## A unique site-selective reaction of ketones with new recyclable hypervalent iodine(III) reagents based on a tetraphenylmethane structure

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General Information. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14B gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO<sub>2</sub> (Merck Silica Gel 60 (230-400 mesh)). Preparative high performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC-908 instrument, equipped with an RI absorbance detector. Tetraphenylmethane  $2^{[1]}$  and iodine(III) compounds PIDA<sup>[2]</sup> and PDAIS<sup>[3]</sup> were prepared according to the literature procedures. All other materials are commercially available and used without further purification.

## **Experimental Section**

Synthesis of recyclable hypervalent iodine(III) reagents 1a-c.

**1,3,5,7-Tetrakis-[4-(diacetoxyiodo)phenyl]methane (1a):** To a stirred solution of 1,3,5,7-tetrakis-(4-iodophenyl)methane **2** (620 mg, 0.75 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (75 mL)-AcOH (75 mL), then *m*CPBA (1.55 g, 9.0 mmol) was added to the mixture at room temperature. The reaction mixture was stirred for 2day under the same reaction conditions. The resultant slightly clouded solution was filtered to give clear solution.  $CH_2Cl_2$  was removed under reduced pressure and hexanes was added to the residue and stirred for 1h to precipitate 1,3,5,7-tetrakis-[4-(diacetoxyiodo)phenyl]-methane **1a**. After filtration, the crude **1a** was washed with hexanes and Et<sub>2</sub>O several times, and dried *in vacuo* to give **1a** (910.8 mg, 94 %).

**1a**: colorless crystal; m.p. (decomp.) 218~220 °C (from AcOH-CH<sub>2</sub>Cl<sub>2</sub>-Hexanes by vapor diffusion method); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 8.02$  (d, <sup>3</sup>*J*(H,H) = 9.6 Hz, 8H; ArH), 7.30 (d, <sup>3</sup>*J* (H,H) = 9.6 Hz, 8H; ArH), 2.02 (s, 24H, OCOCH<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 176.6$ , 147.6, 134.8, 133.0, 119.8, 65.69, 20.5 ppm. IR (KBr): 1686w, 1637.5w, 1647w, 1560m, 1541w, 1521w, 1508w, 1475w, 1458w, 1396w, 1364w, 1288w, 1003w, 912m, 808w, 743m, 669m cm<sup>-1</sup>.; Anal. Calcd for C<sub>41</sub>H<sub>40</sub>I<sub>4</sub>O<sub>16</sub> • 2H<sub>2</sub>O: C, 36.96; H, 3.33. Found: C, 36.80; H, 3.19.

#### 1,3,5,7-Tetrakis-[4-bis(trifluoroacetoxyiodo)phenyl]methane (1b).

To a stirred solution of 1,3,5,7-tetrakis-[4-(diacetoxyiodo)phenyl]methane **1a** (388.9 mg) in CHCl<sub>3</sub> (3 mL) was added trifluoroacetic acid (3 mL) at room temperature. The mixture was stirred for 1.5h under the same reaction conditions. CHCl<sub>3</sub> was removed under reduced pressure, then hexanes-Et<sub>2</sub>O (=10:1) was added. The precipitate was filtered and washed with hexanes-Et<sub>2</sub>O (=10:1) several times, and dried *in vacuo* to give **1b** (479.9 mg, 93%) as a slightly yellow crystal.

**1b**: slightly yellow crystal; m.p. (decomp.) 158~160 (from CH<sub>2</sub>Cl<sub>2</sub>-Hexanes); <sup>1</sup>H

NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H (10/1), 25 °C):  $\delta = 8.19$  (d, <sup>3</sup>*J*(H,H) = 9.6 Hz, 8H; ArH), 7.41 (d, <sup>3</sup>*J* (H,H) = 9.6 Hz, 8H; ArH) ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H (10/1), 25 °C, hexafluorobenzene (-162.9 ppm)):  $\delta = -74.47$  (s, OCOCF<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub> /CF<sub>3</sub>CO<sub>2</sub>H (10/1), 25 °C):  $\delta = 162.31$  (q, <sup>3</sup>*J*(C,F) = 42.3 Hz, C=O), 149.0, 135.6, 133.9, 121.5, 112.85 (q, <sup>1</sup>*J*(C,F) = 286.7 Hz, CF<sub>3</sub>), 65.69 ppm. IR (KBr): 1770 m, 1681 m, 1180 s, 912 w, 806 w, 785 w, 669 m, 657 w cm<sup>-1</sup>. Anal. Calcd for C<sub>41</sub>H<sub>16</sub>F<sub>24</sub>I<sub>4</sub>O<sub>16</sub>: C, 28.50; H, 0.93. Found: C, 28.38; H, 1.31.

#### 1,3,5,7-Tetrakis-[4-{hydroxy(tosyloxy)iodo}phenyl]methane (1c).

To a stirred solution of *p*-toluenesulfonic acid monohydrate (380.4 mg, 2.0 mmol) in CH<sub>3</sub>CN (5 mL) was added 1,3,5,7-tetrakis-[4-(diacetoxyiodo)phenyl]methane **1a** (324.1 mg, 0.25 mmol) at room temperature. The mixture was stirred for 3h under the same reaction conditions. After filtration, the crude **1c** was washed with CH<sub>3</sub>CN and Et<sub>2</sub>O several times, and dried *in vacuo* to give pure **1c** (357.4 mg, 91%).

**1c**: yellow solid; m.p. (decomp.)  $123 \sim 125$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H (10/1), 25 <sup>o</sup>C):  $\delta = 8.20$  (d, <sup>3</sup>*J*(H,H) = 8.7 Hz, 8H; ArH), 7.70 (d, <sup>3</sup>*J* (H,H) = 8.1 Hz, 8H; TsH), 7.41 (d, <sup>3</sup>*J* (H,H)= 8.7 Hz, 8H; ArH), 7.30 (d, <sup>3</sup>*J* (H,H)= 8.1 Hz, 8H; TsH), 2.43 (s, 12H, CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H (10/1), 25 °C):  $\delta = 149.12$ , 145.06, 135.57, 134.69, 133.92, 129.94, 126.47, 121.65, 65.67, 21.34 ppm; IR (KBr): 2923 m, 2482 w, 1598 w, 1571 w, 1481 m, 1396 m, 1145 s, 1105 s, 1028 m, 999 s, 812 s, 681 s cm<sup>-1</sup>.

# *Typical procedure for Oxidation Reaction with 1a*: Oxidation of phenol into [1,4]-benzoquinone<sup>[4]</sup>

To a stirred solution of 3,4,5-trimethoxyphenol (18.4 mg, 0.1 mmol) in  $CH_3CN/H_2O$  (4:1) (1 mL) was added **1a** (32.4 mg, 0.025 mmol) in one portion at room temperature. The mixture was stirred for 30 min. Then, the reaction mixture was filtered, and washed with  $CH_3CN$  several times to give pure **2** as a white solid. The recovery of **2** was nearly quantitative. The filtrate was evaporated in vacuo to give 3,5-dimethoxy-[1,4] benzoquinone (6) (16.1 mg, 96%).

**3,5-Dimethoxy-[1,4] benzoquinone** (6)<sup>[5]</sup>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C ):  $\delta = 5.82$  (s, 2H), 3.82 (s, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 186.8$ , 157.3, 107.4, 56.5 ppm; IR (KBr):1697, 1624, 1380, 1323, 1261, 1220, 1006 cm<sup>-1</sup>.

*L*-Menthone (4)<sup>[6]</sup>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 2.37-2.33$  (m, 1H), 2.15-1.88 (c, 6H), 1.40-1.32 (c, 2H), 1.01 (d, <sup>3</sup>*J* (H,H) = 6.4 Hz, 3H), 0.91 (d, <sup>3</sup>*J* (H,H) = 7.0 Hz, 3H), 0.85 (d, <sup>3</sup>*J* (H,H) = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 212.0$ , 56.1, 51.0, 35.6, 34.1, 28.4, 26.0, 22.3, 21.3, 18.8 ppm.; IR (KBr): 2870 s, 1713 s, 1454 s, 1427 m, 1367 m, 1335 m, 1311 w, 1275 m, 1246 w, 1202 m, 1116 w, 1043 w, 1022 w, 949 w, 930 w, 866 w, 839 w, 748 w cm<sup>-1</sup>.

**2,2'-Dibromo-4,5,4',5'-tetramethoxy-biphenyl** (**11**)<sup>[7]</sup>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.04 (s, 2H), 6.69 (s, 2H), 3.85 (s, 6H), 3.79 (s, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 149.0, 147.9, 133.9, 115.0, 113.8 (2C), 56.1 (2C) ppm; IR (KBr): 3002, 1603, 1505, 1173, 862 cm<sup>-1</sup>.

Toluene-4-sulfonic acid 1-methyl-2-oxo-2-phenyl-ethyl ester (8)<sup>[8]</sup>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  7.88 (dt, <sup>3</sup>*J* (H,H) = 8.1 Hz, 2H), 7.75 (d, <sup>3</sup>*J* (H,H) = 7.2 Hz, 2H), 7.60 (t, <sup>3</sup>*J* (H,H) = 7.2 Hz, 1H), 7.46 (t, <sup>3</sup>*J* (H,H) = 2H), 7.29(d, <sup>3</sup>*J* (H,H) = 8.1 Hz, 2H), 5.79 (q, <sup>3</sup>*J* (H,H) = 7.0 Hz, 1H), 2.41 (s, 3H), 1.60 (d, <sup>3</sup>*J* (H,H) = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 194.38, 144.71, 133.49, 133.23, 132.98, 129.42, 128.38, 128.26, 127.47, 76.94, 21.18, 18.29 ppm; IR (KBr): 1700, 1370, 1170, 830, 760, 660 cm<sup>-1</sup>.

# *Typical procedure for site-selective* -*Tosyloxylation Reaction of ketones with 1a* A mixture of 2-butanone (14.4 mg, 0.2 mmol), **1a** (64.8 mg, 0.050 mmol),

*p*-toluenesulfonic acid monohydrate (38.1 mg, 0.2 mmol), CH<sub>3</sub>CN (2 mL) was heated at 70 in a sealed tube. After 24 h, the mixture was cooled to ambient temperature. MeOH (2 mL) was added to the reaction mixture, then the mixture was filtered. Recovery of **2** was quantitave. After evaporation, crude products were obtained and subjected to <sup>1</sup>H NMR to determine a ratio of **12a** and **13a**. Integrations of the methyl doublet at 1.6 (for **12a**) and methyl triplet 1.1 (for **13a**) indicated that these isomers presented in a ratio of ca. 5.1: 1. Purification by calumn chromatography (SiO<sub>2</sub>/ hexane-AcOEt= 10/1) to give pure **12a** and **13a** as a mixture of two isomers (**12a** : **13a** = 5.1 : 1, see chart 1).

Toluene-4-sulfonic acid 1-methyl-2-oxo-propyl ester (12a) and Toluene-4-sulfonic acid 2-oxo-butyl ester (13a)<sup>[8-10]</sup>: colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.86-7.77 (c, 2H, TsH (12a and 13a)), 7.41-7.32 (c, 2H, TsH (12a and 13a)), 4.76 (q, <sup>3</sup>*J*(H,H) = 7.2 Hz, 1H, OCH (12a)), 4.50 (s, 2H, OCH<sub>2</sub>(13a)), 2.52 (q, <sup>3</sup>*J*(H,H) = 7.2 Hz, 2H, COCH<sub>2</sub>(13a)), 2.52-2.41 (c, 3H, Ts (12a and 13a)), 1.222 (s, 3H, COCH<sub>3</sub>(12a), 1.35 (d, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>(12a)), 1.06 ppm (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, CH<sub>3</sub>(13a)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 205.20, 145.36, 133.16, 130.02, 128.04, 127.89, 80.80, 71.67, 32.41, 29.68, 25.56, 21.67, 17.30, 6.78 ppm; IR (KBr): 1732m, 1362s, 1190s, 1178s, 912w, 820w, 787w, 669s cm<sup>-1</sup>.

Toluene-4-sulfonic acid 1-acetyl-butyl ester (12b) and Toluene-4-sulfonic acid 2-oxo-hexyl ester (13b)<sup>[9, 11]</sup>: colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 7.85$ -7.76 (c, 2H, TsH (12b and 13b)), 7.41-7.32 (c, 2H, TsH (12b and 13b)), 4.61 (q, <sup>3</sup>*J*(H,H) = 4.6 Hz, 1H, O*CH* (12b)), 4.49 (s, 2H, O*CH*<sub>2</sub> (13b)), 2.52-2.41 (c, 3H, Ts (12b and 13b) and CO*CH*<sub>2</sub> (13b)), 2.20 (s, 3H, CO*CH*<sub>3</sub> (12b)), 1.75-1.49 (c, 2H, CH<sub>2</sub> (12b and 13b)), 1.33-1.19 (c, 2H, CH<sub>2</sub> (12b and 13b)), 0.89 (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, 3H, CH<sub>3</sub> (12b)), 0.79 (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, 3H, CH<sub>3</sub> (13b)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 205.37$ , 145.23, 132.75, 129.89, 127.94, 84.24, 71.78, 38.74, 33.49, 29.74, 25.92, 24.95, 22.18, 21.77, 17.90, 13.85, 13.37 ppm; IR (KBr): 1722m, 1367s, 1190s, 1177s, 1018w, 953m,





885m, 816m, 748w, 669s cm<sup>-1</sup>.

Toluene-4-sulfonic acid 1-acetyl-3-methyl-butyl ester (12c) and Toluene-4-sulfonic acid 5-methyl-2-oxo-hexyl ester (13c)<sup>[9, 12]</sup>: colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 7.86-7.76$  (c, 2H, TsH (12c and 13c)), 7.41-7.32 (c, 2H, TsH (12c and 13c)), 4.62 (dd, <sup>3</sup>*J*(H,H) = 9.6, 3.8 Hz, 1H, OCH (12c)), 4.50 (s, 2H, OCH<sub>2</sub> (13c)), 2.52-2.41 (c, 3H, Ts (12c and 13c) and COCH<sub>2</sub> (13c)), 2.20 (s, 3H, COCH<sub>3</sub> (12c)), 1.71-1.33 (c (12c and 13c)), 0.85 (c, 3H, CH<sub>3</sub> (12c and 13c)), 0.65 (c, 3H, CH<sub>3</sub> (12c and 13c)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 205.78$ , 145.40, 132.73, 129.96, 128.07, 83.10, 71.76, 40.11, 36.92, 29.69, 27.49, 25.40, 23.92, 22.96, 22.22, 21.68, 20.80 ppm; IR (KBr): 1719m, 1369m, 1177m, 955w, 883w, 816w, 748w, 669s cm<sup>-1</sup>.

Toluene-4-sulfonic acid 2-oxo-1-phenyl-propyl ester (12d) and Toluene-4-sulfonic acid 2-oxo-3-phenyl-propyl ester (13d): colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta =$ 7.77–7.68 (c, 2H, TsH (12d and 13d)), 7.20-7.45 (c, 7H, ArH and TsH (12d and 13d)), 5.68 (s, 1H, O*CH* (12d)), 4.56 (s, 2H, O*CH*<sub>2</sub>(13d)), 3.81 (s, 2H, CH<sub>2</sub>(13d)), 2.38-2.48 (c, 3H, Ts (12d and 13d)), 2.18 (s, 3H, CH<sub>3</sub> (12d)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta =$ 201.41, 145.15, 133.13, 132.37, 129.77, 129.42, 128.91, 127.93, 127.06, 85.25, 25.63, 21.6 ppm; IR (KBr): 1738s, 1366s, 1190s, 1177s, 1095w, 997w, 995m, 814w, 745m, 669s cm<sup>-1</sup>. FAB-HRMS: Anal. Calcd for C<sub>16</sub>H<sub>17</sub>O<sub>4</sub>S (M+H) 305.0848. Found: 305.0865.; Elemental analysis: Anal. Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>S: C, 63.14; H, 5.30; S, 10.54. Found: C, 62.97; H, 5.40; S, 10.22.

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