{FC}_6\text{H}_4\text{I}(\text{OAc})_2$	7.29 d	-	7.84 t	7.51 m	7.84 t	-	-	-	2.02 s
4- $\text{FC}_6\text{H}_4\text{I}(\text{OAc})_2$	8.09 d	7.19 t	-	7.19 t	8.09 d	-	-	-	2.02 s
2- $\text{MeC}_6\text{H}_4\text{I}(\text{OAc})_2$	-	7.52 d	7.52 t	7.26 t	8.17 d	-	2.72 s	-	1.98 s
2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{I}(\text{OAc})_2$	-	7.31 s	-	7.05 d	8.04 d	-	2.68 s	2.40 s	1.98 s
2- $\text{MeOC}_6\text{H}_4\text{I}(\text{OAc})_2$	-	7.16 d	7.59 t	7.04 t	8.14 d	3.99 s	-	-	1.97 s
3- $\text{MeOC}_6\text{H}_4\text{I}(\text{OAc})_2$	7.65 s	-	7.10 d	7.41 t	7.67 s	3.87 s	-	-	2.02 s

**Table 3.**  $^{13}\text{C}$  NMR chemical shifts for pure (diacetoxyiodo)arenes and coupling constants  $J_{^{19}\text{F}-^{13}\text{C}}$  and  $J_{^{19}\text{F}-\text{C}-^{13}\text{C}}$  (Hz). Cf. our present experimental values with those previously reported incompletely [10, 12].

Product	Chemical shifts of aromatic C atoms in $\delta$ (ppm)					
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
C <sub>6</sub> H <sub>5</sub> I(OAc) <sub>2</sub>	121.58 s	134.94 s	130.96 s	131.74 s	130.96 s	134.94 s
3-FC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	120.65 s	122.56 d $J = 24.6$	161.33 d $J = 253.0$	119.26 d $J = 20.7$	132.33 s	130.87 s
4-FC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	115.64 s	137.74 s	118.59 d $J = 22.6$	164.63 d $J = 253.7$	118.82 d $J = 22.6$	135.95 s
2-MeC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	127.29 s	140.72 s	128.51 s	130.97 s	132.82 s	137.30 s
2,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> I(OAc) <sub>2</sub>	124.09 s	143.73 s	131.78 s	140.66 s	129.40 s	137.32 s
2-MeOC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	113.63 s	156.46 s	112.33 s	134.70 s	122.91 s	137.94 s
3-MeOC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	121.62 s	120.68 s	160.72 s	118.14 s	131.73 s	127.25 s

Product	Chemical shifts of C atoms in substituents in $\delta$ (ppm)				
	CH <sub>3</sub> ( <i>o</i> )	CH <sub>3</sub> ( <i>p</i> )	OCH <sub>3</sub>	CH <sub>3</sub> in OAc	C=O in OAc
C <sub>6</sub> H <sub>5</sub> I(OAc) <sub>2</sub>	-	-	-	20.36 s	176.39 s
3-FC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	-	-	-	20.51 s	176.76 s
4-FC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	-	-	-	20.47 s	176.66 s
2-MeC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	25.68 s	-	-	20.42 s	176.53 s
2,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> I(OAc) <sub>2</sub>	25.56 s	21.64 s	-	20.52 s	176.57 s
2-MeOC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	-	-	57.06 s	20.54 s	176.82 s
3-MeOC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	-	-	55.92 s	20.56 s	176.64 s

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*Sample Availability:* The samples of pure (diacetoxyiodo)arenes, prepared one year ago and kept in a fridge, have deteriorated in full or in part. Hence, they are not available.