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Oxidative Chlorination of Various Iodoarenes to (Dichloroiodo)arenes with Chromium(VI) Oxide as the Oxidant†

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Chromium(VI) oxide dissolved in a mixture of acetic acid with concentrated hydrochloric acid converts, at or near room temperature, iodoarenes to (dichloroiodo)arenes, in a very simple and efficient procedure.

Organic hypervalent iodine reagents play an important role in organic synthesis, as demonstrated by a number of recent reviews.[1–6] The more stable, solid (dichloroiodo)-arenes, $ArICl_2$, *e.g.* (dichloroiodo)benzene, are widely used as potent and fairly selective halogenating and/or oxidizing agents. They have a practical advantage over elemental chlorine, due to their easy and safe handling. Moreover, they may be readily converted to the respective iodosylarenes, (diacyloxyiodo)arenes, (difluoroiodo)arenes, and iodylarenes, used as important reagents in organic syntheses.[1–6] The most common procedure[1–3,7,8] for the synthesis of $ArICl_2$ is by reacting an iodoarene, ArI, with dichlorine in chloroform at 0 °C; the yields are generally excellent when this method is applicable;[1–3,7] the anhydrous conditions previously demanded[8] are not necessary.[9] Quite recently,[10] the repeated preparations of $PhICl_2$ on a 20 kg scale (94% yield, mp 113–117 °C with decomp.) have been conducted by the direct chlorination of PhI at −3 to +4 °C; the substitution of $CHCl_3$ and CCl_4 as solvents for the less toxic CH_2Cl_2 is worth mentioning. $PhICl_2$ could be safely handled without major concerns for its thermal decomposition; under cooled conditions, it was possible to chlorinate 4-aminoacetophenone on a large scale, in 87% yield.

The inconvenient use of gaseous Cl_2 to afford $ArICl_2$ from ArI may be avoided as follows: (i) by using liquid SO_2Cl_2 added to a solution of ArI either in wet diethyl ether,[11] or (better) in 98% acetic acid;[12] (ii) by the action of hydrochloric acid on either iodosylarenes or (diacyloxyiodo)arenes previously otherwise obtained from ArI;[1–3,7] (iii) by the action of a liquid mixture: cobalt(III) acetate–KCl–67% aq. CF_3COOH on PhI;[13] (iv) by the use of hydrochloric acid oxidized *in situ* with sodium perborate in either acetonitrile or carbon tetrachloride containing a dissolved ArI.[14]

$ArICl_2$, yellow crystalline compounds, are light- and heat-sensitive and often unstable to storage. They do not usually give satisfactory microanalyses, and mostly should be used immediately after preparation. Due to their thermal lability, their melting points are rather uncertain, depend upon the rate of heating, and may be those of the parent ArI.[1,2]

We report in this paper a new, very simple, and efficient laboratory method for the conversion of some iodoarenes to (dichloroiodo)arenes, including (dichloroiodo)benzene obtained from iodobenzene in 95% crude yield (reaction time: 1 h; 95% purity). Our method avoids gaseous Cl_2 and, in our opinion, is relatively safe and inexpensive. We used concentrated (36%) hydrochloric acid oxidized *in situ* with different amounts (see Table 1) of chromium(VI) oxide, a common and easily handled oxidant, dissolved in aqueous acetic acid, and acting upon a dissolved (or suspended) iodoarene. The reactions proceeded according to the equation:

$$3\,ArI + 2\,CrO_3 + 12\,HCl \xrightarrow[\text{62–95\% (crude yields)}]{\text{aq. AcOH, room temp., 0.5–5 h}} 3\,ArICl_2 + 2\,CrCl_3 + 6\,H_2O$$

Table 1 Preparative details, crude yields, and melting points (uncorrected) of (dichloroiodo)arenes

Substrate ArI	CrO_3/g	*t*/h	Product $ArICl_2$	Yield (%)	Mp/°C (decomp.) (Lit., mp)
C_6H_5I	1.0	1.0	$C_6H_5ICl_2$	95[a]	111–112 (121),[14] (110–136; 115–127)[18]
4-$MeOC_6H_4I$	1.0	0.5	4-$MeOC_6H_4ICl_2$	62	75–76 (75–78)[14]
3-MeC_6H_4I	1.0	1.0	3-$MeC_6H_4ICl_2$	80	97–98 (100)[14]
4-MeC_6H_4I	1.0	1.0	4-$MeC_6H_4ICl_2$	81	108–111 (97)[14]
4-FC_6H_4I	1.0	2.0	4-$FC_6H_4ICl_2$	95	106–107 (105)[14]
2-ClC_6H_4I	1.0	2.0	2-$ClC_6H_4ICl_2$	78	96–98 (96–97)[18]
3-ClC_6H_4I	1.0	2.0	3-$ClC_6H_4ICl_2$	79	96–98 (99–100)[18]
4-ClC_6H_4I	1.0	1.0	4-$ClC_6H_4ICl_2$	86	110–112 (113)[14]
2,4-$Cl_2C_6H_3I$	3.0	5.0	2,4-$Cl_2C_6H_3ICl_2$	62	96–98 (107)[18]
2-$NO_2C_6H_4I$	3.0	3.0	2-$NO_2C_6H_4ICl_2$	77	92–94 (96)[18]
3-$NO_2C_6H_4I$	3.0[b]	2.0	3-$NO_2C_6H_4ICl_2$	74	94–95 (90)[14]
3-$HO_2CC_6H_4I$	3.0	3.0	3-$HO_2CC_6H_4ICl_2$	94	183–185 (185)[14]
3-$MeO_2CC_6H_4I$	1.0	1.0	3-$MeO_2CC_6H_4ICl_2$	84	108–110
3-$EtO_2CC_6H_4I$	1.0	1.0	3-$EtO_2CC_6H_4ICl_2$	83	98–100
5-Cl-2-$MeOC_6H_3I$	1.0	1.0	5-Cl-2-$MeOC_6H_3ICl_2$	91	100–102 (*ca.* 76)[19]
2-MeO-5-$NO_2C_6H_3I$	3.0	3.0	2-MeO-5-$NO_2C_6H_3ICl_2$	74	105–106
4-MeO-3-$NO_2C_6H_3I$	1.0	1.0	4-MeO-3-$NO_2C_6H_3ICl_2$	94	112–113

[a] When we enlarged the preparative scale twentyfold, the final yields for $PhICl_2$ were 92–94%. [b] On adding alternatively: (a) 1.0 g; (b) 2.0 g; (c) 3.0 g of CrO_3 (2.0 h, room temp.) to the reaction mixtures, the respective crude yields for 3-$NO_2C_6H_4ICl_2$ were as follows: 48, 59 and 74%.

The crude yellow products precipitated by water were collected by filtration, washed well on the filter with ice-cold water to remove $CrCl_3$, HCl, and AcOH, then with carbon tetrachloride to remove most of the unreacted ArI, and

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air-dried in the dark. Iodometric titrations,[7] carried out immediately, showed that they were of 92–98% purity. Hence, they may be used as such in subsequent reactions. So far, we have failed to chlorinate oxidatively 4-iodonitrobenzene, 4-iodobenzonitrile and 2,4,6-trichloroidobenzene.

The same procedure is effective for the aromatic chlorination of activated arenes. For example, we chlorinated 4-nitroanisole, 4-nitroacetanilide and 4-methoxybenzoic acid to obtain the respective pure chlorinated products: 2-chloro-4-nitroanisole (64%), mp 94–95 °C (from ethanol), lit.,[15] mp 93–94 °C; 2-chloro-4-nitroacetanilide (58%), mp 138–139 °C (from ethanol), lit.,[16] mp 139–140 °C; 3,5-dichloro-4-methoxybenzoic acid (42%), mp 202–204 °C (from ethanol), lit.,[17] mp 202–202.5 °C. Their purity was supported by correct elemental analyses (C, H, Cl).

Experimental

The starting iodoarenes, ArI, were either commercial or obtained by reported methods. They were purified prior to use, and analyzed (C, H, I). All the chlorination reactions were carried out **under a fume hood**. The *toxic* residues containing chromium salts were disposed of according to the local safety measures. Working on a small scale, we did not recover or remove chromium salts from the wastes. This should be taken into account, when preparations of larger quantities are required.

The melting points with decomposition (see Table 1) were uncorrected and were measured as follows: after an approximate mp had been taken in a capillary tube, a new sample was introduced about 10 °C below this point, and the temperature was raised at a rate of 10 °C min^{-1}.

General Procedure.—Powdered CrO_3 [either (see Table 1): (a) 1.0 g, 10 mmol, 50% excess; (b) 2.0 g, 20 mmol, 200% excess; (c) 3.0 g, 30 mmol, 350% excess] was dissolved in water (*ca.* 3–5 ml), this was added to glacial acetic acid (15 ml), then an appropriate iodoarene (10 mmol) was either dissolved or suspended, keeping the temperature below 30 °C. Concentrated (36%) hydrochloric acid (14 ml, 160 mmol, 300% excess) was added with vigorous stirring at or near room temp. The reaction mixture turned from orange to deep green, and a precipitate appeared either immediately or within several minutes. The resulting slurry was stirred for 0.5–5.0 h (see Table 1), then the whole was poured into ice–water (100 ml). The yellow precipitate was collected by filtration, washed well with ice-cold water until the washings were colourless and neutral, then with CCl_4. The crude product was air dried‡ in the dark. See Table 1 for the crude yields and melting points (with decomposition). Note: easily oxidizable iodoarenes, *e.g.* 4-iodoanisole and iodotoluenes, should be added to the reaction mixture after the addition of the whole portion of conc. HCl. Otherwise, the final yields of the corresponding $ArICl_2$ are very low.

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‡By drying the crude $ArICl_2$ in a vacuum desiccator, the chlorine percentage was lowered: $ArICl_2 \rightarrow ArI + Cl_2$.