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Esters of 2-Iodoxybenzoic Acid: Hypervalent Iodine Oxidizing Reagents with a Pseudobenziodoxole Structure

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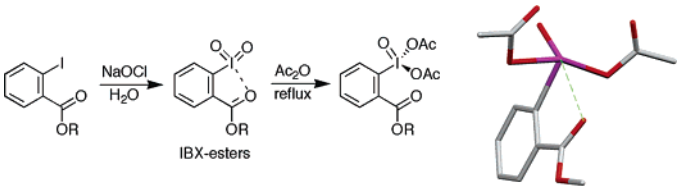

Esters of 2-iodoxybenzoic acid (IBX-esters) were prepared by the hypochlorite oxidation of the corresponding 2-iodobenzoate esters and isolated as chemically stable, microcrystalline products. These hypervalent iodine compounds are potentially valuable oxidizing reagents belonging to a new class of pentavalent iodine compounds with a pseudobenziodoxole structure. Methyl 2-iodoxybenzoate can be further converted to the diacetate or a bis(trifluoroacetate) derivative by treatment with acetic anhydride or trifluoroacetic anhydride, respectively. Single-crystal X-ray diffraction analysis of methyl 2-[(diacetoxy)iodosyl]benzoate **8a** reveals a pseudobenziodoxole structure with three relatively weak intramolecular I···O interactions. The dimethyl and diisopropyl esters of 2-iodoxyisophthalic acid were prepared by oxidation of the respective iodoarenes with dimethyldioxirane. Single-crystal X-ray diffraction analysis of diisopropyl 2-iodoxyisophthalate **6b** showed intramolecular I···O interaction with the carbonyl oxygen of only one of the two carboxylic groups, while NMR spectra in solution indicated equivalency of both ester groups. IBX-esters, methyl 2-[(diacetoxy)iodosyl]benzoate, and 2-iodoxyisophthalate esters can oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate. The bis(trifluoroacetate) derivative can oxidize alcohols to carbonyl compounds without acid catalyst.

Introduction

In the past decade, the chemistry of hypervalent iodine compounds (λ^3- and λ^5-iodanes) has experienced an unprecedented growth.[1] A broad variety of polyvalent iodine reagents have been prepared, and new, highly useful synthetic procedures have been developed. Hypervalent iodine reagents based on the heterocyclic system of benziodoxole represent an especially important class of iodanes with rich and synthetically useful chemistry.[1−3] In particular, the heterocyclic λ^5-iodane, 1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one (**1a**), has received widespread application in organic synthesis as a highly efficient and mild oxidant that can be used for selective oxidation of primary and secondary alcohols and for a variety of other important oxidations.[1−3] Reagent **1a** is commonly referred to as 2-iodoxybenzoic acid (IBX) (structure **1b**), although the tautomeric form **1a** gives the correct representation for the actual structure of this compound. This has been confirmed by X-ray crystallographic analysis, which also indicates a polymeric structure for IBX due to an extended linkage of intermolecular secondary I···O bonding interactions.[4] The

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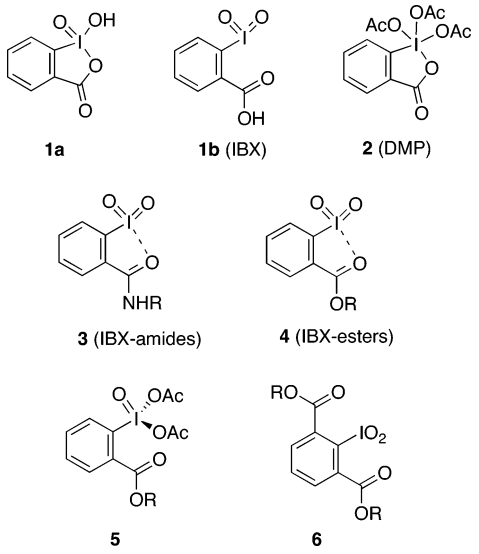
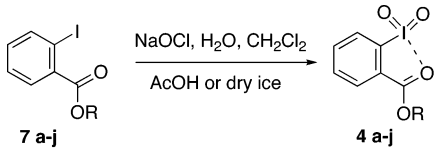
CHART 1. IBX and Its Derivatives



polymeric structure of IBX renders it essentially insoluble in all nonreactive media. The low solubility of IBX and its potentially explosive nature restrict practical application of this valuable reagent. Several research groups have tried to improve IBX by structurally modifying it[1,5] or by developing polymer-supported analogues.[6] The most important derivative of IBX is the commercially available triacetate **2**, commonly known as Dess−Martin periodinane (DMP).[1] DMP is prepared by heating IBX with acetic anhydride, and it has improved solubility compared to IBX. It is, however, moisture sensitive, which imposes certain restrictions on storage and handling of this useful reagent. Recently, we have reported the synthesis and structural analysis of amides and esters of 2-iodoxybenzoic acid, IBX-amides (**3**),[7] and IBX-esters (**4**),[8] which are stable and soluble reagents having oxidizing properties similar to IBX. According to X-ray data, these new derivatives of IBX have a pseudobenziodoxole structure due to iodine−oxygen secondary bonding interactions. In comparison with IBX and other benziodoxoles, pseudobenziodoxoles have much better solubility, which is explained by a partial disruption of their polymeric nature due to the redirection of I···O secondary bonding.[7,8] Very recently, Lee and co-workers reported the preparation of the polymer-supported IBX-esters and IBX-amides, which showed excellent oxidative activity toward benzylic alcohols and were also used for oxidative bromination of activated arenes.[9]

SCHEME 1



4a: R = Me (21%)
4b: R = Et (61%)
4c: R = *i*-Pr (89%)
4d: R = *tert*-Bu (59%)
4e: R = (−)-menthyl (69%)
4f: R = (+)-menthyl (63%)
4g: R = (±)-menthyl (73%)
4h: R = [(1*S*)-*endo*]-(−)-bornyl (63%)
4i: R = 2-adamantyl (83%)
4j: R = 1-adamantyl (66%)

In the present work, we report details on the preparation and chemistry of IBX-esters **4** as well as the preparation and structure of two new iodoxybenzoate derivatives, namely, diacetate derivatives of IBX-esters (**5**) and diesters of 2-iodoxyisophthalic acid (**6**).

Results and Discussion

Preparation of IBX-Esters. Iodoxybenzoates **4a**−**j** were prepared by the hypochlorite oxidation[10] of the respective esters of 2-iodobenzoic acid **7a**−**j** in the presence of acetic acid and dichloromethane (Scheme 1). The methyl and ethyl esters **4a** and **4b**, being essentially insoluble in dichloromethane, precipitated from the reaction mixture and were isolated by filtration in the form of white, microcrystalline solids. All other esters **4c**−**j** were extracted from the reaction mixture with dichloromethane and obtained as colorless or pale-yellow amorphous solids or oils after solvent evaporation. Crystallization of crude products from acetonitrile furnished products **4c**−**j** in white, microcrystalline form, which could be converted back into the amorphous form by dissolving the crystals in CH_2Cl_2 followed by solvent evaporation. An alternative procedure for the hypochlorite oxidation of 2-iodobenzoate esters **7** involves the use of dry ice instead of acetic acid in order to simplify extraction and purification of products **4**. This modification works especially well for the preparation of the isopropyl ester **4c**. By use of either workup protocol, the hypochlorite oxidation procedure allows for the preparation of iodoxybenzoate esters **4** derived from a wide variety of precursors, including primary, secondary, and tertiary alcohols, adamantanols, as well as optically active menthols and borneol. Preparative yields of pure products **4** are generally in the range 60−90%, with the exception of the methyl ester **4a**, which was isolated in a low yield (21%) due to its solubility in the aqueous phase of the reaction mixture. In general, products **4c**−**j** have moderate to high solubility in common organic solvents, such as chloroform, dichloromethane, and acetonitrile. In dichloromethane, for example, the solubilities

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of **4c**, **4d**, and **4e** are 2.9, 0.2, and 1.7 M, respectively. The methyl and ethyl esters **4a** and **4b** are moderately soluble in water and acetonitrile but have a low solubility in dichloromethane (0.003 M for ester **4a**). All esters **4** are stable to hydrolysis and can be stored indefinitely under refrigeration. Treatment of IBX-ester **4c** with trifluoroacetic acid for several hours at room temperature showed that it is not hydrolyzed to IBX under these conditions and demonstrated its chemical stability.

In view of the unstable nature of IBX, which was found to be explode under heating above 200 °C or upon impact,[11] thermal analyses were preformed on several IBX ester samples (**4a**, **4b**, and **4c**) using traditional melting points, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). DCS analysis for **4a** and **4b** show broad endotherms centered at 125 and 100 °C, respectively, which correspond to mass losses of 5.7 and 5.5%, respectively, based on TGA analysis. In both cases, this is consistent with loss of cocrystallized solvent from the sample (likely water, based on combustion analysis). Sample **4c** shows a much weaker endotherm centered at ca. 135 °C, with less than 5% mass loss over the temperature range up to its decomposition. At higher temperatures, DSC analyses of **4a** and **4b** show exotherms characteristic of decomposition, while **4c** shows endotherm (likely melting point) followed immediately by an exotherm (decomposition). Melting-point analyses confirm the chemical decomposition of all three samples into a yellow solid that coats the inner walls of the melting point tube, empirically suggesting some kind of decarboxylation process. While no explosive decomposition has been observed for **4a**−**4c** in any of these experiments, DSC analysis shows that decomposition in all cases is rapid and exothermic, and TGA confirms nearly 100% mass loss upon decomposition. As a result, due caution should be exercised upon heating these samples at temperatures approaching their decomposition points.

The composition, structure, and purity of compounds **4a**−**j** were established through a combination of elemental analysis, spectroscopic data, electrospray ionization (ESI) mass spectrometry, and single-crystal X-ray analysis. In particular, IR spectra of all compounds show the carbonyl stretch at 1640−1680 cm^{-1} and an I=O absorption at 780−740 cm^{-1}. In the ^1H NMR spectra, a characteristic pattern of the aromatic protons between 8.4 and 7.6 ppm and the respective signals of each ester group R are present. The most characteristic signals in ^{13}C NMR spectra of **4** are those of the ipso carbon, $C-IO_2$, found at ca. 149 ppm.

Single-crystal X-ray analysis of iodoxybenzoate esters **4a**, **4c**, and **4d** were reported in our preliminary communication.[8] The X-ray data revealed the key features of crystal and molecular structure of IBX-esters and provided an explanation for the better solubility of compounds **4c** and **4d**: a partial disruption of their polymeric nature due to the redirection of I···O secondary bonding. A broad range of solubility, i.e., **4c** vs **4a**, suggested that molecular structure was not the only factor but that secondary bonding interactions in the solid state (i.e., polymeric vs nonpolymeric) might also play a significant role. The structure of **4c** showed a unit cell consisting of two crystallographically independent molecules. Strong secondary I···O bonding interactions between neighboring molecules affords dimeric pairs. These dimers are then linked together by a combination of strong and weak interactions, forming a polymeric motif, much like that observed for IBX in the solid state.[4] Within each unique molecule of **4c**, an intramolecular close contact between the I(V) center and the oxygen atom of the ester group (I−O 2.81 and 2.69 Å) affords the pseudo-benziodoxole ring. X-ray crystallographic analysis of **4d** showed a centrosymmetric arrangement of four molecules. As observed for **4c**, the secondary I···O bonding interactions that link neighboring molecules are present, as is the intramolecular close contact between the iodine center and the oxygen atom of the ester group (I−O 2.68 and 2.67 Å). Whereas crystals of **4c** and **4d** could be grown from CH_3CN, the more sparingly soluble **4a** provided X-ray quality crystals only from DMSO (it should be noted that complex **4a**·DMSO is considerably more soluble in other solvents than pure **4a**). Analysis of the crystals shows a dimeric structure between two inversion-related molecules. The remaining close contact to the I(V) center, however, occurs with oxygen from a DMSO molecule. As found in the structures of **4c** and **4d**, the *intra*molecular I···O interaction involving the iodonium center and ester oxygen is again significant, with I−O1 = 2.69 Å.

The *intra*molecular I···O bonding motif with the carbonyl oxygen is common to the structures of IBX-esters **4a**, **4c**, and **4d·DMSO** and suggests that the presence of an ester moiety in the ortho position is vital for improved solubility.[12,13] This results from a disruption of *inter*molecular I···O bonds and a concurrent reduction of the polymeric interactions found in some iodyl and iodosyl derivatives.[12] In comparison to the IBX-esters, IBX shows a stronger *intra*molecular I−O interaction with the carboxylate oxygen (2.263(2) Å)[4a] as well as a three-dimensional network based on a combination of intermolecular O−H···O and I···O secondary bonding. It is, therefore, the absence of the hydrogen-bonding interactions in the IBX-esters that appears sufficient to enhance solubility vs IBX. The consequence of this effect can be appreciated by considering the structure of **4c**, which shows that, even with partial oligomeric nature on the basis of I···O bonding, considerable solubility can be maintained.

Preparation and Structure of IBX-Esters Diacetates: Pseudocyclic Dess−Martin Periodinane Analogues. To improve the solubility and the potential reactivity of methyl 2-iodoxybenzoate **4a**, it was converted to the acetate (**8a**) and trifluoroacetate (**8b**) by treatment with the corresponding anhydride under reflux conditions by analogy with the original procedure[14] for the preparation of DMP (Scheme 2).

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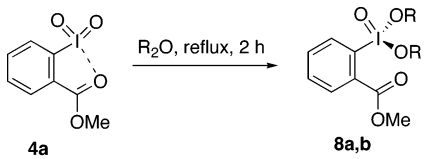
SCHEME 2



8a: R = Ac (71%)
8b: R = CF_3CO (55%)

Products **8a** and **8b** precipitated from the reaction mixture after addition of ether and were isolated by filtration as white, microcrystalline solids. Bis(trifluoroacetate) **8b** is highly hygroscopic and should be handled and stored in dry atmosphere. Both derivatives **8a** and **8b** gradually lose acetyl moieties on storage producing the initial IBX-ester **4a**. The structure and composition of the compounds **8a** and **8b** were established by elemental analysis, spectroscopic data, and single-crystal X-ray analysis for diacetate **8a** (Figure 1). In particular, ^{13}C NMR spectra of products **8a** and **8b** show the signals of additional carbonyl groups at 172 and 158 ppm, respectively, and the signals of the ipso carbon, C−I, at about 150 ppm.

While the solid-state structure of compound **8a** is unique among the known I(V) derivatives that have been characterized to date (IBX, the IBX esters, and DMP analogue **9**), there are also several similarities. For example, the geometry around the hypervalent iodine center retains coordination of the iodine to carbonyl oxygen O6 (2.6676(17) Å), similar to that found in the IBX esters. The bonding interactions between iodine and acetoxy oxygens (O2 and O4), at 2.1249(16) and 2.1088(16) Å, respectively, are similar to that of the alkoxy bond in **9**, at 2.296(7) Å.[15] The apical I=O bond length is also comparable in both cases, at 1.7723(16) Å and 1.776(9) Å for **8a** and **9**, respectively. There are, however, notable differences. The I(V) center of **8a** maintains secondary bonding interactions with *both* acetyl carbonyls at 2.8051(17) and 2.7675(17) Å, providing an unusual heptacoordinate geometry about iodine. Finally, unlike the polymeric structure of IBX and the oligomeric nature of the IBX esters and DMP analogue **9** due to *intermolecular* I···O interactions, the coordination sphere about iodine in **8a** is satisfied completely by *intramolecular* bonding. As a result, the solubility of **8a** in comparison to IBX and IBX esters is somewhat increased.

Preparation and Structural Investigation of the Esters of 2-Iodoxyisophthalic Acid. 2-Iodoxyisophthalate ester **6** can, in principle, provide for the intramolecular coordination of the iodine(V) center with two carbonyl oxygens. It was expected that the additional coordination could lead to the increased redirection of secondary bonding from an *inter*molecular to *intra*molecular mode resulting in improved solubility and modified reactivity of the reagent. The precursors to the target structures, 2-iodoisophthalates **11a** and **11b**, were prepared from the known 2-iodoisophthaloyl dichloride **10**,[16] and the corresponding alcohols. The oxidation of

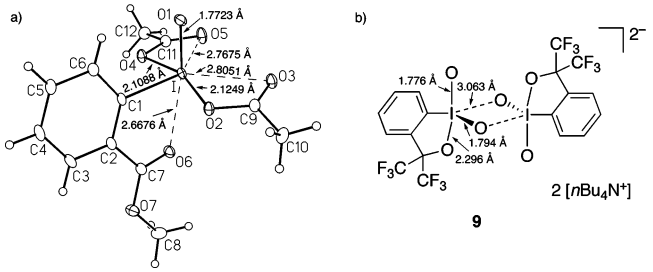
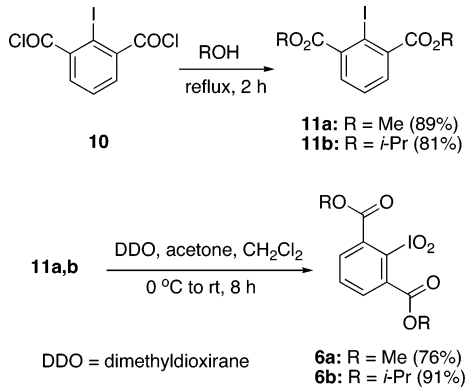


FIGURE 1. (a) Perspective view and selected bond lengths for molecule **8a**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, and hydrogen atoms are shown with arbitrarily small thermal parameters. (b) Structure and selected bond lengths for DMP analogue **9**.[15] Dashed lines I···O indicate secondary bonding interactions.

SCHEME 3



11a: R = Me (89%)
11b: R = *i*-Pr (81%)

DDO = dimethyldioxirane

6a: R = Me (76%)
6b: R = *i*-Pr (91%)

compounds **11a** and **11b** with an acetone solution of dimethyldioxirane (DDO) afforded the final products **6a** and **6b** in high yield (Scheme 3).

Compounds **6a** and **6b** were isolated in the form of white, microcrystalline solids, soluble in organic solvents, including dichloromethane, benzene, and acetone. The rapid heating and impact tests have corroborated their nonexplosive nature.

Compounds **6** were analyzed by NMR, IR, spectroscopy, and ESI-MS. In particular, ^{13}C NMR spectra of each product **6a** and **6b** showed a single signal of the carbonyl carbons at 166.8 and 166.6 ppm, respectively, and the signal of the ipso carbon, C−IO_2, at about 149 ppm. The ^1H NMR spectrum of dimethyl ester **6a** showed a single sharp singlet corresponding to the two identical methoxy groups. Likewise, the signals corresponding to two identical isopropyl groups were present in the ^1H NMR spectrum of diisopropyl ester **6b** at room temperature and at temperatures as low as −80 °C. The structure of diisopropyl 2-iodoxyisophthalate **6b** in the solid state was investigated by single-crystal X-ray analysis (Figure 2).

According to the X-ray structural analysis, **6b** assumes a pseudo-centrosymmetric tetramer in the solid state, composed of four unique molecules linked by secondary bonding interactions. The I=O bond lengths fall in a very narrow range of 1.774(4)−1.811(5) Å. The intermolecular secondary bonding interactions for I(1) and I(2) are analogous: each establishes two relatively strong I···O bonds with neighboring molecules, with bond lengths in the range of 2.497(4)−2.692(5) Å. The intermolecular secondary bonding interactions for I(3) and I(4) are also analogous: each establishes two somewhat weaker

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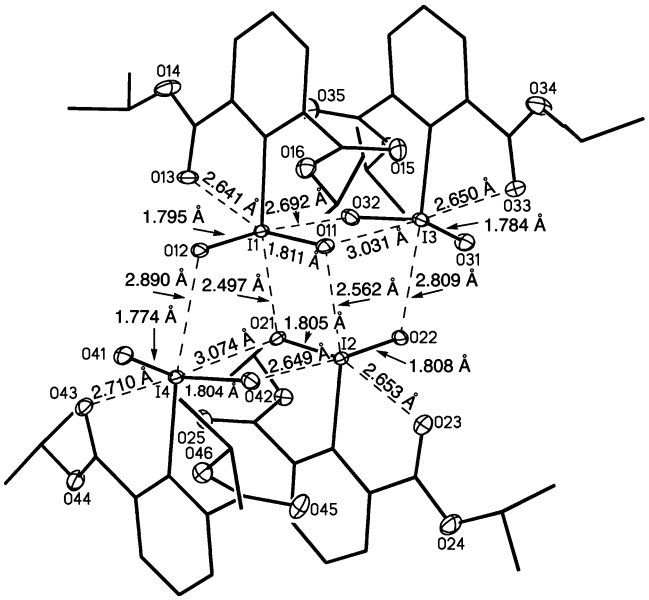

FIGURE 2. Perspective view and selected bond lengths for the four unique molecules in the solid-state tetramer of **6b**. Selected non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level; the others have been removed for clarity. Dashed lines I···O indicate secondary bonding interactions.

I···O bonds with neighboring molecules, with bond lengths in the range of 2.809(4)−3.074(4) Å. Two interesting observations are seen with respect to the participation of the various oxygen atoms in these secondary bonds. First, O(11) and O(21) both form bifurcated bonds with the I(V) atoms of two neighbors, and one of the two close contacts in each case is significantly stronger than the other. Conversely two oxygen atoms, O(31) and O(41), experience no secondary bonding interactions at all.

Unlike that observed for the structure of **8a**, each unique molecule in the tetramer **6b** has only one of the two carbonyl groups in coordination with the hypervalent iodine center, with bond distances ranging from 2.641(5) to 2.710(5) Å. This result contrasts ^{1}H NMR spectroscopic analysis of **6b** in CD_2Cl_2, which showed equivalent carboxylic groups. This degeneracy was maintained down to −80 °C, indicative of a very low energy barrier for the interconversion process.

Oxidation of Alcohols with IBX-Esters. Oxidation of the hydroxyl functional group is one of the most important transformations in organic synthesis. According to literature data,[1] iodylbenzene ($PhIO_2$) as well as other noncyclic iodylarenes are not effective oxidants toward alcohols, due in part to their polymeric nature and, as a consequence, decreased solubility. In contrast to the noncyclic iodylarenes and in agreement with their structural features, the oxidizing reactivity of IBX-esters **4** is closer to the benziodoxole-based pentavalent iodine reagents such as IBX.

The isopropyl ester of 2-iodylbenzoic acid **4c** is the most readily available of the new IBX-esters, and it was therefore chosen to explore the synthetic potential of these oxidants. A range of alcohols could be oxidized to the respective carbonyl compounds by reagent **4c** under mild conditions in the presence of trifluoroacetic acid, $BF_3{\cdot}Et_2O$, or KBr as a catalyst (Table 1). For example, oxidation of benzyl alcohol in the presence of KBr[17] in chloroform at 50 °C cleanly gives benzaldehyde as the only product detected by ^{1}H NMR spectroscopy (Entry 2). A variety of secondary alcohols, such as cyclohexanol and cycloheptanol, are converted to the corresponding ketones in >90% yields as determined by gas chromatography (GC) analysis (entries 4−7). Furthermore, the increased solubility of, e.g., **4c**, greatly expands the range of solvents that can be utilized in comparison IBX. The oxidation of 1-phenylethanol to acetophenone, for example, proceeds in good yield (>65%) using CH_3CN, $CHCl_3$, CH_2Cl_2, and benzene.

Methyl 2-[(diacetoxy)iodosyl]benzoate **8a** (Entry 10) and 2-iodoxyisophthalate esters **6** (Entry 11) oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate. The bis(trifluoroacetate) derivative **8b** (Entry 9) can oxidize alcohols to carbonyl compounds without additional acid catalyst. It can be assumed that the more electrophilic trifluoroacetate species, formed in situ from **4c** or **6** in the presence of trifluoroacetic acid, are the actual reactive intermediates. As it was shown previously, the mechanism of oxidation of alcohols with iodine(V) reagents includes the initial ligand exchange on the iodine atom with intermediate formation of alkoxyiodane species.[15] The enhanced electrophilic reactivity of the iodine(V) center is essential in order to facilitate the initial interaction of the reagent with the molecule of alcohol.

Very recently, we have reported that IBX-esters can also be used as reagents for the clean and selective oxidation of organic sulfides to sulfoxides.[18] This reaction does not require acid catalysis, it proceeds without overoxidation to sulfones, and it is compatible with the presence of the hydroxy group, double bond, phenol ether, benzylic carbon, and various substituted phenyl rings in the molecule of the substrate. The highly selective oxidizing reactivity of IBX-esters, combined with their stability and easiness of preparation, validates potential importance of these compounds as oxidizing reagents for organic synthesis.

Conclusion

In conclusion, we have reported the preparation and chemistry of esters of IBX-esters, new pseudobenziodoxole-based hypervalent iodine reagents. Various IBX-esters **4** can be conveniently prepared by the hypochlorite oxidation of the corresponding 2-iodobenzoate esters and isolated as chemically stable, microcrystalline products. Methyl 2-iodoxybenzoate **4a** can be further converted to the diacetate **8a** or bis(trifluoroacetate) **8b** by the treatment with acetic anhydride or trifluoroacetic anhydride, respectively. X-ray diffraction analysis of the diacetate derivative **8a** reveals a pseudobenziodoxole structure with a relatively weak intramolecular I···O interaction. The methyl and isopropyl esters of 2-iodoxyisophthalic acid (**6a**,**b**) were prepared by oxidation of the respective iodoarenes with dimethyldioxirane. Single-crystal X-ray diffraction analysis of diisopropyl 2-iodoxyisophthalate showed intramolecular I···O interaction with only one

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(18) Koposov, A. Y.; Zhdankin, V. V. *Synthesis* **2005**, 22.

TABLE 1. Oxidation of Alcohols to Carbonyl Compounds with IBX-Esters

entry	reagent[a]	alcohol	catalyst	reaction time (h)	temperature (°C)	yield[b] (%)
1	**4c**	benzyl alcohol	TFA	1	40	100[c]
2	**4c**	benzyl alcohol	KBr	4	50	100[d]
3	**4c**	benzyl alcohol	$BF_3{\cdot}Et_2O$	0.5	20	100[d]
4	**4c**	cyclohexanol	TFA	11	20	95[c]
5	**4c**	cyclohexanol	TFA	2	40	95[c]
6	**4c**	cycloheptanol	TFA	2	40	90[c]
7	**4c**	cyclooctanol	TFA	2	40	95[c]
8	**4c**	cyclooctanol	$BF_3{\cdot}Et_2O$	0.5	20	95[c]
9	**8b**	benzyl alcohol	none	0.5	20	100[d]
10	**8a**	benzyl alcohol	TFA	1	40	100[d]
11	**6b**	benzyl alcohol	TFA	2	40	100[d]

[a] All reactions were performed in dichloromethane using 1 equiv IBX-ester. [b] The respective carbonyl compound and the respective aryliodide were the only products determined by GC or ^{1}H NMR spectroscopic analysis of the reaction mixture. [c] Determined by GC analysis. [d] Determined by ^{1}H NMR spectroscopy.

carbonyl oxygen of the two carboxylic groups, while NMR spectra in solution indicated equivalency of both ester groups. IBX-esters, methyl 2-[(diacetoxy)iodosyl]benzoate, and 2-iodoxyisophthalate esters can oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate. The bis(trifluoroacetate) derivative can oxidize alcohols to carbonyl compounds without additional acid catalyst.

Experimental Section

For general experimental methods and synthesis of starting esters **7a**−**j**, see the Supporting Information.

General Procedure for Oxidation of 2-Iodobenzoate Esters. Dichloromethane (20 mL) was added to a vigorously stirred suspension of the appropriate ester of 2-iodobenzoic acid **7** (5 mmol) and sodium hypochlorite solution ("bleach", 5% NaOCl, 15 mL), and then acetic acid (5 mL) was added dropwise in 10 min at room temperature. The resulting mixture was stirred overnight. The initially formed yellow mixture turned into a white precipitate (**4a** and **4b**) or a colorless solution (**4d**−**4j**). Products **4a** and **4b** were isolated by filtration in analytically pure form as white, microcrystalline solids. Esters **4d**−**j** were extracted from the reaction mixture with dichloromethane (5 × 10 mL). The extract was washed with a saturated aqueous solution of $NaHCO_3$, dried with $MgSO_4$, and evaporated in a vacuum to afford crude products as colorless or pale-yellow amorphous solids or oils. Crystallization of crude products from acetonitrile or CH_2Cl_2/hexanes furnished analytically pure products **4d**−**j** in white, microcrystalline form, which, however, could be converted back into the amorphous form by dissolving the crystals in CH_2Cl_2 followed by solvent evaporation.

Methyl 2-Iodoxybenzoate 4a. Oxidation of methyl 2-iodobenzoate **7a** according to general procedure afforded 0.33 g (21%) of product **4a**, mp 194−196 °C (decomposition). The lower preparative yield for this product is explained by its high solubility in water. IR (KBr): 3063, 1687, 786, 755 cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.28 (dd, J_1 = 7.7 Hz, J_2 = 0.9 Hz, 1H), 8.10 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 8.04 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.76 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 167.2, 150.6, 134.6, 131.7, 129.9, 125.7, 123.0, 53.6. Anal. Calcd for $C_8H_7IO_4{\cdot}H_2O$: C, 30.79; H, 2.91; I, 40.67. Found: C, 30.81; H, 2.92; I, 40.42.

Ethyl 2-Iodoxybenzoate 4b. Oxidation of ethyl 2-iodobenzoate **7b** according to general procedure afforded 0.99 g (61%) of product **4b**, mp 196−198 °C (decomposition; recrystallized from acetonitrile). IR (KBr): 1633, 804, 732 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.27 (d, J = 7.7 Hz, 1H), 8.10 (dd, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H), 8.04 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (DMSO-d_6): δ 162.8, 146.6, 130.6, 127.8, 126.1, 122.1, 119.2, 58.9, 10.0. Anal. Calcd for $C_9H_9IO_4{\cdot}H_2O$: C, 33.15; H, 3.40; I, 38.92. Found: C, 33.11; H, 3.41; I, 39.08.

***tert*-Butyl 2-Iodoxybenzoate 4d.** Oxidation of *tert*-butyl 2-iodobenzoate **7d** according to general procedure afforded 0.99 g (59%) of product **4d**, mp 160−162 °C (decomposition; recrystallized from CH_2Cl_2/hexanes). Solubility in CH_2Cl_2: 5.17 g in 100 g of solvent (up to 0.2 M solutions). IR (KBr): 3057, 2910, 2852, 1672, 1251, 771, 745. ^{1}H NMR ($CDCl_3$): δ 8.43 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 7.3 Hz, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 1.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 167.2, 147.8, 140.9, 131.9, 130.4, 128.0, 127.8, 85.9, 28.1. Anal. Calcd for $C_{11}H_{13}IO_4$: C, 39.31; H, 3.90; I, 37.76. Found: C, 39.39; H, 4.03; I, 37.28.

(−)-Menthyl 2-Iodoxybenzoate 4e. Oxidation of (−)-menthyl 2-iodobenzoate **7e** according to general procedure afforded 1.50 g (69%) of product **4e**, mp 101 °C (decomposition; recrystallized from EtOAc/hexanes); $[\alpha]^{20}_D = -63°$. Solubility in CH_2Cl_2: 54.11 g in 100 g of solvent (up to 1.71 M solutions). IR (KBr): 1679, 774, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.44 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.4, 1H), 7.91 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 5.01 (td, J_1 = 11.0 Hz, J_2 = 4.0 Hz, 1H), 2.18 (d, J = 11 Hz, 1H), 1.88 (m, 1H), 1.75 (m, 2H), 1.58 (m, 2H), 1.11 (m, 3H), 0.92 (m, 6H), 0.75 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.6, 148.6, 135.0, 132.4, 130.3, 126.9, 125.1, 78.7, 47.1, 40.5, 34.1, 31.4, 26.4, 23.5, 21.9, 20.7, 16.5. Anal. Calcd for $C_{17}H_{23}IO_4{\cdot}H_2O$: C, 46.80; H, 5.78. Found: C, 47.14; H, 5.47. ES MS: *m*/*z* (%) 859 (100, $[2M + Na]^+$).

(+)-Menthyl 2-Iodoxybenzoate 4f. Oxidation of (+)-menthyl 2-iodobenzoate **7f** according to general procedure afforded 1.37 g (63%) of product **4f**, mp 100−102 °C (decomposition; recrystallized from EtOAc/hexanes); $[\alpha]^{20}_D = +62°$. IR (KBr): 1675, 773, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.41 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 6.8 Hz, 1H), 7.90 (t, J = 7.3 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 4.97 (td, J_1 = 10.7 Hz, J_2 = 4.4 Hz, 1H), 2.17 (m, 1H), 1.87 (m, 1H), 1.75 (m, 2H), 1.57 (m, 2H), 1.10 (m, 3H), 0.91 (m, 6H), 0.72 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.6, 148.6, 134.9, 132.3, 130.2, 126.9, 125.1, 78.5, 47.0, 40.3, 33.9, 31.2, 26.4, 23.4, 21.9, 20.7, 16.5. Anal. Calcd for $C_{17}H_{23}IO_4{\cdot}H_2O$: C, 46.80; H, 5.78. Found: C, 47.11; H, 5.45. ES MS: *m*/*z* (%) 859 (100, $[2M + Na]^+$), 419 (15, $[M + H]^+$).

(±)-Menthyl 2-Iodoxybenzoate 4g. Oxidation of (±)-menthyl 2-iodobenzoate **7g** according to general procedure afforded 1.59 g (73%) of product **4g**, mp 99−100 °C (decomposition; recrystallized from MeCN/hexanes). IR (KBr): 1679, 774, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$): 8.47 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.91 (t, J = 7.3 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 4.91 (m, 1H), 2.11 (m, 1H), 1.82 (m, 1H), 1.73 (m, 2H), 1.55 (m, 2H), 1.07 (m, 3H), 0.91 (m, 6H), 0.68 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): 167.7, 148.9, 135.1, 132.2, 130.3, 127.0, 125.2, 78.6, 47.1, 40.5, 34.1, 31.6, 26.4, 23.5, 22.0,

20.8, 16.6. Anal. Calcd for $C_{17}H_{23}IO_4$: C, 48.82; H, 5.54. Found: C, 48.71; H, 5.68.

[(1S)-*endo*]-(−)-Bornyl 2-Iodoxybenzoate 4h. Oxidation of [(1S)-*endo*]-(−)-bornyl 2-iodobenzoate **7h** according to general procedure afforded 1.31 g (63%) of product **4h**, mp 164−165 °C (decomposition; recrystallized from MeCN/hexanes). IR (KBr): 3057, 2882, 1678, 1296, 775, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.41 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 5.11 (m, 1H), 2.46 (m, 1H), 2.03 (m, 1H), 1.77 (m, 2H), 1.40 (m, 1H), 1.26 (m, 1H), 1.14 (m, 1H), 0.95 (s, 3H), 0.91 (s, 3H), 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 168.3, 149.4, 134.9, 131.9, 130.1, 126.8, 125.0, 83.8, 49.2, 47.9, 44.8, 36.6, 27.9, 27.7, 19.6, 18.9, 13.7. Anal. Calcd for $C_{17}H_{21}IO_4$: C, 49.05; H, 5.09; I, 30.49. Found: C, 48.94; H, 5.26; I, 29.90.

2-Adamantyl 2-Iodoxybenzoate 4i. Oxidation of 2-adamantyl 2-iodobenzoate **7i** according to general procedure afforded 1.72 g (83%) of product **4i**, mp 138−140 °C (decomposition; recrystallized from CH_2Cl_2/hexanes). IR (KBr): 3061, 2854, 1670, 1289, 763, 752 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.46 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 7.5 Hz, 1H), 7.94 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 5.30 (m, 1H), 2.10 (m, 4H), 1.96 (m, 6H), 1.79 (m, 2H), 1.64 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 167.6, 148.1, 135.2, 132.4, 130.4, 127.0, 124.8, 81.3, 37.1, 36.3, 31.8, 27.1, 26.8. Anal. Calcd for $C_{17}H_{19}IO_4$: C, 49.29; H, 4.62. Found: C, 49.19; H, 4.71.

1-Adamantyl 2-Iodoxybenzoate 4j. Oxidation of 1-adamantyl 2-iodobenzoate **7j** according to general procedure afforded 1.37 g (66%) of product **4j**, mp 120−121 °C (decomposition; recrystallized from CH_2Cl_2/hexanes). IR (KBr): 3061, 2855, 1670, 1290, 763, 752 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.45 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.88 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 2.25 (m, 6H), 2.01 (m, 3H), 1.72 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 166.8, 148.1, 134.6, 132.2, 130.5, 128.1, 124.7, 85.3, 41.3, 35.9, 31.0. Anal. Calcd for $C_{17}H_{19}IO_4$: C, 49.29; H, 4.62; I, 30.64. Found: C, 49.75; H, 4.77; I, 29.09.

Alternative Procedure for Hypochlorite Oxidation. Isopropyl 2-Iodoxybenzoate 4c. To a rigorously stirred suspension of isopropyl ester of 2-iodobenzoic acid (1.45 g, 5 mmol) and sodium hypochlorite solution ("bleach", 5% NaOCl, 15 mL), 20 mL of dichloromethane was added and then excess dry ice over the course of 10 min. The reaction mixture was stirred overnight, the organic layer separated, and the aqueous layer extracted three times with dichloromethane (3 × 10 mL). The combined organic fractions were dried over anhydrous magnesium sulfate, and the solvent was evaporated in a vacuum to afford 1.43 g (89%) of product **4c**, mp 156−157 °C (decomposition; recrystallized from CH_2Cl_2/ether). IR (KBr): 1673, 789, 743 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.34 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 5.31 (m, 1H) 1.35 (d, J = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 167.5, 149.6, 134.9, 131.8, 130.2, 126.8, 124.8, 71.9, 21.8. Anal. Calcd for $C_{10}H_{11}IO_4$: C, 37.29; H, 3.44; I, 39.40. Found: C, 37.21; H, 3.49; I, 39.36.

General Procedure for the Preparation of the Diacetates 8a,b. Methyl ester of IBX **4a** (2.9 g, 10 mmol) and the appropriate anhydride (20 mL) were placed into a round-bottom flask, and the mixture was stirred for 2 h under reflux. After the solution cooled, 50 mL of dry ether was added into the flask and the white precipitate immediately formed. The product was filtered through the filter funnel under argon and dried in vacuo.

Methyl 2-[(Diacetoxy)iodosyl]benzoate 8a. Reaction of compound **4a** with acetic anhydride according to the general procedure afforded 2.81 g (71%) of white hygroscopic product **8a**, mp 150−151 °C (in sealed capillary; with decomposition). IR (NaCl): 3057, 2956, 1659, 1330, 1275, 1256, 833, 748 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.28 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H), 8.09 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.05 (td J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 7.76 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 4.00 (s, 3H), 1.90 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 172.1, 167.4, 150.7, 134.8, 131.9, 130.2, 125.9, 123.3, 53.8, 21.1.

Crystal Data for 8a. X-ray intensity data were collected at −80 °C on a Bruker PLATFORM/SMART 1000 charge-coupled device (CCD) diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a crystal with dimensions of 0.83 × 0.30 × 0.22 mm. $C_{12}H_{13}IO_7$, FW = 396.12 g/mol[3], triclinic space group = $P\bar{1}$ (No. 2), unit cell dimensions a = 8.0018(3) Å, b = 8.7268(4) Å, c = 11.8450(5) Å, α = 91.4834(7)°, β = 107.9121(7)°, γ = 114.6969(7)°, V = 703.56(5) Å^3, Z = 2, ρ_{calcd} = 1.870 g/cm^3, μ = 2.304 mm^{-3}, 2θ max = 52.74°, $R_1(F)$ = 0.0181 for 2805 reflections with $F_0^2 \geq 2\sigma(F_0^2)$, $wR_2(F^2)$ = 0.0481 for 2830 independent reflections ($F_0^2 \geq -3\sigma(F_0^2)$) and 184 parameters, GOF(F^2) = 1.099 ($F_0^2 \geq$ EnDash3$\sigma(F_o^2)$), CCDC 260006. For further details on crystal structure of **8a** see the Crystallographic Information File (deposited as Supporting Information).

Methyl 2-[(Bistrifluoroacetoxy)iodosyl]benzoate 8b. Reaction of methyl ester of IBX **4a** with trifluoroacetic anhydride according to the general procedure afforded 55% of extremely hygroscopic product **8b**, mp 143−145 °C. IR (NaCl): 3065, 2968, 1786, 1669, 1338, 1308, 1162, 852, 781, 750, 730 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.31 (d, J = 7.8 Hz, 1H), 8.10 (m, 2H), 7.80 (t, J = 7.5 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 167.7, 158.4 (q, J = 38.5 Hz), 150.1, 135.1, 132.3, 130.4, 125.7, 123.3, 115.3 (q, J = 289 Hz), 54.1. Anal. Calcd for $C_{12}H_7F_6IO_7$: C, 28.59; H, 1.40. Found: C, 28.33; H, 1.76.

General Procedure for the Preparation of Esters of 2-Iodoisophthalic Acid 11a,b. 2-Iodobenzene-1,3-benzenedicarbonyl dichloride **10** (3.29 g, 10 mmol) was placed into a round-bottom flask. Appropriate alcohol (50 mL) was added into the flask, and mixture was refluxed for 2 h. Then the excess of alcohol was evaporated, and the mixture was separated by column chromatography (ethyl acetate/hexanes 1:2) to afford analytically pure esters **11**.

Dimethyl 2-Iodoisophthalate 11a. Reaction of methanol with 2-iodobenzene-1,3-benzenedicarbonyl dichloride **10** according to general procedure afforded 2.85 g (89%) of product **11a**, mp 49−50 °C (literature value[19] = 49−50 °C). IR (KBr): 2949, 1731, 1434, 1253, 995 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.63 (dd, J_1 = 7.8 Hz, J_2 = 0.7 Hz, 2H), 7.45 (dd, J_1 = 8.3 Hz, J_2 = 7.1 Hz, 1H), 3.96 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.2, 139.8, 131.5, 128.1, 91.9, 53.0.

Diisopropyl 2-Iodoisophthalate 11b. Reaction of 2-propanol with 2-iodobenzene-1,3-benzenedicarbonyl dichloride **10** according to general procedure afforded 3.05 g (81%) of product **11b**, mp 37−38 °C. IR (KBr): 2982, 1724, 1453, 1279, 1105, 938 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.55 (dd, J_1 = 8.3 Hz, J_2 = 1.0 Hz, 2H), 7.42 (dd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, 1H), 5.3 (m, 2H), 1.40 (d, J = 6.1 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 167.5, 140.4, 130.9, 128.0, 91.3, 70.1, 21.9. Anal. Calcd for $C_{14}H_{17}IO_4$: C, 44.70; H, 4.55. Found: C, 44.88; H, 4.60.

Preparation of Dimethyl 2-Iodoxyisophthalate 6a. Freshly prepared dioxirane (30 mL, 0.1 M) was added to the stirred mixture ester **11a** (1 mmol) in 5 mL of methylene chloride at 0 °C. The reaction mixture was stirred at room temperature for additional 8 h. The resulting white precipitate was filtered and washed with diethyl ether and dried in a vacuum to afford 266 mg (76%) of analytically pure **6a**, mp 140−141 °C (with decomposition). IR (KBr): 2956, 1712, 1686, 1437, 1303, 1279, 992, 828, 749 cm^{-1}. ^1H NMR ($CDCl_3$/DMSO-d_6): δ 8.01 (d, J = 7.3 Hz, 2H), 7.73 (td, J_1 = 7.7 Hz, J_2 = 0.7 Hz, 1H), 3.99 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.8, 149.4, 133.0, 131.1, 130.9, 52.9. Anal. Calcd for $C_{10}H_9IO_6$: C, 34.11; H, 2.58; I, 36.04. Found: C, 34.26; H, 2.53; I, 35.76. ESI HRMS: m/z (%) 374.9336 (100%, $[M + Na]^+$).

Preparation of Diisopropyl 2-Iodoxyisophthalate 6b. Freshly prepared dioxirane (30 mL, 0.1 M) was added to the

(19) Whitmore, F. C.; Perkins, R. P. *J. Am. Chem. Soc.* **1929**, *51*, 3352.

stirred mixture ester **11b** (1 mmol) in 5 mL of methylene chloride at 0 °C. The reaction mixture was stirred at room temperature for additional 8 h, then the solvent was evaporated, and the white solid residue was recrystallized with methylene chloride/diethyl ether and dried in a vacuum to afford 370 mg (91%) of analytically pure product **6b**, mp 136−137 °C (with decomposition). IR (KBr): 2980, 1714, 1659, 1283, 1103, 911, 751 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.88 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 5.31 (m, 2H), 1.43 (d, J = 6.1 Hz, 12H). ^{13}C NMR ($CDCl_3$ δ 166.6, 149.3, 133.7, 132.4, 131.9, 72.1, 22.0. Anal. Calcd for $C_{14}H_{17}IO_6$: C, 41.19; H, 4.20; I, 31.09. Found: C, 40.96; H, 4.13; I, 30.90. ESI HRMS: *m/z* (%) 430.9962 (100%, $[M + Na]^+$).

Crystal Data for 6b. X-ray intensity data were collected at −80 °C on a Bruker PLATFORM/SMART 1000 CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a crystal with dimensions of 0.22 × 0.22 × 0.05 mm^3. $C_{56}H_{68}I_4O_{24}$, FW = 1632.70 g/mol^3, orthorhombic space group = $Pna2_1$ (No. 33), unit cell dimensions a = 19.7076(11) Å, b = 14.2272(8) Å, c = 23.5360(13) Å, V = 6599.1(6) $Å^3$, Z = 4, ρ_{calcd} = 1.643 g/cm^3, μ = 1.963 mm^{-3}, 2θ max = 52.76°, $R_1(F)$ = 0.0399 for 2805 reflections with $F_0^2 \geq 2\sigma(F_0^2)$, $wR_2(F^2) = 0.0811$ for 12996 independent reflections ($F_0^2 \geq -3\sigma(F_0^2)$) and 774 parameters, GOF(F^2) = 1.013 ($F_0^2 \geq$ EnDash3$\sigma(F_0^2)$), CCDC 270007. For further details on crystal structure of **6b** see the Crystallographic Information File (deposited as Supporting Information).

General Procedure for Oxidation of Alcohols with Ester 4c. A solution of the appropriate alcohol (0.5 mmol) in methylene chloride (2 mL) was added to a solution of IBX-ester **4c** (0.161 g, 0.5 mmol) in methylene chloride (5 mL). Trifluoroacetic acid (0.06 g, 0.5 mmol) (or $BF_3{\cdot}Et_2O$, 0.07 g, 0.5 mmol) in entries 3 and 8) was then added dropwise to this mixture. The reaction mixture was stirred at 40 °C for 2 h (or as specified in the Table 1). A portion of the crude reaction mixture (1.5 mL) was passed through 1 cm of silica gel suspended in a Pasteur pipet and eluted with CH_2Cl_2 (2−3 mL) and then diluted to 10 mL and analyzed by GC mass spectroscopy.

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Supporting Information Available: Details of experimental procedures, spectroscopic data of the reaction products, and X-ray structures of **6b** and **8a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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