Organoiodine-Catalyzed Oxidative Spirocyclization of Phenols using Peracetic Acid as a Green and Economic Terminal Oxidant

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The use of peracetic acid as a green and economical terminal oxidant in fluoroalcohol solvents could provide a practical iodoarene-catalyzed oxidation of phenols to give spirodienones. Acetic acid and water were the only co-products and waste, and thus this catalytic approach utilizing fluoroalcohol media could simplify the reaction workup procedure for product isolation.

Manuscript received: 13 March 2009. Final version: 30 April 2009.

Introduction

Hypervalent iodine reagents such as phenyliodine diacetate (PIDA) and phenyliodine bis(trifluoroacetate) (PIFA) have been widely recognized as extremely useful and environmentally friendly oxidizing reagents, replacing the highly toxic heavy metal oxidants, i.e. Pb^{IV} , Hg^{II} , and Tl^{III} .^[1] The recent significant breakthrough in their application is the fact that useful stoichiometric organo-oxidants have now been utilized successfully in various oxidations by catalytic means.^[2] As pioneering work, we demonstrated in 2005 that *m*-chloroperbenzoic acid (mCPBA) is a versatile terminal oxidant to construct an efficient II to IIII catalytic cycle for the iodoarene-catalyzed oxidations of phenols.^[3] In the same year, Ochiai's group also reported in the literature the iodobenzene-catalyzed α -acetoxylation of ketones using *m*CPBA in which diacyloxy(phenyl)- λ^3 -iodanes acted as real oxidants.^[4] With the recent growing interest in greener synthetic processes, the catalytic utilization of hypervalent iodine reagents is increasing in importance to broaden the utility of the reagents in organic synthesis, leading to a new route to the development of organocatalysts.

In early studies, [3-5] *m*CPBA initially played a pivotal role as a unique terminal oxidant in catalytic cycles to generate efficiently the active catalytic iodine(III) species from iodoarenes in situ. However, in view of atom economy and cost performance, [6]*m*CPBA is not an ideal terminal oxidant for the catalytic strategy. In addition, commercially available stabilized *m*CPBA, containing large amounts of water, is potentially explosive in the absolutely dry form. Accordingly, optimization of the terminal oxidant to a more favourable one should be the next challenge to be investigated for the realization of a practical, economical, safe, and clean organocatalytic process.





Herein, we report inexpensive and environmentally friendly peracetic acid (PAA) as the terminal oxidant in the iodoarenecatalyzed oxidation of phenols 2 to give spirodienones 3, in which PAA acts as an efficient generator of the reactive aryliodine(III) diacetates 1 from iodoarene catalysts with the aid of fluoroalcohol solvents (Scheme 1).

Result and Discussion

PAA is known as a safe and environmentally friendly oxidant that releases non-toxic acetic acid as the co-product. It is commercially available in dilute acetic acid solutions from some



Entry	Solvent	Time [h]	Yield of 3a [%]
1 ^A	CH ₂ Cl ₂	24	31
2	CH_2Cl_2	24	20
3	Toluene	24	33
4	THF	24	Trace
5	CH ₃ CN	10	8
6	MeOH	24	18
7	TFE	3	66
8	HFIP	1	82
9	None ^B	24	25

^A1 equiv. of trifluoroacetic acid was added.

^B9% peracetic acid solution was used as solvent.

chemical product companies, or alternatively, is prepared from hydrogen peroxide and acetic anhydride before use.^[7] PAA solution is frequently employed in industrial-scale oxidations such as epoxidation or the Baeyer–Villiger reaction. Furthermore, a 0.2–0.3% solution of PAA is widely utilized as a disinfectant in medical use.

With a commercially available ~9% (v/v) PAA solution in acetic acid (net 5 equiv. of PAA was used), we examined the reaction of 3-(4-hydroxyphenyl)propionic acid **2a** using a 10 mol-% amount of iodobenzene (Table 1). The reaction was performed at ~35°C to suitably induce the oxidation ability of PAA towards iodoarenes.^[8] Relying on the optimized reaction conditions established in the case of *m*CPBA,^[3a] we first started our survey of the reaction in dichloromethane, which gave only disappointing results in the obtained yield of **3a** (entries 1 and 2). We therefore next tried to perform the reaction using 2,2,2trifluoroethanol (TFE).^[3b] At this stage, we noted the remarkable effect of the fluorinated alcohol solvent^[9,10] on the catalytic phenol oxidation with PAA.

As shown in Table 1, systematic screening of the solvents was used to verify the yield of the spirodienone product **3a**. Other conventional non-polar or polar solvents such as toluene, THF, acetonitrile, and methanol were employed with generally unsatisfactory results (entries 3–6). In contrast, simple replacement of dichloromethane by TFE remarkably improved the yield of the obtained product **3a** (entry 7). The use of a more polar and acidic fluoroalcohol, 1,1,1,3,3,3- hexafluoroiso-propanol (HFIP), as solvent^[11] led to a further increase in the yield to reach 82% (entry 8); the conditions gave the product **3a** in a better yield than that under the previously optimized conditions using *m*CPBA.^[3a] Finally, the PAA solution was also examined as solvent (entry 9).

Regarding the catalyst, 4-iodotoluene showed the best result in both turnover number (TON) and turnover frequency (TOF) in the reaction among those examined. The effect of the iodoarene catalysts on the reaction of **2a** to **3a** at 5 mol-% of the catalysts was established as follows: iodobenzene (1 h, 80%), 4-iodotoluene (1 h, 88%), 4-iodoanisole (5 h, 50%), 4fluoroiodobenzene (2 h, 68%), 4-nitroiodobenzene (24 h, 40%). 649

In the last case, the presence of the electron-withdrawing group on the aromatic ring clearly inhibited the smooth generation of the corresponding iodine(III) by the action of PAA. Thus, the iodine atom in the catalyst must be moderately activated towards the terminal oxidant, similarly to the case with *m*CPBA.^[3] No reaction, needless to say, was observed under the catalyst-free conditions.

With the optimized conditions in hand, we confirmed the versatility of the method using several types of phenol derivatives **2** with 5 mol-% of 4-iodotoluene. It has been established that PAA could serve as the efficient terminal oxidant in HFIP for the oxidative C–O bond-forming reaction of phenols **2** to construct a wide range of spirodienone lactone structures (Table 2). The oxidative transformation of various phenol derivatives **2** could indeed occur smoothly in good to excellent yields under short reaction times. In particular, the acid-sensitive spirodienone that decomposed in strongly acidic conditions^[3a] was obtained in an acceptable yield under milder conditions (entry f). The less polar TFE was used for the naphthol derivatives because background side reactions attributed to the oxidations of the naphthol ring were dominant in HFIP to give a complex mixture (entry k).

The catalytic conditions with PAA were also compatible with a nitrogen-containing substrate $4^{[12]}$ without any optimization to furnish the spiro C–N bond (Scheme 2). The spirodienone structures of 3 and 5 are known to exist as the core components of various biologically active compounds and natural products and are key intermediates in biosynthetic processes.^[13]

Our catalytic method with PAA generates only easily removable acetic acid and water as co-products. This makes the product isolation step simpler, and the almost-pure products were obtained by a simple aqueous workup. Any tedious purification procedures such as column chromatography were not necessary, and the used HFIP could be reused repeatedly after distillation; these merits would provide a highly practical and environmentally benign method for the organocatalytic oxidation of phenols.

To determine the existence of hypervalent iodine(III) species in the catalytic cycle, we conducted the following experiments (Scheme 3). In the absence of phenols **2**, 4-iodotoluene was heated with PAA (5 equiv. relative to 4-iodotoluene) in HFIP (0.25 M) at 35°C for 1 h. The exclusive formation of the corresponding iodine(III) could be confirmed this time by isolation of trivalent 4-(diacetoxyiodo)toluene **1a** (90% yield, see Experimental Section) as expected. However, the same operation in dichloromethane was less effective and partial formation of **1a** was detected (**1a**: 47% yield). These results clearly suggest that HFIP accelerates the formation of the active catalytic species **1** during the reactions. In addition, the fluoroalcohols can also facilitate smooth generation of reactive phenoxenium ion intermediates mediated by the hypervalent iodine(III) reagents, leading to the products **3**.^[14]

Conclusions

The main goal of the catalytic approach is to design a practical and sustainable process by using low-cost and environmentally friendly terminal oxidants. In the present work, we have established PAA as a green and economical terminal oxidant in the iodoarene-catalyzed oxidation of phenols. When using PAA in fluoroalcohol media, that is, HFIP and TFE, it functions as an efficient generator of the active iodine(III) species **1**. The use of PAA results in the formation of only non-toxic acetic acid and water, and hence we believe that the present system

Table 2. 4-Iodotoluene-catalyzed spirocyclization of various phenol derivatives 2 using PAA as terminal oxidant

Conditions: phenols 2 (1 mmol), 4-iodotoluene (5 mol-%), AcOOH (5 equiv.) in HFIP (6 mL) at 35°C for 1 h

Entry	Phenol 2 $R^1 \rightarrow R^2$ $R^3 \rightarrow CO_2 H$		Product 3 $R^1 \rightarrow R^2$ $R^3 \rightarrow Q$ $R^4 \rightarrow Q$		Yield [%] ^A
	R ¹	R ²	R ³	R ⁴	
a b c d e f g h	H Me H Br OMe Br Br Br	H H H H Br Me	H H Me H H Me Me	H H Me H H H H	88 72 80 75 83 46 81 97
i		-CO ₂ H			87
j	Me	он Ме -cO ₂ H	Me –	Me	79 ^B
k ^C		рн -со₂н			62

^AIsolated yield of the products **3**.

^BThe products were obtained as a 51:49 mixture of the diastereoisomers.

^C2,2,2-Trifluoroethanol was used as solvent.





Scheme 2.

basis of PAA with fluoroalcohol media could become a valuable organocatalytic process in line with the recent directions of green synthesis.

Experimental

Melting points (mp) were measured using a Büchi B-545 apparatus. Infrared spectra (IR) were recorded on a Hitachi 270–50 spectrometer; absorptions are reported in reciprocal

centimetres. ¹H and ¹³C NMR spectra were recorded on a JEOL JMN-300 spectrometer operating at 300 MHz in CDCl₃ at 25°C with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad singlet, m = multiplet), coupling constant (Hz), and integration. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. The column chromatography and TLC were carried out on Merck Silica gel 60 (230–400 mesh) using hexane/AcOEt as eluent; the spots were detected

by UV irradiation (254, 365 nm). The 9% v/v PAA solution was purchased from Sigma–Aldrich Japan. All commercially available reagents and solvents were used as received without further purification.

General Experimental Procedure for Compounds 3

To a stirred solution of 3-(4-hydroxyphenyl)propionic acid **2a** (166.2 mg, 1.0 mmol) and catalyst 4-iodotoluene (10.9 mg, 0.05 mmol) in HFIP was added commercially available PAA solution (9% v/v in acetic acid, 2.2 mL, ~5 mmol). The reaction mixture was then stirred for 1 h while the reaction temperature was maintained at ~35°C. After the reaction was complete, AcOEt was added and the organic layer was washed with water, saturated aqueous NaHCO₃, and then dried over anhydrous Na₂SO₄. Evaporation of the solvent under vacuum afforded the almost pure product, 1-oxaspiro[4,5]deca-6,9-diene-2,8-dione **3a**, which was further purified by short column chromatography on silica-gel to give pure **3a** (144.5 mg, 0.88 mmol) in 88% yield.

3a:^[3] colourless solid; mp: 106–107°C. ν_{max} (KBr)/cm⁻¹ 3048, 2955, 2930, 2855, 1782, 1678. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 2.37 (d, *J* 8.3, 2H), 2.78 (d, *J* 8.3, 2H), 6.28 (d, *J* 10.0, 2H), 6.85 (d, *J* 10.0, 2H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 27.8, 32.1, 78.4, 129.0, 145.5, 175.2, 184.0.

3b: colourless solid; mp: 115–116°C. ν_{max} (KBr)/cm⁻¹ 3535, 2925, 1776, 1676, 1649, 1450, 1396, 1367, 1296, 1226, 1178, 1153, 1109, 1020, 960. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 1.98 (s, 3H), 2.36 (d, *J* 8.1, 2H), 2.78 (d, *J* 8.1, 2H), 6.28 (d, *J* 10.2, 1H), 6.61–6.63 (m, 1H), 6.82 (dd, *J* 9.9, 3.3, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 15.5, 28.0, 32.2, 79.0, 129.0, 136.1, 140.8, 145.2, 175.4, 184.8. (Anal. calc. for C₁₀H₁₀O₃: C 67.41, H 5.66. Found: C 67.32, H 5.63%.)

3c: colourless solid; mp: 79–80°C. ν_{max} (KBr)/cm⁻¹ 2970, 1790, 1674, 1633, 1456, 1386, 1344, 1278, 1218, 1147, 1068, 1017, 975. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 1.02 (d, *J* 6.6, 3H), 2.44 (dd, *J* 17.1, 11.7, 1H), 2.62–2.75 (m, 1H), 2.85 (q, *J* 8.3, 1H), 6.32–6.40 (m, 2H), 6.79 (d, *J* 10.2, 2H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 13.5, 35.4, 39.4, 81.7, 130.2, 142.6, 145.8, 174.4, 184.3. (Anal. calc. for C₁₀H₁₀O₃: C 67.41, H 5.66. Found: C 67.35, H 5.67%.)

3d: colourless solid; mp: 122–123°C. ν_{max} (KBr)/cm⁻¹ 3541, 2968, 2933, 1787, 1672, 1633, 1610, 1460, 1388, 1278, 1257, 1215, 1151, 1068, 1017, 945. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 1.29 (d, *J* 6.9, 3H), 2.10 (t, *J* 12.5, 1H), 2.51 (dd, *J* 13.2, 8.7, 1H), 2.90–2.97 (m, 1H), 6.29 (t, *J* 10.8, 2H), 6.79 (dd, *J* 9.9, 3.0, 1H), 6.89 (dd, *J* 9.9, 3.0, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 15.4, 34.3, 40.4, 76.1, 128.7, 129.5, 144.9, 146.9, 177.8, 184.1. (Anal. calc. for C₁₀H₁₀O₃: C 67.41, H 5.66. Found: C 67.23, H 5.68%.)

3e: colourless solid; mp: 173–174°C. ν_{max} (KBr)/cm⁻¹ 3051, 1782, 1676, 1643, 1608, 1456, 1419, 1380, 1340, 1296, 1220, 1172, 1140, 1070, 1020, 960. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 2.43 (t, *J* 8.4, 2H), 2.81 (t, *J* 6.0, 2H), 6.43 (d, *J* 10.8, 1H), 6.89 (dd, *J* 10.2, 3.0, 1H), 7.30 (d, *J* 3.0, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 27.7, 31.9, 80.1, 125.8, 127.7, 145.7, 145.8, 174.5, 177.0. (Anal. calc. for C₉H₇BrO₃: C 44.47, H 2.90, Br 32.87. Found: C 44.31, H 3.02, Br 32.77%.)

3f: colourless solid; mp: 89–90°C. ν_{max} (KBr)/cm⁻¹ 2937, 2909, 2851, 2833, 1770, 1682. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 2.41 (t, *J* 8.7, 2H), 2.78 (t, *J* 8.7, 2H), 3.70 (s, 3H), 5.72 (d, *J* 2.8, 1H), 6.26 (d, *J* 10.0, 1H), 6.84 (dd, *J* 10.0, 2.8, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 28.3, 33.3, 55.2, 80.9, 112.8, 128.2, 145.8, 151.0, 175.2, 179.6. (Anal. calc. for C₁₀H₁₀O₄: C 61.85, H 5.19. Found: C 61.79, H 5.22%.)

3g: colourless solid; mp: 103–104°C. ν_{max} (KBr)/cm⁻¹ 2931, 1793, 1685, 1596, 1458, 1419, 1319, 1263, 1218, 1151, 1124, 975. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 1.10 (d, *J* 6.9, 3H), 2.46 (dd, *J* 16.5, 11.4, 1H), 2.73–2.93 (m, 2H), 6.45–6.51 (m, 1H), 7.22–7.25 (m, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 13.8, 35.1, 39.6, 84.7, 123.8, 123.9, 143.7, 146.5, 171.5, 173.3. (Anal. calc. for C₁₀H₈Br₂O₃: C 35.75, H 2.40, Br 47.57. Found: C 35.71, H 2.45, Br 47.27%.)

3h (diastereomixture):^[3] colourless oil. ν_{max} (KBr)/cm⁻¹ 2966, 2927, 1793, 1676, 1614, 1421, 1332, 1267, 1209, 1139, 977. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 0.96 (t, *J* 5.8, 3H), 1.94 (s, 3H), 2.35–2.46 (m, 1H), 2.60–2.83 (m, 2H), 7.20–7.36 (m, 2H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 13.4, 13.7, 16.1, 16.2, 35.1, 35.2, 39.2, 39.5, 83.4, 83.6, 126.1, 126.2, 136.3, 136.5, 138.0, 141.4, 143.2, 146.1, 174.0, 174.1, 178.2 (×2).

3i: colourless solid; mp: 183–184°C. ν_{max} (KBr)/cm⁻¹ 3057, 1768, 1672. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 6.43 (d, *J* 10.2, 2H), 6.66 (d, *J* 9.9, 2H), 7.31 (d, *J* 7.5, 1H), 7.64 (td, *J* 7.2, 0.9, 1H), 7.73 (td, *J* 7.2, 0.9, 1H), 8.00 (d, *J* 7.5, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 80.3, 122.4, 125.5, 126.7, 129.8, 130.6, 135.1, 144.2, 146.4, 168.9, 184.1. (Anal. calc. for C₁₃H₈O₃: C 73.58, H 3.80. Found: C 73.57, H 4.00%.)

3*j* (diastereomixture): colourless solid; mp: 76–77°C. ν_{max} (KBr)/cm⁻¹ 2970, 2931, 2358, 2339, 1778, 1672, 1633, 1398, 1211, 1147. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 0.97 (t, *J* 5.1, 3H), 2.09 (s, 3H), 2.37–2.50 (m, 1H), 2.79–2.91 (m, 2H), 6.21 (d, *J* 1.5, 1H), 6.35 (dd, *J* 9.0, 2.1, 1H), 6.76 (d, *J* 10.2). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 13.8, 17.5, 55.8, 38.1, 84.6, 128.9, 130.5, 143.6, 155.2, 174.5, 184.3.

3k:^[15] colourless solid; mp: 135–136°C. ν_{max} (KBr)/cm⁻¹ 1770, 1672, 1228. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 2.55 (t, *J* 8.4, 2H), 2.86–3.02 (m, 2H), 6.46 (d, *J* 10.2, 1H), 7.06 (d, *J* 10.2, 1H), 7.49–7.57 (m, 2H), 7.68 (dd, *J* 7.5, 1.5, 1H), 8.15 (dd, *J* 7.8, 1.2, 1H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 28.5, 36.6, 80.1, 125.4, 126.8, 128.5, 129.1, 129.7, 133.5, 142.6, 146.4, 175.8, 183.2.

5:^[12a] colourless solid; mp: 115–116°C. ν_{max} (KBr)/cm⁻¹ 2879, 1666, 1629, 1344, 1157, 1095. $\delta_{\rm H}$ (CDCl₃, 300 MHz) 2.03–2.09 (m, 4H), 2.43 (s, 3H), 3.69 (t, *J* 6.9, 2H), 6.17 (d, *J* 10.2), 6.71 (d, *J* 10.2), 7.29 (d, *J* 8.3), 7.67 (d, *J* 8.3). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 21.6, 23.5, 40.4, 49.1, 63.7, 127.8, 127.9, 129.6, 136.2, 143.9, 150.1, 185.3.

Preparation of 4-(Diacetoxyiodo)toluene **1a** in HFIP with PAA (Scheme 3)

A stirring solution of HFIP (2 mL) containing 4-iodotoluene (109 mg, 0.5 mmol) and 9% (v/v) PAA solution (2.2 mL, 2.5 mmol) was heated at 35°C for 1 h. The solvent was evaporated, and the resulting oily mixture was washed with water and then extracted with chloroform. The organic layer containing the product was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was triturated with hexane to give 4-(diacetoxyiodo)toluene **1a** as a fine powder, which was collected by filtration (151 mg, 0.45 mmol, 90% yield).

Ia: white powder; mp: 107–109°C (lit.^[16] 106–108°C). $\delta_{\rm H}$ (CDCl₃, 300 MHz) 1.92 (s, 6H), 2.37 (s, 3H), 7.22 (d, *J* 7.8, 2H), 7.91 (d, *J* 7.8, 2H). $\delta_{\rm C}$ (CDCl₃, 75 MHz) 21.1, 22.2, 119.2, 132.5, 135.8, 143.5, 177.2.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research (A) and for Young Scientists (B), and a grant for Scientific Research on Priority Areas 'Advanced Molecular Transformations of Carbon Resources' from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. TD also acknowledges support from the Industrial Technology Research Grant Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan and the Japan Chemical Innovation Institute (JICC).

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