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Preparation, structure, and oxidative reactivity of (dichloroiodo)pyridines: recyclable hypervalent iodine reagents

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Dedicated to Prof. Kenneth K. Laali on the occasion of his 65th birthday

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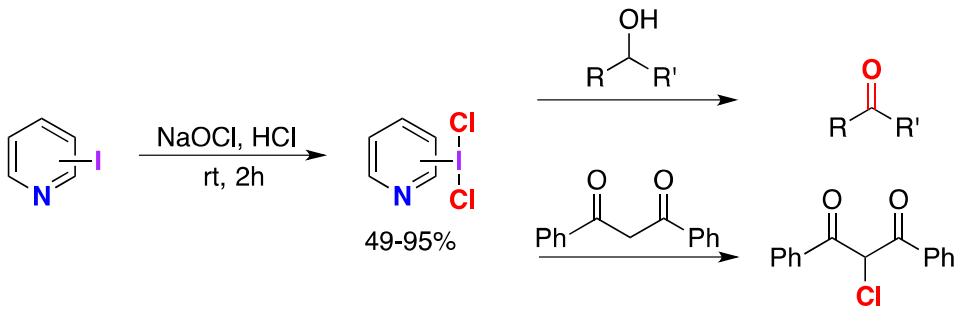
Abstract

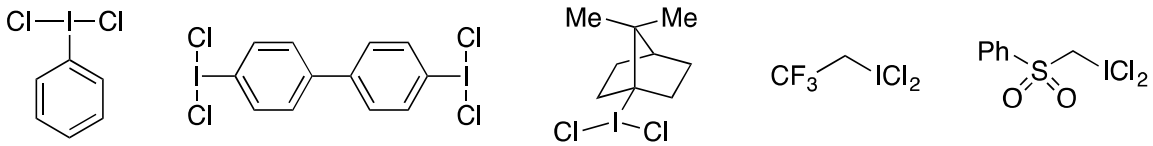
New pyridine-based hypervalent iodine reagents, (dichloroiodo)pyridines, were prepared by chlorination of 2-, 3-, or 4-iodopyridines with NaOCl-HCl at room temperature. Structures of 2-(dichloroiodo)pyridine and 2-(dichloroiodo)-3-propoxypyridine were established by X-ray crystallography. The new (dichloroiodo)pyridines can be used as efficient reagents for oxidation of alcohols to carbonyl compounds and also as chlorinating reagents. The reduced form of the reagents such as 2-iodo-3-propoxypyridine, can be recovered from the reaction mixture in good yields by an acid-base liquid-liquid biphasic protocol.



Keywords: Hypervalent iodine, iodopyridine, (dichloroiodo)arenes, oxidation, recyclable reagents

Introduction

Organohypervalent iodine compounds are widely used in organic synthesis as versatile and environmentally friendly reagents for various oxidative transformations.[1-7] In particular, (dichloroiodo)arenes, $ArICl_2$, are commonly applied as efficient oxidants or chlorinating reagents.[8] (Dichloroiodo)benzene **1** is one of the most common reagents that can be conveniently prepared by direct chlorination of iodobenzene.[9] Numerous alternative procedures for oxidative chlorination of iodobenzene are also known, and a particularly useful method employs the combination of hydrochloric acid and inorganic oxidants such as NaClO or $NaClO_2$.[10-13] Numerous (dichloroiodo)arenes and other organic iododichlorides (e.g., compounds **2**-**5** shown in Scheme 1) have been prepared by chlorination of the corresponding iodides using similar procedures.[14-17]



1 **2** **3** **4** **5**

Scheme 1. Representative examples of organic iododichlorides.

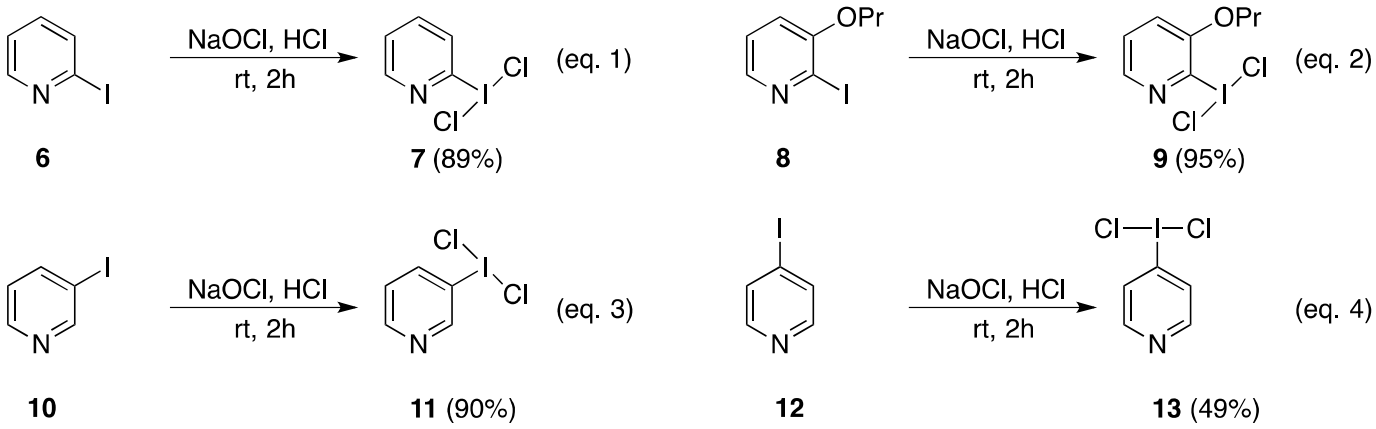
Recently, several pyridine-based hypervalent iodine compounds have been prepared and investigated.[18-23] Most of these compounds are pyridine-derived iodonium salts, which can be used as effective electrophilic pyridine transfer reagents toward various organic substrates. The chemistry of pyridine-based hypervalent iodine compounds of general type $PyIX_2$ remains undeveloped. Previously, our group reported the preparation of pyridine-based pentavalent iodine reagents, 2-iodylpyridines, by oxidation of corresponding 2-iodopyridines using 3,3-dimethyldioxirane. We have demonstrated that 2-iodylpyridines are useful oxidizing reagents towards alcohols or sulfides.[24] However, to the best our knowledge, the pyridine based trivalent iodine reagents such as 2-(dichloroiodo)pyridine have not been reported. In the present paper, we report the synthesis, structural characterization, and reactivity of several (dichloroiodo)pyridine derivatives. These compounds can be used as efficient recyclable oxidants towards alcohols or chlorinating reagents towards electron-rich organic substrates.

Results and Discussion

In our initial experiments, we have found that the reaction of 2-iodopyridine **6** with the HCl-NaOCl combination for 2 hours at room temperature yields 2-(dichloroiodo)pyridine **7** in 89% yield (Scheme 2, eq. 1). The solid-state structure of **7** was established by single crystal X-ray crystallography (Figure 1). According to the X-ray crystallographic data, compound **7** has a T-shaped geometry of the iodine(III) center (the Cl1-I1-Cl2 bond angle is 177.21(4)^o), and the bond distances between iodine and chlorine atoms are 2.4488(13) Å (I1-Cl1) and 2.5274(12) Å (I1-Cl2). This molecular arrangement is similar to the previous reported structure of $PhICl_2$ **1**.[25] The ICl_2 fragment in **7** is significantly rotated out of the pyridine plane (50.14(11)^o). There are no close intermolecular contacts in the structure of **7** (the closest intermolecular I-Cl contact is 3.627 Å). The analogous reaction of 2-iodo-3-propoxypyridine **8** under similar conditions gave the expected product **9** in 95% yield

(Scheme 2, eq. 2). A single-crystal X-ray study of **9** revealed that this compound also has T-shaped geometry with the Cl1-I1-Cl2 angle of 170.12(5)°. Compound **9** has a pseudocyclic structure with an intramolecular interaction of 3.084(8) Å between the iodine center and the alkoxy group oxygen atom (Figure 1).[24,26-29] Similar to **7**, the ICl_2 fragment is rotated out of the pyridine plane (85.46(9)). Two intermolecular I-Cl contacts at about 3.5 Å are present in the X-ray structure of **9** forming a trigonal-bipyramidal motif.

The chlorination of 3-iodopyridine **10** under similar conditions afforded 3-(dichloroiodo)pyridine **11** in 90% yield (Scheme 2, eq. 3), and the reaction of 4-iodopyridine **12** produced the expected dichloride **13** in 49% yield (Scheme 2, eq. 4).



Scheme 2. Preparation of (dichloroiodo)pyridines.

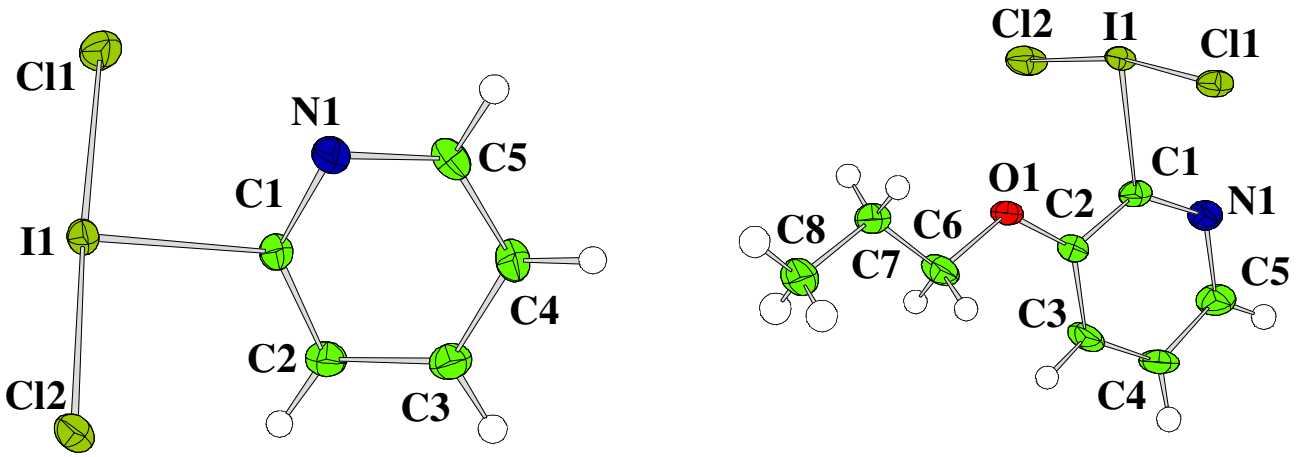


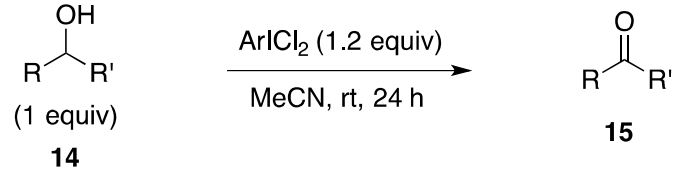
Figure 1. X-ray crystal structures of 2-(dichloroiodo)pyridines **7** and **9**.

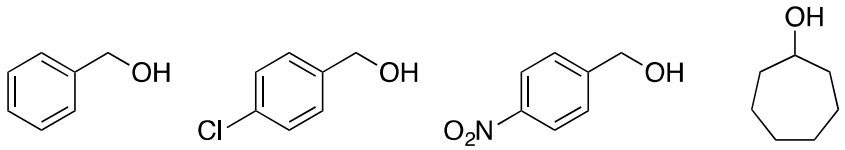
In general, dichloroiodoarene compounds, $ArICl_2$, can serve as useful oxidants or efficient chlorinating reagents towards various organic substrates.[11,30] We have investigated the oxidation of alcohols and oxidative chlorination of electron-rich organic substrates using (dichloroiodo)pyridines as reagents. The reaction of benzyl alcohol **14a** with 2-iodopyridine dichloride **7** in acetonitrile solution at room temperature gave

benzaldehyde **15a**, isolated from reaction mixture as the 2,4-dinitrophenylhydrazone derivative in good yield (Table 1). As expected, the oxidation of benzyl alcohol **14a** using other dichloroiodopyridines also produced benzaldehyde in good yields. In the reactions of *para*-chloro- **14b** or *para*-nitro-benzyl alcohol **14c** under similar conditions, the respective products were obtained in low to moderate yields. When the reaction of cycloheptanol **14d** was performed using dichloroiodopyridines under these conditions, the expected ketone was obtained in moderate yields. Compared to the reactions of (dichloroiodo)benzene **1** under the same conditions, the new (dichloroiodo)pyridines afforded respective carbonyl compounds in comparable or better yields.

In the reaction of benzyl alcohol **14a** with $PhICl_2$ (**1**) in the presence of 2-iodopyridine (**6**) as additive, the yield of benzaldehyde was improved up to 81%. This result implies that the pyridine moiety present in iodopyridines or (dichloroiodo)pyridines is facilitating the oxidation. Previously, Wicha and co-workers reported that the addition of pyridine resulted in increased reactivity of $PhICl_2$ (**1**).[31]

Table 1. Oxidation of alcohols **14** using (dichloroiodo)pyridines[a]





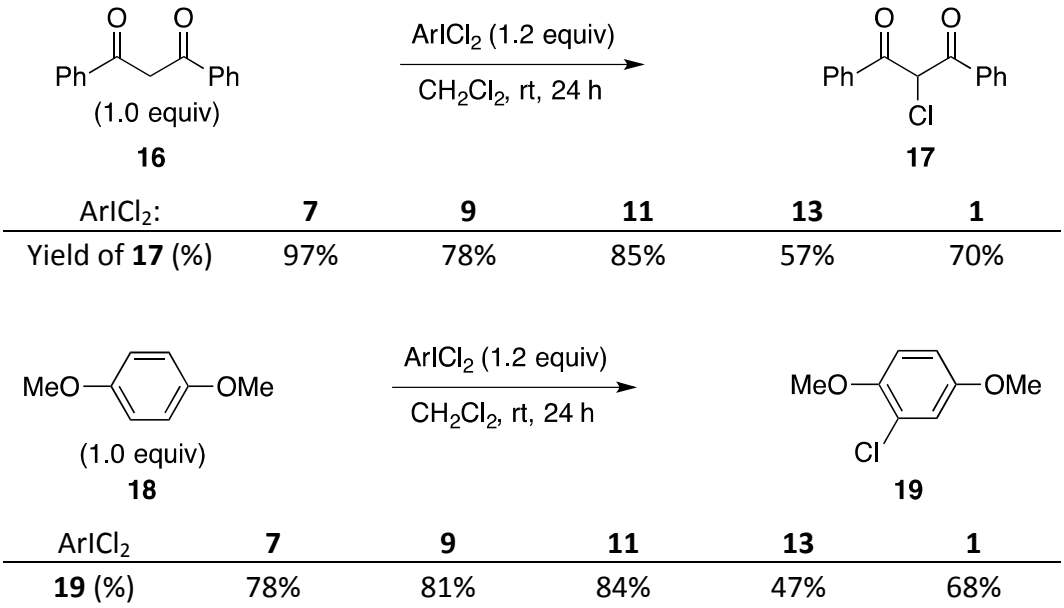
14a **14b** **14c** **14d**

	Product **15** (%)[b]			
$ArICl_2$	C_6H_5CHO **15a**	*p*-ClC_6H_4CHO **15b**	*p*-$NO_2C_6H_4CHO$ **15c**	*Cyc*-$C_7H_{12}O$ **15d**
7	98%	62%	30%	52%
9	84%	69%	19%	37%
11	87%	97%	39%	41%
13	84%	61%	13%	30%
1	57% (81%)[c]	66%	24%	29%

[a] Reaction conditions: $ArICl_2$ (0.300 mmol) and alcohol **14** (0.250 mmol) stirred in acetonitrile (2.0 mL) at room temperature for 24 hours. [b] Isolated yields as 2,4-dinitrophenylhydrazone derivatives of **15**.
[c] In the presence of 2-iodopyridine **6** (1.2 equiv).

In the next step, we have investigated the reactivity of (dichloroiodo)pyridines as chlorine atom transfer reagents towards organic substrates. The reaction of dibenzoylmethane **16** with 2-(dichloroiodo)pyridine **7** gave the corresponding α-mono chloride **17** in good yield. As expected, the reactions of dibenzoylmethane **16** with other (dichloroiodo)pyridine reagents also produced product **17** in moderate yield. In the reactions of 1,4-dimethoxybenzene **18** with (dichloroiodo)pyridines, the corresponding product of monochlorination **19** was obtained in moderate yield. Compared to the reactions of (dichloroiodo)benzene **1** or analogous

(dichloroiodo)arenes under similar conditions, the (dichloroiodo)pyridine reagents showed better reactivity and higher yields.[32-34] Among the chlorination reactions, the reactions of 4-(dichloroiodo)pyridine **13** gave the lowest yields because of the low solubility of this reagent in methylene chloride.



$ArICl_2$:	**7**	**9**	**11**	**13**	**1**
Yield of **17** (%)	97%	78%	85%	57%	70%

$ArICl_2$	**7**	**9**	**11**	**13**	**1**
19 (%)	78%	81%	84%	47%	68%

Scheme 2. Oxidative chlorination using (dichloroiodo)pyridine reagents.

Finally, we have demonstrated that 2-(dichloroiodo)-3-propoxypyridine **9** can be used as a recyclable reagent. The reduced form of reagent **9**, 2-iodo-3-propoxypyridine **8**, can be easily recovered from the reaction mixture in over 85% yield by a simple acid-base liquid-liquid biphasic protocol. The recovered compound **8** can be converted to 2-(dichloroiodo)-3-propoxypyridine **9** using standard procedure.[24]

Conclusions

In summary, we have prepared new (dichloroiodo)pyridines from respective iodopyridines by chlorination with the HCl/NaOCl combination. Structures of 2-(dichloroiodo)pyridine **7** and 2-(dichloroiodo)-3-propoxypyridine **9** were established by X-ray crystallography. According to the crystal data, both compounds have the typical for hypervalent iodine T-shape structure. Compound **9** has a pseudocyclic structure with a short intramolecular interaction between oxygen atom and iodine center. The new (dichloroiodo)pyridines can be used as efficient reagents for oxidation of alcohols to carbonyl compounds and also as chlorinating reagents. The reduced form of the reagents, in particular, 2-iodo-3-propoxypyridine, can be recovered from the reaction mixture in good yields by an acid-base liquid-liquid biphasic protocol.

Experimental Section

General. All reactions were performed under dry argon atmosphere with flame-dried glassware. Dichloromethane and acetonitrile were distilled from CaH_2 immediately prior to use. All commercial reagents were ACS reagent grade and used without further purification. Melting points were determined in an open

capillary tube with a Mel-temp II melting point apparatus. NMR spectra were recorded on a Varian Inova 500 MHz (^{1}H NMR). Chemical shifts are reported in parts per million (ppm) and referenced relative to the tetramethylsilane. The known compounds, 3-propoxy-2-iodopyridine (**8**)[24] and dichloroiodobenzene (**1**)[9] were prepared according to the reported procedures.

General Procedure for preparation of (dichloroiodo)pyridines

Aqueous 12M HCl solution (1.5 mL) was added to a mixture of iodoarene (1.4 to 2.0 mmol) with 5.85% aqueous NaOCl (8.0 mL). The reaction was stirred at room temperature for 2 h (reaction completion was controlled by TLC), and the reaction mixture changed from a light yellow solution to a yellow suspension. After completion of the reaction, the resulting yellow precipitate was separated by filtration. The precipitate was washed with hexane and dried in vacuum to afford analytically pure (dichloroiodo)pyridine product**.**

2-(Dichloroiodo)pyridine (**7**). Chlorination of 2-iodopyridine **6** (410 mg, 2.00 mmol) according to the general procedure afforded 490 mg (89%) of product **7**, isolated as a yellow solid: mp 79.5-81.1 ^{o}C (from methylene chloride); IR (KBr) cm^{-1} 3077, 1556, 1444, 1412; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (dd, *J* 4.9 Hz, 1.8 Hz, 1H), 8.19 (dd, *J* 8.3 Hz, 0.5 Hz, 1H), 7.84 (ddd, *J* 8.3 Hz, 7.4 Hz, 1.8 Hz, 1H), 7.59 (ddd, *J* 7.4 Hz, 4.9 Hz, 0.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8,144.8, 141.5, 129.9, 127.6; Anal. Calcd for$C_5H_4Cl_2IN$: C, 21.77; H, 1.46; N, 5.08. Found: C, 22.04; H,1.30; N, 5.08%.

Single crystals of product **7** suitable for X-ray crystallographic analysis were obtained by slow evaporation of MeCN-CH_2Cl_2 solution. For details on crystal structure of compound **7** see the CIF file in Supporting Information. Selected crystallographic data for **7**: Triclinic P-1 a 4.0281(3) Å, b 8.6219(6) Å, c 11.7755(11) Å, α = 73.583(5)^o, β = 88.270(6)^o, γ = 80.810(6)^o, V = 387.20(5) Å^3, Z = 2, R (I>2.0/σ(I)) = 0.0204, R_w (all) = 0.0640, CCDC 1563656.

2-(Dichloroiodo)-3-propoxypyridine (**9**). Chlorination of 2-iodo-3-propoxypyridine **8** (375 mg, 1.43 mmol) according to the general procedure afforded 452 mg (95 %) of product **9**, isolated as a yellow solid: mp 89.1-90.5 ^{o}C (from methylene chloride); IR (KBr) cm^{-1} 3071, 2964, 2877, 1559, 1443, 1411, 1290, 1043; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, *J* 4.4 Hz, 1.4 Hz, 1H), 7.53 (dd, *J* 8.3 Hz, 4.4 Hz, 1H), 7.41 (dd, *J* 8.3 Hz, 1.4 Hz, 1H), 4.21 (t, *J* 6.3 Hz, 2H), 2.06-1.93 (m, 2H), 1.16 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 141.4, 139.2, 128.9, 121.8, 72.2, 22.3, 10.5; Anal. Calcd for$C_8H_{10}INCl_2$: C, 28.77; H, 3.02; N, 4.19. Found: C, 28.77; H,2.89; N, 4.15.

Single crystals of product **9** suitable for X-ray crystallographic analysis were obtained by slow evaporation of MeCN-CH_2Cl_2 solution. For details on crystal structure of compound **9** see the CIF file in Supporting Information. Selected crystallographic data for **9**: Orthorhombic, $P2_12_12_1$, a = 8.0475(5) Å, b = 10.3684(5) Å, c = 13.9105(9) Å, V = 1160.69(12) Å^3, Z = 4, R (I>2.0/σ(I)) = 0.0379, R_w (all) = 0.0659, CCDC 1563657.

3-(Dichloroiodo)pyridine (**11**)[35]: Chlorination of 3-iodopyridine **10** (410 mg, 2.00 mmol) according to the general procedure afforded 498 mg (90%) of product **11**, isolated as a yellow solid: mp 130.5-132.0 ^{o}C (from methylene chloride) (lit,[35] mp 128-129 ^{o}C); IR (neat) cm^{-1} 3007, 2986, 2921, 1568, 1459; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.10 (s, 1H), 8.87-8.78 (m, 1H), 8.73 (d, *J* 7.0 Hz, 1H), 7.75-7.63 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 151.8, 149.5, 142.9, 128.1, 96.3; HRMS (APCI-positive ionization): calcd for $C_5H_5{}^{35}Cl_2IN$ ($[M+H]^+$): 275.8844, found: 275.8860.

4-(Dichloroiodo)pyridine (**13**): Chlorination of 4-iodopyridine **12** (410 mg, 2.00 mmol) according to the general procedure afforded 270 mg (49%) of product **10**, isolated as yellow solid: mp 109.5-110.1 ^{o}C (from methylene chloride); IR (neat) cm^{-1} ; 3103, 2915, 2846, 1617, 1481; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.49 (d, *J* 5.0 Hz, 2H),

8.40 (d, *J* 5.0 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 142.2, 136.3, 120.3; HRMS (APCI-positive ionization): calcd for $C_5H_5I^{35}Cl_2N$ ($[M+H]^+$): 275.8844, found: 275.8816.

General procedure for oxidation of alcohols using (dichloroiodo)arenes

Alcohol **14** (0.250 mmol) was added to a solution of (dichloroiodo)arene (0.300 mmol) in acetonitrile (2 mL). The reaction was stirred at room temperature for 24 h. After completion of the reaction, a standard solution of 1.5 mL of 2,4-dinitrophenylhydrazine (prepared from 200mg of 2,4-dinitrophenylhydrazine, 1 mL of H_2SO_4, 10 mL of EtOH, and 2 mL of H_2O) was added. The precipitate of 2,4-dinitrophenylhydrazone derivative **15** was filtered, washed with water, and dried in vacuum.

2,4-Dinitrophenylhydrazone of benzaldehyde (**15a**)**:**[24] Reaction of benzyl alcohol **14a** (27 mg, 0.250 mmol) according to the general procedure afforded 2,4-dinitrophenylhydrazone of **15a** (57-98%), isolated as a light orange solid: mp 231.7-233.2 °C (from ethanol) (lit,[24] mp 235.8-237.0 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.7 (s, 1H), 8.86 (d, *J* 0.3 Hz, 1H), 8.70 (s, 1H), 8.37 (dd, *J* 10.0 Hz, 0.3 Hz, 1H), 8.10 (d, *J* 10.0 Hz, 1H), 7.79 (dd, *J* 7.5 Hz, 2.0 Hz, 2H), 7.50-7.42 (m, 3H).

2,4-Dinitrophenylhydrazone of *p*-chlorobenzaldehyde (**15b**):[36] Reaction of *p*-chlorobenzyl alcohol **14b** (36 mg, 0.250 mmol) according to the general procedure afforded 2,4-dinitrophenylhydrazone of **15b** (61-97%), isolated as a light orange solid: mp 256.0-258.7 °C (from ethanol) (lit,[36] mp 264.0 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.7 (s, 1H), 8.86 (d, *J* 0.3 Hz, 1H), 8.69 (s, 1H), 8.37 (dd, *J* 9.5 Hz, 0.3 Hz, 1H), 8.10 (d, *J* 9.5 Hz, 1H), 7.81 (d, *J* 8.3 Hz, 2H), 7.55 (d, *J* 8.3 Hz, 2H).

2,4-Dinitrophenylhydrazone of *p*-nitrobenzaldehyde (**15c**):[37] Reaction of *p*-nitrobenzyl alcohol **14c** (38 mg, 0.250 mmol) according to the general procedure afforded 2,4-dinitrophenylhydrazone of **15c** (13-39%), isolated as a light orange solid: mp 293.5-295.0 °C (from ethanol) (lit,[37] mp 278.0-280.0 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.8 (s, 1H), 8.88 (d, *J* 0.3 Hz, 1H), 8.81 (s, 1H), 8.42 (dd, *J* 9.8 Hz, 0.3 Hz, 1H), 8.32 (d, *J* 8.5 Hz, 2H), 8.17 (d, *J* 9.8 Hz, 1H), 8.05 (d, *J* 8.5 Hz, 2H).

2,4-Dinitrophenylhydrazone of cycloheptanone (**15d**):[24] Reaction of cycloheptanol **14d** (29 mg, 0.250 mmol) according to the general procedure afforded 2,4-dinitrophenylhydrazone of **15d** (29-52%), isolated as a yellow solid: mp 146.8-148.3 °C (from ethanol) (lit,[24] mp 147.0-147.2 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.0 (s, 1H), 9.13 (d, *J* 2.5 Hz, 1H), 8.30 (dd, *J* 9.8 Hz, 2.5 Hz, 1H), 7.99 (d, *J* 9.8 Hz, 1H), 2.68-2.52 (m, 4H), 1.94-1.80 (m, 2H), 1.77-1.51 (m, 6H).

General procedure for chlorination of dibenzoylmethane 16 using (dichloroiodo)arenes

Dibenzoylmethane **16** (0.250 mmol) was added to a solution of $ArICl_2$ (0.300 mmol) in dichloromethane (2 mL). The reaction was stirred at room temperature for 24 h. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 5 : 1) afforded analytically pure mono-chlorination product **17**.

2-Chloro-1,3-diphenylpropane-1,3-dione (**17**):[38] Reaction of dibenzoylmethane **16** (56 mg, 0.250 mmol) according to the general procedure afforded product **17** (57-97%), isolated as a yellow solid: mp 77.1-79.5 °C (from methylene chloride) (lit,[38] mp 86.0-87.0 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* 8.0 Hz, 4H), 7.63-7.58 (m, 2H), 7.47 (t, *J* 7.8 Hz, 4H), 6.41 (s, 1H).

General procedure for chlorination of 1,4-dimethoxybenzene 18 using (dichloroiodo)arenes

1,4-Dimethoxybenzene **18** (0.250 mmol) was added to a solution of (dichloroiodo)arene (0.300 mmol) in dichloromethane (2 mL). The reaction was stirred at room temperature for 24 h. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) was added, and the mixture was extracted with dichloromethane. The

organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 10 : 1) afforded analytically pure mono-chlorination product **19**.

2-Chloro-1,4-dimethoxybenzene (**19**):[39] Reaction of 1,4-dimethoxybenzene **18** (35 mg, 0.250 mmol) according to the general procedure afforded product **19** (47-84%), isolated as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (d, *J* 3.0 Hz, 1H), 6.86 (d, *J* 9.0 Hz, 1H), 6.77 (dd, *J* 9.0 Hz, 3.0 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H).

Recovery of 2-iodo-3-propoxypyridine 8

After completion of the reaction of benzyl alcohol **14a** with reagent **9**, 20% H_2SO_4 (3.0-5.0 mL) was added. The mixture was extracted with dichloromethane. Treatment of the organic layer according to general procedures for oxidation of benzyl alcohol or chlorination afforded product **15a**. To the aqueous layer 20% NaOH (5.0-7.0 mL) was added, and then the mixture was extracted with dichloromethane. The organic solution was dried over anhydrous Na_2SO_4 and concentrated in vacuum to give 2-iodo-3-propoxypyridine **8** (70 mg, 89%).

After completion of the reaction of 1,4-dimethoxybenzene **18** with reagent **9**, 20% H_2SO_4 (3.0-5.0 mL) was added. The mixture was extracted with dichloromethane. Treatment of the organic layer according to general procedures for chlorination of 1,4-dimethoxybenzene afforded product **19**. To the aqueous layer 20% NaOH (5.0-7.0 mL) was added, and then the mixture was extracted with dichloromethane. The organic solution was dried over anhydrous Na_2SO_4 and concentrated in vacuum to give 2-iodo-3-propoxypyridine **8** (67 mg, 85%).

Acknowledgements

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Supplementary Material

NMR spectra of all reagents and products are given in the associated Supplementary Data File. The crystal data files can be retrieved from the Cambridge Crystallography Data Center as CCDC numbers 1563656 (compound **7**) and 1563657 (compound **9**).

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