Short Articles

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One-Pot Preparations of (Dichloroiodo)arenes from Some Arenes

Piotr Luliński, Nicolas Obeid, and Lech Skulski*

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

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Arenes (ArH) were substituted with some transient $\mathbf{I^{3+}}$ species, generated in situ in appropriate, *anhydrous* $I_2/NaIO_4$ or $NaIO_3/AcOH/Ac_2O$/concd H_2SO_4 mixtures, to form soluble organoiodine(III) intermediates, $ArISO_4$. Next, excess concd hydrochloric acid was added to precipitate out the title $ArICl_2$, and isolated in 46–88% optimized crude yields.

(Dichloroiodo)arenes ($ArICl_2$) have been finding growing importance in organic synthesis as moderate and selective chlorinating and/or oxidizing agents. Moreover, they may be converted to other important hypervalent iodine reagents, e.g. ArIO, $ArIO_2$, $ArI(OAc)_2$, diaryliodonium salts, etc.[1,2]

$ArICl_2$, yellow crystalline compounds, are light- and heat-sensitive and often unstable to be storaged; some more stable $ArICl_2$, e.g. $PhICl_2$, may be stored in a cooler for a few days. They do not usually give satisfactory microanalyses, and their melting/decomposition points are uncertain, depending upon the purity of their freshly prepared batches, the time elapsed since their preparation, and the rate of heating.[1–3]

In 1886 Willgerodt[3] developed the most common method up to now for preparing $ArICl_2$, by passing a stream of Cl_2 through solutions of ArI in $CHCl_3$. Recently, Japanese industrial chemists[4] repeatedly produced $PhICl_2$ from PhI (in 94% crude yield) on a 20 kg scale using the classic Willgerodt method.[3]

In order to avoid any hazardous use of gaseous Cl_2 to afford $ArICl_2$ from ArI, a number of various either ***two-phase*** (CCl_4/concd aq HCl) or monophasic ***liquid-phase*** methods were reported.[1,2] A full account of all those methods is given in our latest review (Ref. 2, pp. 1346–1352).

However, all former methods[1–4] demanded the application of *costly* iodoarenes (ArI) as the starting substrates, to be subsequently chlorinated at their iodine atoms. In this paper we present a quite novel, one-pot (two-stage) method for preparing eleven $ArICl_2$ from the corresponding **arenes** (ArH), used by us as the starting substrates (Table 1). ArH were at first, oxidatively substituted in *anhydrous* $I_2/NaIO_4$ or $NaIO_3/AcOH/Ac_2O$/concd H_2SO_4, mixtures (vide infra) with some transient *iodine(III)* species, $\mathbf{I^{3+}}$, to form in situ the respective organoiodine(III) intermediates, $ArISO_4$ (Scheme 1).

$$\mathrm{ArH} + \mathbf{I^{3+}} \xrightarrow[-\mathrm{H^+}]{} \mathrm{ArI^{2+}} \xrightarrow[-2\mathrm{H^+}]{\mathrm{H_2SO_4}} \mathrm{ArISO_4}$$

Scheme 1.

Next, excess concd (36%) hydrochloric acid was added to the resulting (final) reaction mixtures, containing soluble $ArISO_4$ intermediates, to precipitate out the corresponding $ArICl_2$, isolated in 46–88% crude yields (Scheme 2).

$$\mathrm{ArISO_4}\,(\textit{not isolated}) + 2\,\mathrm{HCl} \longrightarrow \downarrow \mathbf{ArICl_2} + \mathrm{H_2SO_4}$$

Scheme 2.

Table 1. Yields (possibly optimized) and Melting Points (with decomposition) of Crude (Dichloroiodo)arenes Prepared from Arenes, as well as Four Variable Reactions Parameters (cf. Ref. 5)

Substrate, ArH	Product, $ArICl_2$[a)]	Yield/%	Oxidant	Concd H_2SO_4[b)]	Time/h; Temp/°C[c)]	Mp/°C	Lit, mp/°C
PhH	$PhICl_2$	88	$NaIO_4$	1.07 mL; 20 mmol	2, r.t.	112–113	111–112[8]
PhH	$PhICl_2$	87	$NaIO_3$	4.26 mL; 80 mmol	2, r.t.	111–112	111–112[8]
PhF	$4\text{-}FC_6H_4ICl_2$	70	$NaIO_4$	2.13 mL; 40 mmol	2, r.t.	105–106	106–107[8]
PhCl	$4\text{-}ClC_6H_4ICl_2$	70	$NaIO_4$	2.13 mL; 40 mmol	2, r.t.	110–112	110–112[8]
PhBr	$4\text{-}BrC_6H_4ICl_2$	75	$NaIO_4$	2.13 mL; 40 mmol	2, r.t.	119–122	123–124[7]
PhBr	$4\text{-}BrC_6H_4ICl_2$	63	$NaIO_3$	4.26 mL; 80 mmol	2, r.t.	123–126	123–124[7]
PhI	$4\text{-}IC_6H_4ICl_2$	81	$NaIO_4$	3.20 mL; 60 mmol	2, r.t.	126–129	136–138[7]
$PhCO_2H$	$3\text{-}HO_2CC_6H_4ICl_2$	86	$NaIO_4$	4.26 mL; 80 mmol	3, r.t.	185–186	183–185[8]
$PhCO_2H$	$3\text{-}HO_2CC_6H_4ICl_2$	80	$NaIO_3$	5.33 mL; 100 mmol	2, r.t.	183–185	183–185[8]
$PhCO_2Me$	$3\text{-}MeO_2CC_6H_4ICl_2$	69	$NaIO_4$	4.26 mL; 80 mmol	3, r.t.	117–118	108–110[8]
$PhCO_2Me$	$3\text{-}MeO_2CC_6H_4ICl_2$	64	$NaIO_3$	5.33 mL; 100 mmol	2, r.t.	117–118	108–110[8]
$PhCO_2Et$	$3\text{-}EtO_2CC_6H_4ICl_2$	74	$NaIO_4$	4.26 mL; 80 mmol	3, r.t.	102–103	98–100[8]
$PhCF_3$	$3\text{-}F_3CC_6H_4ICl_2$	57	$NaIO_4$	7.99 mL; 150 mmol	1, r.t.; 3, 65	85–87	81–83[10]
PhOMe	$4\text{-}MeOC_6H_4ICl_2$	57	$NaIO_4$	0.27 mL; 5 mmol	0.5, r.t.; 2, 60	75–76	75–76[8]
$1,3\text{-}Cl_2C_6H_4$	$2,4\text{-}Cl_2C_6H_3ICl_2$	46	$NaIO_4$	4.26 mL; 80 mmol	2, r.t.	93–95	96–98[8]

a) Satisfactory homogeneities of the crude $ArICl_2$ were checked with TLC, after their reduction to the corresponding iodoarenes. b) The amount of concd H_2SO_4 added dropwise to each of the cooled and stirred reaction mixtures. c) Time of stirring the individual reaction mixture at given temperature to complete the iodination reaction, *after* the addition of concd H_2SO_4.

To explain the present method, it is necessary to recall our former paper;[5] alternatively, see our review,[2] p. 1337, where the supposed structures of the $\mathbf{I}^{3+}$ species and $ArISO_4$ intermediates are also shown and explained. In our former work,[5] we oxidatively substituted halobenzenes and deactivated arenes in *anhydrous* liquid systems, $I_2/NaIO_4$ or $NaIO_3/AcOH/Ac_2O/$ concd H_2SO_4, in which the said transient species, $\mathbf{I}^{3+}$, played a predominant role in electrophilic substitutions of the reacted arenes, ArH. These species were generated there as Scheme 3.

$$2\,I_2 + 3\,I(VII) \longrightarrow 7\,\mathbf{I}^{3+}$$

(***stoichiometry with*** $\boldsymbol{NaIO_4}$ ***used as oxidant***);

$$I_2 + 3\,I(V) \longrightarrow 5\,\mathbf{I}^{3+}$$

(***stoichiometry with*** $\boldsymbol{NaIO_3}$ ***used as oxidant***);

Scheme 3.

Next, the said strongly electrophilic $\mathbf{I}^{3+}$ species readily substituted ArH (Scheme 1). After pouring the resulting reaction mixtures into excess aq. Na_2SO_3 solutions, the corresponding *iodoarenes* were afforded: $ArISO_4 + Na_2SO_3 + H_2O \rightarrow \mathbf{ArI} + Na_2SO_4 + H_2SO_4$. Alternatively, the same resulting reaction mixtures were reacted upon with excess aq ammonium acetate solutions to afford *(diacetoxyiodo)arenes*:[2,6] $ArISO_4 + 2AcONH_4 \rightarrow \mathbf{ArI(OAc)_2} + (NH_4)_2SO_4$. Consequently, in the present work we added excess concd (36%) hydrochloric acid to the same resulting (final) reaction mixtures to precipitate out the corresponding *(dichloroiodo)arenes*, $\mathbf{ArICl_2}$ (Scheme 2). For more details see Experimental and Table 1.

Our novel, ***environmentally benign*** method for the preparation of crude $ArICl_2$ from the respective ***arenes*** (Table 1) avoids the hazardous application of gaseous Cl_2 and chlorinated solvents, and the use of *costly* iodoarenes, previously applied as starting substrates for preparing $ArICl_2$. Strongly acidic wastes obtained in the present method, after their neutralization and dilution, did *not* contain any toxic by-products, in contrast to many former methods.[1,2] Thus, our present method would be particularly suitable for *large-scale preparations* of, for example, (dichloroiodo)benzene; cf. Ref. 4. Of course, only those isomeric $RC_6H_4ICl_2$ may predominantly be obtained from the monosubstituted benzenes, RC_6H_5, which are formed in agreement with common orientation rules in the electrophilic substitutions of the used RC_6H_5 (Table 1) by the said strongly electrophilic $\mathbf{I}^{3+}$ transient species (Scheme 1).

Experimental

The melting/decomposition points of crude $ArICl_2$ (Table 1) were uncorrected and were determined as previously described.[7,8] All commercial reagents and solvents (Aldrich) were purified or dried, if necessary, prior to use. Diiodine was *finely powdered* in order to facilitate its dissolution in the reaction mixtures.

Optimized Procedures for the Preparation of $\mathbf{ArICl_2}$ from Arenes, ArH. $NaIO_4$ (1.41 g, 6.6 mmol; 10% excess) [or: $NaIO_3$ (1.43 g, 7.2 mmol; 20% excess)] and I_2 (1.12 g, 4.4 mmol; 10% excess) [or: I_2 (0.61 g, 2.4 mmol; 20% excess), when $NaIO_3$ was used as an oxidant] were suspended in a stirred mixture of glacial AcOH (10 mL) with Ac_2O (5 mL) cooled to 5 °C. *Varied quantities* (see Table 1) of concd (98%) H_2SO_4 were very slowly added dropwise with vigorous stirring while keeping the temperature below 10 °C. An appropriate arene (14 mmol; 0% excess) [or: arene (10 mmol; 0% excess), when $NaIO_3$ was used as an oxidant] was added portionwise or dropwise with stirring. Then, the *notably individualized reaction conditions* shown in Table 1 [i. e. the differentiated times of a further stirring at given temperatures to complete the iodinating reactions] were applied for each of the arenes iodinated (cf. Ref. 5). Dark-brown initial reaction mixtures faded to be finally yellowish. The resulting reaction mixtures, containing optimized quantities of the respective $ArISO_4$ intermediates, were cooled to ca. 5 °C, and concd (36%) hydrochloric acid (15 mL, ca. 170 mmol) was added with stirring while keeping the temperature at 5–10 °C. After ca. 30 min, the resulting suspensions were poured into stirred ice-water (ca. 300 g). After 15 min, yellow precipitates were collected by filtration, washed well with ice-cold water, until the filtrates were *neutral*, then with a little CCl_4, and air-dried[9] *in the dark*. Their melting points (Table 1) were taken immediately in the way explained in Refs. 7 and 8. The crude yields (Table 1) were calculated from the total amounts of the *arenes*, used in strictly stoichiometric quantities (0% excess). Iodometric titrations[3] indicated that the freshly prepared crude $ArICl_2$ had 90–96% purity.

Note. Exceptionally, PhI (3.14 g, 15.4 mmol; 10% excess) was oxidatively iodinated, but with strictly stoichiometric quantities of $NaIO_4$ (1.28 g, 6.0 mmol; 0% excess) and I_2 (1.02 g, 4.0 mmol; 0% excess); see Table 1 for the other reaction parameters. The crude yield for 4-$IC_6H_4ICl_2$ (Table 1) was calculated from the total amount of the *diiodine* consumed.

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