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Iodoarene-catalyzed Oxidative Transformations Using Molecular Oxygen

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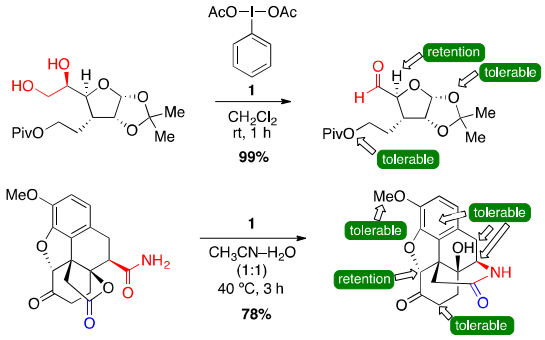
Molecular oxygen serves as a useful oxidant for glycol scission of 1,2-diols and Hofmann rearrangement of primary amides using pentamethyliodobenzene as a catalyst. Use of isobutyraldehyde and Lewis basic nitriles under O_2 enabled iodine(I)/(III) catalytic cycle, where *in situ*-generated peracid acts as a terminal oxidant.

Introduction

Hypervalent iodine compounds have been widely used in organic synthesis. Aryl-λ^3-iodanes with two heteroatom ligands (ArI(X)Y) now occupy a privileged position in oxidative transformations for organic synthesis because of their excellent oxidizing ability towards a wide range of organic compounds, low toxicity, and stability to heat and moisture.[1] For example, oxidative cleavage of 1,2-diols (glycol scission) and Hofmann rearrangement of primary amides proceed cleanly under mild conditions, providing a unique and valuable entry to synthetically complex organic molecules.[2,3] Nicolaou and co-workers have elegantly demonstrated that (diacetoxyiodo)benzene (**1**) enables highly chemoselective glycol scission of 1,2-diols while leaving a wide range of functionalities intact (Scheme 1).[2a] Fukuyama *et al.* have successfully established a late-stage Hofmann rearrangement by using **1** as a key step leading to total syntheses of (–)-oxycodone and (–)-oseltamivir.[3i,j] However, from the viewpoints of reagent cost and by-products formation, use of catalytic amount of ArI(X)Y-type λ^3-iodane would be preferable, but this is not yet well established.

Recent developments in simple methodologies for *in situ* generation of λ^3-iodanes with commercially available terminal oxidants have greatly enhanced their synthetic utility.[4] We have also reported iodobenzene-catalyzed oxidative transformations, including α-acetoxylation of ketones,[5] oxidative cleavage of carbon–carbon multiple bonds,[6] and Hofmann rearrangement of primary carboxamides.[7] However, these methods generally need notoriously explosive peracids, such as peracetic acid or *m*-CPBA.[1g-i,8,9] Several alternative terminal oxidants have also been reported. 1) Oxone® was developed as a safer terminal oxidant, but its use was essentially limited to aqueous media because of poor solubility in organic solvents.[1g-i,8,10,11] 2) Positive halogen sources such as *N*-bromosuccinimide (NBS) and Selectfluor® were reported as fungible oxidants, [4d,4i,4m,4n] but their synthetic utility is restricted by their high cost (NBS: 23$/mol; Selectfluor®: 935$/mol).[12] Therefore, replacement of them with molecular O_2 is an attractive solution.[13] We report herein the first example of O_2-mediated oxidative transformations (glycol scission and Hofmann rearrangement) under mild reaction conditions, in which isobutyraldehyde and pentamethyliodobenzene act as O_2-mediator and catalyst, respectively.



Scheme 1. Recent sophisticated examples of oxidative transformations using stoichiometric amount of $PhI(OAc)_2$.

Results and discussion

Aldehyde is gradually oxidized to carboxylic acid by molecular O_2 through peracid **4** (Scheme 2a).[14,15] It occurred to

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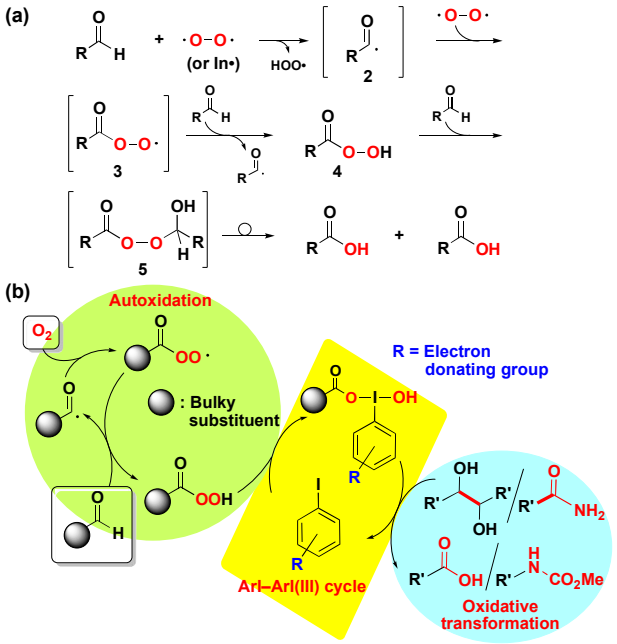
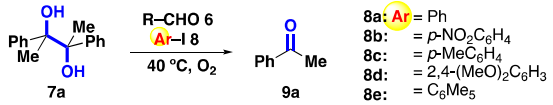
us that the *in situ*-generated peracid would be a suitable oxidant for iodoarene catalysis if undesired consumption of peracid *via* Criegee intermediate **5**[16] was suppressed. We thought that the key to control the formation of peracid might be the use of sterically hindered aldehyde. In our initial study, the autoxidation of isobutyraldehyde (**6a**) under an O_2 atmosphere (1 atm) in 1,2-dichloroethane (DCE) at 40 °C was quite fast, and after only 1 h perisobutyric acid was formed as a prominent species (Fig. S1). Further reaction with iodobenzene (**8a**) proceeded at a reasonable rate to afford a mixture of hypervalent iodine(III) species in high yield (5 h, 75%). Encouraged by these results, we applied this approach to the oxidative cleavage of 1,2-diols (Table 1).



Scheme 2. (a) Mechanism of autoxidation of aldehyde. (b) Working hypothesis.

In the presence of 10 mol% of **8a** and 3 eq of **6a**, exposure of 1,2-diol **7a** to molecular O_2 (1 atm) in DCE at 40 °C resulted in glycol scission to give acetophenone (**9a**) in 45% yield (entry 1). This is the first example of iodoarene-catalyzed O_2-mediated glycol scission. Use of other non-polar solvents did not improve the yield of **9a** (entries 2–4), but afforded significant amounts of Baeyer-Villiger oxidation (BVO) product, isopropyl formate and isobutyric acid.[16] In contrast, acetonitrile (possessing a greater hydrogen bond acceptor basicity, β value = 0.40)[17] dramatically improved the yield of **9a** (entry 5).[18] In this system, electron-rich iodoarenes showed excellent catalytic activity, probably due to a greatly enhanced rate of formation of iodine(III) species, as well as suppression of over-oxidation of **9a** (*e.g.*, α-hydroxylation, BVO, and so on) (entries 6–8). However, highly electron-rich 2,4,6-(trimethoxy)iodobenzene and aliphatic iodobutane, resulted in a decreased yield of **9a** (30-33%), probably because of degradation of the catalyst.[7] Among various iodoarenes, pentamethyliodobenzene (**8e**) was the best (entry 9). Although both aliphatic and aromatic aldehydes can be used, best result was obtained by **6a** (entries 12–16). This is attractive from a synthetic viewpoint, because **6a** is an inexpensive petroleum-derived aldehyde (3$/mol).[12,19] Note that the reaction proceeds smoothly even in air or in the dark (entries 17 and 18). Importantly, the *in situ*-generated peracid is a *transient species and could not be detected at all at the end of the reaction*, enabling the reaction to be safely scaled-up (entry 19).[20] Gratifyingly, the amount of **6a** can be reduced to 1.5 eq on 10 mmol scale (entry 20).

Table 1 Catalytic oxidative cleavage of 1,2-diol **7a**[a]



Entry	solvent	Ar–I **8** (mol%)	R–CHO **6** (R =)	time (h)	yield (%)[b]
1	DCE	**8a** (10)	**6a** (*i*-Pr)	25	45
2	$CHCl_3$	**8a** (10)	**6a** (*i*-Pr)	9	43
3	PhH	**8a** (10)	**6a** (*i*-Pr)	11	0
4	CyH	**8a** (10)	**6a** (*i*-Pr)	7	0
5	MeCN	**8a** (10)	**6a** (*i*-Pr)	48	99
6	MeCN	**8b** (10)	**6a** (*i*-Pr)	72	43
7	MeCN	**8c** (10)	**6a** (*i*-Pr)	24	100
8	MeCN	**8d** (10)	**6a** (*i*-Pr)	11	100
9	MeCN	**8e** (10)	**6a** (*i*-Pr)	10	100
10	MeCN	**8e** (5)	**6a** (*i*-Pr)	24	100
11	MeCN	–	**6a** (*i*-Pr)	24	9
12	MeCN	**8e** (5)	**6b** (Me)	48	66
13	MeCN	**8e** (5)	**6c** (n-pent)	32	95
14	MeCN	**8e** (5)	**6d** (*t*-Bu)	24	86[c]
15	MeCN	**8e** (5)	**6e** (Ph)	24	92[c]
16	MeCN	**8e** (5)	**6e** (3-ClC_6H_4)	24	54[c]
17[d]	MeCN	**8e** (5)	**6a** (*i*-Pr)	24	100
18[e]	MeCN	**8e** (5)	**6a** (*i*-Pr)	24	90
19[f]	MeCN	**8e** (5)	**6a** (*i*-Pr)	48	90 (74)
20[f,g]	MeCN	**8e** (5)	**6a** (*i*-Pr)	48	77 (68)

[a] Conditions: **7a** (0.24 mmol, 0.2 M)/**6** (3 eq)/O_2 (1 atm). [b] GC yields. Isolated yield is given in parentheses. [c] ^{1}H NMR yields. [d] In the dark. [e] In air. [f] **7a** (10 mmol) was used. [g] **6a** (1.5 eq) was used.

With these optimized conditions in hand, we studied the scope of the new protocol, which proved effective for the glycol scisson of a wide range of 1,2-diols (Table 2). Dihydrobenzoin (**7b**) was cleanly converted to benzoic acid (**9b**) in 76% yield after Pinnick oxidative workup. The electronic effect at benzylic carbons had little influence on the reactivity of diols and various dihydrobenzoins with an electron-donating group (*p*-MeO or Me) or an electron-withdrawing group (Cl or CF_3) on the phenyl ring were also smoothly cleaved to give the corresponding carboxylic acids **9c-f** within 24 h in good yields. In addition, various *mono*- and *di*-substituted diols **7g-j** were

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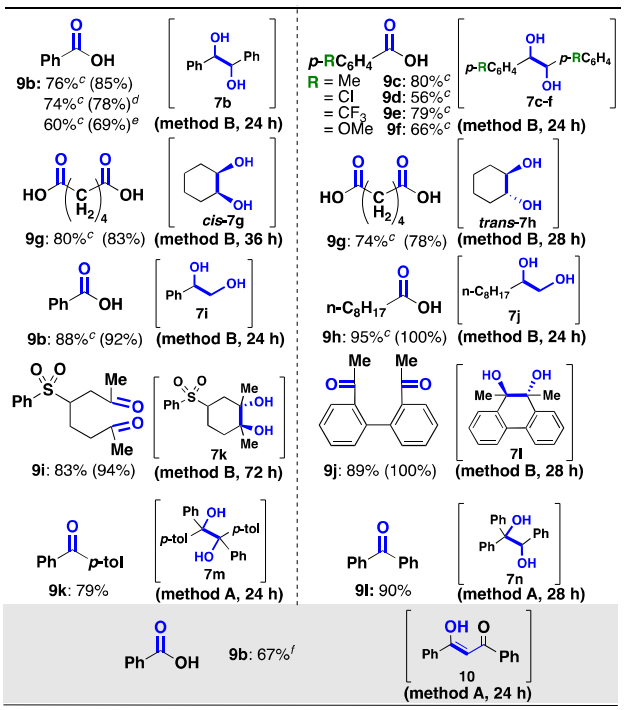
compatible with the reaction conditions. Sterically congested tri- and tetra-substituted diols **7k**-**n** were not deleterious to the reaction. It is interesting to note that typical oxidants for glycol scissions, such as $NaIO_4$, generally cannot cleave cyclic *trans*-diols with a large and rigidly held distance between two oxygen atoms, whereas our methods were also effective for such substrates (**7k** and **7l**).[2e] It should be noted that under the optimized conditions (method A, Table 1, entry 10), the use of 1,2-diols possessing α-C–H bonds caused low reproducibility, probably because of inhibition of autoxidation of **6a**. For these cases, a slightly modified reaction conditions (method B) greatly improved the efficiency/reproducibility of the reaction, in which pre-mixing of aldehyde **6a** and O_2 for 3 h prior to the addition of substrate in a less polar solvent system (DCE–*t*-BuCN (9:1)) was used. The reaction conditions were quite robust: we found no significant decrease of the yield in air or with excess water (10 eq). Interestingly, this system can be applied to convert 1,3-diketone **10** to **9b**, which is not feasible in the absence of iodoarene **8e**.[21,22]

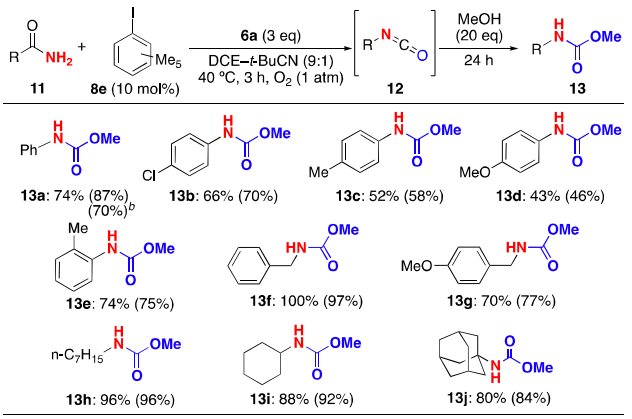
Table 2 Iodoarene-catalyzed oxidative cleavage of 1,2-diols under O_2[a,b]



[a] Conditions, diol **7**/**8e**/**6a**/O_2 (1 atm). Method A: **7** (0.24 mmol)/**8e** (5 mol%)/**6a** (3 eq)/MeCN. Method B: **7** (0.1 mmol)/**8e** (20 mol%)/**6a** (5 eq)/DCE–*t*-BuCN (9:1). Structures in brackets are starting materials. [b] Isolated yields. ^{1}H NMR yields are given in parentheses. [c] Isolated yields determined after Pinnick oxidation of the reaction mixture. [d] In air. [e] H_2O (10 eq) was added. [f] **6a** (5 eq).

We recently reported the iodoarene-catalyzed Hofmann rearrangement of carboxamides using *m*-CPBA as a terminal oxidant.[7] However, this protocol is still unsatisfactory in terms of its rather low functional group compatibility: for example, 1) strong Brønsted acid, HBF_4 was essential for the smooth catalytic reaction, and hence, acid–sensitive functional groups cannot survive. In addition, 2) aromatic amides cannot be used, because of over-oxidation.[23] The present system using O_2 overcomes these drawbacks. Exposure of benzamide (**11a**) to **8e** (10 mol%) and **6a** (3 eq) under O_2 resulted in the generation of the corresponding isocyanate **12a**, which was trapped by methanol to give methyl *N*-phenylcarbamate (**13a**) in 74% yield (Table 3). Remarkably, the reaction could be reproduced in air without significant decrease in yield (**13a**: 70%). A variety of amides, including both electron-rich and electron-deficient benzamides, as well as aliphatic 1°-, 2°-, and 3°-alkyl carboxamides, could be utilized. Hofmann rearrangement of alkyl- and aryl carboxamide using a stoichiometric amount of **1** generally requires a strong base such as KOH in order to suppress unwanted side reactions, such as urea formation, oxidation of the aromatic ring, *etc.*,[1b,3] whereas no formation of any *N*,*N*'-dialkylureas or benzoquinone was observed in this system, partly due to the weakly acidic or neutral conditions (pH 4-6).[24]

Table 3 Hofmann rearrangement of carboxamide **11**.[a]



[a] Isolated yields. ^{1}H NMR yields are given in parentheses. [b] In air.

Conclusions

In summary, we have succeeded in utilizing O_2 as the terminal oxidant for the first time. This system opens up facile access to synthetically versatile oxidative cleavage of various 1,2-diols and Hofmann rearrangement of carboxamides in up to quantitative yield by reacting the substrate in the presence of 3 eq of *i*-PrCHO **6a** and a catalytic amount of iodoarene **8e** under 1 atm of O_2/air at 40 °C. This protocol is applicable to gram-scale synthesis and its functional group tolerance compares favorably with that of previously reported protocols. Studies to expand the scope of the catalytic oxidative transformations and to elucidate the reaction mechanism are ongoing in our laboratory.

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Notes and references

1 (*a*) G. F. Koser, *Halonium Ions* in The Chemistry of Functional Groups, Supplement D, eds. S. Patai, Z. Rappoport, John Wiley & Sons, New York, 1983, Ch. 18, p. 721; (*b*) A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH Publishers, New York, 1992; (*c*) P. J Stang, V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (*d*) M. Ochiai, In *Chemistry of Hypervalent Compounds,* ed. K. Akiba, VCH Publishers, New York, 1999; (*e*) *Hypervalent Iodine Chemistry*, ed. T. Wirth, Topics in Current Chemistry, **224**, Springer, Berlin, 2003; (*f*) V. V. Zhdankin, P. Stang, *Chem. Rev.*, 2008, **108**, 5299; (*g*) V. V. Zhdankin, *Hypervalent Iodine Chemistry*, John Wiley & Sons, New York, 2014; (*h*) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328; (*i*) *Hypervalent Iodine Chemistry*, ed. T. Wirth, Topic in Current Chemistry, **373**, Springer, Berlin, 2016.

2 (*a*) K. C. Nicolaou, V. A. Adsool, C. R. H. Hale, *Org. Lett.*, 2010, **12**, 1552; (*b*) R. Criegee, H. Beuker, *Justus Liebigs Ann. Chem.*, 1939, **541**, 218; (*c*) S. Spyroudis, A. Varvoglis, *Synthesis*, 1975, 445; (*d*) M. Okawara, Y. Kurusu, E. Imoto, *Kogyo Kagaku Zasshi,* 1962, **65**, 816; (*e*) S. J. Angyal, R. J. Young, *J. Am. Chem. Soc.*, 1959, **81**, 5251; (*f*) K. H. Pausacker, *J. Chem. Soc.*, 1953, 107.

3 (*a*) A. S. Radhakrishna, M. E. Parham, R. M. Riggs, G. M. Loudon, *J. Org. Chem.*, 1979, **44**, 1746; (*b*) G. M. Loudon, A. S. Radhakrishna, M. R. Almond, J. K. Blodgett, R. H. Boutin, *J. Org. Chem.*, 1984, **49**, 4272; (*c*) A. L. J. Beckwith, L. K. Dyall, *Aust. J. Chem.*, 1990, **43**, 451; (*d*) R. M. Moriarty, C. J. Chany, R. K. Vaid, O. Prakash, S. M. Tuladhar, *J. Org. Chem.*, 1993, **58**, 2478; (*e*) H. Togo, T. Nabana, K. Yamaguchi, *J. Org. Chem.*, 2000, **65**, 8391; (f) I. M. Lazbin, G. F. Koser, *J. Org. Chem.*, 1986, **51**, 2669; (*g*) A. Vasudevan, G. F. Koser, *J. Org. Chem.*, 1988, **53**, 5158; (*h*) A. S. Radhakrishna, C. G. Rao, R. K. Varma, B. B. Singh, S. P. Bhatnagar, *Synthesis*, 1983, 538; (*i*) A. Kimishima, H. Umihara, A. Mizoguchi, S. Yokoshima, T. Fukuyama, *Org. Lett.*, 2014, **16**, 6244; (*j*) N. Satoh, T. Akiba, S. Yokoshima, T. Fukuyama, *Angew. Chem., Int. Ed.*, 2007, **46**, 5734; (*k*) J. W. Hilborn, Z.-H. Lu, A. R. Jurgens, Q. K. Fang, P. Byers, S. A. Wald, C. H. Senanayake, *Tetrahedron Lett.*, 2001, **42**, 8919.

4 For selected examples: (*a*) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem., Int. Ed.*, 2005, **44**, 6193; (*b*) A. P. Thottumkara, M. S. Bowsher, T. K. Vinod, *Org. Lett.*, 2005, **7**, 2933; (*c*) Y. Yamamoto, H. Togo, *Synlett,* 2006, 798; (*d*) D. C. Braddock, G. Cansell, S. A. Hermitage, *Chem. Commun.*, 2006, 2483. Selected asymmetric oxidations: (*e*) T. Dohi, A. Maruyama, N. Takenaga, K. Senami, Y. Minamitsuji, H. Fujioka, S. B. Caemmerer, Y. Kita, *Angew. Chem., Int. Ed.*, 2008, **47**, 3787; (*f*) S. M. Altermann, R. D. Richardson, T. K. Page, R. K. Schmidt, E. Holland, U. Mohammed, S. M. Paradine, A. N. French, C. Richter, A. M. Bahar, B. Witulski, T. Wirth, *Eur. J. Org. Chem.*, 2008, 5315; (*g*) S. Quideau, G. Lyvinec, M. Marguerit, K. Bathany, A. Ozanne-Beaudenon, T. Buffeteau, D. Cavagnat, A. Chénedé, *Angew. Chem., Int. Ed.,* 2009, **48**, 4605; (*h*) M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem., Int. Ed.,* 2010, **49**, 2175; (*i*) D. C. Fabry, M. Stodulski, S. Hoerner, T. Gulder, *Chem. Eur. J.*, 2012, **18**, 10834; (*j*) M. Shimogaki, M. Fujita, T. Sugimura, *Eur. J. Org. Chem.,* 2013, 7128; (*k*) K. A. Volp, A. M. Harned, *Chem. Commun.*, 2013, **49**, 3001; (*l*) S. Suzuki, T. Kamo, K. Fukushi, T. Hiramatsu, E. Tokunaga, T. Dohi, Y. Kita, N. Shibata, *Chem. Sci.,* 2014, **5**, 2754; (*m*) A. Alhalib, S. Kamouka, W. J. Moran, *Org. Lett.,* 2015, **17**, 1453; (*n*) I. G. Molnár, R. Gilmour, *J. Am. Chem. Soc.,* 2016, **138**, 5004.

5 M. Ochiai, Y. Takeuchi, T. Katayama, T. Sueda, K. Miyamoto, *J. Am. Chem. Soc.*, 2005, **127**, 12244.

6 K. Miyamoto, Y. Sei, K. Yamaguchi, M. Ochiai, *J. Am. Chem. Soc.*, 2009, **131**, 1382.

7 K. Miyamoto, Y. Sakai, S. Goda, M. Ochiai, *Chem. Commun.,* 2012, **48**, 982.

8 H. Hussain, I. R. Green, I. Ahmed, *Chem. Rev.,* 2013, **113,** 3329.

9 Many serious accidents due to explosion/fire during the use of percarboxylic acid have been reported. See: (*a*) N. A. Milas, A. McAlevy, *J. Am. Chem. Soc.,* 1934, **56**, 1221; (*b*) L. S. Silbert, E. Siegel, D. Swern, *Org. Synth.,* 1964, **44**, 81; (*c*) A. I. Meyers, S. Schwartzman, G. L. Olson, H.-C. Cheung, *Tetrahedron Lett.,* 1976, **17**, 2417; (*d*) R. B. King, W. M. Douglas, A. Efraty, *Org. Synth.,* 1977, **56**, 1.

10 H. Hussain, I. R. Green, I. Ahmed, *Chem. Rev.,* 2013, **113**, 3329.

11 IBS-catalyzed oxidation does not require the aqueous media. M. Uyanik, T. Mutsuga, K. Ishihara, *Molecules,* 2012, **17**, 8604.

12 Data taken from TCI America: http://www.tcichemicals.com/en/ns/index.html.

13 Several studies on iodoarene-catalyzed oxidation of alcohol using O_2 have been reported. (*a*) R. Mu, Z. Liu, Z. Yang, Z. Liu, L. Wu, Z.-L. Liu, *Adv. Synth. Catal.,* 2005, **347**, 1333; (*b*) C. I. Herrerías, T. Y. Zhang, C.-J. Li, *Tetrahedron,* 2006, **47**, 13. But, according to the following reports by Ishihara and Iwabuchi, those reaction mechanisms do not seem to involve a iodine(III)-catalyzed pathway. (*c*) M. Uyanik, R. Fukatsu, K. Ishihara, *Chem. Asian J.,* 2010, **5**, 456; (*d*) M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa, Y. Iwabuchi, *J. Am. Chem. Soc.*, 2011, **133**, 6497.

14 (*a*) *Purification of Laboratory Chemicals*, eds. W. L. F. Armarego, C. L. L. Chai, Elsevier, Oxford, 2009; (*b*) J. R. McNesby, C. A. Heller Jr., *Chem. Rev.,* 1954, **54**, 325.

15 C. Marteau, F. Ruyffelaere, J.-M. Aubry, C. Penverne, D. Favier, V. Nardello-Rataj, *Tetrahedron,* 2013, **69**, 2268.

16 (*a*) A. Baeyer, V. Villiger, *Ber. Dtsch. Chem. Ges.,* 1899, **32**, 3625. For reviews, see: (*b*) G. R. Krow, *Org. React.,* 1993, **43**, 251; (*c*) G. Strukul, *Angew. Chem., Int. Ed.,* 1998, **37**, 1198; (*d*) M. Renz, B. Meunier, *Eur. J. Org. Chem.,* 1999, 737; (*e*) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Chem. Rev.*, 2004, **104**, 4105.

17 C. Reichardt, *Solvent and Solvent Effects in Organic Chemistry*, Wiley, Weinheim, 1979.

18 Lewis basic solvent, CH_3CN probably suppresses hydrogen bonding, which has been suggested to be the key factor for undesired Criegee intermediate formation. See: (*a*) F. Grein, A. C. Chen, D. Edwards, C. M. Crudden, *J. Org. Chem.*, 2006, **71**, 861. For theoretical calculation for BVO of aldehyde, see: (*b*) M. Ochiai, A. Yoshimura, K. Miyamoto, S. Hayashi, W. Nakanishi, *J. Am. Chem. Soc.*, 2010, **132**, 9236.

19 Transition metal-catalyzed C–H oxidation using *in situ*-generated peracetic acid from inexpensive CH_3CHO and O_2 was reported by Murahashi and co-workers, see: (*a*) S.-I. Murahashi, T. Naota, N. Komiya, *Tetrahedron Lett.*, 1995, **36**, 8059; (*b*) S.-I. Murahashi, X.-G. Zhou, N. Komiya, *Synlett*, 2003, 321.

20 The absence of any peracid in the reaction mixture was confirmed by both ^{1}H NMR measurement and KI test.

21 $PhI(OAc)_2$ undergoes oxidative cleavage of 1,3-diketone, see: B. Podolešov, *J. Org. Chem.*, 1984, **49**, 2644.

22 Photo-induced oxidative cleavage of 1,3-diketones using I_2 under O_2, see: N. Tada, M. Shomura, L. Cui, T. Nobuta, T. Miura, A. Itoh, *Synlett*, 2011, 2896.

23 A large amount of benzoquinone was observed during the reaction of benzamide under our previous reaction conditions. See, reference 7. See also: A. A. Zagulyaeva, C. T. Banek, M. S. Yusubov, V. V. Zhdankin, *Org. Lett.,* 2010, **12**, 4644.