Tetrahedron 66 (2010) 9688–9693

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A simple method for the oxidation of primary alcohols with *o*-iodoxybenzoic acid (IBX) in the presence of acetic acid

Cheng-Kun Lin, Ta-Jung Lu *

Department of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan ROC

ARTICLE INFO

Article history:
Received 14 August 2010
Received in revised form 17 October 2010
Accepted 18 October 2010
Available online 11 November 2010

Keywords:
o-Iodoxybenzoic acid (IBX)
Oxidation
Aldehydes

ABSTRACT

A simple method for the oxidation of primary alcohols to aldehydes using *o*-iodoxybenzoic acid (IBX) with the addition of stoichiometric acetic acid has been developed. Addition of acetic acid significantly accelerated the reaction rate. Under these conditions, primary aliphatic, benzylic, and allylic alcohols are smoothly converted to aldehydes in high yields (90–97%).

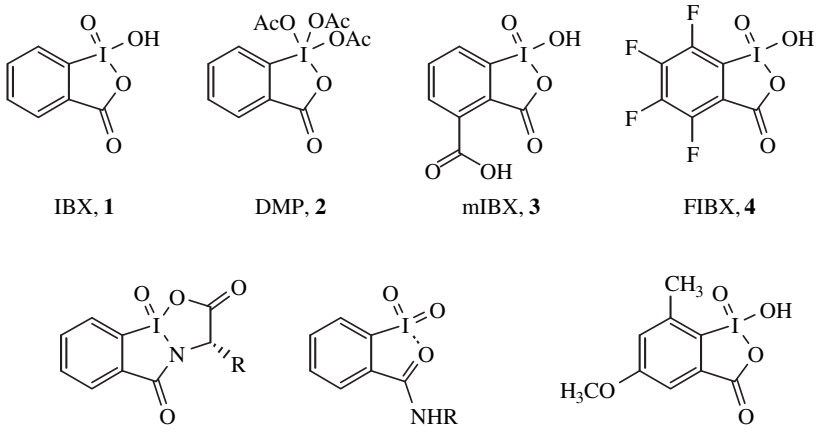
1. Introduction

Transformation of alcohols into the corresponding carbonyl compounds is an important subject in organic synthesis. Many methods and a wide variety of oxidizing agents have been developed including chromium oxidants [pyridinium chlorochromate (PCC, Corey's reagent),[1] pyridinium dichromate (PDC),[2] Jones oxidation (CrO_3, H_2SO_4),[3] Collins reagent ($CrO_3 \cdot py_2$)[4]], dimethyl sulfoxide-promoted oxidations [Pfitzner–Moffatt protocol (DMSO, DCC),[5] Swern oxidation (DMSO, oxalyl chloride),[6] Parikh–Doering procedure (DMSO, $SO_3 \cdot py$)[7]], Corey–Kim protocol,[8] hypervalent iodine reagents,[9] tetra-*n*-propylammonium perruthenate (TPAP),[10] 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO),[11] Oppenauer oxidation,[12] and active manganese dioxide.[13] However, some of the foregoing processes are carried out under strong acidic conditions and some oxidations of primary alcohols cannot stop at the aldehyde stage. In addition, some methods are performed under inconvenient conditions (low reaction temperatures, inert atmosphere, dry solvents, and moisture-sensitive reagents). Among these methodologies, hypervalent iodine reagents are particularly attractive and have drawn a growing attention as oxidizing agents because of their mildness, efficiency, wide functional group tolerance, selectivity, easy accessibility, and stability against air and moisture.[14]

In 1893, a hypervalent iodine reagent, *o*-iodoxybenzoic acid (IBX, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide, **1**) was first prepared by Hartmann and Meyer.[15] Probably due to its insolubility in most organic solvents, its mild oxidizing ability was rarely used in synthetic reactions until Frigerio and Santagostino reported the oxidation of alcohols to carbonyl compounds by IBX dissolving in dimethyl sulfoxide in 1994.[16] Recently, Pivnitsky disclosed that dimethyl formamide is a convenient alternative solvent to dimethyl sulfoxide to simplify product isolation procedure because of the lower volatility of dimethyl sulfoxide.[17] The poor solubility of IBX in organic solvents has been improved by converting it into its derivatives such as the well-known Dess–Martin periodinane (DMP, **2**),[18] modified IBX (mIBX, **3**),[19] tetrafluoro-IBX (FIBX, **4**),[20] amino acid-derived benziodazole oxides **5**,[21] IBX amides **6**,[22] and modified *o*-methyl-substituted IBX **7** (Scheme 1).[23] For IBX oxidation of alcohols, there are an increasing number of improved protocols. For instances, the oxidations were conducted with IBX in the presence of stoichiometric amount of dimethyl sulfoxide,[24] under solvent-free conditions,[25] in stabilized form (sIBX),[26] in the presence of catalytic amount of Oxone®,[27] in a water/dichloromethane mixture in the presence of a phase-transfer catalyst,[28] at elevated temperatures in most organic solvents,[29] in ionic liquids,[30] in water/acetone in the presence of β-cyclodextrin,[31] and in polymer-supported forms.[32] Unfortunately, there are some existing problems, among these synthetic routes, such as the elevation of reaction temperature may cause expulsion of IBX[33] and the decomposition of the starting materials, the preparations of the solid-supported IBX and IBX derivatives are laborious, and the successive aqueous extraction removal of some additives is required.

* Corresponding author. Tel.: +86 886 4 22850533; fax: +86 886 4 22862547; e-mail address: tjlu@dragon.nchu.edu.tw (T.-J. Lu).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.10.053



Scheme 1. IBX derivatives.

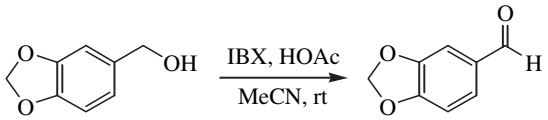
In the course of our study on the asymmetric synthesis of α-amino acids, we were required to prepare an α-hydroxy ketone from the corresponding diol as our chiral auxiliary.[34] An interesting outcome caught our attention when we noticed that the yields of IBX oxidation of diols varied with the scale of the reaction. When the reaction was carried out with less than 5 mmol of the starting diol, 2.5 equiv of IBX, and 5 equiv of dimethyl sulfoxide at room temperature for 1 day resulting in the formation of more than 95% isolated yield of the product. However, when the amount of the diol was increased to more than 10 mmol, under the same conditions, the yield decreased to around 80%. We found that replacing dimethyl sulfoxide by acetic acid resulted in improving yield to 93%. In addition, the product was clean enough for further use without the need of purification. As a result, we set forth to investigate the reaction conditions of IBX oxidation of primary alcohols in the presence of acetic acid. Herein, we report a new and practical protocol of IBX oxidation using acetic acid.

2. Results and discussion

First, 3 equiv of IBX and acetic acid were employed for different primary alcohols and the oxidations were complete in 4–15 h in 93–99% yields. However, in the absence of acetic acid, longer reaction time was needed (additional 7.5–13.5 h) to consume all the starting materials. The oxidations using different amounts of IBX and acetic acid in acetonitrile[35] at room temperature were performed to study the optimal reaction conditions and the results were summarized in Table 1. When 3 equiv of IBX was employed in the presence of equal amount of acetic acid, with vigorous stirring, piperonyl alcohol was smoothly oxidized to piperonal within 3 h in 97% yield (Table 1, entry 1). When the reaction was conducted with 3 equiv of IBX without the addition of acetic acid, the reaction time required to finish the oxidation was 4.5 h (entry 2). Decreasing the amounts of IBX and acetic acid to 2, 1.5, and 1.2 equiv, the yields were comparable to entry 1 but with shorter reaction time (entries 3, 4, and 6). Changing the ratio of IBX and acetic acid from 1:1 to 1:2, the reaction rate did not change (entries 4 and 5). Comparison of entries 6, 7, and 8, in the absence or in catalytic amount (0.3 equiv) of acetic acid, the yields fell by 17% and 14%, respectively. At the same time, we also attempted to use stronger acid than acetic acid, such as *p*-toluenesulfonic acid and trifluoroacetic acid in catalytic amount (0.3 equiv), but unidentified impurities were detected along with the formation of 87% of piperonal. When the reaction was performed with 1.1 equiv of IBX and acetic acid, longer reaction time was required to achieve 93% of conversion of the starting material. The reaction did not go completion even when the reaction time was extended to 10 h (entry 9). From the results of Table 1, the addition of acetic acid significantly accelerates the rate of oxidation. In addition, the conditions of entry 6 were chosen as the reaction conditions to examine the scope of substrate of the oxidation.

All the primary alcohols investigated were converted efficiently by IBX in the presence of acetic acid into the corresponding aldehydes in good yields (90–97%) without over-oxidation to acids (Table 2). However, in the absence of acetic acid, using same reaction time, the yields decreased to 39–84%. The reaction time is found to be dependent on the nature of the substrate. The first step of IBX oxidation is a nucleophilic addition of the oxygen atom of alcohols to the iodine atom of IBX. Therefore, a substituent on the benzene ring of the benzyl alcohol, either electron-donating or -withdrawing, the reaction time changed significantly (entries 1–14). Moreover, an *ortho* substituent on the benzyl alcohol, steric hindrance plays a major role. Accordingly, the same substituent on the *para* position of benzyl alcohol reacts faster than that on the *ortho* position (entries 2–13). Due to both electronic and steric effects, there is a significant rate decrease of the oxidation reaction when a benzene ring containing an *ortho* electron-withdrawing group is utilized (entries 6, 8, 10, and 12). On the other hand, *para*

Table 1
Optimization of oxidation conditions



Entry	IBX[a] (equiv)	HOAc (equiv)	Time[b] (h)	Isolated yield[c] (%)
1	3	3	3	97
2	3	—	4.5	96
3	2	2	2	95
4	1.5	1.5	2	95
5	1.5	3	2	94
6	1.2	1.2	2	97
7	1.2	—	2	80
8[d]	1.2	0.3	2	83
9	1.1	1.1	5	90[e]

[a] IBX was prepared according to Santagostino procedure.[36]
[b] The reaction progress was monitored by ^{1}H NMR.
[c] The reported yields are isolated yields after the crude mixture was passed through a short path of silica gel.
[d] When replacing acetic acid by TsOH·H_2O or TFA, the yield was 87% along with unidentified impurity.
[e] The conversion was 93% even expanding the reaction time to 10 h.

Table 2
Oxidation of alcohols with IBX in the presence or absence of acetic acid in MeCN[a]

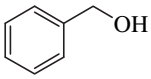
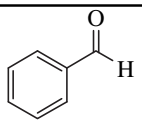
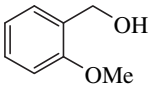
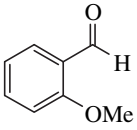
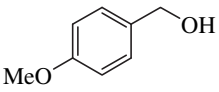
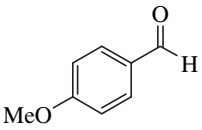
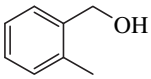
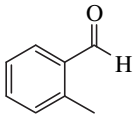
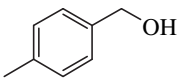
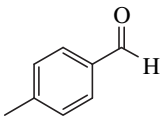
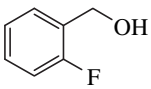
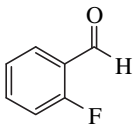
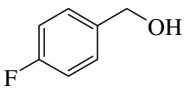
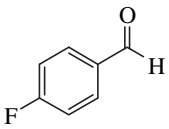
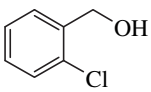
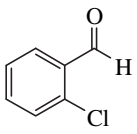
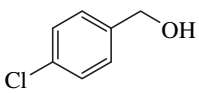
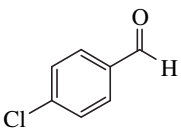
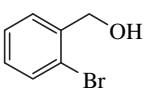
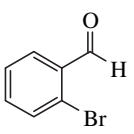
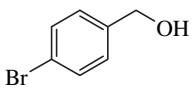
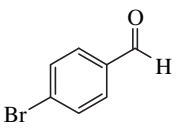
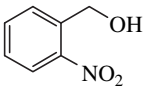
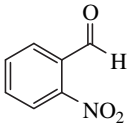
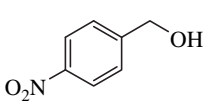
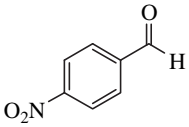
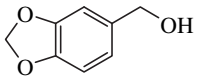
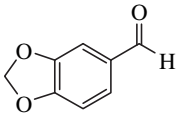
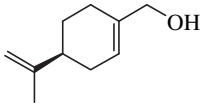
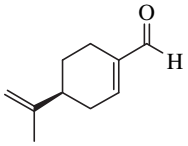
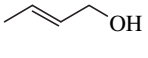
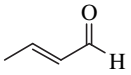
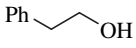
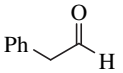
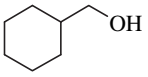
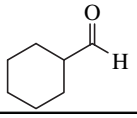
Entry	Substrate	Product	With HOAc		Without HOAc	
			Time (h)	Yield[b] (%)	Time (h)	Yield[b] (%)
1			5	94	5	80
2			5	95	5	81
3			2.5	95	2.5	75
4			6	95	6	81
5			3	95	3	82
6			9	93	9	65
7			8	92	8	82
8			6	95	6	60
9			3	97	3	84
10			8	93	8	83
11			5	95	5	80
12			8	96	8	73

Table 2 (*continued*)

Entry	Substrate	Product	With HOAc		Without HOAc	
			Time (h)	Yield[b] (%)	Time (h)	Yield[b] (%)
13			4	96	4	83
14			2	97	2	80
15			2	90	2	39
16			4	91	4	41
17			9	93	9	55
18			11	92	11	59

[a] The ratio of alcohols, IBX, and HOAc is 1:1.2:1.2.
[b] The reported yields are isolated yields after the crude mixture was passed through a short path of silica gel.

electron-donating substituent on the benzene ring only exhibits electronic donating effect and faster oxidation is observed (entries 3, 5, and 14). Moreover, the oxidation of benzylic (entries 1–14) and allylic (entries 15 and 16) alcohols is faster than that of the aliphatic ones (entries 17 and 18). Among all cases, there is a dramatic improvement of yields (10–51%) by the addition of acetic acid.

It is noteworthy that the addition of acetic acid in other solvent systems did not show marked improvements in reaction times and yields for the IBX oxidation of alcohols. For example, the oxidation of alcohols by IBX in DMSO in the presence of acetic acid similar reaction time was needed to give comparable yields of aldehyde products compared with those in the absence of acetic acid. However, these reactions required more amounts (2–3 equiv) of IBX for the oxidation to go completion as opposed to only 1.2 equiv of IBX were needed when acetonitrile was used. The oxidation was also carried out in DMF as the solvent under the similar reaction conditions as those using DMSO but demanded more solvent because of the poor solubility of IBX in DMF. In addition, the boiling point of acetonitrile (81 °C) is much lower that that of DMSO (189 °C) and DMF (153 °C), which renders it easily removed after the reaction.

The role of acetic acid in this oxidation reaction presumably is an external proton source to assist the formation and dissociation of water molecule from the intermediate derived from alcohols and IBX based on the work of Frigerio and Palmisan,[14] in which the mechanism of IBX oxidation of alcohols involved the liberation of 1 mol of water molecule. We reasoned that the addition of acetic acid in the oxidation reaction would aid the elimination of water resulting in acceleration of the oxidation.

3. Conclusion

In conclusion, a new, practical, and effective protocol for the oxidation of primary alcohols to the corresponding aldehydes using IBX and acetic acid has been developed. This protocol presents a mild, simple, and convenient methodology for the conversion of primary alcohols to the corresponding aldehydes using IBX, which is a cheap, mild, and easily available reagent. Among all the reactions, there is a dramatic improvement of yields (10–51%) by the addition of acetic acid. A wide range of primary alcohols can be oxidized to the corresponding aldehydes in excellent yields demonstrating the usefulness of our method.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 MHz spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS) as internal standard. Spectra in $CDCl_3$ are referenced to the residual solvent peaks at δ 0.00 (^{1}H) and 77.0 (^{13}C). Coupling constants are reported in hertz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). High-resolution mass spectrometry (HRMS) analyses were determined on a Jeol JMS-HX 110 spectrometer. The optical rotations were measured in $CHCl_3$ solution with a cuvette of 1 dm length on a Perkin–Elmer 241 polarimeter. IR spectra were recorded with a Bruker Tensor 27 FT-IR and only structurally important peaks are

listed. Melting points were measured on a Mel-Temp II with a capillary melting point tube. Thin-layer chromatography (TLC) plates visualized by exposure to ultraviolet light at 254 nm and/or immersion in a staining solution (phosphomolybdic acid) followed by heating on a hot plate. Flash chromatography was carried out utilizing silica gel 60, 70–230 mesh ASTM. All reagents and solvents are commercially available and were used without further purification. IBX was prepared according to the literature procedure.[36]

4.2. General procedure

A suspension of the alcohol (1 mmol), IBX (1.2 mmol), and acetic acid (1.2 mmol) in acetonitrile (5 mL) was stirred vigorously at room temperature. The reaction progress was monitored by TLC plate or ^{1}H NMR. After completion of the reaction, sodium bicarbonate (100 mg) was added to the mixture. The resulting mixture was passed through a short path of silica gel using ethyl acetate as the eluent. After removal of the solvent, desired aldehyde was obtained.

4.2.1. Benzaldehyde. Yield: 100 mg (94%). Colorless oil. IR (KBr, neat): 3073 (m), 2827 (m), 2745 (m), 1696 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.01 (s, 1H), 7.75–7.79 (m, 2H), 7.60–7.42 (m, 3H); ^{13}C NMR (100 MHz): δ 192.2, 136.2, 134.1, 129.8, 128.7; MS: *m*/*z* 106 (M$^+$, 62.8), 105 (91.9), 91 (44.7), 77 (100.0); HRMS *m*/*z* calcd C_7H_6O for M$^+$ 106.0419, found M$^+$ 106.0422.

4.2.2. 2-Methoxybenzaldehyde. Yield: 129 mg (95%). White solid. Mp=36–41 °C; IR (KBr, $CHCl_3$): 3011 (m), 2843 (m), 2758 (m), 1690 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.48 (s, 1H), 7.82 (dd, *J*=8.0, 1.6 Hz, 1H), 7.54 (td, *J*=8.0, 1.6 Hz, 1H), 7.02–6.98 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz): δ 188.9, 161.3, 136.0, 128.4, 124.6, 120.5, 111.4, 55.7; MS: *m*/*z* 136 (M$^+$, 100.0), 135 (55.6), 77 (84.9); HRMS *m*/*z* calcd $C_8H_8O_2$ for M$^+$ 136.0524, found M$^+$ 136.0531.

4.2.3. 4-Methoxybenzaldehyde. Yield: 129 mg (95%). Colorless oil. IR (KBr, neat): 3011 (w), 2826 (w), 2738 (w), 1700 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.81 (s, 1H), 7.76 (d, *J*=8.8 Hz, 2H), 7.02 (d, *J*=8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz): δ 190.5, 164.4, 131.6, 129.8, 114.0, 55.5; MS: *m*/*z* 136 (M$^+$, 68.0), 135 (100.0), 77 (38.9); HRMS *m*/*z* calcd for $C_8H_8O_2$ M$^+$ 136.0524, found M$^+$ 136.0517.

4.2.4. 2-Methylbenzaldehyde. Yield: 114 mg (95%). Colorless oil. IR (KBr, neat): 3030 (w), 2850 (w), 2733 (w), 1698 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.29 (s, 1H), 7.80 (d, *J*=4.4 Hz, 1H), 7.49–7.44 (m, 1H), 7.37–7.32 (m, 1H), 7.28 (d, *J*=4.4 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz): δ 192.8, 140.3, 133.9, 133.5, 131.9, 131.6, 126.2, 20.1; MS: *m*/*z* 120 (M$^+$, 40.3), 119 (48.8), 91 (100.0), 65 (27.4); HRMS *m*/*z* calcd for C_8H_8O M$^+$ 120.0575, found M$^+$ 120.0570.

4.2.5. 4-Methylbenzaldehyde. Yield: 114 mg (95%). Colorless oil. IR (KBr, neat): 3040 (m), 2825 (m), 2736 (m), 1700 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.96 (s, 1H), 7.75 (d, *J*=8.0 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz): δ 192.0, 145.4, 134.0, 129.8, 129.7, 21.8; MS: *m*/*z* 120 (M$^+$, 80.9), 119 (100.0), 91 (61.1), 65 (52.0); HRMS *m*/*z* calcd for C_8H_8O M$^+$ 120.0575, found M$^+$ 120.0567.

4.2.6. 2-Fluorobenzaldehyde. Yield: 115 mg (93%). Colorless oil. IR (KBr, neat): 3069 (m), 2858 (m), 2763 (m), 1699 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.35 (s, 1H), 7.89–7.82 (m, 1H), 7.77–7.61 (m, 1H), 7.27–7.17 (m, 2H); ^{13}C NMR (100 MHz): δ 187.3, 169.9, 136.7, 128.8, 124.6, 124.4, 117.0; MS: *m*/*z* 124 (M$^+$, 24.5), 123 (100.0), 95 (32.6), 75 (26.2); HRMS *m*/*z* calcd for C_7H_5FO M$^+$ 124.0324, found M$^+$ 124.0322.

4.2.7. 4-Fluorobenzaldehyde. Yield: 114 mg (92%). Colorless oil. IR (KBr, neat): 3071 (w), 2827 (w), 2742 (w), 1701 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.98 (s, 1H), 7.93–7.89 (m, 2H), 7.25–7.20 (m, 2H); ^{13}C NMR (100 MHz): δ 189.9, 167.4, 164.8, 132.4, 132.1, 116.0, 115.5; MS: *m*/*z* 124 (M$^+$, 69.1), 123 (100.0), 95 (73.8), 75 (43.0); HRMS *m*/*z* calcd for C_7H_5FO M$^+$ 124.0324, found M$^+$ 124.0319.

4.2.8. 2-Chlorobenzaldehyde. Yield: 134 mg (95%). Colorless oil. IR (KBr, neat): 3069 (w), 2849 (w), 2761 (w), 1697 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.43 (s, 1H), 7.86 (td, *J*=8.0, 1.6 Hz, 1H), 7.52–7.35 (m, 3H); ^{13}C NMR (100 MHz): δ 189.8, 137.7, 135.2, 132.2, 130.3, 129.5, 127.3; MS: *m*/*z* 140 (M$^+$, 69.0), 139 (100.0), 111 (56.3), 75 (43.9), 50 (35.3); HRMS *m*/*z* calcd for C_7H_5ClO M$^+$ 140.0029, found M$^+$ 140.0031.

4.2.9. 4-Chlorobenzaldehyde. Yield: 136 mg (97%). White solid. Mp=43–46 °C; IR (KBr, $CHCl_3$): 3056 (m), 2833 (ms), 2727 (ms), 1709 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.96 (s, 1H), 7.82 (d, *J*=8.0 Hz, 2H), 7.48 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz): δ 190.7, 141.1, 134.9, 131.0, 129.4; MS: *m*/*z* 140 (M$^+$, 83.3), 139 (100.0), 111 (57.6), 75 (77.1), 50 (39.1); HRMS *m*/*z* calcd C_7H_5ClO for M$^+$ 140.0029, found M$^+$ 140.0026.

4.2.10. 2-Bromobenzaldehyde. Yield: 172 mg (93%). Colorless oil. IR (KBr, neat): 3019 (m), 2862 (m), 2757 (m), 1698 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.23 (s, 1H), 7.86–7.79 (m, 1H), 7.56–7.49 (m, 1H), 7.33–7.28 (m, 2H); ^{13}C NMR (100 MHz): δ 191.3, 135.3, 133.6, 133.2, 130.1, 127.9, 126.8; MS: *m*/*z* 184 (M$^+$, 60.1), 183 (100.0), 155 (39.2), 75 (48.8), 50 (67.6); HRMS *m*/*z* calcd for C_7H_5BrO M$^+$ 183.9524, found M$^+$ 183.9531.

4.2.11. 4-Bromobenzaldehyde. Yield: 176 mg (95%). White solid. Mp=56–58 °C; IR (KBr, $CHCl_3$): 3077 (w), 2820 (m), 2766 (m), 1694 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.99 (s, 1H), 7.74 (d, *J*=8.4 Hz, 2H), 7.68 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz): δ 191.2, 135.2, 132.3, 130.8, 129.7; MS: *m*/*z* 184 (M$^+$, 81.9), 185 (100.0), 183 (94.7), 155 (48.1), 76 (41.5), 50 (56.1); HRMS *m*/*z* calcd for C_7H_5BrO M$^+$ 183.9524, found M$^+$ 183.9527.

4.2.12. 2-Nitrobenzaldehyde. Yield: 145 mg (96%). Pale yellow solid. Mp=40–43 °C; IR (KBr, $CHCl_3$): 3061 (w), 2860 (w), 2749 (w), 1700 (s), 1532 (s), 1344 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.42 (s, 1H), 8.12–7.78 (m, 5H); ^{13}C NMR (100 MHz): δ 188.2, 149.6, 134.2, 133.8, 131.4, 129.7, 124.5; MS: *m*/*z* 151 (M$^+$, 0.27), 121 (77.9), 93 (50.0), 76 (69.4), 65 (100.0), 51 (83.1); HRMS *m*/*z* calcd for $C_7H_5NO_3$ M$^+$ 151.0629, found M$^+$ 151.0272.

4.2.13. 4-Nitrobenzaldehyde. Yield: 145 mg (96%). Pale yellow solid. Mp=105–106 °C; IR (KBr, $CHCl_3$): 3070 (w), 2850 (ms), 2733 (w), 1703 (s), 1549 (m), 1345 (m) cm^{-1}; ^{1}H NMR (400 MHz): δ 10.16 (s, 1H), 8.37 (d, *J*=8.8 Hz, 2H), 8.05 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (100 MHz): δ 190.1, 151.2, 140.0, 130.4, 124.0; MS: *m*/*z* 151 (M$^+$, 0.35), 121 (79.1), 93 (49.9), 76 (71.6), 65 (100.0), 51 (79.9); HRMS *m*/*z* calcd for $C_7H_5NO_3$ M$^+$ 151.0629, found M$^+$ 151.0271.

4.2.14. Piperonal. Yield: 146 mg (97%). White solid. Mp=35–37 °C; IR (KBr, $CHCl_3$): 3078 (w), 2843 (w), 2740 (w), 1688 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.73 (s, 1H), 7.36 (dd, *J*=8.0, 1.6 Hz, 1H), 7.25 (d, *J*=1.6 Hz, 1H), 6.88 (d, *J*=8.0 Hz, 1H), 6.09 (s, 2H); ^{13}C NMR (100 MHz): δ 190.0, 153.1, 148.4, 131.8, 128.5, 108.2, 107.0, 102.1; MS: *m*/*z* 150 (M$^+$, 95.1), 149 (100.0), 121 (39.6), 63 (44.5); HRMS *m*/*z* calcd for $C_8H_6O_3$ M$^+$ 150.0317, found M$^+$ 150.0325.

4.2.15. (S)-(−)-Perillaldehyde. Yield: 135 mg (90%). Colorless oil. $[\alpha]_D^{23}$ −112 (*c* 1.00, $CHCl_3$); IR (KBr, neat): 3081 (w), 2932 (ms), 2843 (w), 2720 (w), 1690 (s) cm^{-1}; ^{1}H NMR (400 MHz): δ 9.46 (s, 1H), 6.86–6.84 (m, 1H), 4.78–4.74 (m, 2H), 2.50–2.44 (m, 2H), 2.31–2.15 (m, 3H), 1.97–1.90 (m, 1H), 1.79 (s, 3H), 1.57–1.37 (m, 1H); ^{13}C NMR

(100 MHz): δ 193.7, 150.6, 148.3, 141.3, 109.7, 40.8, 31.6, 26.4, 21.8, 20.7; MS: *m*/*z* 150 (M^+, 20.1), 107 (39.0), 79 (59.2), 68 (100.0); HRMS *m*/*z* calcd for $C_{10}H_{14}O$ M^+150.1045, found M^+150.1039.

4.2.16. Crotonaldehyde. Yield: 64 mg (91%). Colorless oil. IR (KBr, neat): 3039 (w), 2811 (w), 2727 (w), 1700 (s) cm^{-1}; ^1H NMR (400 MHz): δ 9.50 (d, *J*=7.8 Hz, 1H), 6.88 (qd, *J*=15.6, 6.8 Hz, 1H), 6.15 (qdd, *J*=15.6, 7.8, 1.6 Hz, 1H), 2.03 (dd, *J*=6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz): δ 194.0, 154.3, 134.6, 18.6; MS: *m*/*z* 70 (M^+, 12.7), 69 (100.0), 57 (17.4); HRMS *m*/*z* calcd for C_4H_6O M^+ 70.0419, found M^+ 70.0411.

4.2.17. Phenylacetaldehyde. Yield: 112 mg (93%). Colorless oil. IR (KBr, neat): 3029 (m), 2945 (m), 2823 (m), 2726 (m), 1720 (s) cm^{-1}; ^1H NMR (400 MHz): δ 9.65 (s, 1H), 7.38–7.28 (m, 5H), 3.61 (s, 2H); ^{13}C NMR (100 MHz): δ 199.0, 131.6, 129.3, 128.6, 127.6, 127.0, 50.3; MS: *m*/*z* 120 (M^+, 27.9), 91 (100.0), 65 (18.4); HRMS *m*/*z* calcd for C_8H_8O M^+ 120.0575, found M^+ 120.0570.

4.2.18. Cyclohexanecarboxaldehyde. Yield: 103 mg (92%). Colorless oil. IR (KBr, neat): 2910 (s), 2855 (ms), 2707 (ms), 1725 (s) cm^{-1}; ^1H NMR (400 MHz): δ 9.60 (s, 1H), 1.88–1.83 (m, 1H), 1.93–1.21 (m, 10H); ^{13}C NMR (100 MHz): δ 203.9, 48.9, 25.2, 24.1; MS: *m*/*z* 112 (M^+, 15.1), 111 (47.6), 96 (73.7), 83 (91.6), 55 (100.0); HRMS *m*/*z* calcd for $C_7H_{12}O$ M^+ 112.0888, found M^+ 112.0881.

Acknowledgements

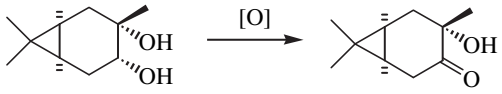
Financial support by the National Science Council of the Republic of China is gratefully acknowledged.

Supplementary data

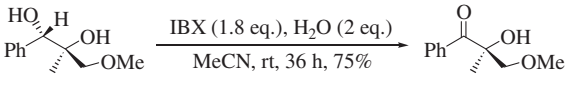
Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.10.053.

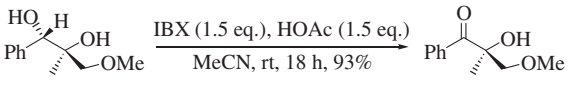
References and notes

1. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647–2650.
2. Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *20*, 399–402.
3. (a) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39–45; (b) Heilbron, S. I.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1949**, 604–607.
4. (a) Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, *9*, 3363–3366; (b) Collins, J. C.; Hess, W. W. *Org. Synth.* **1972**, *52*, 5–9.
5. Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 3027–3028.
6. (a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651–1660; (b) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482; (c) Mancuso, A. J.; Brownfain, D. S.; Swern, D. *J. Org. Chem.* **1979**, *44*, 4148–4150.
7. Parikh, J. R.; Doering, W. v. E. *J. Am. Chem. Soc.* **1967**, *89*, 5505–5507.
8. Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586–7587.
9. (a) Wirth, T.; Hirt, H. U. *Synthesis* **1999**, 1271–1287; (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523–2584; (c) Stang, P. J. *J. Org. Chem.* **2003**, *68*, 2997–3008; (d) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656–3665.
10. (a) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625–1627; (b) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639–666.
11. (a) Ganem, B. *J. Org. Chem.* **1975**, *40*, 1998–2000; (b) Ma, Z.; Bobbitt, J. M. *J. Org. Chem.* **1991**, *56*, 6110–6114; (c) Nooy, A. E. J. d.; Besemer, A. C.; Bekkum, H. v. *Synthesis* **1996**, 1153–1174.
12. (a) Oppenauer, R. V. *Recl. Trav. Chim.* **1937**, *56*, 137–144; (b) Graauw, C. F. d.; Peters, J. A.; Bekkum, H. v.; Huskens, J. *Synthesis* **1994**, 1007–1017; (c) Graves, C. R.; Zeng, B.-S.; Nguyen, S. T. *J. Am. Chem. Soc.* **2006**, *128*, 12596–12597.
13. (a) Fatiadi, A. J. *Synthesis* **1976**, 65–104; (b) Fatiadi, A. J. *Synthesis* **1976**, 133–167.
14. Frigerio, M.; Santagostino, M.; Sputore, S.; Palmisano, G. *J. Org. Chem.* **1995**, *60*, 7272–7276.
15. Hartmann, C.; Meyer, V. *Chem. Ber.* **1893**, *26*, 1727–1732.
16. Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019–8022.
17. Lapitskaya, M. A.; Vasiljeva, L. L.; Pivnitsky, K. K. *Mendeleev Commun.* **2008**, *18*, 309–311.
18. (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156; (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.
19. Thottumkara, A. P.; Vinod, T. K. *Tetrahedron Lett.* **2002**, *43*, 569–572.
20. Richardson, R. D.; Zayed, J. M.; Altermann, S.; Smith, D.; Wirth, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 6529–6532.
21. Zhdankin, V. V.; Smart, J. T.; Zhao, P.; Kiprof, P. *Tetrahedron Lett.* **2000**, *41*, 5299–5302.
22. 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.
23. Moorthy, J. N.; Singhal, N.; Senapati, K. *Tetrahedron Lett.* **2008**, *49*, 80–84.
24. Chen, J. J.; Aduda, V. *Synth. Commun.* **2007**, *37*, 3493–3499.
25. Moorthy, J. N.; Singhal, N.; Venkatakrishnan, P. *Tetrahedron Lett.* **2004**, *45*, 5419–5424.
26. Ozanne, A.; Pouységu, L.; Depernet, D.; François, B.; Quideau, S. *Org. Lett.* **2003**, *5*, 2903–2906.
27. Thottumkara, A. P.; Bowsher, M. S.; Vinod, T. K. *Org. Lett.* **2005**, *7*, 2933–2936.
28. (a) Kuhakarn, C.; Kittigowittana, K.; Pohmakotr, M.; Reutrakul, V. *Tetrahedron* **2005**, *61*, 8995–9000; (b) Kuhakarn, C.; Kittigowittana, K.; Ghabkham, P.; Pohmakotr, M.; Reutrakul, V. *Synth. Commun.* **2006**, *36*, 2887–2892.
29. More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001–3003.
30. (a) Karthikeyan, G.; Perumal, P. T. *Synlett* **2003**, 2249–2251; (b) Liu, Z.; Chen, Z.-C.; Zheng, Q.-G. *Org. Lett.* **2003**, *5*, 3321–3323; (c) Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Narsaiah, A. V. *Tetrahedron* **2004**, *60*, 2131–2135.
31. Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. *J. Org. Chem.* **2003**, *68*, 2058–2059.
32. (a) Mülbaier, M.; Giannis, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4393–4394; (b) Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4395–4397; (c) Lei, Z.; Denecker, C.; Jegasothy, S.; Sherrington, D. C.; Slater, N. K. H.; Sutherland, A. J. *Tetrahedron Lett.* **2003**, *44*, 1635–1637.
33. Plumb, J. B.; Harper, D. J. *Chem. Eng. News* **1990**, *68*, 3.
34. Swern oxidation, Jones reagent, and Parikn–Doring oxidation have been attempted for the following transformation but all gave unsatisfactory yields of the desired product.



35. A variety of solvents, such as THF, DCM, EtOAc, acetone, acetonitrile, and DMSO have been examined but acetonitrile was found to be the solvent of choice in our studies. IBX oxidation in acetonitrile was utilized in the preparation of the α-hydroxy ketone in our study on the synthesis of α-amino acids. In this study, the addition of 2 equiv of water was necessary to give 75% of the desired product (Lu, T.-J.; Lin, C.-K. J. Org. Chem., **2008**, *73*, 9527–9534, eq. 1). The reaction yield was greatly improved (93%) by replacing water with acetic acid (unpublished results, eq. 2).





36. Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537–4538.