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Transition metal-mediated oxidations utilizing monomeric iodosyl- and iodylarene species

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ABSTRACT

Several transition metal-mediated oxidations using hypervalent iodine species are reported. A convenient procedure for preparation of iodylarenes via $RuCl_3$-catalyzed oxidation of iodoarenes has been developed. This procedure allows the generation of highly reactive monomeric iodine(V) species, which are excellent oxidants toward alcohols and hydrocarbons in situ. A broad range of substrates can be oxidized to carbonyl compounds by a tandem catalytic system based on the Ru(III)-catalyzed reoxidation of ArIO to $ArIO_2$ using Oxone® as oxidant. It was shown that electrophilic iodine(III) species, originating from oligomeric iodosylbenzene sulfate $(PhIO)_3SO_3$, are efficient oxygenating agents in catalytic oxidation of aromatic hydrocarbons in the presence of metalloporphyrin complexes.

1. Introduction

Hypervalent iodine compounds have found wide application as versatile and environmentally friendly oxidizing reagents in organic chemistry.[1] It has also been found that transition metals have a dramatic catalytic effect on some oxidations with hypervalent iodine reagents. In 1979 Groves and co-workers reported that iodosylbenzene, $(PhIO)_n$, is the most efficient source of oxygen in oxygenation of hydrocarbons in the presence of iron(III) porphyrin complexes,[2] and since then iodosylarenes and other hypervalent iodine reagents have been widely used as stoichiometric oxidants in the reactions mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.[3] Recent examples of transition metal-catalyzed oxidations employing iodosylbenzene include the hydroxylation of hydrocarbons,[4] the transition metal-mediated epoxidation of alkenes,[5] oxidation of alcohols to carbonyl compounds,[6,7] δ-sultone formation through Rh-catalyzed C–H insertion,[8a] and oxidation of organic sulfides to sulfoxides.[8b,c]

[Bis(acyloxy)iodo]arenes are also commonly used as stoichiometric oxidants in the reactions catalyzed by transition metal salts and complexes. (Diacetoxyiodo)benzene (DIB) is occasionally employed instead of iodosylbenzene as the terminal oxidant in biomimetic oxygenations catalyzed by metalloporphyrins and other transition metal complexes.[9] Primary and secondary alcohols can be selectively oxidized to the corresponding carbonyl compounds by DIB in the presence of transition metal catalysts, such as $RuCl_3$,[10] polymer-micelle incarcerated ruthenium catalysts,[11a] chiral-Mn(salen)-complexes,[11b,c] Mn(TPP)CN/Im catalytic system,[11d] and (salen)Cr(III) complexes.[11e] The epoxidation of alkenes, such as stilbenes, indene, and 1-methylcyclohexene, using DIB in the presence of chiral binaphthyl ruthenium(III) catalysts (5 mol %) has also been reported.[11f]

The mechanisms and applications of Pd-catalyzed reactions of DIB and other hypervalent iodine reagents in synthetically useful organic transformations were recently reviewed by Deprez and Sanford.[12a] Particularly useful are the Pd-catalyzed oxidation reactions, including the oxidative functionalization of C–H bonds and the 1,2-aminooxygenation of olefinic substrates.[12] Representative examples of these catalytic oxidations are illustrated by the selective acetoxylation of C–H bonds adjacent to coordinating functional groups,[12b] and by the $Pd(OAc)_2$-catalyzed intramolecular aminoacetoxylation in the reaction of γ-aminoolefins with DIB.[12c] The key mechanistic step in these catalytic transformations includes the DIB promoted oxidation of Pd(II) to the Pd(IV) species, as proved by the isolation and X-ray structural identification of stable Pd(IV) complexes prepared by the reaction of $PhI(O_2CPh)_2$ with Pd(II) complexes containing chelating 2-phenylpyridine ligands.[12o] Several examples of Pd-catalyzed chlorinations of organic substrates using (dichloroiodo)benzene have also been reported.[12p,q]

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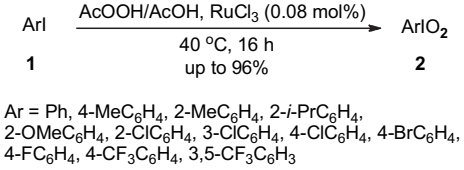
Our interest in the study of transition metal-mediated oxidations using hypervalent iodine reagents originated in 2006, when we had found a simple and efficient procedure for the Ru-catalyzed oxidation of alcohols to carbonyl compounds using (diacetoxyiodo)benzene as stoichiometric oxidant.[10a] This reaction involved an initial instantaneous $RuCl_3$-catalyzed disproportionation of DIB to iodobenzene and iodylbenzene with the latter acting as the actual stoichiometric oxidant toward alcohols. In the present work we report our further studies on the application of organoiodine(III) and organoiodine(V) compounds in the transition metal-catalyzed oxidations of alcohols and aromatic hydrocarbons.

2. Results and discussion

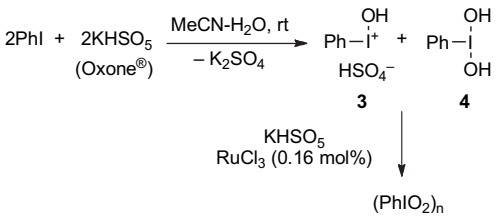
2.1. Transition metal-mediated oxidations utilizing iodine(V) species

Our studies of the $RuCl_3$-catalyzed disproportionation of DIB to iodobenzene and iodylbenzene[10a] resulted in the development of a facile experimental procedure for the preparation of iodylarenes via $RuCl_3$-catalyzed oxidation of iodoarenes with peracetic acid (Scheme 1).[13]



Scheme 1. Preparation of iodylarenes via $RuCl_3$-catalyzed oxidation of iodoarenes with peracetic acid.

Further studies have demonstrated that the use of Oxone® as the oxidant instead of peracetic acid leads to even milder reaction conditions. In a typical procedure, treatment of iodobenzene with Oxone® in aqueous acetonitrile at room temperature in the presence of $RuCl_3$ (0.16 mol %) results in the formation of iodylbenzene $(PhIO_2)_n$, which can be isolated from the reaction mixture in a 59% preparative yield (Scheme 2). We suggest that this reaction starts with the initial oxidation of iodoarene to the iodine(III) species **3** (protonated PhIO) and **4** (hydrated PhIO) by Oxone® at room temperature.



Scheme 2. $RuCl_3$-catalyzed oxidation of iodobenzene with Oxone®.

A special experiment shows that PhI reacts with Oxone® instantaneously at room temperature in the absence of $RuCl_3$ producing a yellow solution. The ESI mass-spectrometry study of this solution indicates the presence of hypervalent iodine(III) species, hydroxy(phenyl)iodonium ion **3**, and iodosylbenzene, along with unreacted iodobenzene (Fig. 1). The same iodine(III) electrophilic species are present in the aqueous solutions of oligomeric iodosylbenzene sulfate $(PhIO)_3SO_3$ (see ESI mass spectrum of $(PhIO)_3SO_3$ in Section 2.2), which can be prepared by simple treatment of commercially available (diacetoxyiodo)benzene with aqueous hydrogen sulfate and isolated as a thermally stable, yellow crystalline solid, which can be used as a reagent for oxidative functionalization of organic substrates.[14a–e] The use of $(PhIO)_3SO_3$ in metalloporphyrin or phthalocyanine-catalyzed oxygenations is described in Section 2.2 of this article. The preparation and reactions of protonated iodosylbenzene monomer, $PhI(OH)BF_4$, which can be stabilized by complexation with 18C6 crown ether, has previously been reported by Ochiai.[1r] Very recently, we have developed a mild and convenient procedure for preparation of [bis(trifluoroacetoxy)iodo]perfluoroalkanes and [bis(trifluoroacetoxy)iodo]arenes based on the room temperature oxidation of ArI to ArI(III)-species with Oxone® (Scheme 2).[14f]

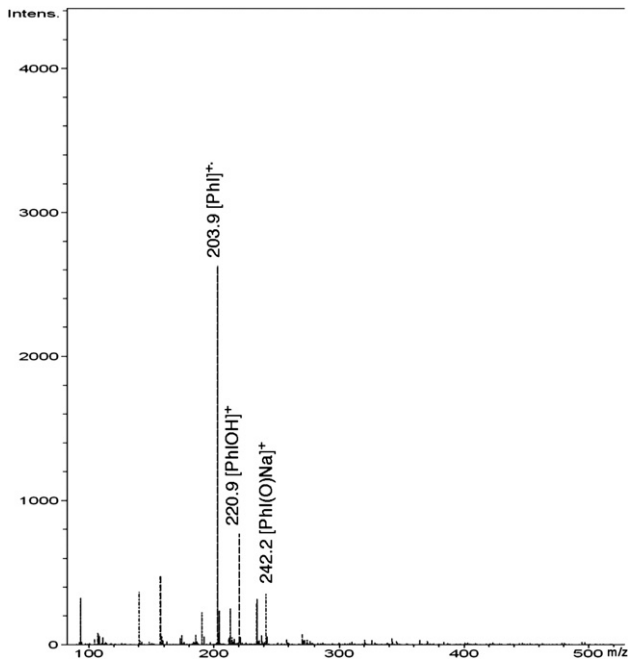


Figure 1. ESI mass spectrum of PhI/Oxone® mixture in aqueous acetonitrile in the absence of $RuCl_3$.

We assume that in the presence of $RuCl_3$ the initially formed species **3** and **4** are further converted to iodylbenzene via a Ru-catalyzed oxidation with Oxone®. It is likely that the intermediate oxoruthenium complexes are responsible for catalytic oxidation of the initially formed iodine(III) species **3** and **4** to the iodine(V) species. An experimental evidence toward catalytic oxidation of PhIO to $PhIO_2$ mediated by the oxoruthenium species has previously been documented,[15a] and the generation and identification of highly reactive ruthenium(V)-oxo species were reported in the literature.[15b–d] The polymeric, insoluble iodylbenzene, $(PhIO_2)_n$,[16] is the final, isolated product that slowly precipitates from this reaction (Scheme 2); however, the exact nature of the initially formed monomeric iodine(V) species in Scheme 2 remains unknown. Most likely, these species are represented by some activated form of monomeric $PhIO_2$ (e.g., protonated, hydrated, or a peroxysulfate derivatives shown in Fig. 2), which show extremely high oxidative reactivity toward organic substrates.

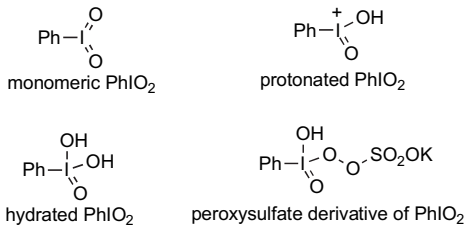
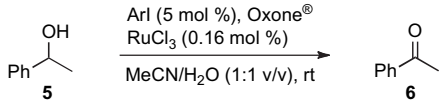


Figure 2. Hypothetical active monomeric iodine(V) species generated from PhI/Oxone® mixture in aqueous acetonitrile in the presence of $RuCl_3$.

In our initial research we have utilized the monomeric $PhIO_2$ species as a highly reactive stoichiometric oxidant toward the oxidation of alcohols.[10a] Further studies of this reaction have led us to the development of extremely mild and efficient tandem catalytic system for the oxidation of alcohols and hydrocarbons based on a Ru(III)-catalyzed reoxidation of ArIO to $ArIO_2$ using Oxone® as a stoichiometric oxidant.[17]

Taking into account that the Ru(III)-catalyzed oxidation of alcohols usually occurs only at temperatures above 80 °C,[18] while iodylarenes are effective oxidants at room temperature,[1f,k] we investigated the oxidation of alcohols using ArI/$RuCl_3$ tandem catalytic system. The reaction was optimized using 1-phenylethanol **5** as a model substrate (Table 1). As expected, in the absence of PhI and in the presence of $RuCl_3$ (0.16 mol %), or in the presence of PhI without $RuCl_3$ the oxidation of substrate **5** at room temperature proceeds very slowly (Table 1, entries 1 and 2). The combined application of PhI and $RuCl_3$ results in almost instantaneous oxidation of phenylethanol **5** to acetophenone **6** with a 100% conversion reached in less than 20 min (entry 3). The optimized reaction requires at least 1 mol equiv of Oxone® (2 equiv of active oxygen); the use of smaller amounts of Oxone® leads to incomplete conversion (entry 4) due to its noticeable decomposition with loss of oxygen gas under reaction conditions. Several other iodoarenes tested in this reaction showed a comparable to PhI high catalytic activity (entries 5–8).

Table 1
Effect of ArI and $RuCl_3$ on the oxidation of 1-phenylethanol to acetophenone with Oxone®[a]



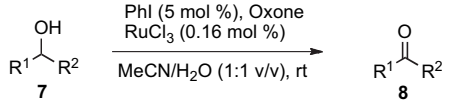
Entry	ArI	Oxone® (mol equiv)	Time (h)	Conversion (%)[b]
1	None	1.5	0.3	12[c]
2	PhI[d]	1.0	1.0	0
3	PhI	1.0	0.3	100
4	PhI	0.67	1.0	83
5	2-$IC_6H_4SO_3H$	1.25	0.3	100
6	4-$IC_6H_4SO_3H$	1.15	0.3	100
7	4-$IC_6H_4SO_3Na$	1.25	0.6	100
8	3-$IC_6H_4CO_2H$	1.22	1.0	99

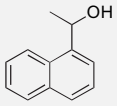
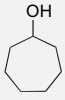
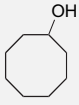
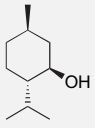
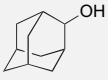
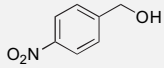
[a] All reactions were performed at room temperature in MeCN/H_2O (1:1 v/v) using 0.1 mmol of 1-phenylethanol, 0.16 mol % of $RuCl_3$, and 5 mol % of ArI unless otherwise noted.
[b] The conversion was determined by GC analysis. According to GC acetophenone **6** was the only product resulting from the oxidation of 1-phenylethanol **5** under these conditions.
[c] Also contains 8% of styrene and 80% of unreacted alcohol.
[d] No $RuCl_3$ added.

A variety of alcohols **7** are smoothly oxidized under optimized reaction conditions to afford the respective oxidation products **8** in excellent isolated yields at room temperature (Table 2). Similar to the high-temperature ArI/Oxone® procedure,[19] our protocol affords ketones from the secondary alcohols (entries 1–9) and mainly carboxylic acids from primary alcohols (entries 10 and 11). Shorter reaction time, however, allows to oxidize benzyl alcohol predominantly to benzaldehyde (entry 12). The use of smaller quantities of Oxone® and shortening reaction time in the oxidation of other primary alcohols (cf. entries 10 and 11) also leads to the predominant formation of aldehydes.

Selective oxidation of activated and unactivated C–H bonds is of particular interest for organic chemists. The pentavalent iodine reagent, IBX, has been demonstrated to be a reagent of choice for the oxidation of benzylic C–H bonds.[20] Recently, the oxidation of benzylic C–H bonds has been performed under catalytic conditions by the in situ formed IBX using Oxone® as a terminal oxidant at 70–80 °C for 8–48 h.[21] We investigated the oxidation of C–H

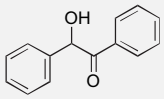
Table 2
PhI/$RuCl_3$-cocatalyzed oxidation of alcohols[a]



Entry	Alcohol **7**	Oxone® (mol equiv)	Time (h)	Yield of **8** (%)[b]
1		1.2	0.3	100
2		1.2	10	96
3		2.0	7	100
4		1.0	2	92
5		1.2	0.8	100
6		1.0	0.5	100
7		1.05	0.5	100
8		1.0	0.8	99
9		1.0	0.8	100
10		2.4	4	96[c]
11	$CH_3(CH_2)_7OH$	1.1	16	100[d]
12		1.25	1.5	80[e]
13		1.2	1	82[f]
14		1.6	1	90[f]
15		1.4	10	100[f]

(*continued on next page*)

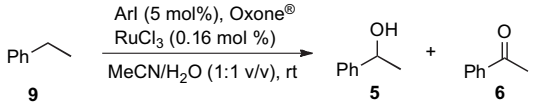
Table 2 (*continued*)

Entry	Alcohol **7**	Oxone® (mol equiv)	Time (h)	Yield of **8** (%)[b]
16		1.0	2	93[f]
17		4.5	18	87[f,g]

[a] All reactions were performed at room temperature in MeCN/H_2O (1:1 v/v) using 1 mmol of alcohol, 0.16 mol % of $RuCl_3$ and 5 mol % of PhI unless otherwise noted.
[b] Yields of isolated pure products **8** are shown unless otherwise noted.
[c] 4-$NO_2C_6H_4CO_2H$ is the only product formed under these conditions.
[d] $CH_3(CH_2)_6CO_2H$ is the only isolated product.
[e] Isolated yield of 2,4-dinitrophenylhydrazone of benzaldehyde.
[f] Yield of product was determined by GC analysis using the initially added PhI as an internal standard (after reductive treatment of the reaction mixture with $Na_2S_2O_3$).
[g] Also contains 13% of benzoic acid.

bonds using ArI/$RuCl_3$ tandem catalytic system. The reaction was optimized using ethylbenzene **9** as a model substrate (Table 3). As expected, in the absence of PhI and in the presence of $RuCl_3$, or in the presence of PhI and in the absence of $RuCl_3$ the oxidation of substrate **9** at room temperature does not occur or proceeds very

Table 3
Effect of ArI and $RuCl_3$ on the oxidation of ethylbenzene **9** with Oxone®[a]



9 **5** **6**

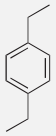
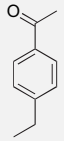
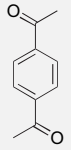
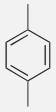
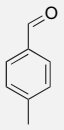
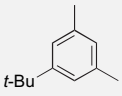
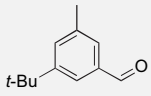
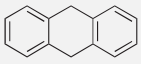
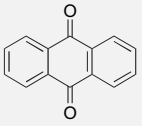
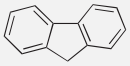
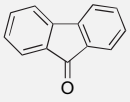
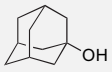
Entry	ArI	Oxone® (mol equiv)	Time (h)	Products (%)[b]
1	None	1.05	3.3	**5** (1%), **6** (8%)
2	PhI[c]	1.05	24.0	**5** (0%), **6** (0%)
3	PhI	1.05	3.3	**5** (0.5%), **6** (27%)
4	2-$IC_6H_4SO_3H$	1.05	3.3	**5** (1%), **6** (31%)
5	4-$IC_6H_4SO_3H$	1.05	3.3	**5** (0.5%), **6** (17%)
6	2-$IC_6H_4CO_2H$	1.05	3.3	**5** (1%), **6** (30%)
7	3-$IC_6H_4CO_2H$	1.03	3.3	**5** (0%), **6** (18%)
8	4-$IC_6H_4CF_3$	1.05	3.3	**5** (0%), **6** (13%)
9	4-IC_6H_4Br	1.05	3.3	**5** (0%), **6** (21%)
10	PhI	2.10[d]	4.0	**5** (0%), **6** (50%)
11	None	2.10[d]	4.0	**5** (0%), **6** (14%)
12	PhI[e]	4.2[f]	11.5	**5** (0%), **6** (80%)

[a] All reactions were performed at room temperature in MeCN/H_2O (1:1 v/v) using 0.1 mmol of ethylbenzene **5**, 5 mol % of ArI, and 0.16 mol % of $RuCl_3$ unless otherwise noted.
[b] Product yields were determined by GC analysis; unreacted ethylbenzene **9** was the only other product present in all entries.
[c] No $RuCl_3$ added.
[d] 1.05 mol equiv of Oxone® added initially and the second portion 1.05 mol equiv added after 2 h.
[e] 10 mol % of PhI was used.
[f] 0.9 mol equiv of Oxone® added initially, the second portion 1.1 mol equiv added after 2 h, the third portion 1.1 mol equiv added 4 h later, and the final portion 1.1 mol equiv added 3 h later.

slowly (Table 3, entries 1, 2, and 11). The combined application of PhI and $RuCl_3$ results in a 27% conversion of ethylbenzene **9** to acetophenone **6** (entry 3). The optimized reaction conditions leading to 80% conversion of substrate **9** to product **6** require the addition of 4.2 mol equiv of Oxone® in small portions over 11 h and the use of 10 mol % of PhI (entry 12). Out of several other iodoarenes tested in this reaction, 2-iodosulfonic acid and 2-iodobenzoic acid showed slightly better catalytic effect than iodobenzene (entries 4–9); however, a noticeable amount of by-product **5** was observed with these catalysts.

The results of the oxidation of several other hydrocarbons under optimized catalytic conditions are summarized in Table 4. In general, moderate to high yields of aromatic ketones are obtained in these oxidations under very mild reaction conditions (entries 1–8).

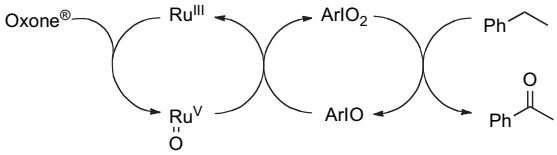
Table 4
PhI/$RuCl_3$-cocatalyzed oxidation of hydrocarbons[a]

Entry	Substrate	Oxone® (equiv)	Time (h)	Products	Yield (%)[b]
1		6.1[c]	26		80
2		2.06	3		77
					11
3		1.0[c]	24		18[d]
4		1.2	6		23
5		2.0[c,e]	1		95
6		1.2[c]	1		69
7		8.2[c]	20		72
8		4.7[c]	20		38[d]
9		2.5[c]	8		1.5[d]

[a] All reactions were performed at room temperature in MeCN/H_2O (1:1 v/v) using 1.0 mmol of a hydrocarbon, 0.16 mol % of $RuCl_3$ and 5 mol % of PhI unless otherwise noted.
[b] Yields of isolated products are shown; unreacted hydrocarbons were also present in all entries.
[c] Oxone® was added in small portions during the indicated time period.
[d] Yield was determined by GC analysis.
[e] 10 mol % of PhI was used.

Compared to the high-temperature IBX/Oxone® procedure,[21] our protocol is much more selective and generally does not afford products of C–C bond cleavage and carboxylic acids. The oxidation of an unactivated C–H bond in adamantane under these conditions proceeds with a low conversion affording 1-adamantanol in only 1.5% yield (entry 9).

A plausible, simplified mechanism for these catalytic oxidations is shown in Scheme 3 that includes two catalytic redox cycles. The



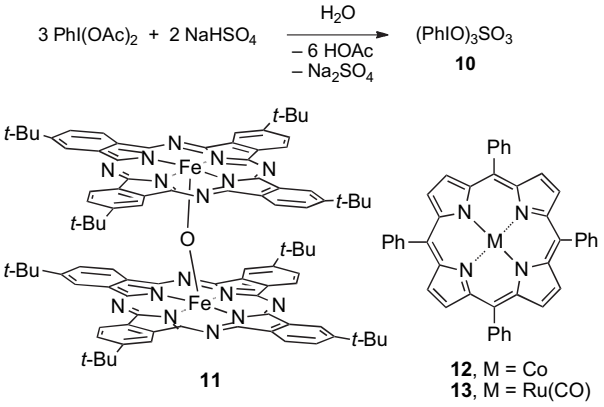
Scheme 3. Tandem catalytic system for the oxidation of organic substrates with Oxone®.

reaction starts with the initial oxidation of ArI to ArIO and then to $ArIO_2$ by the Oxone®/Ru(III,V) system as inferred from Schemes 1 and 2. The generated in situ, highly active monomeric $ArIO_2$ species (Fig. 2) are responsible for actual oxidation of organic substrates by known mechanisms.[20,21] We propose that the intermediate oxoruthenium complexes are responsible for the reoxidation of the initially formed ArIO to $ArIO_2$ (Scheme 3). An experimental evidence toward catalytic oxidation of PhIO to $PhIO_2$ mediated by the oxoruthenium species has previously been documented,[15a] and the generation and identification of highly reactive ruthenium(V)-oxo species was reported in the literature.[15b–d] It is also possible that the oxidation of organic substrates with $ArIO_2$ in this system is additionally catalyzed by ruthenium species. Several examples of transition metal-catalyzed oxidations using $ArIO_2$ as a stoichiometric oxidant have been reported.[7,10,14e]

2.2. Transition metal-catalyzed oxidations utilizing iodine(III) species

Among hypervalent iodine(III) reagents, iodosylbenzene, $(PhIO)_n$, is particularly important as an efficient oxygen transfer agent that has found widespread application in various oxygenation reactions.[1,22] Since 1979 $(PhIO)_n$ has been widely used as a terminal oxidant in the reactions mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.[2,3] Despite its usefulness as an oxidant, practical applications of iodosylbenzene are hampered by its low solubility in nonreactive media,[22] as well as low thermal stability and explosive properties upon moderate heating.[23]

We have investigated relative reactivity of iodosylbenzene and a readily available, stable oligomeric iodosylbenzene sulfate **10** in the oxygenation of anthracene to anthraquinone catalyzed by μ-oxo diiron-phthalocyanine complex **11**, Co(II)-tetraphenylporphyrin **12** or Ru(II)-tetraphenylporphyrin **13** (Scheme 4).[14e] The oligomeric



Scheme 4. Oligomeric iodosylbenzene sulfate **10**, Fe(III)-phthalocyanine complex **11**, Co(II)-tetraphenylporphyrin **12**, and Ru(II)-tetraphenylporphyrin **13**.

iodosylbenzene sulfate **10** was prepared by simple treatment of commercially available (diacetoxyiodo)benzene with aqueous hydrogen sulfate and isolated as a thermally stable, yellow crystalline solid.[14a,b] The structure of reagent **10** was previously established by single crystal X-ray diffraction and confirmed by mass-spectrometry in solution.[14a] In particular, the ESI mass-spectrometry study of compound **10** in aqueous solution indicates mainly the presence of hydroxy(phenyl)iodonium ion **3** along with dimeric and trimeric protonated iodosylbenzene units (Fig. 3).

The μ-oxo diiron-phthalocyanine complex **11** was prepared using direct high-temperature reaction between 4-*tert*-butylphthalonitrile and iron(II) acetate as described previously,[24a–c] while Co(II)-tetraphenylporphyrin **12** and Ru(II)-carbonyl tetraphenylporphyrin **13** were used from commercial sources. It was shown recently that porphyrin and phthalocyanine iron (III) μ-oxo-,[24d–f] and μ-nitrido-dimers,[24g,h] which were earlier considered as catalytically inactive compounds, in many cases have high catalytic activity in different oxidation reactions. Previously, we have reported the use of complexes **11**–**13** in catalytic oxidations of alcohols.[7]

We have investigated catalytic oxidation of anthracene **14** to anthraquinone **15** using complexes **11**–**13** as catalysts and oligomeric iodosylbenzene sulfate **10** as the oxidant in comparison with iodosylbenzene as the common oxygenating reagent (Scheme 5). The use of iodosylbenzene in this reaction in the presence of transition metal complexes was previously reported in the literature.[25]

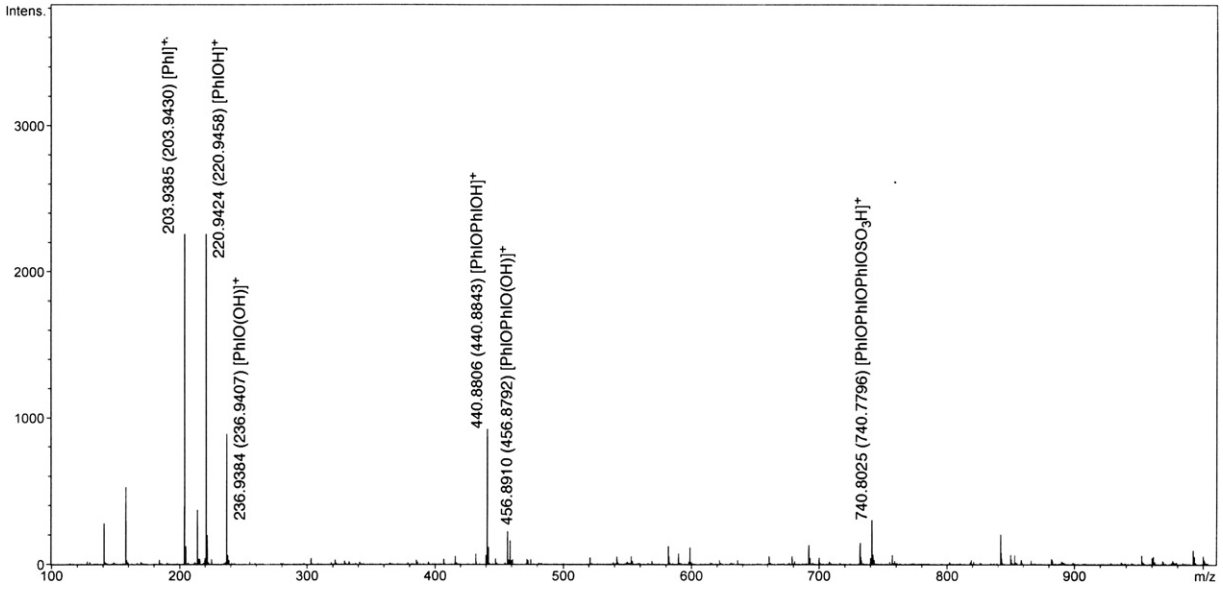
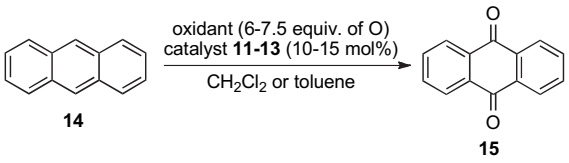


Figure 3. HR-ESI mass spectrum of oligomeric iodosylbenzene sulfate **10** in aqueous acetonitrile (calculated mass shown in parenthesis).



Scheme 5. Catalytic oxidation of anthracene **14** to anthraquinone **15**.

The oxidation of anthracene was carried out in dry dichloromethane or in toluene using 2.0–2.5 times excess (6.0–7.5 mol equiv of active oxygen per one molecule of anthracene **14**) with 0.10–0.15 equiv of the appropriate catalyst (Table 5). After indicated time, the catalyst was removed by flash chromatography and the obtained solution was analyzed by GC–MS to determine the conversion of anthracene **14** to anthraquinone **15**. According to the GC–MS and NMR data, anthraquinone **15** and iodobenzene resulting from the reduction of hypervalent iodine reagents were the only products formed under these reaction conditions. Dichloromethane was found to be the best solvent for the oxidations in the presence of metalloporphyrins **12** and **13**. Toluene was used for the reactions catalyzed by μ-oxo diiron-phthalocyanine **11** due to the instability of complex **11** in dichloromethane solutions. The results of the oxidations are summarized in Table 5.

Table 5
Metalloporphyrin or phthalocyanine-catalyzed oxidations of anthracene **14** to anthraquinone **15** using hypervalent iodine(III) reagents[a]

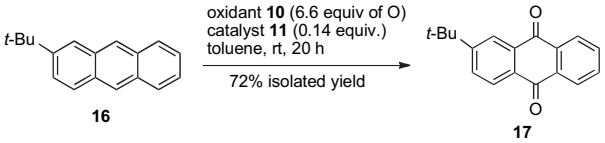
Entry	Reagent	Catalyst (mol %)	Solvent	Time (h)	Yield of **15** (%)[b]
1	**10**	None	PhMe	24	0
2	**10**	**11** (10)	PhMe	2	100
3	**10**	**12** (10)	CH_2Cl_2	2	100
4	**10**	**13** (10)	CH_2Cl_2	1	100
5	$(PhIO)_n$	None	PhMe	24	0
6	$(PhIO)_n$	**11** (10)	PhMe	5	100
7	$(PhIO)_n$	**12** (15)	CH_2Cl_2	2	26
8	$(PhIO)_n$	**13** (15)	CH_2Cl_2	3	7
9	$(PhIO)_n$	**13** (15)	CH_2Cl_2	24	100

[a] All reactions were performed at room temperature using 2.5 mol equiv of reagent **10** or 7.5 mol equiv of $(PhIO)_n$.
[b] Yield was determined by GC analysis.

First of all, we have found that the oxidation of anthracene with hypervalent iodine reagents in the absence of catalysts at room temperature in toluene or dichloromethane proceeds extremely slow and does not show any measurable conversion to anthraquinone after 24 h (entries 1 and 5). The addition of 0.1 mol equiv of catalysts **11**–**13** leads to a significant increase in the reaction rate. The oligomeric iodosylbenzene sulfate **10** shows high reactivity in catalytic oxidations at room temperature in the presence of any of the catalysts **11**–**13** (10 mol %), while the reaction in the absence of catalysts at room temperature does not occur (entry 1). The best catalytic effect is observed in the presence of Ru(II)-porphyrin **13** (entry 4; 100% conversion in 1 h). The reactivity of oxidant **10** in the presence of catalysts **11** and **12** is slightly lower (entries 2 and 3; 100% conversion in 2 h). Iodosylbenzene is less reactive as the source of oxygen under identical reaction conditions (entries 6–9) with a 100% conversion reached after 5 h using catalyst **11** (entry 6) and only after 24 h when using catalyst **13** (entry 9).

The data presented in Table 5 clearly indicate that the oligomeric iodosylbenzene sulfate **10** is the best oxidant, significantly more reactive than the commonly used iodosylbenzene. The slower reaction with iodosylbenzene can partially be explained by its polymeric structure, $(PhIO)_n$, requiring initial depolymerization, while the structure of sulfate **10** consists of smaller oligomeric units of PhIO (cf. Fig. 3), which have more electrophilic character due to the ionic nature of this reagent. The ruthenium(II) complex **13** shows the highest catalytic activity in oxidations with reagent **10**; however, the availability and low cost of iron(III) complex **11** as compared to the ruthenium porphyrin **13** make it a potentially useful reagent for biomimetic catalytic transformations.

In order to demonstrate the general character of the optimized reaction conditions, we performed the oxidation of 2-*tert*-butylanthracene **16** using oxidant **10** in the presence of the μ-oxo diiron-phthalocyanine complex **11** (Scheme 6). Compared to the oxidation of anthracene **14**, the reaction of 2-*tert*-butylanthracene **16** was slower, probably due to steric hindrance caused by the *tert*-butyl group, with a 100% conversion reached only after 20 h at room temperature. The GC analysis of the reaction mixture indicated the presence of a single product of oxidation, 2-*tert*-butylanthraquinone **17**, along with iodobenzene resulting from the reduction of reagent **10**. 2-*tert*-Butylanthraquinone **17** was isolated from the reaction mixture by preparative column chromatography on silica gel as yellow needles in 72% yield and identified by comparison with authentic sample.[26]



Scheme 6. Catalytic oxidation of 2-*tert*-butylanthracene **16** to 2-*tert*-butylanthraquinone **17** using oligomeric iodosylbenzene sulfate **10** as the oxidant.

3. Conclusions

In summary, we have reported a series of transition metal-mediated oxidations using hypervalent iodine species. Based on the facile $RuCl_3$-catalyzed disproportionation of (diacetoxyiodo)benzene to iodobenzene and iodylbenzene, we have developed a convenient experimental procedure for the preparation of iodylarenes via $RuCl_3$-catalyzed oxidation of iodoarenes with peracetic acid. Further studies have demonstrated that the use of Oxone® as the oxidant instead of peracetic acid leads to even milder reaction conditions allowing the generation of the highly reactive monomeric iodine(V) species in situ at room temperature. Based on these observations, we have developed extremely mild and efficient tandem catalytic system for the oxidation of alcohols and hydrocarbons based on a Ru(III)-catalyzed reoxidation of ArIO to $ArIO_2$ using Oxone® as a stoichiometric oxidant. Due to the mild reaction conditions our protocol is highly selective and generally does not afford products of C–C bond cleavage. Finally, we have shown that the electrophilic iodine(III) species, originating from oligomeric iodosylbenzene sulfate **10**, are efficient oxygenating agents in catalytic oxidation of aromatic hydrocarbons in the presence of metalloporphyrin or phthalocyanine complexes. Reagent **10**, which can be conveniently prepared from (diacetoxyiodo)benzene and $NaHSO_4$ in aqueous solution, can be used as a safe and convenient alternative to the potentially explosive iodosylbenzene in the biomimetic oxidations mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.

4. Experimental section

4.1. General

All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Toluene and dichloromethane were distilled from CaH_2 and stored over molecular sieves. Catalyst **11**,[24a,b] iodosylbenzene sulfate **10**[14a,b] and iodosylbenzene[22] were prepared by known methods. GC–MS analysis was carried out with a HP 5890A Gas Chromatograph using a 5970 Series mass selective detector. Mass spectrometric (ESI–MS)

analyses were obtained at the University of Minnesota Minneapolis Mass Spectrometry Facility, using BioTOF II mass spectrometer. NMR spectra were recorded on Varian INOVA instrument with 500 MHz frequency for ^{1}H NMR and 125 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million and referenced to TMS as an internal standard.

4.2. General procedure for the preparation of iodylarenes 2 via $RuCl_3$-catalyzed oxidation of iodoarenes 1 with peracetic acid (Scheme 1)

The mixture of acetic anhydride (16 mL) and 35% H_2O_2 (4 mL) was stirred at 40 °C for 4 h, then the appropriate iodoarene (5 mmol) was added and the mixture was stirred at 40 °C for additional 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, the resulting solid precipitate was collected by filtration, washed with Et_2O, and dried in vacuo to give product **2** as white microcrystalline solid. Samples for elemental analysis were additionally recrystallized from boiling water.

4.2.1. Representative data for products ***2****. 4.2.1.1. 1-Iodyl-2-isopropylbenzene.* Oxidation of 1-iodo-2-isopropylbenzene (1.23 g, 5.0 mmol) according to the general procedure afforded 0.50 g (36%) of product, isolated as microcrystalline solid, mp 173–175 °C. ^{1}H NMR (DMSO-d_6): δ 7.94 (d, J=7.5 Hz, 1H), 7.57 (m, 3H), 3.22 (septet, 6.5 Hz, 1H), 1.29 (d, 7.0 Hz, 6H). ^{13}C NMR (DMSO-d_6): δ 148.7, 147.0, 132.1, 127.1, 126.9, 122.6, 33.0, 23.7. Anal. Calcd for $C_9H_{11}IO_2 \cdot 0.75H_2O$: C, 37.07; H, 4.32. Found: C, 37.04; H, 3.92.

4.2.1.2. 1-Iodyl-4-trifluoromethylbenzene. Oxidation of 1-iodo-4-trifluoromethylbenzene (1.36 g, 5.0 mmol) under general conditions afforded 1.26 g (83%) of product, isolated as microcrystalline solid, mp 213–215 °C (with decomposition). ^{1}H NMR (DMSO-d_6): δ 8.17 (d, J=8.0, 2H), 7.95 (d, J=8.1 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 155.4 (d, J=1.5 Hz), 131.1 (d, J=31.7 Hz), 127.5, 125.7 (q, J=3.8 Hz), 123.8 (q, J=271 Hz). Anal. Calcd for $C_7H_4F_3IO_2 \cdot 0.25H_2O$: C, 27.25; H, 1.47. Found: C, 27.00; H, 1.23.

4.2.1.3. 1-Iodyl-3,5-bis(trifluoromethyl)benzene. Oxidation of 1-iodo-3,5-bis(trifluoromethyl)benzene (1.70 g, 5.0 mmol) under general conditions afforded 1.69 g (91%) of product, isolated as microcrystalline solid, mp 206–209 °C (with decomposition). ^{1}H NMR (DMSO-d_6): δ 8.58 (s, 2H), 8.3 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 153.8, 130.2 (q, J=33.2 Hz), 127.5 (d, J=3.4 Hz), 124.8 (q=3.6 Hz), 123.0 (q, J=273.3 Hz). Anal. Calcd for $C_8H_3F_6IO_2$: C, 25.83; H, 0.81. Found: C, 25.48; H, 0.83.

4.3. $RuCl_3$-catalyzed oxidation of iodobenzene to iodylbenzene using Oxone® (Scheme 2)

To a mixture of iodobenzene (0.204 g, 1 mmol) and Oxone® (0.33 g, 0.54 mmol) in 3 mL of aqueous acetonitrile ($MeCN/H_2O$, 1:1) an aqueous solution of $RuCl_3$ (10 μL of standard 0.16 M solution; 0. 0016 mmol) was added via syringe under stirring at room temperature. After stirring for 30 min the second portion of Oxone® (0.32 g, 0.52 mmol) was added and then after additional 50 min the third portion of Oxone® (0.11 g, 0.18 mmol) was added. The reaction mixture was stirred for 2 h 20 min (the reaction was monitored by TLC by disappearance of PhI), and then the precipitate was filtered, washed with cold water, and dried to afford 0.14 g (59%) of iodylbenzene, mp 229–230 °C (crystallized from hot water; explodes at mp); IR (KBr): 731, 713 (IO_2); ^{1}H NMR (DMSO-d_6) δ 7.92 (m, 2H) 7.59 (m, 3H); ^{13}C NMR (DMSO-d_6) δ 150.8 (C–IO_2), 131.7, 129.1, 126.6. Literature data: mp 235 °C (expl.).[27]

4.4. Typical preparative procedure for PhI/$RuCl_3$-cocatalyzed oxidation of alcohols (Table 2)

Table 2, entry 2. To a mixture of benzhydrol (184 mg, 1 mmol), PhI (0.5 mL of standard solution; 0.05 mmol; 5 mol %), and Oxone® (0.737 g, 1.2 mmol) in 3 mL of acetonitrile and 3 mL of water, an aqueous solution of $RuCl_3$ (10 μL of standard solution; 0.0016 mmol; 0.16 mol %) was added under stirring at room temperature. The reaction mixture was stirred for 10 h (the reaction was monitored by TLC by disappearance of benzhydrol). Then 15 mL of ethyl acetate and 20 mL of water were added and the mixture was stirred for 5 min. The organic solution was separated and the aqueous phase was extracted with ethyl acetate (2×15 ml). Organic phases were combined, washed with NaCl (saturated solution, 20 ml), dried over Na_2SO_4 (anhydrous). Removal of the solvent under vacuum afforded 175 mg (96%) of benzophenone. The oxidation of other alcohols (Table 2) was performed using a similar procedure. All products were identified by comparison with commercially available samples and some volatile carbonyl products were additionally identified as 2,4-dinitrophenylhydrazones.

4.5. Typical preparative procedure for PhI/$RuCl_3$-cocatalyzed oxidation of aromatic hydrocarbons (Table 4)

Table 4, entry 1. To a mixture of propylbenzene (120 mg, 1 mmol), PhI (0.5 mL of standard solution; 0.05 mmol; 5 mol %), and $RuCl_3$ (10 μL of standard solution; 0.0016 mmol; 0.16 mol %) in 3 mL of acetonitrile and 3 mL of water, Oxone® (total 3.74 g; 6.1 mmol) was added in five portions during 22 h under stirring at room temperature. The reaction mixture was stirred for additional 4 h (the reaction was monitored by TLC by disappearance of propylbenzene). Then 15 mL of ethyl acetate and 20 mL of water were added and the mixture was stirred for 5 min. The organic solution was separated, and the aqueous phase was extracted with ethyl acetate (2×15 ml). Organic phases were combined, washed with NaCl (saturated solution, 20 ml), dried over Na_2SO_4 (anhydrous). Removal of the solvent under vacuum afforded 107 mg (80%) of propiophenone. The oxidation of other hydrocarbons (Table 4) was performed using a similar procedure. All products were identified by comparison with commercially available samples and some carbonyl products were additionally identified as 2,4-dinitrophenylhydrazones.

4.6. ArI/$RuCl_3$-cocatalyzed oxidation of organic substrates (general procedure for GC–MS experiments)

To a mixture of an organic substrate (0.1 mmol), ArI (50 μL of 0.1 M solution in MeCN; 0.005 mmol; 5 mol %), and Oxone® (0.062–0.277 g, 0.1–0.45 mmol; see Tables) in 0.3 mL of acetonitrile and 0.3 mL of water, an aqueous solution of $RuCl_3$ (1.0 μL of standard solution; 0.00016 mmol; 0.16 mol %) was added under stirring at room temperature. The reaction mixture was stirred for a period of time indicated in the Tables (the reactions were monitored by TLC by disappearance of organic substrate). Then 2 mL of ethyl acetate and 2 mL of 5%-aqueous solution of sodium thiosulfate were added and the mixture was stirred for 5 min. The organic solution was separated and analyzed using GC–MS. Products were identified by comparison with commercially available samples.

4.7. Typical procedure for catalytic oxidation of anthracene (Scheme 5)

A solution of anthracene **14** (0.10–0.15 mmol) in toluene or dichloromethane (3–5 mL) was mixed with the appropriate catalyst **11**–**13** (0.010–0.015 mmol) and the hypervalent iodine oxidant (6–7.5 equiv of O), with stirring, at room temperature (see Table 5).

Samples of the reaction mixture (50 μL) were collected every 30 min, filtered through 2–3 cm of silica gel suspended in a Pasteur pipette, washed with a mixture of ethyl acetate and hexane (2:3 v/v), and analyzed using GC–MS.

4.8. Catalytic oxidation of 2-*tert*-butylanthracene (Scheme 6)

A solution of 2-*tert*-butylanthracene **16** (16 mg, 0.068 mmol) in toluene (2.5 mL) was mixed with Fe(III)-phthalocyanine complex **11** (15 mg, 0.0094 mmol) and reagent **10** (110 mg, 0.15 mmol) and was stirred 24 h at room temperature. The solvent was removed and the residue was separated by column chromatography on silica gel (ethyl acetate/hexane, 1:20) to give 13 mg (72%) of 2-*tert*-butylanthraquinone **17** as yellow needles, mp 101–102.5 °C (lit.[26] mp: 103–104 °C).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.04.046.

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