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Oxidation of Alcohols to Aldehydes or Ketones with 1-Acetoxy-1,2-benziodoxole-3(1*H*)-one Derivatives

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Keywords: Oxidation / Hypervalent compounds / Iodine / Alcohols / Aldehydes / Ketones

Various benzylic and aliphatic alcohols were smoothly oxidized to the corresponding aromatic aldehydes and ketones as well as aliphatic ketones by treatment with 1-acetoxy-5-nitro-1,2-benziodoxole-3(1*H*)-one (**ANBX**), 1-acetoxy-5-bromo-1,2-benziodoxole-3(1*H*)-one (**ABBX**), 1-acetoxy-5-chloro-1,2-benziodoxole-3(1*H*)-one (**ACBX**), and 1-acetoxy-5-fluoro-1,2-benziodoxole-3(1*H*)-one (**AFBX**). These new trivalent iodine compounds were prepared from 5-substituted 2-iodobenzoic acids and *meta*-chloroperoxybenzoic acid (*m*-CPBA). **ANBX** and **ABBX** were the most effective reagents for this oxidation of alcohols, and this present reaction is very attractive because of the ease of product isolation and the reusability of the reagents.

Introduction

Because of their environmentally benign character and highly selective oxidizing ability, hypervalent iodine compounds have recently become more and more popular.[1] The Dess–Martin periodinane [1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(*1H*)-one][2] and 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (2-iodoxybenzoic acid, IBX)[3] are examples of pentavalent iodine compounds (I^V) that are used for the efficient oxidation of alcohols. The Dess–Martin periodinane, in particular, is the most popular and best reagent for the selective oxidation of alcohols that contain a variety of functional groups to give the corresponding aldehydes or ketones, as these reactions can be carried out in dichloromethane or chloroform at room temperature. However, the Dess–Martin periodinane and IBX are heat- and shock-sensitive reagents, and, therefore, all experimental operations must be carried out behind a safety shield to protect from explosions.[2c] In this regard, it is difficult to use these compounds for the large-scale oxidation of alcohols. Recently, the 2,2,6,6-tetramethylpiperidine-1-oxyl-catalyzed (TEMPO-catalyzed) oxidation of alcohols by treatment with (diacetoxyiodo)benzene (**DIB**) at room temperature to give aldehydes or ketones has become very popular in organic synthesis.[4] However, in this case, the reaction mixture must be purified by column chromatography to remove the coproduct iodobenzene and an oxoammonium salt of TEMPO, which is the actual active species for the oxidation. Herein, as part of our study of new trivalent iodine compounds for organic synthesis,[5] we would like to report the preparation of the new compounds 1-acetoxy-5-nitro-1,2-benziodoxole-3(1*H*)-one (**ANBX**),[6] 1-acetoxy-5-bromo-1,2-benziodoxole-3(1*H*)-one (**ABBX**), 1-acetoxy-5-chloro-1,2-benziodoxole-3(1*H*)-one (**ACBX**), and 1-acetoxy-5-fluoro-1,2-benziodoxole-3(1*H*)-one (**AFBX**, see Figure 1) as well as the employment of these trivalent iodine compounds under mild conditions for the oxidation of various alcohols.

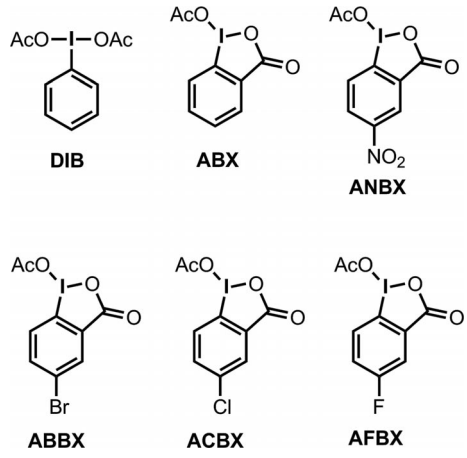

Figure 1. Trivalent iodine compounds.

Results and Discussion

(Diacetoxyiodo)benzene, which is the most typical and popular trivalent iodine compound, is often used in organic synthesis because of its wide synthetic utility and nonexplosive character. However, **DIB** does not oxidize alcohols smoothly. For example, when *p*-methylbenzyl alcohol was

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http://reaction-2.chem.chiba-u.jp/index.html

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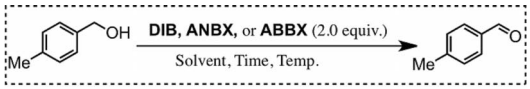
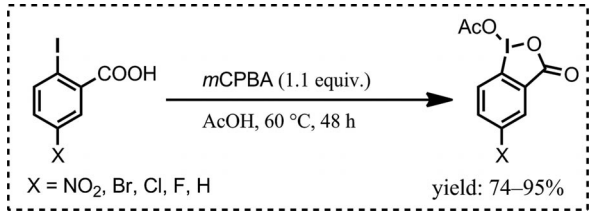
Table 1. Optimization for oxidation of *p*-methylbenzyl alcohol with **DIB**, **ANBX**, and **ABBX**.



Entry	Trivalent iodine	Solvent time, temp.	Yield[a] [purity][b]
1	**DIB**	DMF 24 h, 60 °C	19%
2	**DIB**	$CHCl_3$ 24 h, 60 °C	32%
3	**DIB**	CH_3CN 24 h, 60 °C	27%
4	**DIB**	THF 24 h, 60 °C	19%
5	**DIB**	CH_2Cl_2 24 h, 40 °C	31%
6	**ANBX** (1.2 equiv.)	DMF 12 h, r.t.	52% –
7	**ANBX** (1.2 equiv.)	DMF 12 h, 60 °C	71% [62%]
8	**ANBX** (1.5 equiv.)	DMF 24 h, r.t.	64% –
9	**ANBX** (1.5 equiv.)	DMF 24 h, 60 °C	87% [84%]
10	**ANBX**	**DMF 24 h, 60 °C**	**97% [98%]**
11	**ANBX**	$CHCl_3$ 24 h, 60 °C	23% –
12	**ANBX**	CH_3CN 24 h, 60 °C	6% –
13	**ANBX**	THF 24 h, 60 °C	4% –
14	**ANBX**	CH_2Cl_2 24 h, 40 °C	18% –
15	**ANBX**	**DMSO 24 h, 60 °C**	**95% [94%]**
16	**ABBX** (1.5 equiv.)	$CHCl_3$ 24 h, r.t.	38% –
17	**ABBX** (1.5 equiv.)	$CHCl_3$ 24 h, 60 °C	66% –
18	**ABBX**	$CHCl_3$ 24 h, r.t.	71% [69%]
19	**ABBX**	**$CHCl_3$ 24 h, 60 °C**	**90% [90%]**
20	**ABBX**	CH_3CN 24 h, 60 °C	21% –
21	**ABBX**	THF 24 h, 60 °C	14% –
22	**ABBX**	**DMF 24 h, 60 °C**	**94% [93%]**
23	**ABBX**	CH_2Cl_2 24 h, 40 °C	72% [69%]
24	**ABBX**	**DMSO 24 h, 60 °C**	**89% [88%]**
25	**ABBX**	NMP 24 h, 60 °C	46% –

[a] Purified yield. [b] Purity after extraction of the reaction mixture with Et_2O/hexane and removal of the solvent. [c] NMP = *N*-methyl-2-pyrrolidone.

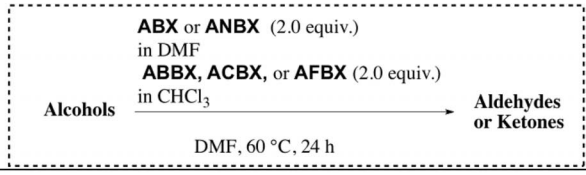
treated with **DIB** in *N*,*N*-dimethylformamide (DMF), $CHCl_3$, CH_3CN, or tetrahydrofuran (THF) at 60 °C for 24 h or in CH_2Cl_2 at 40 °C for 24 h, *p*-methylbenzaldehyde was obtained in yields of 19–31%, and mostly the starting material was recovered as shown in Table 1 (see Entries 1–5). The poor oxidizing ability of **DIB** with alcohols is because the electron density at the iodine atom is not sufficiently low. To enhance the oxidizing ability of trivalent iodine compounds, the new substances **ANBX**, **ABBX**, **ACBX**, and **AFBX** that have two electron-withdrawing groups on the benzene ring, that is, a carboxy group along with a nitro, bromo, chloro, or fluoro group, were proposed (see Figure 1). **ANBX**, **ABBX**, **ACBX**, and **AFBX** were easily prepared in high yields by using our previous method that employs the oxidation of 2-iodo-5-nitrobenzoic acid, 5-bromo-2-iodobenzoic acid, 5-chloro-2-iodobenzoic acid, and 5-fluoro-2-iodobenzoic acid, respectively, with *m*-chloroperoxybenzoic acid (*m*-CPBA) in acetic acid (see Scheme 1).[7] First, the reactivity of **ANBX** and **ABBX** was examined with regard to the oxidation of *p*-methylbenzyl alcohol. **ANBX** showed a high reactivity when the reaction was performed in either DMF or dimethyl sulfoxide (DMSO) at 60 °C for 24 h to give *p*-methylbenzaldehyde in good yields (see Table 1, Entries 10 and 15). **ABBX** also showed a high reactivity not only in DMF and DMSO but also in $CHCl_3$ at 60 °C for 24 h to give *p*-methylbenzaldehyde in good yields (see Table 1, Entries 19, 22, and 24). However, both cases required 2 equiv. of **ANBX** or **ABBX** for the effective oxidation of the alcohol. Overall, **ANBX** showed the best reactivity in DMF and DMSO among the examined solvents $CHCl_3$, CH_3CN, CH_2Cl_2, tetrahydrofuran (THF), DMF, and DMSO (see Table 1, Entries 6–15), and DMF was a slightly better solvent than DMSO (see Table 1, Entries 10 and 15). This is a consequence of the moderate solubility of **ANBX** in DMF and DMSO under warm conditions, as **ANBX** is scarcely soluble in THF, CH_3CN, CH_2Cl_2, or $CHCl_3$. On the other hand, **ABBX** is a slightly soluble in $CHCl_3$ in addition to DMF and DMSO. Therefore, the oxidation of the alcohol by treatment with **ABBX** proceeded smoothly not only in DMF and DMSO but also in $CHCl_3$ (see Table 1, Entries 19, 22, and 24).



Scheme 1. Preparation of **ANBX**, **ABBX**, **ACBX**, **AFBX**, and **ABX**.

On the basis of the optimum reaction conditions, the reactivities of the known compound 1-acetoxy-1,2-benziodoxole-3(1*H*)-one (**ABX**) and **ANBX** in DMF along with

Table 2. Oxidation of alcohols with **ABX**, **ANBX**, **ABBX**, **ACBX**, and **AFBX**.



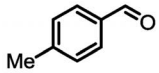
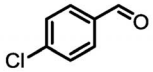
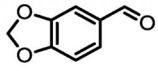
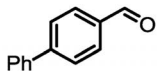
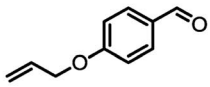
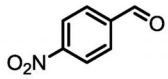
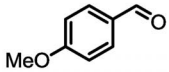
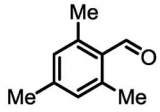
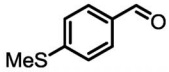
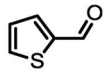
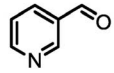
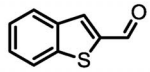
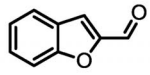
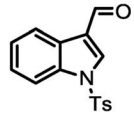
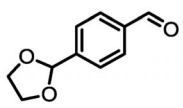
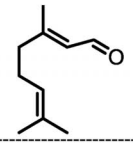
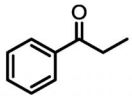
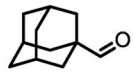
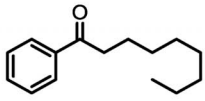
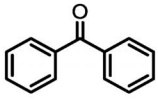
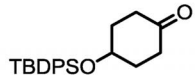
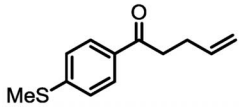
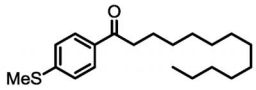
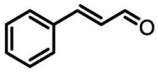
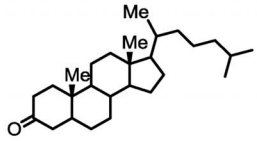
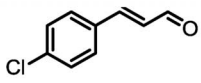
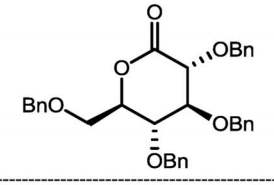
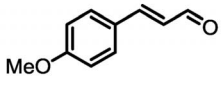
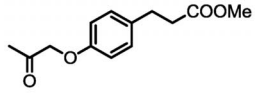
Entry	Aldehyde or ketone	Trivalent iodine	Yield[a] [purity][b]
1		**ABX**	88% [87%]
2		**ANBX**	97% [98%]
3		**ANBX**	95%[c] [96%][c]
4		**ABBX**	90% [90%]
5		**ABBX**	87%[d] [86%][d]
6		**ACBX**	84% [83%]
7		**AFBX**	84% [84%]
8		**ABX**	90% [90%]
9		**ANBX**	93% [93%]
10		**ANBX**	92%[c] [93%][c]
11		**ABBX**	92% [92%]
12		**ABBX**	88%[d] [87%][d]
13		**ABX**	92% [92%]
14		**ANBX**	92% [92%]
15		**ANBX**	91%[c] [92%][c]
16		**ABBX**	94% [93%]
17		**ABBX**	89%[d] [88%][d]
18		**ABX**	84% [83%]
19		**ANBX**	91% [91%]
20		**ABBX**	90% [90%]
21		**ABX**	82% [80%]
22		**ANBX**	90% [90%]
23		**ABBX**	91% [92%]
24		**ABX**	81% [80%]
25		**ANBX**	95% [95%]
26		**ABBX**	94% [93%]
27		**ABX**	84% [83%]
28		**ANBX**	97% [96%]
29		**ABBX**	96% [96%]
30		**ABX**	82% [82%]
31		**ANBX**	98% [98%]
32		**ABBX**	94% [93%]
33		**ABX**	76% [74%]
34		**ANBX**	82%[e] [80%][e]
35		**ABBX**	86% [84%]
36		**ABX**	83% [82%]
37		**ANBX**	98% [98%]
38		**ABBX**	93% [91%]
39		**ANBX**	86% [85%]
40		**ABBX**	82% [81%]
41		**ANBX**	97% [97%]
42		**ABBX**	93% [92%]
43		**ANBX**	93% [93%]
44		**ABBX**	94% [93%]
45		**ANBX**	86% [85%]
46		**ABBX**	85% [84%]

Table 2. *(Continued)*

Entry	Aldehyde or ketone	Trivalent iodine	Yield[a] [purity][b]	Entry	Aldehyde or ketone	Trivalent iodine	Yield[a] [purity][b]
47		**ANBX**	89% [88%]	69		**ANBX**	93% [93%]
48		**ABBX**	85% [84%]	70		**ABBX**	94% [94%]
49		**ABX**	68% [68%]	71		**ABX**	29%
50		**ANBX**	87% [86%]	72		**ANBX**	88% [87%]
51		**ABBX**	84% [83%]	73		**ABBX**	82% [80%]
52		**ANBX**	86% [86%]	74		**ANBX**	74% [73%]
53		**ABBX**	81% [80%]	75		**ABBX**	72% [70%]
54		**ABX**	76% [76%]	76		**ANBX**	77% [76%]
55		**ANBX**	89% [89%]	77		**ABBX**	74% [73%]
56		**ABBX**	84% [85%]	78		**ABX**	19%[f]
57		**ANBX**	91% [90%]	79		**ANBX**	81%[f] [80%][f]
58		**ABBX**	90% [88%]	80		**ABBX**	78%[f] [76%][f]
59		**ANBX**	93% [93%]	81		**ACBX**	71%[f] [71%][f]
60		**ABBX**	89% [89%]	82		**AFBX**	67%[d][f] [67%][f]
61		**ABX**	80% [79%]	83		**ABX**	15%
62		**ANBX**	89% [90%]	84		**ANBX**	75% [75%]
63		**ABBX**	88% [88%]	85		**ABBX**	76% [76%]
64		**ABX**	83% [82%]	86		**ABX**	24%
65		**ANBX**	87% [88%]	87		**ANBX**	84% [83%]
66		**ABBX**	87% [87%]	88		**ABBX**	79% [79%]
67		**ANBX**	76% [74%]	89		**ANBX**	84% [84%]
68		**ABBX**	81% [80%]	90		**ABBX**	78% [77%]

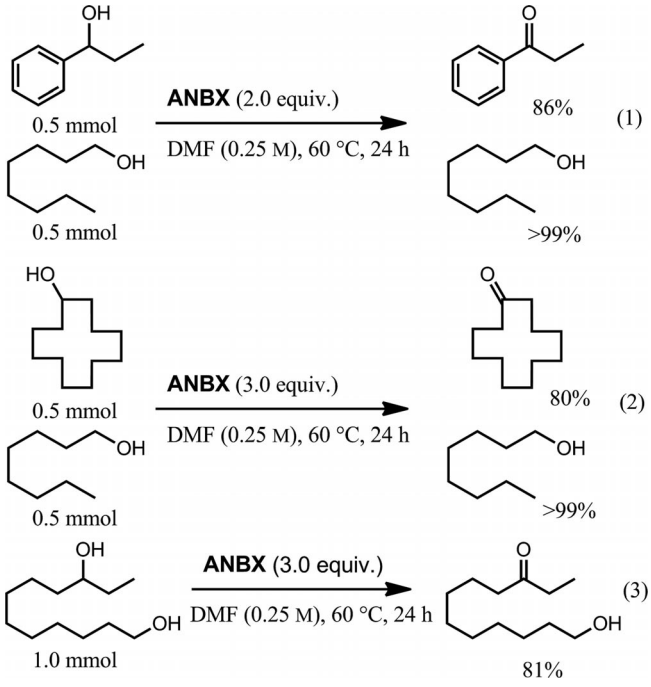
[a] Purified yield. [b] Purity after extraction of the reaction mixture with Et_2O/hexane and removal of the solvent. [c] Recovered and regenerated **ANBX** was used. [d] Recovered and regenerated **ABBX** was used. [e] **ANBX** (1.6 equiv.) was used. [f] **ABX**, **ANBX**, **ABBX**, **ACBX**, or **AFBX** (3.0 equiv.) was used.

those of **ABBX**, **ACBX**, and **AFBX** in $CHCl_3$ were compared with regard to the oxidation of *p*-methylbenzyl alcohol (see Table 2, Entries 1, 2, 4, 6, and 7). **ABX**, **ABBX**, **ACBX**, and **AFBX** showed high reactivities to form *p*-methylbenzaldehyde in good yields. **ANBX** in DMF showed the best reactivity to furnish *p*-methylbenzaldehyde in higher yields than those obtained with **ABX**, **ABBX**, **ACBX**, or **AFBX**. Here, **ABX** is slightly soluble in DMF, as is **ANBX**,

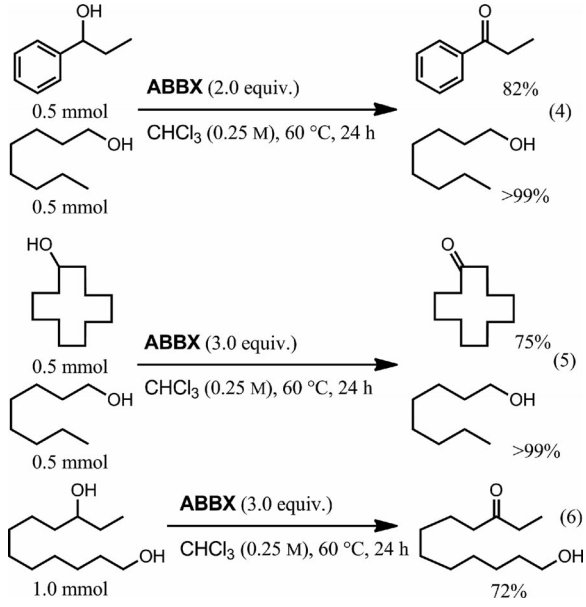
but it is scarcely soluble in $CHCl_3$. On the other hand, similar to **ABBX**, **ACBX** and **AFBX** are slightly soluble in $CHCl_3$. The present oxidation reactions offer two tremendous advantages. The first is that the aldehyde could be obtained in high yield with high purity by a simple extraction of the reaction mixture with diethyl ether/hexane after quenching with aqueous $NaHCO_3$. The second is that acidification of the aqueous solution induces the precipitation of 2-iodo-5-nitrobenzoic acid and 5-bromo-2-iodobenzoic acid in high yields, and upon treatment *m*CPBA, **ANBX** and **ABBX** could be regenerated in high yields and reused in the same oxidation reaction to give *p*-methylbenzaldehyde in 95 and 87% yields, respectively, with high purity (see Table 2, Entries 3 and 5). Thus, after recovery and regeneration, **ANBX** and **ABBX** could be repeatedly used in the same reaction. In addition, **ABX**, **ACBX**, and **AFBX** were recovered in moderate yields (60–75%). *p*-Chlorobenzyl alcohol was also treated with **ABX** and **ANBX** in DMF as well as with **ABBX** in $CHCl_3$ to provide *p*-chlorobenzaldehyde in good yields with high purity (see Table 2, Entries 8, 9, and 11). The regenerated **ANBX** and **ABBX** also gave the aldehyde in good yields with high purity (see Table 2, Entries 10 and 12). Other benzylic alcohols that contain acetal, phenyl, allyl, nitro, methoxy, trimethyl, and methylthio groups on the aromatic ring as well as heteroaromatic benzylic alcohols, such as 2-thiophenemethanol, 3-pyridinemethanol, 2-benzothiophenemethanol, 2-benzofuranmethanol, and *N*-tosyl-3-indolemethanol, were treated with **ABX** and **ANBX** in DMF and **ABBX** in $CHCl_3$ at 60 °C for 24 h to give the corresponding aromatic aldehydes in good yields. **ANBX** in DMF and **ABBX** in $CHCl_3$, in particular, gave the corresponding aldehydes in high yields with high purity (see Table 2, Entries 13–48) by simple extraction of the reaction mixture followed by removal of the solvent.

Under these conditions, the thiomethyl moiety of the aromatic aldehyde did not oxidize (see Table 2, Entries 33–35). Next, the oxidation of benzylic secondary alcohols by treatment with **ANBX** in DMF and **ABBX** in $CHCl_3$ was carried out at 60 °C for 24 h to give the corresponding aromatic ketones in good yields with high purities, and, again, this occurred by simple extraction of the reaction mixture followed by removal of the solvent (see Table 2, Entries 49–60). In these cases as well, the thiomethyl and olefinic groups were not affected during the oxidation (see Table 2, Entries 57 and 58). **ABX** in DMF gave the corresponding aromatic ketones in moderate to good yields (see Table 2, Entries 49 and 54). The treatment of cinnamyl alcohol, *p*-chlorocinnamyl alcohol, and *p*-methoxycinnamyl alcohol with **ABX** and **ANBX** in DMF as well as **ABBX** in $CHCl_3$ also gave the corresponding cinnamaldehydes in good yields, and **ANBX** and **ABBX** showed high reactivities to provide the corresponding α,β-unsaturated aldehydes in good yields with high purity (see Table 2, Entries 61–68). Then, aliphatic alcohols such as geraniol, which is an allylic alcohol that contains another olefinic group, 1-adamantanemethanol, borneol, cyclohexanol that contains an *O*-*tert*-butyldiphenylsilyl (TBDPS) group at 4-position, cyclododecanol, and β-cholestanol were treated with **ANBX** in DMF and **ABBX** in $CHCl_3$ at 60 °C for 24 h to form the corresponding aliphatic aldehydes and ketones in good yields (see Table 2, Entries 69–85). When the reactivities of **ABX**, **ANBX**, **ABBX**, **ACBX**, and **AFBX** were again compared with respect to the oxidation of cyclododecanol, we found that **ABX** showed poor reactivity, whereas **ACBX** and **AFBX** showed moderate reactivities, and **ANBX** and **ABBX** showed high reactivities to provide cyclododecanone in good yields (see Table 2, Entries 78–82). In this case, **ANBX** showed the best reactivity. Thus, **ABX** is not an efficient oxidant for the oxidation reaction of aliphatic secondary alcohols (see Table 2, Entries 71, 78, 83). Finally, 2,3,4,6-tetra-*O*-benzyl-D-glucose and 1-[2′-(4′′-methoxycarbonyl)-ethylphenoxy]-2-propanol, which contain ether and ester groups, underwent oxidation by treatment with **ANBX** and **ABBX** to give the corresponding lactone and ketone, respectively, in good yields (see Table 2, Entries 87–90). Again, **ABX** showed poor reactivity (see Table 2, Entry 86). Overall, **ANBX** in DMF gave slightly higher yields than **ABBX** in $CHCl_3$. However, **ABBX** can be used when the oxidation is carried out in $CHCl_3$.

Neither of the trivalent iodine compounds **ANBX** or **ABBX** could oxidize primary alcohols such as 1-octanol and 1-decanol, and the starting alcohols were recovered quantitatively. However, adamantanemethanol, a neopentyl-type aliphatic alcohol, could be oxidized. This is probably a consequence of the higher electron density of the oxygen atom of an aliphatic secondary alcohol in comparison to that of an aliphatic primary alcohol. Therefore, **ANBX** and **ABBX** could selectively oxidize benzylic alcohols and aliphatic secondary alcohols to give the corresponding aromatic aldehydes and ketones as well as aliphatic ketones, respectively. When a mixture of 1-phenyl-1-propanol and 1-octanol was treated with **ANBX** (2 equiv.) in DMF at 60 °C for 24 h, propiophenone was obtained in 86% yield along with 1-octanol in 99% yield [see Scheme 2, Equation (1)], and when a mixture of cyclododecanol and 1-octanol was treated with **ANBX** (3 equiv.) in DMF at 60 °C for 24 h, cyclododecanone was obtained in 80% yield along with 1-octanol in 99% yield [see Scheme 2, Equation (2)]. Moreover, when 1,10-dihydroxydodecane was treated with **ANBX** (3 equiv.) in DMF at 60 °C for 24 h, 1-hydroxydodecan-10-one was obtained in 81% yield [see Scheme 2, Equation (3)]. Similarly, when a mixture of 1-phenyl-1-propanol and 1-octanol was treated with **ABBX** (2 equiv.) in $CHCl_3$ at 60 °C for 24 h, propiophenone was obtained in 82% yield together with 1-octanol in 99% yield [see Scheme 3, Equation (4)], and when a mixture of cyclododecanol and 1-octanol was treated with **ABBX** (3 equiv.) in $CHCl_3$ at 60 °C for 24 h, cyclododecanone was obtained in 75% yield together with 1-octanol in 99% yield [see Scheme 3, Equation (5)]. Moreover, when 1,10-dihydroxydodecane was treated with **ABBX** (3 equiv.) in $CHCl_3$ at 60 °C for 24 h, 1-hydroxydodecan-10-one was obtained in 72% yield [see Scheme 3, Equation (6)]. Therefore, **ANBX** and **ABBX** can be used for the selective oxidation of secondary alcohols.



Scheme 2. Selective oxidation of secondary alcohols with **ANBX**.



Scheme 3. Selective oxidation of secondary alcohols with **ABBX**.

Conclusions

The new trivalent iodine compounds **ANBX**, **ABBX**, **ACBX**, and **AFBX** were prepared, and their reactivities were compared when employed in the oxidation of alcohols. As a result, **ANBX** in DMF and **ABBX** in either $CHCl_3$ or DMF showed high reactivities when used in the oxidation of benzylic primary alcohols, benzylic secondary alcohols, and aliphatic secondary alcohols to give the corresponding aldehydes and ketones in good yields with high purity by employing a simple ether/hexane extraction of the reaction mixture and subsequent removal of the solvent. Moreover, the coproducts 5-nitro-2-iodobenzoic acid and 5-bromo-2-iodobenzoic acid could be recovered by acidification of the aqueous reaction solution, and **ANBX** and **ABBX** could be regenerated and reused for the same oxidation reaction to give once again the aldehyde or ketone in good yields with high purity. Thus, **ANBX** and **ABBX** can be used as efficient oxidants of benzylic primary alcohols, benzylic secondary alcohols, and aliphatic secondary alcohols that contain various functional groups.

Experimental Section

General Methods: The ^1H and ^{13}C NMR spectroscopic data were recorded with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in δ (ppm) downfield from TMS. Mass spectra were recorded with JMS-T100GCV, JMS-HX110, and Thermo LTQ Orbitrap XL spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were recorded with a Yamato Melting Point Apparatus Model MP-21. Silica gel $60F_{254}$ (Merck) was used for TLC, and silica gel 60 (Kanto Kagaku Co.) was used for short column chromatography.

General Procedure for the Preparation of New Trivalent Iodine Compounds: To a solution of 2-iodo-5-nitrobenzoic acid (1.46 g, 5.0 mmol) in a mixture of AcOH (20 mL) and Ac_2O (20 mL) was added *m*-CPBA (1.46 g, 5.5 mmol). The mixture was stirred at 60 °C for 48 h. Upon completion, Et_2O (40 mL) was added to the reaction mixture at 0 °C, and the resulting mixture was filtered to afford 1-acetoxy-5-nitro-1,2-benziodoxol-3(1*H*)-one (1.67 g, 95% yield).

Large-Scale Preparation of ANBX: To a solution of 2-iodo-5-nitrobenzoic acid (5.85 g, 20.0 mmol) in a mixture of AcOH (80 mL) and Ac_2O (80 mL) was added *m*-CPBA (5.84 g, 22.0 mmol). The mixture was stirred at 60 °C for 48 h. Upon completion, Et_2O (160 mL) was added to the reaction mixture at 0 °C, and the resulting mixture was filtered to afford 1-acetoxy-5-nitro-1,2-benziodoxol-3(1*H*)-one (6.12 g, 87% yield).

1-Acetoxy-5-nitro-1,2-benziodoxol-3(1*H*)-one (ANBX): (1.67 g, 95% yield); m.p. 175–179 °C. IR (neat): $\tilde{\nu}$ = 1697, 1665, 1525, 1346 cm^{-1}. ^1H NMR (500 MHz, [D$_7$]DMF): δ = 1.96 (s, 3 H), 8.26 (d, J = 8.9 Hz, 1 H), 8.67 (d, J = 2.3 Hz, 1 H), 8.78 (dd, J = 2.3 Hz, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_7$]DMF): δ = 20.84, 125.52, 128.20, 128.81, 128.85, 134.31, 150.81, 166.82, 172.53 ppm. HRMS (ESI): calcd. for $C_9H_7O_6NI$ $[M + H]^+$ 351.9313; found 351.9320.

1-Acetoxy-5-bromo-1,2-benziodoxol-3(1*H*)-one (ABBX): (1.80 g, 94% yield); m.p. 176–179 °C. IR (neat): $\tilde{\nu}$ = 1682, 1668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 7.85 (d, J = 8.7 Hz, 1 H), 8.01 (dd, J = 2.3 Hz, J = 8.6 Hz, 1 H), 8.38 (d, J = 2.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.21, 116.41, 126.57, 130.63, 130.92, 136.04, 138.86, 166.63, 176.40 ppm. HRMS (ESI): calcd. for $C_9H_7O_4BrI$ $[M + H]^+$ 384.8567; found 384.8560.

1-Acetoxy-5-chloro-1,2-benziodoxol-3(1*H*)-one (ACBX): (1.56 g, 92% yield); m.p. 193–195 °C. IR (neat): $\tilde{\nu}$ = 1703, 1659, 1259 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 7.69 (dd, J = 1.8 Hz, J = 8.0 Hz, 1 H), 7.99 (d, J = 1.7 Hz, 1 H), 8.15 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.30, 119.00, 127.68, 129.33, 132.06, 133.59, 142.76, 167.09, 176.58 ppm. HRMS (ESI): calcd. for $C_9H_7O_4ClI$ $[M + H]^+$ 340.9072; found 340.9071.

1-Acetoxy-5-fluoro-1,2-benziodoxol-3(1*H*)-one (AFBX): (1.20 g, 74% yield); m.p. 139–142 °C. IR (neat): $\tilde{\nu}$ = 1696, 1632 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 7.43 (ddd, $J_{H,H}$ = 7.7 Hz, $J_{H,H}$ = 7.7 Hz, $J_{H,F}$ = 2.3 Hz, 1 H), 7.76 (dd, $J_{H,H}$ = 7.5 Hz, $J_{H,F}$ = 1.6 Hz, 1 H), 8.22 (dd, $J_{H,F}$ = 5.2 Hz, $J_{H,H}$ = 8.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.26, 117.32 (d, $J_{C,F}$ = 28.7 Hz), 119.36 (d, $J_{C,F}$ = 22.9 Hz), 119.69 (d, $J_{C,F}$ = 10.5 Hz), 125.41, 134.53 (d, $J_{C,F}$ = 9.5 Hz), 167.11, 167.47 (d, $J_{C,F}$ = 261.3 Hz), 176.55 ppm. HRMS (ESI): calcd. for $C_9H_7O_4FI$ [M + H]$^+$ 324.9368; found 324.9364.

Typical Procedure for the Oxidation of Alcohols to Aldehydes or Ketones in DMF: To a solution of 4-methylbenzyl alcohol (122.1 mg, 1.0 mmol) in DMF (4 mL) was added 1-acetoxy-5-nitro-1,2-benziodoxol-3-(1*H*)-one (703.8 mg, 2.0 mmol). The mixture was stirred at 60 °C for 24 h. Upon completion, the reaction mixture was added to aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with a mixture of Et_2O/hexane (1:1; 3× 10 mL). The combined organic layers were dried with Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave 4-methylbenzaldehyde (116.4 mg, 97% yield, 98% purity). The purity was estimated by ^{1}H NMR spectroscopic analysis. To recover the **ANBX**, the aqueous layer was acidified (pH ≈ 2) by using aqueous HCl (1 M solution, 15 mL), and the resulting mixture was filtered to afford 2-iodo-5-nitrobenzoic acid (538.9 mg, >92% yield). Oxidation of 2-iodo-5-nitrobenzoic acid with *m*CPBA again afforded **ANBX** (>92% yield).

Typical Procedure for the Oxidation of Alcohols to Aldehydes or Ketones in $CHCl_3$: To a solution of 4-methylbenzyl alcohol (122.1 mg, 1.0 mmol) in $CHCl_3$ (4 mL) was added 1-acetoxy-5-bromo-1,2-benziodoxol-3-(1*H*)-one (767.7 mg, 2.0 mmol). The mixture was stirred at 60 °C for 24 h. Upon completion, the reaction mixture was added to aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with $CHCl_3$ (3× 10 mL). The combined organic layers were dried with Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave 4-methylbenzaldehyde (108.0 mg, 90% yield, 90% purity). The purity was estimated by ^{1}H NMR spectroscopic analysis. To recover the **ABBX**, the aqueous layer was acidified (pH ≈ 2) by using aqueous HCl (1 M solution, 15 mL), and the resulting mixture was filtered to afford 2-iodo-5-bromobenzoic acid (593.0 mg, >91% yield). Oxidation of 2-iodo-5-bromobenzoic acid with *m*CPBA again afforded **ABBX** (>93% yield).

Aldehydes and Ketones Resulting from the Oxidation of Alcohols with ABBX

4-Methylbenzaldehyde: (108.0 mg, 90% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2827, 2734, 1702, 809 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.33 (d, J = 7.9 Hz, 2 H), 7.78 (d, J = 7.9 Hz, 2 H), 9.97 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.50, 129.33, 129.46, 133.81, 145.15, 191.62 ppm.

4-Chlorobenzaldehyde: (128.8 mg, 92% yield); m.p. 48–49 °C (commercially available, m.p. 47–50 °C). IR (Nujol): $\tilde{\nu}$ = 2727, 1710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.4 Hz, 2 H), 7.83 (d, J = 8.4 Hz, 2 H), 9.98 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.93, 130.36, 134.16, 140.39, 190.31 ppm.

Piperoylaldehyde: (141.0 mg, 94% yield); m.p. 37–39 °C (commercially available, m.p. 36–38 °C). IR (Nujol): $\tilde{\nu}$ = 2725, 1685 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.07 (s, 2 H), 6.93 (d, J = 7.9 Hz, 1 H), 7.32 (d, J = 1.6 Hz, 1 H), 7.41 (dd, J = 7.9 Hz, 1.6 Hz, 1 H), 9.80 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.02, 106.77, 108.24, 128.55, 131.77, 148.60, 153.00, 190.17 ppm.

4-Phenylbenzaldehyde: (163.8 mg, 90% yield); m.p. 57–58 °C (commercially available, m.p. 58 °C). IR (Nujol): $\tilde{\nu}$ = 2726, 1708, 833 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, J = 7.2 Hz, 1 H), 7.47 (t, J = 7.2 Hz, 2 H), 7.62 (d, J = 7.2 Hz, 2 H), 7.73 (d, J = 8.2 Hz, 2 H), 7.93 (d, J = 8.2 Hz, 2 H), 10.04 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.94, 127.26, 128.06, 128.60, 129.85, 134.77, 139.26, 146.74, 191.49 ppm.

4-(Allyloxy)benzaldehyde:[8a] Oil (147.4 mg, 91% yield). IR (neat): $\tilde{\nu}$ = 2787, 1686, 1596, 1251, 1157, 829 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.62 (d, J = 5.2 Hz, 2 H), 5.33 (d, J = 10.6 Hz, 1 H), 5.44 (d, J = 17.4 Hz, 1 H), 6.00–6.10 (m, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 7.83 (d, J = 8.6 Hz, 2 H), 9.88 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 68.90, 114.89, 118.27, 129.91, 131.87, 132.18, 163.49, 190.71 ppm.

4-Nitrobenzaldehyde: (141.9 mg, 94% yield); m.p. 101–103 °C (commercially available, m.p. 102–107 °C). IR (neat): $\tilde{\nu}$ = 2827, 1702, 1536, 1343, 1194, 813, 737 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.9 Hz, 2 H), 8.40 (d, J = 8.6 Hz, 2 H), 10.19 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.20, 130.40, 139.99, 151.02, 190.26 ppm.

4-Methoxybenzaldehyde: (130.6 mg, 96% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2840, 1698, 1602, 1511, 1263, 1162 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 7.01 (d, J = 8.7 Hz, 2 H), 7.84 (d, J = 8.8 Hz, 2 H), 9.89 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.54, 114.26, 129.91, 131.94, 164.56, 190.76 ppm.

2,4,6-Trimethylbenzaldehyde: (139.2 mg, 94% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2921, 1681, 1607, 780 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.56 (s, 6 H), 6.87 (s, 2 H), 10.54 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.10, 21.05, 129.51, 130.10, 141.03, 143.37, 192.49 ppm.

4-(Methylthio)benzaldehyde: (130.7 mg, 86% yield); oil (commercially available, oil), IR (neat): $\tilde{\nu}$ = 2829, 1691, 1588, 1090, 808 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H), 9.91 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 14.51, 125.04, 129.89, 132.80, 147.81, 191.15 ppm.

2-Thiophenecarboxaldehyde: (104.1 mg, 93% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2820, 2761, 1671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, J = 4.8, 3.8 Hz, 1 H), 7.75–7.82 (m, 2 H), 9.95 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.22, 135.03, 136.21, 143.94, 182.89 ppm.

Nicotinaldehyde: (87.7 mg, 82% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2839, 1699, 1588, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.54 (m, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 8.87 (d, J = 8.6 Hz, 1 H), 9.10 (s, 1 H), 10.14 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.45, 131.02, 135.49, 151.55, 154.27, 190.49 ppm.

Benzo[*b*]thiophen-2-carbaldehyde: (150.7 mg, 93% yield); m.p. 34–35 °C (commercially available, m.p. 35–36 °C). IR (neat): $\tilde{\nu}$ = 2823, 1665, 1515, 1133, 747, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.6 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.81 (d, J = 7.6 Hz, 1 H), 7.86 (d, J = 7.7 Hz, 1 H), 7.92 (s, 1 H), 10.03 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$:): δ = 122.92, 124.96, 126.01, 127.89, 134.36, 138.21, 142.23, 142.93, 184.44 ppm.

Benzofuran-2-carbaldehyde:[8b] Oil (137.2 mg, 93% yield). IR (neat): $\tilde{\nu}$ = 2827, 1677, 1555, 1118, 831, 750, 732 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, J = 7.8 Hz, 1 H), 7.52 (t, J = 7.8 Hz, 1 H), 7.57 (s, 1 H), 7.60 (d, J = 7.8 Hz, 1 H), 7.75 (d, J = 7.8 Hz, 1 H), 9.87 (s, 1 H) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ = 112.62, 117.84, 123.60, 124.13, 126.56, 129.16, 152. 58, 156.16, 179.7 ppm.

1-Tosyl-1*H*-indole-3-carbaldehyde:[8c] (254.2 mg, 85% yield); m.p. 144–146 °C. IR (neat): $\tilde{\nu}$ = 2824, 1678, 1376, 1098, 1080, 969, 743, 658 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.32–7.42 (m, 2 H), 7.85 (d, J = 8.1 Hz, 2 H), 7.95 (d, J = 8.3 Hz, 1 H), 8.24 (s, 1 H), 8.25 (d, J = 7.4 Hz, 1 H), 10.09 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.62, 113.20, 122.27, 122.55, 125.01, 126.22, 126.26, 127.19, 130.29, 134.23, 135.15, 136.29, 146.15, 185.42 ppm.

4-(1,3-Dioxolan-2-yl)benzaldehyde:[8d] (151.3 mg, 85% yield); m.p. 108–109 °C. IR (neat): $\tilde{\nu}$ = 2827, 1698, 1204, 1078 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.05–4.15 (m, 4 H), 5.88 (s, 1 H), 7.65 (d, J = 8.1 Hz, 2 H), 7.90 (d, J = 8.2 Hz, 2 H), 10.03 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 65.38, 102.77, 127.04, 129.76, 136.82, 144.33, 191.96 ppm.

Propiophenone: (112.6 mg, 84% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 1686 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.3 Hz, 3 H), 3.00 (q, J = 7.3 Hz, 2 H), 7.45 (t, J = 7.7 Hz, 2 H), 7.55 (t, J = 7.7 Hz, 1 H), 7.96 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.72, 31.25, 127.44, 128.02, 132.35, 136.39, 200.28 ppm.

1-Phenylnonan-1-one: (176.7 mg, 81% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 1685, 689 cm^{-1}. ^1H NMR (400 MHz $CDCl_3$): δ = 0.88 (t, J = 6.0 Hz, 3 H), 1.20–1.40 (m, 10 H), 1.67–1.77 (m, 2 H), 2.92 (t, J = 7.3 Hz, 2 H), 7.41 (t, J = 7.2 Hz, 2 H), 7.50 (t, J = 7.2 Hz, 1 H), 7.94 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.86, 22.44, 24.24, 28.97, 29.15, 29.26, 31.62, 38.28, 127.75, 128.24, 132.53, 136.80, 199.92 ppm.

Benzophenone: (152.9 mg, 84% yield); m.p. 49–52 °C (commercially available, m.p. 49 °C). IR (Nujol): $\tilde{\nu}$ = 1657 cm^{-1}. ^1H NMR (400 MHz $CDCl_3$): δ = 7.48 (t, J = 7.5 Hz, 4 H), 7.58 (t, J = 7.5 Hz, 2 H), 7.80 (d, J = 7.5 Hz, 4 H) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ = 128.20, 129.98, 132.35, 137.51, 196.70 ppm.

1-[4′-(Methylthio)phenyl]pent-4-en-1-one: (185.4 mg, 90% yield); m.p. 56–58 °C. IR (neat): $\tilde{\nu}$ = 1677, 1404, 1065 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46–2.53 (m, 4 H), 3.03 (t, J = 7.4 Hz, 2 H), 5.01 (d, J = 10.2 Hz, 1 H), 5.08 (d, J = 17.3 Hz, 1 H), 5.84–5.96 (m, 1 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.88 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.46, 27.98, 37.22, 115.01, 124.66, 128.17, 132.89, 137.11, 145.49, 198.00 ppm. HRMS (ESI): calcd. for $C_{12}H_{15}OS$ $[M + H]^+$ 207.0838; found 207.0836.

1-[4′-(Methylthio)phenyl]tridecan-1-one: (284.9 mg, 89% yield); m.p. 78–80 °C. IR (neat): $\tilde{\nu}$ = 1680, 1394, 1232 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H), 1.20–1.40 (m, 18 H), 1.68–1.75 (m, 2 H), 2.52 (s, 3 H), 2.91 (t, J = 7.5 Hz, 2 H), 7.27 (d, J = 8.8 Hz, 2 H), 7.87 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.07, 14.69, 22.64, 24.45, 29.29, 29.34, 29.44, 29.46, 29.57 (2 C), 29.61, 31.86, 38.36, 124.89, 128.42, 133.31, 145.42, 199.53 ppm. HRMS (ESI): calcd. for $C_{20}H_{33}OS$ $[M + H]^+$ 321.2247; found 321.2242.

***trans*-Cinnamaldehyde:** (116.2 mg, 88% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2816, 2743, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.72 (dd, J = 7.7, 16.1 Hz, 1 H), 7.41–7.46 (m, 3 H), 7.48 (d, J = 16.1 Hz, 1 H), 7.54–7.60 (m, 2 H), 9.71 (d, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.31, 128.42, 128.93, 131.09, 133.81, 152.60, 193.52 ppm.

***trans*-*p*-Chlorocinnamaldehyde:** (144.4 mg, 87% yield); m.p. 61–63 °C (commercially available, m.p. 60–63 °C). IR (neat): $\tilde{\nu}$ = 2826, 1693, 1078, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.68 (dd, J = 7.7, 16.8 Hz, 1 H), 7.40 (d, J = 8.8 Hz, 2 H), 7.43 (d, J = 16.8 Hz, 1 H), 7.50 (d, J = 8.6 Hz, 2 H), 9.70 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.79, 129.28, 129.51, 132.36, 137.09, 150.96, 193.28 ppm.

***trans*-*p*-Methoxycinnamaldehyde:** (131.2 mg, 81% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2827, 1665, 1596, 1246, 1122, 813 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.60 (dd, J = 7.8, 15.9 Hz, 1 H), 6.94 (d, J = 8.9 Hz, 2 H), 7.42 (d, J = 15.8 Hz, 1 H), 7.52 (d, J = 8.9 Hz, 2 H), 9.65 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.34, 114.44, 126.36, 126.63, 130.25, 152.66, 162.08, 193.62 ppm.

Geranial: (142.9 mg, 94% yield); oil (commercially available, oil). IR (neat): $\tilde{\nu}$ = 2768, 1673 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.61 (s, 3 H), 1.69 (s, 3 H), 2.17 (s, 3 H) 2.17–2.27 (m, 4 H), 5.03–5.14 (m, 1 H), 5.88 (d, J = 7.9 Hz, 1 H), 9.99 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.87, 16.99, 24.92, 25.02, 39.89, 121.86, 126.68, 132.14, 163.07, 190.54 ppm.

1-Adamantanecarboxaldehyde:[8e] (134.5 mg, 82% yield); m.p. 140–142 °C. IR (Nujol): $\tilde{\nu}$ = 2815, 2698, 1722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.68–1.80 (m, 12 H), 2.03–2.09 (m, 3 H), 9.32 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.31, 35.80, 36.52, 44.82, 206.09 ppm.

Camphor: (109.5 mg, 72% yield); m.p. 170–173 °C (commercially available, m.p. 172–180 °C). IR (Nujol): $\tilde{\nu}$ = 1749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 3 H), 0.91 (s, 3 H), 0.96 (s, 3 H), 1.30–1.45 (m, 2 H), 1.68 (td, J = 12.5, 4.0 Hz, 1 H), 1.84 (d, J = 18.4 Hz, 1 H), 1.90–2.00 (m, 1 H), 2.09 (t, J = 4.0 Hz, 1 H), 2.35 (dt, J = 18.4, 4.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.08, 18.98, 19.61, 26.89, 29.75, 42.89, 43.14, 46.62, 57.53, 219.53 ppm.

4-(*tert*-Butyldiphenylsilyloxy)cyclohexanone: (260.6 mg, 74% yield); m.p. 100–102 °C. IR (neat): $\tilde{\nu}$ = 1703, 1037, 1002, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 9 H), 1.74–1.80 (m, 2 H), 1.92–1.98 (m, 2 H), 2.18–2.25 (m, 2 H), 2.70–2.80 (m, 2 H), 4.14–4.17 (m, 1 H), 7.39 (t, J = 7.5 Hz, 4 H), 7.45 (t, J = 7.5 Hz, 2 H), 7.68 (d, J = 7.5 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.09, 26.79, 33.56, 36.77, 66.71, 127.52, 129.63, 133.71, 135.49, 211.54 ppm. HRMS (ESI): calcd. for $C_{22}H_{28}O_2NaSi$ $[M + Na]^+$ 375.1751; found 375.1749.

Cyclododecanone: (142.0 mg, 78% yield); m.p. 60–62 °C (commercially available, m.p. 61 °C). IR (neat): $\tilde{\nu}$ = 1702, 1470 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.20–1.36 (m, 14 H), 1.66–1.76 (m, 4 H), 2.46 (t, J = 6.2 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.99, 22.21, 23.87, 24.25, 24.40, 40.01, 212.46 ppm.

5α-Cholestan-3-one: (293.6 mg, 76% yield); m.p. 123–125 °C (commercially available, m.p. 128–129 °C). IR (Nujol): $\tilde{\nu}$ = 1719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$,): δ = 0.68 (s, 3 H), 0.69–0.76 (m, 1 H), 0.84–0.92 (m, 9 H), 1.01 (s, 3 H), 0.94–1.18 (m, 9 H), 1.23–1.44 (m, 9 H), 1.46–1.60 (m, 4 H), 1.66–1.74 (m, 1 H), 1.78–1.89 (m, 1 H), 1.96–2.12 (m, 3 H), 2.21–2.44 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.43, 12.04, 18.64, 21.42, 22.53, 22.79, 23.79, 24.19, 27.98, 28.21, 28.95, 31.69, 35.36, 35.61, 35.76, 36.11, 38.17, 38.54, 39.47, 39.88, 42.56, 44.70, 46.68, 53.78, 56.23, 212.12 ppm.

2,3,4,6-Tetra-*O*-benzyl-D-glucono-1,5-lactone: Oil (425.2 mg, 79% yield). IR (neat): $\tilde{\nu}$ = 1755, 1454, 1165, 1094, 738, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.64–3.75 (m, 2 H), 3.88–3.98 (m, 2 H), 4.12 (d, J = 6.1 Hz, 1 H), 4.43–4.76 (m, 8 H), 4.98 (d, J = 11.3 Hz, 1 H), 7.15–7.41 (m, 20 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 68.21, 73.52, 73.69 (2 C), 73.91, 76.01, 77.30, 78.12, 80.92, 127.79 (3 C), 127.91, 127.96 (3 C), 128.08, 128.37, 128.41 (2 C), 128.45, 136.90, 137.46 (2 C), 137.55, 169.31 ppm. HRMS (ESI): calcd. for $C_{34}H_{35}O_6$ $[M + H]^+$ 539.2428; found 539.2423.

Methyl 3-[4′-(2′′-Oxopropoxy)phenyl]propanoate: Oil (184.1 mg, 78% yield). IR (neat): $\tilde{\nu}$ = 1730, 1509, 1169, 1065 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 2.60 (t, J = 7.7 Hz, 2 H), 2.90 (t, J = 7.7 Hz, 2 H), 3.65 (s, 3 H), 4.51 (s, 2 H), 6.81 (d, J = 8.7 Hz, 2 H), 7.11 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.51, 29.92, 35.74, 51.52, 73.01, 114.44, 129.37, 133.64, 156.13, 173.21, 205.81 ppm. HRMS (ESI): calcd. for $C_{13}H_{16}O_4Na$ $[M + Na]^+$ 259.0941; found 259.0936.

1-Hydroxydodecan-10-one: (142.1 mg, 71% yield); m.p. 48–51 °C. IR (neat): $\tilde{\nu}$ = 3333, 2916, 1699, 1059 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.4 Hz, 3 H), 1.25–1.42 (m, 10 H), 1.55–1.65 (m, 4 H), 2.38–2.50 (m, 4 H), 3.64 (t, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.79, 23.85, 25.64, 29.17, 29.28 (2 C), 29.32, 32.70, 35.80, 42.35, 62.93, 212.06 ppm. HRMS (ESI): calcd. for $C_{12}H_{25}O_2$ $[M + H]^+$ 201.1849; found 201.1850.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra for **ANBX**, **ABBX**, **ACBX**, **AFBX**, and all aldehydes and ketones.

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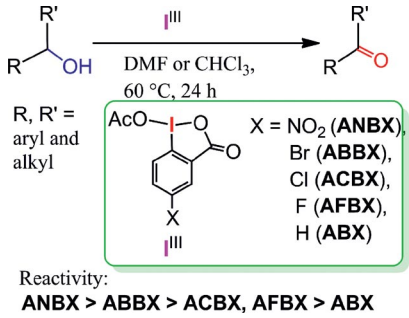
The trivalent iodine compounds 1-acetoxy-5-nitro-1,2-benziodoxole-3(1*H*)-one (**ANBX**), 1-acetoxy-5-bromo-1,2-benziodoxole-3(1*H*)-one (**ABBX**), 1-acetoxy-5-chloro-1,2-benziodoxole-3(1*H*)-one (**ACBX**), and 1-acetoxy-5-fluoro-1,2-benziodoxole-3(1*H*)-one (**AFBX**) were used for the oxidation of benzylic alcohols and aliphatic secondary alcohols to give the corresponding aldehydes and ketones.



Oxidation of Alcohols

Keywords: Oxidation / Hypervalent compounds / Iodine / Alcohols / Aldehydes / Ketones

