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$RuCl_3$-Catalyzed Oxidation of Iodoarenes with Peracetic Acid: New Facile Preparation of Iodylarenes

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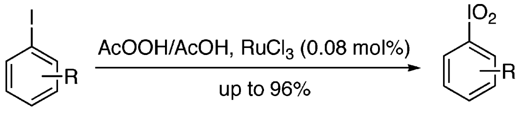
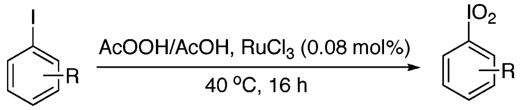


R = H, 4-Me, 2-Me, 2-*i*-Pr, 2-OMe, 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-F, 4-CF_3, 3,5-CF_3

New facile methodology for the preparation of pentavalent iodine compounds using peracetic acid as an oxidant in the presence of catalytic amounts of ruthenium trichloride is described. The new procedure allows the preparation of several previously unknown iodylarenes bearing strongly electron-withdrawing CF_3 groups in the aromatic ring.

Iodylarenes, $ArIO_2$, have attracted a significant current interest as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically useful oxidative transformations.[1] The best known representative of this class of compounds is 2-iodoxybenzoic acid, IBX (which exists in the benziodoxole tautomeric form); however, a variety of other iodylarenes, including the parent iodylbenzene,[2a] have found some synthetic application. During the last several years the preparation and synthetic utilization of numerous new iodylarenes have been reported.[2b−j] A typical procedure for the preparation of iodylarenes involves the oxidation of an iodoarene with a strong oxidizing reagent.[1a,f,g] Several experimental methods for the preparation of iodylbenzene have been reported in the literature including the disproportionation of iodosobenzene,[3a] or oxidations of iodobenzene with potassium peroxysulfate in concentrated sulfuric acid,[3b] sodium periodate,[3c,d] peracetic acid at 100 °C,[3e] and some other powerful and generally unsafe oxidizing systems. We now report a facile and convenient method for the preparation of iodylarenes by ruthenium-catalyzed oxidation of aryl iodides under mild conditions.

SCHEME 1. $RuCl_3$-Catalyzed Preparation of Iodylarenes



R = H, 4-Me, 2-Me, 2-*i*-Pr, 2-OMe, 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-F, 4-CF_3, 3,5-CF_3

In the course of our recent studies on the $RuCl_3$-catalyzed oxidation of alcohols with (diacetoxyiodo)benzene, we have also discovered that this reaction proceeds via an initial instantaneous Ru-catalyzed disproportionation of $PhI(OAc)_2$ to iodobenzene and iodylbenzene with the latter acting as the actual stoichiometric oxidant toward alcohols.[4] A similar example of the ruthenium-catalyzed disproportionation of PhIO yielding $PhIO_2$ and PhI was previously described in the literature.[5] Based on these observations, we have developed a $RuCl_3$-catalyzed direct one-pot conversion of ArI to $ArIO_2$ using peracetic acid as a stoichiometric oxidant (Scheme 1). This mild and convenient procedure combines in one-pot the known peracetic oxidation of ArI to $ArI(OAc)_2$[6] and the immediate disproportionation of the iodine(III) species in the presence of $RuCl_3$ leading to $ArIO_2$ as the final product.

This procedure (Scheme 1) requires much milder conditions (gentle warming to 40 °C) compared to the known noncatalytic oxidation of PhI to $PhIO_2$ with peracetic acid at 100 °C.[3e] Because of the milder conditions, the procedure is compatible with the presence of the electron-donating alkyl and alkoxy groups in the aromatic ring and can be applied for the preparation of methyl-, isopropyl-, and methoxy-substituted iodylarenes (Table 1, entries 2, 3, 5, 6). At the same time, this method allows the preparation of iodylarenes from iodoarenes bearing electron-withdrawing substituents, such as halogen atoms and CF_3 groups, in the aromatic ring (Table 1, entries

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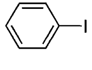
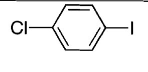
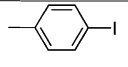
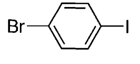
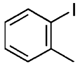
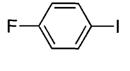
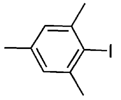
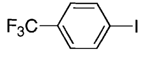
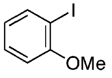
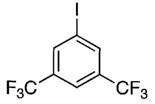
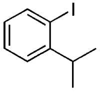
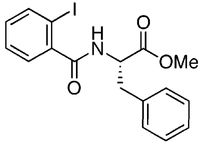
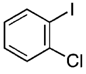
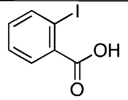
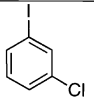
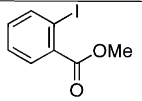
TABLE 1. Oxidation of Aryl Iodides with Peracetic Acid in the Presence of Ruthenium Trichloride

Entry	Substrate	Yield of $ArIO_2$ (%)[a,b]	m.p. (°C)	Entry	Substrate	Yield of $ArIO_2$ (%)[a,b]	m.p. (°C)
1		89	227 (dec)	9		90	230 (dec)
2		94	213 (dec)	10		96	227 (dec)
3		64	193 (dec)	11		87	234 (dec)
4		0[c]		12		83	213-216 (dec)
5		23[d]		13		91	206-209 (dec)
6		36[e]		14		0[c]	
7		89	209 (dec)	15		0 (85[f])	224 (dec)[f]
8		91	222-223 (dec)	16		0 (75[f])	224 (dec)[f]

[a] Isolated yields of analytically pure products. [b] All previously reported $ArIO_2$ were identified by comparison of their IR and NMR spectra with literature data (refs 3c,d); for analytical and spectroscopic characterization of new products (entries 6, 12, 13) see the Supporting Information. [c] Decomposition with formation of black tar was observed. [d] Significant decomposition occurred; yield determined by NMR. [e] Unreacted starting material (about 50%) was present in the reaction mixture. [f] 2-Iodosylbenzoic acid (1-hydroxy-(1H)-benzo-1,2-iodoxol-3-one) was isolated.

7−13). The most impressive result was the facile preparation of the previously unknown 1-iodyl-4-trifluoromethylbenzene (entry 12) and 1-iodyl-3,5-bis(trifluoromethyl)benzene (entry 13) in excellent yields.

The procedure in general is limited to the nonsterically hindered substrates. The attempted preparation of the unknown 1-iodyl-2,4,6-trimethylbenzene by the oxidation of 1-iodo-2,4,6-trimethylbenzene (entry 4, Table 1) resulted in complete decomposition with the formation of a black tar, probably, due to the low stability of the target iodylarene. At the same time, the preparation of the sterically hindered, previously unknown 1-iodyl-2-isopropylbenzene was successful (entry 6). It should be noted, however, that the oxidation of 1-iodo-2-isopropylbenzene was slow and a substantial amount of unreacted iodide was present in the reaction mixture even after 16 h.

The oxidation of 2-iodobenzoic acid (entry 15), and its derivatives (entries 14 and 16) has also failed to afford the desired iodine(V) derivatives. In the case of the 2-iodobenzamide derivative, a complete decomposition was observed, most likely because of the instability of the amido group under reaction conditions. The attempted preparation of 2-iodoxybenzoic acid (IBX) from 2-iodobenzoic acid (entry 15) and its ester (entry16) resulted in the formation of 2-iodosylbenzoic acid (IBA), which indicates that only noncyclic iodine(III) intermediates can disproportionate in the presence of $RuCl_3$.

The mechanism of the Ru-catalyzed disproportionation of iodine(III) compounds has been previously discussed in the literature. It is assumed, in particular, that the intermediate oxo ruthenium complexes are responsible for the oxygen transfer steps in the mechanism of disproportionation of iodine(III) species.[4,5] It is unlikely that $RuCl_3$ has any catalytic effect on the initial oxidation of ArI to $ArI(OAc)_2$. The uncatalyzed oxidation of iodoarenes with peracetic acid occurs at 30−40 °C in about 1 h, which is comparable with the conditions of the catalytic reaction (Scheme 1).

In conclusion, we reported the new facile methodology for the preparation of iodylarenes using peracetic acid as an oxidant in the presence of catalytic amounts of ruthenium trichloride. This new procedure allows the preparation of several previously unknown iodylarenes bearing strongly electron-withdrawing CF_3 groups in the aromatic ring, as well as the preparation of the sterically hindered 1-iodyl-2-isopropylbenzene.

Experimental Section

General Procedure for Preparation of Iodylarenes. Iodoarene (5 mmol) was added at 40 °C to a freshly prepared solution of peracetic acid in acetic acid (prepared by stirring a mixture of acetic anhydride (16 mL) and 35% H_2O_2 (4 mL) at 40 °C for 4 h), and the resulting mixture was stirred at 40 °C for 1 h. Then the solution of $RuCl_3$ in water (10 μL, 0.04 mmol/mL) was added, and the reaction was stirred at the same temperature for 16 h. Diethyl ether (80 mL) was added to the mixture after cooling to room temperature; the resulting white, microcrystalline precipitate of $ArIO_2$ was collected by filtration, washed with Et_2O, and dried in vacuum. Additional purification can be performed by crystallization from boiling water. ***Caution:*** *Dry iodylarenes are potentially hazardous compounds, which may explode upon impact, scratching with a spatula, or heating, and therefore should be handled with appropriate precautions.*

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Supporting Information Available: The general procedure of the oxidation of iodoarenes, full characterization data for new iodylarenes (1-iodyl-2-isopropylbenzene, 1-iodyl-4-trifluoromethylbenzene, and 1-iodyl-3,5-bis(trifluoromethyl)benzene), NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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