JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

Preparation, X-ray Structure, and Reactivity of 2-Iodylpyridines: Recyclable Hypervalent Iodine(V) Reagents

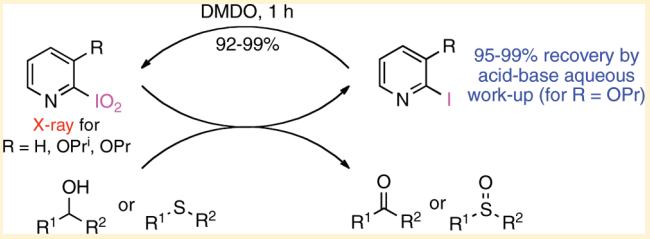
Akira Yoshimura,[†] Christopher T. Banek,[†] Mekhman S. Yusubov,[‡] Victor N. Nemykin,*[,†] and Viktor V. Zhdankin*[,†]

[†]Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, United States

[‡]The Siberian State Medical University and The Tomsk Polytechnic University, 634050 Tomsk, Russia

Supporting Information

ABSTRACT: 2-Iodylpyridine and four examples of 3-alkoxy-2-iodylpyridines were prepared by oxidation of the respective 2-iodopyridines with 3,3-dimethyldioxirane. Structures of 2-iodylpyridine, 2-iodyl-3-isopropoxypyridine, and 2-iodyl-3-propoxypyridine were established by single-crystal X-ray diffraction analysis. 2-Iodyl-3-propoxypyridine has moderate solubility in organic solvents (e.g., 1.1 mg/mL in acetonitrile) and can be used as a recyclable reagent for oxidation of sulfides and alcohols. The reduced form of this reagent, 2-iodo-3-propoxypyridine, can be effectively separated from the reaction mixture by treatment with diluted sulfuric acid and recovered from the acidic aqueous solution by adding aqueous sodium hydroxide.



1. INTRODUCTION

Hypervalent iodine reagents have emerged as versatile and environmentally benign reagents for various synthetically useful oxidative transformations.[1] Particularly useful are hypervalent iodine(V) compounds (λ^5-iodanes), such as Dess−Martin periodinane (DMP), 2-iodoxybenzoic acid (IBX), and their analogues, which are selective oxidants commonly used in the synthesis of natural products.[2] However, despite their importance, IBX and its derivatives are not perfect reagents and have some serious drawbacks. IBX is potentially explosive,[3] and it is insoluble in common organic solvents due to the strong intermolecular secondary bonding creating a three-dimensional polymeric structure. DMP is highly sensitive to moisture, which makes difficult storage and handling of this oxidant. In addition, IBX, DMP, and analogues are not perfect with respect to the principles of Green Chemistry since they are normally used as the nonrecyclable, stoichiometric reagents.[4] Numerous research groups have tried to improve hypervalent iodine(V)-based reagents by developing their polymer-supported analogues,[5] such as polymer-supported variants of IBX,[5a−f] IBX-amides,[5g−j] IBX-esters,[5g,h] *N*-(2-iodylphenyl)acylamides,[5k] and 2-iodylphenol ethers.[5l] Despite the utility of the polymer-supported iodine(V) reagents, they still have several disadvantages. These reagents require a multistep preparation and have lower reactivity compared to the corresponding monomeric analogies, and moreover, the repeated use of these polymers leads to significant degradation due to the benzylic oxidation of the polystyrene chain. Accordingly, substantial recent research efforts have been devoted to the development of simple, nonpolymeric, recyclable iodanes, which show reactivities similar to those of the original hypervalent iodine reagents and do not have the disadvantages of the polymeric reagents.[6] All previously reported nonpolymeric recyclable iodanes belong to iodine(III) compounds, and the reduced form of these reagents can be effectively recovered from the reaction mixture using liquid/liquid biphase fluorous techniques,[6a−d] liquid/solid,[6e−m] or liquid/liquid base−acid biphasic protocols.[6n−t]

In this paper, we present the synthesis, structural characterization, and reactivity of first nonpolymeric recyclable hypervalent iodine(V) reagents based on the readily available derivatives of 2-iodopyridine. These new reagents are useful for oxidation of sulfides and alcohols, and the reduced form of these reagents can be effectively recovered from the reaction mixture using liquid/liquid acid−base biphasic protocols.

2. RESULTS AND DISCUSSION

2.1. Preparation and Structural Investigation of 2-Iodylpyridines. 2-Iodylpyridines **2a**−**e** were prepared by oxidation of the respective 2-iodopyridines **1** with 3,3-dimethyldioxirane (DMDO) similarly to the previously reported procedure (Scheme 1).[7] The starting 2-iodopyridine **1a** was from a commercial source, while 2-iodopyridine ethers **1b**−**e** were prepared in high yields by the alkylation of commercially available 3-hydroxy-2-iodopyridine with appropriate alkyl halides under basic conditions by the known procedure.[8]

Products **2** precipitated from the reaction mixture and were isolated in excellent yields in analytically pure form as white

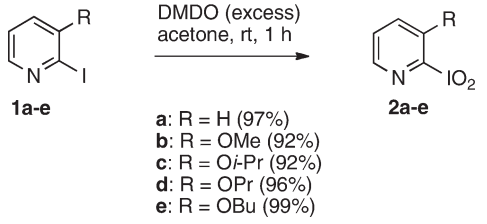
Received: January 23, 2011
Published: April 04, 2011

 © 2011 American Chemical Society

microcrystalline solids by filtration followed by washing with acetone and drying in vacuum. All products were analyzed by NMR, IR, elemental analysis, and compounds **2a**, **2c**, and **2d**, by X-ray crystallography. In particular, ^{13}C NMR spectra of products **2** showed characteristic signals of the C-IO_2 *ipso*-carbon at about 152 ppm, which is typical of iodylarenes.[7,9] The C−O *ipso*-carbon for the ethers **2c**−**e** showed at 156−158 ppm. IR spectra of all compounds **2** showed two intense peak of IO_2 at 780−770 and 750 cm^{-1}. 2-Iodylpyridines **2a**−**e** are stable at room temperature and do not possess explosive properties upon heating or impact. A slow decomposition is observed during heating of the compound **2** in a capillary tube above the melting point. Compounds **2d** and **2e** are soluble in dichloromethane, chloroform, and acetonitrile, while products **2a**−**c** have a relatively low solubility in organic solvents.

Structures of 2-iodylpyridines **2a**, **2c**, and **2d** were established by single-crystal X-ray crystallography (Figures 1−3). X-ray data of products **2a**, **2c**, and **2d** demonstrate the presence of, typical for iodine(V) compounds, complex intra- and/or intermolecular interactions. Although all compounds were crystallized using water as a solvent or in the presence of moist air, only compounds **2a** and **2c** have water molecules in the unit cells, while the *n*-propyl-containing compound **2d** crystallizes without any solvent molecules. In all three molecules studied, I═O and I−C bond distances are in the typical range of 1.80 and 2.15 Å, respectively, which is characteristic for iodyl compounds.[7,9a,9b,9d−9f,9i] Similarly, O═I═O bond angles in **2a**, **2c**, and **2d** (101−102°) are close to those expected for iodine(V) pseudoheterocycle angles with one I═O bond located within the pyridine ring plane and the other I═O bond being almost perpendicular to it. In addition, similar to the described earlier *o*-substituted iodylphenol ethers,[7b] compounds **2c** and **2d** have intramolecular I···O(ether) contacts ranging between 2.909 and 3.053 Å. In general, the first coordination sphere for compounds **2a**, **2c**,

Scheme 1. Preparation of 2-Iodylpyridines 2a−e



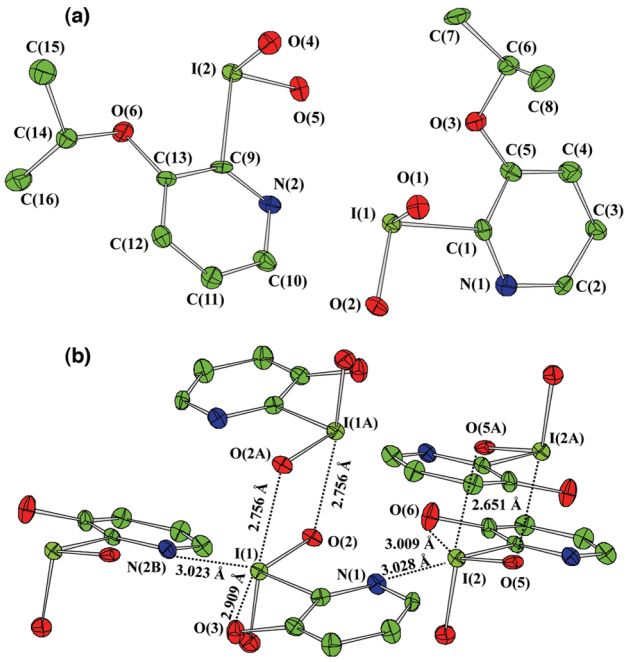


Figure 2. (a) Perspective view of 2-iodyl-3-isopropoxypyridine **2c** (two independent molecules per unit cell) with 50% ellipsoid probability. Selected distances [Å] and angles [°]: I(1)−C(1) 2.144(6), I(2)−C(9) 2.158(5), I(1)−O(1) 1.810(5), I(1)−O(2) 1.797(4), I(2)−O(4) 1.798(5), I(2)−O(5) 1.798(4), C(1)−I(1)−O(1) 97.2(2), C(1)−I(1)−O(2) 96.0(2), C(9)−I(2)−O(4) 95.0(2), C(9)−I(2)−O(5) 96.0(2), O(1)−I(1)−O(2) 102.3(2), O(4)−I(2)−O(5) 101.2(2). (b) Intra- and intermolecular secondary bonding in **2c**. Selected distances [Å]: I(1)···O(2A) 2.756(5), I(2)−O(5A) 2.651(4), I(1)−N(2B) 3.023(5), I(2)−N(1) 3.028(5), I(1)−O(3) 2.909(5), I(2)−O(6) 3.009(5).

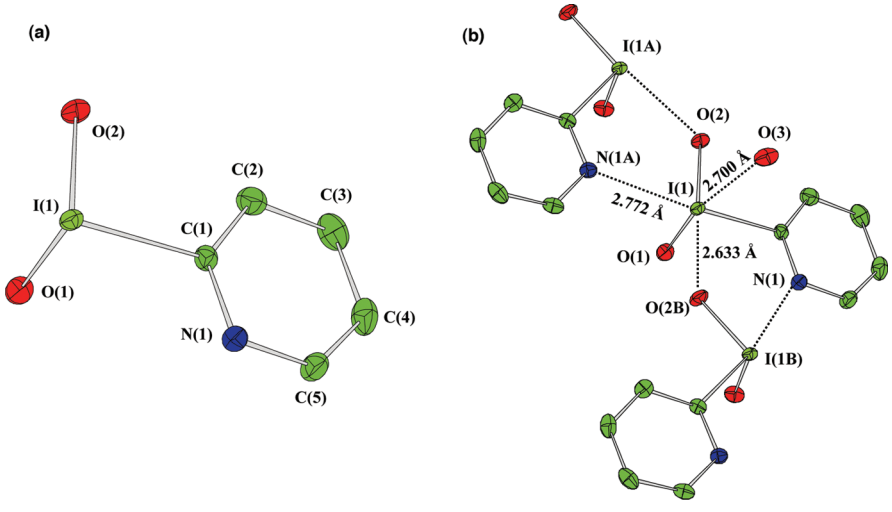


Figure 1. (a) Perspective view of 2-iodylpyridine **2a** with 50% ellipsoid probability. Selected distances [Å] and angles [°]: I(1)−C(1) 2.152(2), I(1)−O(1) 1.8101(16), I(1)−O(2) 1.8179(17), C(1)−I(1)−O(1) 94.35(8), C(1)−I(1)−O(2) 92.86(8), O(1)−I(1)−O(2) 101.70(8). (b) Intra- and intermolecular secondary bonding in **2a**. Selected distances [Å]: I(1)···O(2B) 2.6326(16), I(1)···O(3) 2.6999(17), I(1)−N(1A) 2.772(2).

dx.doi.org/10.1021/jo200163m |*J. Org. Chem.* 2011, 76, 3812–3819

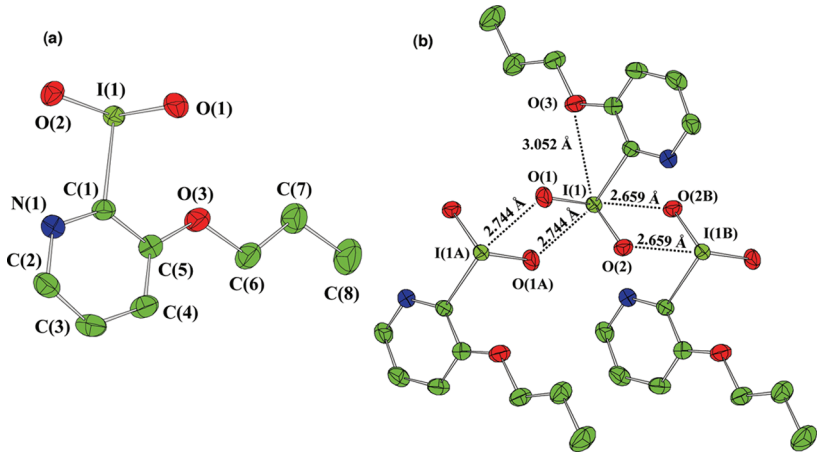


Figure 3. (a) Perspective view of 2-iodyl-3-propoxypyridine **2d** with 50% ellipsoid probability. Selected distances [Å] and angles [°]: I(1)−C(1) 2.1500(18), I(1)−O(1) 1.8049(13), I(1)−O(2) 1.8028(14), C(1)−I(1)−O(1) 96.51(7), C(1)−I(1)−O(2) 95.66(7), O(1)−I(1)−O(2) 101.60(7). (b) Intra- and intermolecular secondary bonding in **2d**. Selected distances [Å]: I(1)···O(2B) 2.6592(14), I(1)···O(1A) 2.744(1), I(1)−O(3) 3.052(2).

and **2d** can be described as distorted octahedral configuration with three covalent bonds and three relatively long intra- and/or intermolecular contacts. It is interesting to see, however, that the pyridine ring nitrogen atom is involved into the intermolecular interactions in molecules **2a** and **2c**, because such N···I short contacts have never previously been reported for organoiodine(V) compounds and are relatively uncommon for iodine(III) compounds.[10] For example, the N···I distances in the complexes of alkynyliodonium tetrafluoroborates with 1,10-phenanthroline are in the range of 2.9−3.2 Å.[10g] The first coordination sphere of the iodine atom in **2a** consists of two short I═O bonds, one I−C bond, and three intermolecular contacts (Figure 1). The shortest one (2.633 Å) originates from the O(2B) atom of the neighboring molecule, while the second oxygen atom of the O═I═O fragment does not participate in intermolecular bonding. In addition, the nitrogen N(1A) atom from the pyridine ring of another neighboring molecule provides quite short additional secondary bonding (2.772 Å). Finally, the iodine atom also interacts with the solvent water oxygen atom O(3) at 2.700 Å distance. As a result, each molecule of **2a** interacts with two other neighboring molecules and solvent water forming a polymeric zigzag chain.

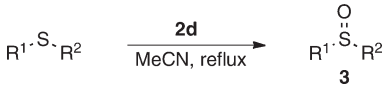
The solvate water molecules, on the other hand, are not involved in intermolecular bonding in compound **2c** (Figure 2). Instead, they are involved in formation of the solvent channel, which separates double-helix type polymeric chains of **2c**. These solvent channels are ordered by the hydrogen bonds between hydrogen atoms of water molecules and perpendicular to the pyridine ring plane O(1) and O(4) oxygen atoms of the O═I═O fragment. Although there are two independent molecules of **2c** observed per unit cell, their intra- and intermolecular coordination motifs are similar. Each iodine center has three covalent bonds (two I═O bonds with ∼1.8 Å bond distances and one I−C bond with ∼2.15 Å bond distance), one intramolecular O(ether)···I bond (∼3.0 Å), and two intermolecular bonds (one short, i.e., 2.651−2.756 Å, I═O···I bond and one long, i.e., 3.023−3.028 Å, N···I bond). Overall, each molecule of **2c** interacts with three other neighboring molecules forming double-helix polymeric chains isolated by the solvent water channels.

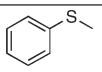
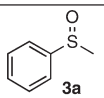
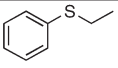
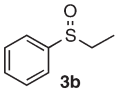
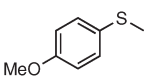
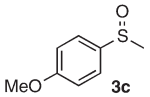
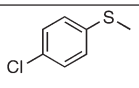
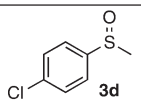
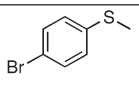
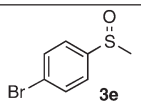
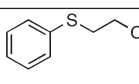
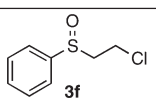
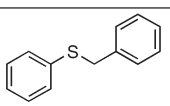
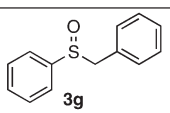
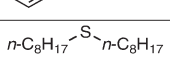
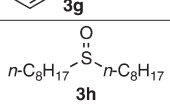
The secondary interactions between the molecules of **2d** are quite different from those observed in **2a** and **2c** (Figure 3). First, solvent molecules are absent in the unit cell. Second, and more important, nitrogen atoms are not involved into intermolecular network. Indeed, the closest observed for **2d** N···I distance is ∼3.43 Å, which is significantly larger than the sum of the van der Waals radii of the iodine and nitrogen atoms. Instead, in addition to three covalent bonds and one short intramolecular O(ether)···I contact, each molecule of **2d** forms two short (2.659−2.744 Å) intermolecular contacts with two oxygen atoms located at two neighboring I═O fragments (Figure 3). Such secondary interactions result in the polymeric zigzag conformation of **2d**. Since the nitrogen atom of the pyridine ring in **2d** is not involved in the secondary bonding, it is available for solvent−solute interaction, which could be responsible for the higher solubility of **2d** compared to compounds **2a** and **2c**.

2.2. Oxidations with 2-Iodylpyridines. We investigated the oxidation of sulfides to sulfoxides and alcohols to aldehydes or ketones using compound **2d** because this compound has good solubility in organic solvents (0.8 mg/mL in dichloromethane and 1.1 mg/mL in acetonitrile). The oxidation of sulfides was initially carried out with 0.6 equiv of reagent **2d** under conditions previously used in the similar reactions of IBX-esters,[11] 2-iodylphenol ethers,[7b] and IBX-amides.[7a] However, the yield of sulfoxides **3** under these conditions was relatively low, only 50−79%, even after 24 h (Table 1, entries 1 and 2), which is probably explained by partial decomposition of reagent **2d** during reaction. We have found that the yield of sulfoxides can be significantly improved by performing the oxidation with 1.0 equiv of reagent **2d** in acetonitrile under reflux conditions. Under these conditions, the oxidation of methyl phenyl sulfide is complete in 1.5 h affording product **3a** in quantitative yield (Table 1, entry 3). Similar reactions of several other aryl alkyl sulfides give the respective sulfoxides **3** in high isolated yields (Table 1, entries 4−9). The oxidation of a dialkyl sulfide affords the respective sulfoxide in a lower yield (Table 1, entry 10).

The reaction conditions for the oxidation of alcohols with reagent **2d** were optimized using 1-phenyl ethanol (Table 2, entries 1−3). Similarly to the oxidation of sulfides, the best yields are obtained by performing the oxidation with 1.0 equiv of

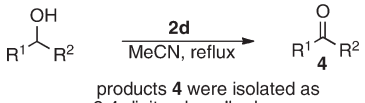
Table 1. Oxidation of Sulfides to Sulfoxides with 2d[a]



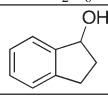
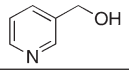
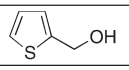
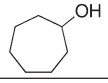
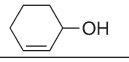
Entry	Sulfide	Time (h)	Sulfoxide **3**	Yield (%)[b]
1		1.5	 **3a**	50[c]
2		24	 **3a**	79[c]
3		1.5	 **3a**	100
4		1.5	 **3b**	100
5		1	 **3c**	82
6		2.5	 **3d**	100
7		2.5	 **3e**	82
8		2.5	 **3f**	89
9		2.5	 **3g**	95
10		2.5	 **3h**	62

[a] Reaction conditions: sulfide (0.1 mmol), reagent **2d** (0.1 mmol), MeCN (1 mL), reflux, unless noted otherwise. [b] Yields of isolated products. [c] 0.6 equiv of reagent **2d** was used.

Table 2. Oxidation of Alcohols with 2d[a]



products **4** were isolated as 2,4-dinitrophenylhydrazones

Entry	Alcohol	Time (h)	**4**	Yield (%)[b]
1	PhCH(OH)Me	3	**4a**	53[c]
2	PhCH(OH)Me	24	**4a**	60[c]
3	PhCH(OH)Me	3	**4a**	80
4	$PhCH_2OH$	2	**4b**	91
5	*p*-$MeOC_6H_4CH_2OH$	4	**4c**	89
6	*m*-$NO_2C_6H_4CH_2OH$	3	**4d**	73
7		2.5	**4e**	99
8		24	**4f**	66
9		15	**4g**	72
10	$PhCH_2CH_2CH_2OH$	3	**4h**	69
11		3	**4i**	82
12	EtCH(OH)Et	2.5	**4j**	(61)[d]
13	*n*-$C_8H_{17}OH$	2	**4k**	(75)[d]
14		2.5	**4l**	(66)[d]

[a] Reaction conditions: alcohol (0.1 mmol), reagent **2d** (0.1 mmol), MeCN (1 mL), reflux, unless noted otherwise. [b] Preparative yields of 2,4-dinitrophenylhydrazone derivatives of **4**. [c] 0.6 equiv of reagent **2d** was used. [d] Numbers in parentheses show yields determined from ^{1}H NMR spectra of the reaction mixture.

reagent **2d** in acetonitrile under reflux conditions (Table 2, entry 3). To standardize the procedure and obtain reliable information about preparative yields of the relatively volatile products **4**, we isolated aldehydes **4b**−**d** and **f**−**h** and ketones **4a**,**c**,**i** as solid 2,4-dinitrophenylhydrazone derivatives after addition of a standard solution of 2,4-dinitrophenylhydrazine to the reaction mixture. Isolated yields of the hydrazone derivatives of products **4** obtained by the oxidation of various alcohols with reagent **2d** under standard conditions are shown in Table 2, entries 1−11. The yields of carbonyl products formed in the oxidation of 3-pentanol, 1-octanol, and 2-cyclohexenol (entries 12−14) were determined from ^{1}H NMR spectra of reaction mixtures after removal of solvent. In general, the oxidation of primary and secondary benzylic and aliphatic alcohols proceeds selectively affording the respective carbonyl compounds in good yields. The oxidation of alcohols derived from heteroaromatic compounds proceeds much slower (Table 2, entries 8 and 9). No overoxidation of primary alcohols to carboxylic acids or esters was observed under these conditions.

The reactivity of reagent **2d** in the oxidations of sulfides and alcohols is generally similar to the reactivity of 2-iodylphenol ethers.[7b] However, compared to previously reported nonpolymeric organoiodine(V) oxidants,[7,9] reagent **2d** has the advantage of being easily recyclable from the reaction mixture using a simple acid−base liquid−liquid biphasic protocol. We found that the reduced form of reagent **2d**, 2-iodo-3-propoxypyridine **1d**, can be effectively separated from the reaction mixture (after initial addition of aqueous solution of $Na_2S_2O_3$ in order to reduce the excessive reagent **2d**) by treatment with diluted sulfuric acid and recovered in 95−99% from the acidic aqueous solution by the addition of aqueous sodium hydroxide followed by extraction with ethyl acetate. The recovered 2-iodo-3-propoxypyridine **1d** can be reoxidized to 2-iodyl-3-propoxypyridine **2d** by DMDO in almost quantitative yield (Scheme 1).

3. CONCLUSIONS

In summary, we have prepared 2-iodylpyridine **2a** and four 3-alkoxy-2-iodylpyridines **2b**−**e** by oxidation of the respective 2-iodopyridines with 3,3-dimethyldioxirane. Structures of 2-iodylpyridine **2a**, 2-iodyl-3-isopropoxypyridine **2c**, and 2-iodyl-3-propoxypyridine **2d** were established by single-crystal X-ray diffraction analysis. According to X-ray structural data, the nitrogen atom of the pyridine moiety is involved in intermolecular

dx.doi.org/10.1021/jo200163m |*J. Org. Chem.* 2011, 76, 3812–3819

interactions with hypervalent iodine atom in molecules **2a** and **2c** but not in the molecule **2d**. 2-Iodyl-3-propoxypyridine **2d** has good solubility in organic solvents and can be used as a recyclable reagent for oxidation of sulfides and alcohols. The reduced form of this reagent, 2-iodo-3-propoxypyridine **1d**, can be effectively separated from the reaction mixture by treatment with diluted sulfuric acid and recovered in 95−99% from the acidic aqueous solution by neutralizing it with aqueous sodium hydroxide.

4. EXPERIMENTAL SECTION

All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Dimethyldioxirane (as 0.1 M solution in acetone) was prepared from commercial acetone and oxone by a known method.[12] 2-Iodopyridine **1a** was from a commercial source, and 3-alkoxy-2-iodopyridines **1b**−**e** were prepared in high yields by the alkylation of commercially available 3-hydroxy-2-iodopyridine with appropriate alkyl halides under basic conditions by the known procedure.[8] All other reagents and solvents were of commercial quality from freshly opened containers. NMR spectra were recorded at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts (δ) are reported in parts per million.

General Procedure for Preparation of 2-Iodopyridines (1b−e)[8]. To a solution of 2-iodo-3-hydroxypyridine in dry DMF was added potassium carbonate or sodium hydride under stirring. After 10 min the appropriate alkyl bromide or alkyl iodide was added to the reaction mixture. The reaction was stirred at 50 °C for 3 h. The solvent was evaporated in vacuum, and the residue was extracted with ethyl acetate and separated by column chromatography using 1:3 mixture EtOAc/hexanes to afford analytically pure product **1**.

*2-Iodo-3-methoxypyridine (**1b**)*[8a]. Reaction of iodomethane (0.75 g, 5.4 mmol) and NaH (0.22 g, 5.4 mmol) with 2-iodo-3-hydroxypyridine (1.00 g, 4.5 mmol) according to the general procedure afforded 0.76 g (71%) of product **1b**, isolated as white colorless needles (recrystallized from dichloromethane): mp 57.7−58.3 °C (lit.[2] 55−57 °C). ^{1}H NMR ($CDCl_3$): δ 8.01 (dd, J = 4.5, 1.5 Hz, 1H), 7.21 (dd, J = 8.3, 4.5 Hz, 1H), 7.01 (dd, J = 8.3, 1.5 Hz, 1H), 3.91 (s, 3H).

*2-Iodo-3-isopropoxypyridine (**1c**)*[8a]. Reaction of 2-bromopropane (0.72 g, 5.9 mmol) and K_2CO_3 (2.80 g, 20 mmol) with 2-iodo-3-hydroxypyridine (1.00 g, 4.5 mmol) according to the general procedure afforded 0.86 mg (73%) of product **1c** as colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.97 (dd, J = 4.5, 1.5 Hz, 1H), 7.16 (dd, J = 8, 4.5 Hz, 1H), 6.99 (dd, J = 8, 1.5 Hz, 1H), 4.56 (sept, J = 6 Hz, 1H), 1.41 (d, J = 6 Hz, 6H). ^{13}C NMR ($CDCl_3$): 153.9, 142.5, 123.3, 119.8, 114, 72.6, 21.9.

*2-Iodo-3-propoxypyridine (**1d**)*[8a]. Reaction of 1-iodopropane (1.15 g, 6.8 mmol) and K_2CO_3 (3.10 g, 23 mmol) with 2-iodo-3-hydroxypyridine (1.00 g, 4.5 mmol) according to the general procedure afforded 0.84 g (73%) of product **1d** as colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.97 (dd, J = 4.8, 1 Hz, 1H), 7.16 (dd, J = 7.9, 4.8 Hz, 1 H), 6.97 (dd, J = 7.9, 1 Hz, 1H), 3.99 (t, J = 6.3 Hz, 2H), 1.88 (m, 2H), 1.26 (t, J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): 154.7, 142.4, 123.4, 117.7, 112.3, 70.9, 22.4, 10.7.

*2-Iodo-3-butoxypyridine (**1e**)*[8b]. Reaction of 1-bromobutane (0.93 g, 6.8 mmol) and K_2CO_3 (3.10 g, 23 mmol) with 2-iodo-3-hydroxypyridine (1.00 g, 4.5 mmol) according to the general procedure afforded 1.07 g (85%) of product **1e** as colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.98 (dd, J = 4.5, 1.5 Hz, 1H), 7.17 (dd, J = 8, 4.5 Hz, 1H), 6.97 (dd, J = 8, 4.5 Hz, 1H), 4.03 (t, J = 6.5 Hz, 2H), 1.84 (m, 2H), 1.57 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): 154.8, 142.4, 123.4, 117.7, 112.3, 69.1, 31, 19.3, 13.8.

General Procedure for Oxidation of 2-Iodopyridines. A freshly prepared solution of dimethyldioxirane[12] in acetone was added to a stirred mixture of the appropriate 2-iodopyridine derivative **1** at room temperature. The reaction mixture immediately changed from colorless solution to white suspension. The mixture was stirred at room temperature for 1 h, and the resulting white microcrystalline precipitate was separated by filtration. The precipitate was washed with acetone and dried in vacuum to afford analytically pure product **2**.

*2-Iodylpyridine (**2a**).* Oxidation of a commercial sample of 2-iodopyridine **1a** (0.40 g, 1.95 mmol) according to the general procedure afforded 0.45 g (97%) of product **2a**, isolated as white crystals: mp 99.3−101.2 °C (dec). IR (KBr) cm^{-1} 3134, 1571, 1455, 1411, 758, 738. ^{1}H NMR (DMSO-d_6): δ 8.53 (d, J = 5 Hz, 1H), 8.12 (td, J = 9.3, 2 Hz, 1H), 7.98 (d, J = 9.3 Hz, 1H), 7.61 (dd, J = 9.3, 5 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ 170.9, 150.3, 139.6, 127.2, 121.1. Anal. Calcd for $C_5H_4INO_2$: C, 25.34; H, 1.70; I, 53.55; N, 5.91. Found: C, 25.23; H, 1.84; I, 53.62; N, 5.74.

Single crystals of product **2a** suitable for X-ray crystallographic analysis were obtained by slow crystallization from water. X-ray diffraction data were collected on a Bruker APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at −100 °C. Absorption corrections were applied to the data using the DIFABS method. The structure was solved by the Patterson method and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **2a**: $C_5H_4INO_2$ x H_2O, M = 255.01, monoclinic, space group $P21/c$, a = 6.2624(7) Å, b = 14.4474(16) Å, c = 8.0465(9) Å, β = 107.3260(10)°, V = 694.98(13) Å^3, Z = 4, T = 173 K, $\mu(\lambda$ = 0.80000 Å) = 4.552 mm^{-1}, d_{calc} = 2.437 g/cm^3, 1659 reflections measured, 1587 unique, R_1 = 0.0138, wR_2 =0.0337 ($I > 3\sigma(I)$), R_1 = 0.0148, wR_2 = 0.0344 (all data), GOF = 1.0552. For further details on crystal structure of compound **2a**, see the CIF file.

*2-Iodyl-3-methoxypyridine (**2b**).* Oxidation of 2-iodo-3-methoxypyridine **1b** (0.21 g, 0.88 mmol) according to the general procedure afforded 0.22 g (92%) of product **2b**, isolated as white crystals: mp 147−147.4 °C (dec). IR (KBr) cm^{-1} 3076, 3045, 2939, 2852, 1556, 1458, 1408, 1278, 1002, 772, 753. ^{1}H NMR (DMSO-d_6): δ 8.27 (dd, J = 4.5, 1.5 Hz, 1H), 7.72 (dd, J = 8.5, 1.5 Hz, 1H), 7.63 (dd, J = 8.5, 4.5 Hz, 1H), 3.9 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 156.1, 152.3, 141.2, 127.8, 120.9, 57. Anal. Calcd for $C_6H_6INO_3$: C, 26.99; H, 2.26; N, 5.25. Found: C, 27.07; H, 2.16; N, 5.22.

*2-Iodyl-3-isopropoxypyridine (**2c**).* Oxidation of 2-iodo-3-isopropoxypyridine **1c** (0.20 g, 0.76 mmol) according to the general procedure afforded 0.20 g (92%) of product **2c**, isolated as white crystals: mp 110.8−111.5 °C (dec); IR (KBr) cm^{-1} 3071, 2982, 2948, 1550, 1454, 1409, 1280, 1103, 790, 770, 757. ^{1}H NMR (DMSO-d_6): δ 8.25 (dd, J = 4.5, 1.5 Hz, 1H), 7.76 (dd, J = 8.5, 1.5 Hz, 1H), 7.6 (dd, J = 8.5, 4.5 Hz, 1H), 4.84 (sept, J = 6 Hz, 1H), 1.34 (d, J = 6 Hz, 6H). ^{13}C NMR (DMSO-d_6): δ 157.7, 152, 142, 129, 123.4, 73.7, 22.3. Anal. Calcd for $C_8H_{10}INO_3$: C, 32.56; H, 3.42; N, 4.75. Found: C, 32.46; H, 3.36; N, 4.87.

Single crystals of product **2c** suitable for X-ray crystallographic analysis were obtained by slow crystallization from a hexane−dichloromethane solution in a refrigerator. X-ray diffraction data were collected on Rigaku RAPID II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at −150 °C. Absorption corrections were applied to the data using a multiscan method. The structure was solved by the Patterson method and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **2c**: $C_8H_{10}INO_3$ x $2H_2O$, M = 331.10, triclinic, space group P-1, a = 9.1841(3) Å, b = 10.3130(5) Å, c = 12.2949(8) Å, α = 82.634(6)°, β = 85.041(6)°, γ = 82.063(6)°, V = 1141.04(10) Å^3, Z = 4, T = 123 K, $\mu(\lambda$ = 0.80000 Å) = 2.809 mm^{-1}, d_{calc} = 1.927 g/cm^3, 32 057 reflections measured, 5201 unique, R_1 = 0.0432, wR_2 = 0.0926 ($I > 2\sigma(I)$), R_1 = 0.0573, wR_2 = 0.1031 (all data), GOF = 0.9781. For further details on the crystal structure of compound **2c**, see the CIF file.

*2-Iodyl-3-propoxypyridine (**2d**).* Oxidation of 2-iodo-3-propoxypyridine **1d** (0.22 g, 0.87 mmol) according to the general procedure

afforded 0.24 g (96%) of product **2d**, isolated as white crystals: mp 116.5−117 °C (with decomposition). IR (KBr) cm^{-1} 3063, 2950, 2910, 1548, 1462, 1420, 1280, 1002, 773, 760. ^1H NMR ($CDCl_3$): δ 8.3 (d, J = 4 Hz, 1 H), 7.46 (m, 1H), 7.38 (d, J = 8 Hz, 1H), 4.14 (t, J = 6.3 Hz, 2H), 1.9 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR (DMSO-d_6): δ 156.3, 152.3, 141.2, 127.8, 121.5, 71.0, 21.6, 10.2. Anal. Calcd for $C_8H_{10}INO_3$: C, 32.56; H, 3.42; N, 4.75. Found: C, 32.53; H, 3.38; N, 4.69.

Single crystals of product **2d** suitable for X-ray crystallographic analysis were obtained by slow crystallization from a hexane−dichloromethane solution in a refrigerator. X-ray diffraction data were collected on Rigaku RAPID II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Absorption corrections were applied to the data using a multiscan method. The structure was solved by the Patterson method and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **2d**: $C_8H_{10}INO_3$, M = 295.08, monoclinic, space group $P21/n$, a = 6.57260(10) Å, b = 12.6845(2) Å, c = 11.8472(8) Å, β = 97.126(7)°, V = 980.07(7) $Å^3$, Z = 4, T = 298 K, $\mu(\lambda$ = 0.80000 Å) = 3.243 mm^{-1}, d_{calc} = 2.000 g/cm^3, 18 700 reflections measured, 2259 unique, R_1 = 0.0145, wR_2 = 0.0346 ($I > 2\sigma(I)$), R_1 = 0.0166, wR_2 = 0.0353 (all data), GOF = 1.0008. For further details on the crystal structure of compound **2d**, see the CIF file.

*3-Butoxy-2-iodylpyridine (**2e**).* Oxidation of 3-butoxy-2-iodopyridine **1e** (0.15 g, 0.54 mmol) according to the general procedure afforded 0.17 g (99%) of product **2e**, isolated as white crystals: mp 117.6−117.8 °C (dec). IR (KBr) cm^{-1} 3036, 2958, 2886, 1553, 1449, 1413, 1296, 1064, 781, 766. ^1H NMR ($CDCl_3$): δ 8.3 (d, J = 4.5 Hz, 1H), 7.51 (dd, J = 8.5, 4.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 4.2 (t, J = 6.5 Hz, 2H), 1.87 (m, 2H), 1.54 (m, 2H), 1.0 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 158.9, 152.9, 142.8, 121.7, 70.5, 30.7, 19.1, 13.8. Anal. Calcd for $C_9H_{12}INO_3$: C, 34.97; H, 3.91; N, 4.53. Found: C, 34.80; H, 3.87; N, 4.48.

General Procedure for the Oxidation of Sulfides with 2-Iodyl-3-propoxypyridine (2d). To a solution of 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN was added the appropriate sulfide (0.1 mmol). The reaction was stirred at reflux for several hours (see Table 1). Then saturated aqueous $Na_2S_2O_3$ (1.5 mL) was added, the mixture was extracted with ethyl acetate, and the organic phase dried over anhydrous $MgSO_4$ and concentrated. Purification by flash column chromatography (hexane−ethyl acetate, 3:1) gave pure product **3**.

*Methyl Phenyl Sulfoxide (**3a**)*[13]. Reaction of methyl phenyl sulfide (12 mg, 0.1 mmol) according to the general procedure afforded 14 mg (100%) of product **3a**, isolated as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.67−7.65 (m, 2H), 7.54−7.51 (m, 3H), 2.73 (s, 3H).

*Ethyl Phenyl Sulfoxide (**3b**)*[14]. Reaction of ethyl phenyl sulfide (14 mg, 0.1 mmol) according to the general procedure afforded 15 mg (100%) of product **3b**, isolated as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.62−7.61 (m, 2H), 7.54−7.50 (m, 3H), 2.94−2.87 (m, 1H), 2.81−2.73 (m, 1H), 1.2 (t, J = 7.5 Hz, 3H).

*4-Methoxyphenyl Methyl Sulfoxide (**3c**)*[15]. Reaction of 4-methoxyphenyl methyl sulfide (15 mg, 0.1 mmol) according to the general procedure afforded 14 mg (82%) of product **3c**, isolated as a brown oil. ^1H NMR ($CDCl_3$): δ 7.6 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H), 2.73 (s, 3H).

*4-Chlorophenyl Methyl Sulfoxide (**3d**)*[15]. Reaction of 4-chlorophenyl methyl sulfide (16 mg, 0.1 mmol) according to the general procedure afforded 17 mg (100%) of product **3d**, isolated as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.6 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 2.72 (s, 3H).

*4-Bromophenyl Methyl Sulfoxide (**3e**)*[16]. Reaction of 4-bromophenyl methyl sulfide (20 mg, 0.1 mmol) according to the general procedure afforded 18 mg (82%) of product **3e**, isolated as colorless needles (recrystallized from hexane−dichloromethane); 82.4−83.3 °C (lit.[16b] 82.5−84 °C). ^1H NMR ($CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 2.72 (s, 3H).

*2-Chloroethyl Phenyl Sulfoxide (**3f**)*[17]. Reaction of 2-chloroethyl phenyl sulfide (17 mg, 0.1 mmol) according to the general procedure afforded 17 mg (89%) of product **3f**, isolated as an amorphous solid. ^1H NMR ($CDCl_3$): δ 7.66−7.64 (m, 2H), 7.58−7.53 (m, 3H), 4−3.95 (m, 1H), 3.69−3.64 (m, 1H), 3.19−3.15 (m, 2H).

*Benzyl Phenyl Sulfoxide (**3g**)*[18]. Reaction of benzyl phenyl sulfide (20 mg, 0.1 mmol) according to the general procedure afforded 21 mg (95%) of product **3g**, isolated as colorless crystals (recrystallized from hexane−dichloromethane); 122.4−123.6 °C (lit.[10,11] 122−123 °C). ^1H NMR ($CDCl_3$): δ 7.48−7.37 (m, 5H), 7.3−7.23 (m, 3H), 6.98 (d, J = 7.5 Hz, 2H), 4.1 (d, J = 12.5 Hz, 1H), 4.0 (d, J = 12.5 Hz, 1H).

*Dioctylsulfoxide (**3h**)*[17,19]. Reaction of dioctylsulfide (26 mg, 0.1 mmol) according to the general procedure afforded 17 mg (63%) of product **3h**, isolated as colorless needles (recrystallized from hexane−dichloromethane); 70.5−71 °C (lit.[19] 75−76 °C). ^1H NMR ($CDCl_3$): δ 2.72−2.59 (m, 4H), 1.8−1.73 (m, 4H), 1.45−1.38 (m, 4H), 1.35−1.25 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H).

General Procedure for the Oxidation of Alcohols with 2-Iodyl-3-propoxypyridine (2d). To a solution of 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN was added the appropriate alcohol (0.1 mmol). The reaction mixture was stirred at reflux for several hours. After the reaction was complete, a standard solution of 1.5 mL of 2,4-dinitrophenylhydrazine (prepared from 200 mg of 2,4-dinitrophenylhydrazine, 1 mL of concd H_2SO_4, 10 mL of EtOH, and 2 mL of H_2O) was added. The precipitate of 2,4-dinitrophenylhydrazone **4** was filtered, washed with water, and dried in vacuum.

*2,4-Dinitrophenylhydrazone of Acetophenone (**4a**)*[20,21]. Reaction of 1-phenylethanol (12 mg, 0.1 mmol) according to the general procedure afforded 24 mg (80%) of product **4a**, isolated as orange needles (recrystallized from hexane−dichloromethane): mp 246−246.7 °C (lit.[21] mp 248−249 °C). ^1H NMR ($CDCl_3$): δ 11.37 (s, 1H), 9.18 (d, J = 1.8 Hz, 1H), 8.37 (dd, J = 9.5, 1.8 Hz, 1H), 8.14 (d, J = 9.5 Hz, 1H), 7.9−7.84 (m, 2H), 7.52−7.4 (m, 3H) 2.48 (s, 3H).

*2,4-Dinitrophenylhydrazone of Benzaldehyde (**4b**)*[21,22]. Reaction of benzyl alcohol (11 mg, 0.1 mmol) according to the general procedure afforded 26 mg (91%) of product **4b**, isolated as light orange needles (recrystallized from hexane−dichloromethane): 235.8−237 °C (lit.[22] 241−242 °C). ^1H NMR ($CDCl_3$): δ 11.33 (s, 1H), 9.16 (s, 1H), 8.44−8.3 (m, 1H), 8.22−8.04 (m, 2H), 7.84−7.73 (m, 2H), 7.56−7.4 (m, 3H), 7.32−7.2 (m, 2H).

*2,4-Dinitrophenylhydrazone of p-Methoxybenzaldehyde (**4c**)*[22,23]. Reaction of *p*-methoxybenzyl alcohol (14 mg, 0.1 mmol) according to the general procedure afforded 28 mg (89%) of product **4c**, isolated as red needles (recrystallized from hexane−dichloromethane): mp 254.1−255 °C (lit.[23] mp 256−257 °C). ^1H NMR ($CDCl_3$) δ 11.28 (s, 1H), 9.15 (s, 1H), 8.34 (d, J = 10 Hz, 1H), 8.08 (d, J = 10 Hz, 1H), 7.72 (d, J = 6.8 Hz, 2H), 6.48 (d, J = 6.8 Hz, 2H), 3.88 (s, 3H).

*2,4-Dinitrophenylhydrazone of m-Nitrobenzaldehyde (**4d**)*[22]. Reaction of *m*-nitrobenzyl alcohol (15 mg, 0.1 mmol) according to the general procedure afforded 24 mg (73%) of product **4d**, isolated as a yellow solid (recrystallized from ethanol): mp 282−283 °C (lit.[22] mp 292−293 °C). ^1H NMR (DMSO-d_6): δ 11.80 (s, 1H), 8.89 (d, J = 2.5 Hz, 1H), 8.83 (s, 1H), 8.57 (s, 1H), 8.44 (dd, J = 9.8, 2.5 Hz, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.25 (d, J = 7.7 Hz, 1H), 8.16 (d, J = 9.8 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H).

*2,4-Dinitrophenylhydrazone of 1-Indanone (**4e**)*[23]. Reaction of 1-indanol (13 mg, 0.1 mmol) according to the general procedure afforded 31 mg (99%) of product **4e**, isolated as orange needles (recrystallized from hexane−dichloromethane): mp 259−259.6 °C (lit.[23] mp 256−258 °C). ^1H NMR ($CDCl_3$): δ 11.11 (s, 1H), 9.17 (d, J = 2.5 Hz, 1H), 8.36 (d, J = 9.5 Hz, 1H), 8.13 (d, J = 9.5 Hz, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.46−7.35 (m, 3H), 3.28 (t, J = 6.1 Hz, 2H), 2.99 (t, J = 6.1 Hz, 2H).

*2,4-Dinitrophenylhydrazone of Nicotinaldehyde (**4f**)*[22,23]. Reaction of 3-pyridinylmethanol (11 mg, 0.1 mmol) according to the general

procedure afforded 19 mg (66%) of product **4f**, isolated as orange plates (recrystallized from hexane−dichloromethane): mp 257.4−258 °C (lit.[23] mp 259−261 °C). ^{1}H NMR ($CDCl_3$): δ 11.40 (s, 1H), 9.17 (s, 1H), 8.94 (s, 1H), 8.69 (d, J = 5 Hz, 1H), 8.40 (d, J = 9 Hz, 1H), 8.18−8.08 (m, 3H), 7.46−7.38 (m, 1H).

*2,4-Dinitrophenylhydrazone of Thiophene-2-carbaldehyde (**4g**)*[23]. Reaction of 2-thiophenylmethanol (11 mg, 0.1 mmol) according to the general procedure afforded 21 mg (72%) of product **4e**, isolated as orange plates (recrystallized from hexane−dichloromethane): mp 223−224.3 °C (lit.[23] mp 239−241 °C). ^{1}H NMR ($CDCl_3$): δ 11.29 (s, 1H), 9.15 (d, J = 2.3 Hz, 1H), 8.37 (dd, J = 9.5, 2.3 Hz, 1H), 8.31 (s, 1H), 8.03 (d, J = 9.5 Hz, 1H), 7.49 (d, J = 4.3 Hz, 1H), 7.37 (d, J = 4.3 Hz, 1H), 7.13 (m, 2H).

*2,4-Dinitrophenylhydrazone of 3-Phenyl-1-propanal (**4h**)*[23]. Reaction of 3-phenyl-1-propanol (14 mg, 0.1 mmol) according to the general procedure afforded 21 mg (69%) of product **4h**, isolated as orange plates (recrystallized from hexane−dichloromethane): mp 160−161 °C (lit.[23] mp 156−157 °C). ^{1}H NMR ($CDCl_3$): δ 11.02 (s, 1H), 9.12 (s, 1H), 8.3 (d, J = 9.8 Hz, 1H), 7.90 (d, J = 9.8 Hz, 1H), 7.56 (s, 1H), 7.35−7.31 (m, 2H), 7.26−7.24 (m, 3H), 2.98 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H).

*2,4-Dinitrophenylhydrazone of Cycloheptanone (**4i**)*[20,23]. Reaction of cycloheptanol (11 mg, 0.1 mmol) according to the general procedure afforded 18 mg (62%) of product **4i**, isolated as yellow needles (recrystallized from hexane−dichloromethane): mp 147−147.2 °C (lit.[23] mp 147−148 °C). ^{1}H NMR ($CDCl_3$): δ 11.05 (s, 1H), 9.13 (d, J = 2.5 Hz, 1H), 8.3 (dd, J = 9.5, 2.5 Hz, 1H), 7.99 (d, J = 9.5 Hz, 1H), 2.66−2.60 (m, 2H), 2.59−2.54 (m, 2H), 1.92−1.82 (m, 2H), 1.76−1.62 (m, 6H).

*3-Pentanone (**4j**).* Reaction of 3-pentanol (9 mg, 0.1 mmol) with 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN, after 2.5 h reflux followed by evaporation of solvent, afforded 3-pentanone in 61% yield as determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^{1}H NMR of the product is identical to the spectra published in the Spectral Database for Organic Compounds, SDBS (http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng).

*Octanal (**4k**).* Reaction of 1-octanol (13 mg, 0.1 mmol) with 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN, after 2 h reflux followed by evaporation of solvent, afforded 1-octanal in 75% yield as determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^{1}H NMR of the product is identical to the spectra published in the Spectral Database for Organic Compounds, SDBS (http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng).

*2-Cyclohexene-1-one (**4l**).* Reaction of 2-cyclohexene-1-ol (10 mg, 0.1 mmol) with 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN, after 2.5 h reflux followed by evaporation of solvent, afforded 2-cyclohexene-1-one in 66% yield as determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^{1}H NMR of the product is identical to the spectra published in the Spectral Database for Organic Compounds, SDBS (http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng).

Typical Procedure for the Oxidation of Organic Sulfides with the Recovery of 2-Iodo-3-propoxypyridine (1d). To a solution of 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN was added benzyl phenyl sulfide (20 mg, 0.1 mmol). The reaction mixture was stirred at reflux for 2.5 h, and then a saturated aqueous solution of $Na_2S_2O_3$ (1.5 mL) and 20% H_2SO_4 (3−5 mL) were added. The mixture was extracted with ethyl acetate, and the organic phase was dried over anhydrous $MgSO_4$ and concentrated to give pure product **3g** (20 mg, 91%). The aqueous layer was mixed with 20% NaOH (5−7 mL) and then extracted with ethyl acetate The organic extract was dried over anhydrous $MgSO_4$ and concentrated in vacuum to give 26 mg (99%) of 2-iodo-3-propoxypyridine **1d**.

Typical Procedure for the Oxidation of Alcohols with the Recovery of 2-Iodo-3-propoxypyridine (1d). To a solution of 2-iodyl-3-propoxypyridine **2d** (30 mg, 0.1 mmol) in 1 mL of dry MeCN was added 1-phenylethanol (12 mg, 0.1 mmol). The reaction mixture was stirred at reflux for 3 h, and then saturated aqueous solution of $Na_2S_2O_3$ (1.5 mL) and 20% H_2SO_4 (3−5 mL) were added. The mixture was extracted with ethyl acetate, and to the organic phase, 2−3 mL of standard solution of 2,4-dinitrophenylhydrazine was added. The precipitate of 2,4-dinitrophenylhydrazone **4a** was filtered, washed with water, and dried in vacuum, to give **4a** (22 mg, 73%). To the aqueous layer was added 20% NaOH (5−7 mL), and then the mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuum to give 2-iodo-3-propoxypyridine (25 mg, 95%).

■ ASSOCIATED CONTENT

Supporting Information. X-ray data for compounds **2a**, **2c**, and **2d** (CIF) and copies of NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*vzhdanki@d.umn.edu; vnemykin@d.umn.edu.

■ ACKNOWLEDGMENT

This work was supported by a research grant from the National Science Foundation (CHE-1009038) and by NSF-MRI award (MRI - 0922366). VVZ and MSY are also thankful to the Government of Russia for support of their cooperative research program on hypervalent iodine chemistry (FCP, GK 02.740.11.5211; Zayavka 2010-1.5-000-010-044).

■ REFERENCES

(1) For books and selected reviews on hypervalent iodine chemistry, see:(a) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997. (b) *Hypervalent Iodine Chemistry*; Wirth, T., Ed.; Springer-Verlag, Berlin, 2003. (c) Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89–102. (d) Koser, G. F. *Adv. Heterocycl. Chem.* **2004**, *86*, 225–292. (e) Moriarty, R. M. *J. Org. Chem.* **2005**, *70*, 2893–2903. (f) Quideau, S.; Pouysegu, L.; Deffieux, D. *Synlett* **2008**, 467–495. (g) Ladziata, U.; Zhdankin, V. V. *ARKIVOC* **2006**, No. ix, 26–58. (h) Ciufolini, M. A.; Braun, N. A.; Canesi, S.; Ousmer, M.; Chang, J.; Chai, D. *Synthesis* **2007**, 3759–3772. (i) Zhdankin, V. V. *Sci. Synth.* **2007**, *31a* (Ch. 31.4.1), 161–234. (j) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299–5358. (k) Ladziata, U.; Zhdankin, V. V. *Synlett* **2007**, 527–537. (l) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073–2085. (m) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, 4229–4239. (n) Yusubov, M. S.; Zhdankin, V. V. *Mendeleev Commun.* **2010**, *20*, 185–191. (o) Zhdankin, V. V. *ARKIVOC* **2009**, No. i, 1–62. (p) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086–2099. (q) Ngatimin, M.; Lupton, D. W. *Aust. J. Chem.* **2010**, *63*, 653–658. (r) Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *Tetrahedron* **2010**, *66*, 5745–5752. (s) Satam, V.; Harad, A.; Rajule, R.; Pati, H. *Tetrahedron* **2010**, *66*, 7659–7706. (t) Uyanik, M.; Ishihara, K. *Aldrichimica Acta* **2010**, *43*, 83–91. (u) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9052–9070. (v) Merritt, E. A.; Olofsson, B. *Synthesis* **2011**, 517–538. (w) Brand, J. P.; Gonzalez, D. F.; Nicolai, S.; Waser, J. *Chem. Commun.* **2011**, *47*, 102–115.

(2) For a recent Perspective on organoiodine(V) reagents in organic synthesis, see: Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 1185–1197.

(3) IBX can explode under impact or heating above 200 °C. See: (a) Plumb, J. B.; Harper, D. J. *Chem. Eng. News* **1990**, *68*, 3. (b) Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537–4538.

(4) In the only available report, it has been shown that IBX can be recovered in a low yield (about 50%) after reaction with alcohols in ethyl acetate: More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001–3003.

(5) (a) Muelbaier, M.; Giannis, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4393–4394. (b) Sorg, G.; Mengei, A.; Jung, G.; Rademann, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4395–4397. (c) Lei, Z. Q.; Ma, H. C.; Zhang, Z.; Yang, Y. X. *React. Funct. Polym.* **2006**, *66*, 840–844. (d) Lei, Z.; Denecker, C.; Jegasothy, S.; Sherrington, D. C.; Slater, N. K. H.; Sutherland, A. J. *Tetrahedron Lett.* **2003**, *44*, 1635–1637. (e) Bromberg, L.; Zhang, H.; Hatton, T. A. *Chem. Mater.* **2008**, *20*, 2001–2008. (f) Bernini, R.; Mincione, E.; Crisante, F.; Barontini, M.; Fabrizi, G. *Tetrahedron Lett.* **2009**, *50*, 1307–1310. (g) Chung, W.-J.; Kim, D.-K.; Lee, Y.-S. *Tetrahedron Lett.* **2003**, *44*, 9251–9254. (h) Jang, H.-S.; Chung, W.-J.; Lee, Y.-S. *Tetrahedron Lett.* **2007**, *48*, 3731–3734. (i) Kim, D.-K.; Chung, W.-J.; Lee, Y.-S. *Synlett* **2005**, 279–282. (j) Lecarpentier, P.; Crosignani, S.; Linclau, B. *Mol. Diversity* **2005**, *9*, 341–351. (k) Ladziata, U.; Willging, J.; Zhdankin, V. V. *Org. Lett.* **2006**, *8*, 167–170. (l) Karimov, R. R.; Kazhkenov, Z.-G. M.; Modjewski, M. J.; Peterson, E. M.; Zhdankin, V. V. *J. Org. Chem.* **2007**, *72*, 8149–8151.

(6) (a) Podgoršek, A.; Jurisch, M.; Stavber, S.; Zupan, M.; Iskra, J; Gladysz, J. A. *J. Org. Chem.* **2009**, *74*, 3133–3140. (b) Tesevic, V.; Gladysz, J. A. *J. Org. Chem.* **2006**, *71*, 7433–7440. (c) Tesevic, V.; Gladysz, J. A. *Green Chem.* **2005**, *7*, 833–836. (d) Rocaboy, C.; Gladysz, J. A. *Chem.—Eur. J.* **2003**, *9*, 88–95. (e) Yusubov, M. S.; Drygunova, L. A.; Zhdankin, V. V. *Synthesis* **2004**, 2289–2292. (f) Tohma, H.; Maruyama, A.; Maeda, A.; Maegawa, T.; Dohi, T.; Shiro, M.; Morita, T.; Kita, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3595–3598. (g) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Shiro, M.; Kita, Y. *Chem. Commun.* **2005**, 2205–2207. (h) Moroda, A.; Togo, H. *Tetrahedron* **2006**, *62*, 12408–12414. (i) Takenaga, N.; Goto, A.; Yoshimura, M.; Fujioka, H.; Dohi, T.; Kita, Y. *Tetrahedron Lett.* **2009**, *50*, 3227–3229. (j) Dohi, T.; Morimoto, K.; Ogawa, C.; Fujioka, H.; Kita, Y. *Chem. Pharm. Bull.* **2009**, *57*, 710–713. (k) Dohi, T.; Morimoto, K.; Takenaga, N.; Maruyama, A.; Kita, Y. *Chem. Pharm. Bull.* **2006**, *54*, 1608–1610. (l) Dohi, T.; Morimoto, K.; Takenaga, N.; Goto, A.; Maruyama, A.; Kiyono, Y.; Tohma, H.; Kita, Y. *J. Org. Chem.* **2007**, *72*, 109–116. (m) Li, X.-Q.; Zhang, C. *Synthesis* **2009**, 1163–1169. (n) Kirschning, A.; Yusubov, M. S.; Yusubova, R. Y.; Chi, K.-W.; Park, J. Y. *Beilstein J. Org. Chem.* **2007**, *3*, 19. (o) Yusubov, M. S.; Yusubova, R. Y.; Kirschning, A.; Park, J. Y.; Chi, K.-W. *Tetrahedron Lett.* **2008**, *49*, 1506–1509. (p) Yusubov, M. S.; Funk, T. V.; Yusubova, R. Y.; Zholobova, G.; Kirschning, A.; Park, J. Y.; Chi, K.-W. *Synth. Commun.* **2009**, *39*, 3772–3784. (q) Yusubov, M. S.; Gilmkhanova, M. P.; Zhdankin, V. V.; Kirschning, A. *Synlett* **2007**, 563–566. (r) Yusubov, M. S.; Funk, T. V.; Chi, K.-W.; Cha, E.-H.; Kim, G. H.; Kirschning, A.; Zhdankin, V. V. *J. Org. Chem.* **2008**, *73*, 295–297. (s) Yusubov, M. S.; Yusubova, R. Y.; Funk, T. V.; Chi, K.-W.; Kirschning, A.; Zhdankin, V. V. *Synthesis* **2010**, 3681–3685.

(7) (a) Zhdankin, V. V.; Koposov, A. Y.; Netzel, B. C.; Yashin, N. V.; Rempel, B. P.; Ferguson, M. J.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 2194–2196. (b) Koposov, A. Y.; Karimov, R. R.; Geraskin, I. M.; Nemykin, V. N.; Zhdankin, V. V. *J. Org. Chem.* **2006**, *71*, 8452–8458.

(8) (a) Mongin, F.; Trecourt, F.; Mongin, O.; Queguiner, G. *Tetrahedron* **2002**, *58*, 309–314. (b) Milburn, R. R.; Hussain, S. M. S.; Prien, O.; Ahmed, Z.; Snieckus, V. *Org. Lett.* **2007**, *9*, 4403–4406.

(9) (a) Zhdankin, V. V.; Litvinov, D. N.; Koposov, A. Y.; Luu, T.; Ferguson, M. J.; McDonald, R.; Tykwinski, R. R. *Chem. Commun.* **2004**, 106–107. (b) Koposov, A. Y.; Litvinov, D. N.; Zhdankin, V. V. *Tetrahedron Lett.* **2004**, *45*, 2719–2721. (c) Zhdankin, V.; Goncharenko, R. N.; Litvinov, D. N.; Koposov, A. Y. *Arkivoc* **2005**, No. iv, 8–18. (d) Zhdankin, V. V.; Koposov, A. Y.; Litvinov, D. N.; Ferguson, M. J.; McDonald, R.; Luu, T.; Tykwinski, R. R. *J. Org. Chem.* **2005**, *70*, 6484–6491. (e) Koposov, A. Y.; Nemykin, V. N.; Zhdankin, V. V. *New J. Chem.* **2005**, *29*, 998–1000. (f) Ladziata, U.; Koposov, A. Y.; Lo, K. Y.; Willging, J.; Nemykin, V. N.; Zhdankin, V. V. *Angew. Chem., Int. Ed.* **2005**, *44*, 7127–7131. (g) Ladziata, U.; Carlson, J.; Zhdankin, V. V. *Tetrahedron Lett.* **2006**, *47*, 6301–6304. (h) Koposov, A. Y.; Karimov, R. R.; Pronin, A. A.; Skrupskaya, T.; Yusubov, M. S.; Zhdankin, V. V. *J. Org. Chem.* **2006**, *71*, 9912–9914. (i) Mailyan, A. K.; Geraskin, I. M.; Nemykin, V. N.; Zhdankin, V. V. *J. Org. Chem.* **2009**, *74*, 8444–8447.

(10) To our knowledge, no X-ray crystal structures with N···I interactions in organoiodine(V) compounds have previously been reported. For X-ray structures of iodine(III) compounds with I···N inter- or intramolecular interactions, see: (a) Balthazor, T. M.; Godar, D. E.; Stults, B. R. *J. Org. Chem.* **1979**, *44*, 1447–1449. (b) Zhdankin, V. V.; Arbit, R. M.; Lynch, B. J.; Kiprof, P.; Young, V. G. *J. Org. Chem.* **1998**, *63*, 6590–6596. (c) Zhdankin, V. V.; Arbit, R. M.; Lynch, B. J.; Kiprof, P.; Young, V. G. *J. Org. Chem.* **1998**, *63*, 6590–6596. (d) Zhdankin, V. V.; Arbit, R. M.; Lynch, B. J.; Kiprof, P.; Young, V. G. *J. Org. Chem.* **1998**, *63*, 6590–6596. (e) Zhdankin, V. V.; Koposov, A. Y.; Su, L. S.; Boyarskikh, V. V.; Netzel, B. C.; Young, V. G. *Org. Lett.* **2003**, *5*, 1583–1586. (f) Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martin, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2367–2368. (g) Ochiai, M.; Suefuji, T.; Miyamoto, K.; Shiro, M. *Chem. Commun.* **2003**, 1438–1439. (h) Ochiai, M.; Nakano, A.; Yoshimura, A.; Miyamoto, K.; Hayashi, S.; Nakanishi, W. *Chem. Commun.* **2009**, 959–961. (i) Suefuji, T.; Shiro, M.; Yamaguchi, K.; Ochiai, M. *Heterocycles* **2006**, *67*, 391–397.

(11) Koposov, A. Y.; Zhdankin, V. V. *Synthesis* **2005**, 22–24.

(12) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber* **1991**, *124*, 2377.

(13) Ochiai, M.; Miyamoto, K.; Shiro, M.; Ozawa, T.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 13006–13007.

(14) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970–6971.

(15) Hanson, P.; Hendrickx, R. A. A. J.; Smith, J. R. L. *Org. Biomol. Chem.* **2008**, *6*, 745–761.

(16) (a) Oh, K.; Knabe, W. E. *Tetrahedron* **2009**, *65*, 2966–2974. (b) Cooke, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 2739–2745.

(17) Koposov, A. Y.; Karimov, R. R.; Geraskin, I. M.; Nemykin, V. N.; Zhdankin, V. V. *J. Org. Chem.* **2006**, *71*, 8452–8458.

(18) (a) Rama Raju, B.; Sarkar, S.; Chandramoulali Reddy, U.; Saikia, A. K. *J. Mol. Catal. A Chem.* **2009**, *308*, 169–173. (b) Oae, S.; Onishi, Y.; Kozuka, S.; Tagaki, W. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 364–366.

(19) Shaabani, A.; Bazgir, A.; Soleimani, K.; Salehi, P. *Synth. Commun.* **2003**, *33*, 2935–2944.

(20) Lue, P.; Fan, W.; Zhou, X. *Synthesis* **1989**, 692–693.

(21) Newman, M. S.; Weinberg, A. E. *J. Am. Chem. Soc.* **1957**, *79*, 2814–2819.

(22) Mohapatra, S. C.; Tehlan, S.; Hundal, M. S.; Mathur, P. *Inorg. Chim. Acta* **2008**, *361*, 1897–1907.

(23) Yusubov, M. S.; Chi, K.-W.; Park, J. Y.; Karimov, R.; Zhdankin, V. V. *Tetrahedron Lett.* **2006**, *47*, 6305–6308.