Iodobenzene-Catalyzed α -Acetoxylation of Ketones. In Situ Generation of Hypervalent (Diacyloxyiodo)benzenes Using *m*-Chloroperbenzoic AcidMasahito Ochiai,^{*} Yasunori Takeuchi, Tomoko Katayama, Takuya Sueda, and Kazunori Miyamoto

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Scheme S1. Attempted Deuteration of Acetophenone in the Absence of $\text{BF}_3\text{-Et}_2\text{O}$

Figure S1. Time courses for oxidation of iodobenzene with *m*-CPBA in the absence of $\text{BF}_3\text{-Et}_2\text{O}$ (determined by ^1H NMR analyses). Reaction conditions: iodobenzene (0.024 M) in $\text{CD}_3\text{CO}_2\text{D}$ and *m*-CPBA (10 equiv) at 23 °C under argon. (a) (○) without D_2O , and (b) (●) with D_2O (50 equiv).

Figure S2. Time courses for the deuteration of acetophenone in the presence of $\text{BF}_3\text{-Et}_2\text{O}$ (determined by ^1H NMR analyses). Reaction conditions: acetophenone (0.25 M) in $\text{CD}_3\text{CO}_2\text{D}$, $\text{BF}_3\text{-Et}_2\text{O}$ (3 equiv) at 23 °C under argon. (a) (●) without D_2O , and (b) (○) with D_2O (5 equiv).

Figure S3. Time courses for oxidation of iodobenzene with *m*-CPBA (determined by ^1H NMR analyses). Reaction conditions: iodobenzene (0.25 M) in $\text{CD}_3\text{CO}_2\text{D}$, *m*-CPBA (1 equiv), and $\text{BF}_3\text{-Et}_2\text{O}$ (1 equiv) at 25 °C under argon. (a) (○) without D_2O , and (b) (●) with D_2O (5 equiv).

Figure S4. Ligand exchange between $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OCO-}m\text{-ClC}_6\text{H}_4)_2$ (determined by ^1H NMR analyses). Conditions: $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OCO-}m\text{-ClC}_6\text{H}_4)_2$ (each 6 mM) in CDCl_3 at 22 °C. (○) $\text{PhI}(\text{OAc})_2$, (●) $\text{PhI}(\text{OCO-}m\text{-ClC}_6\text{H}_4)_2$, and (▲) $\text{PhI}(\text{OAc})\text{OCO-}m\text{-ClC}_6\text{H}_4$.

Table S1. Effects of Acids on Catalytic α -Acetoxylation of Acetophenone^a

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{Me} \end{array} \xrightarrow[\text{AcOH, 25-30 } ^\circ\text{C, 24 h, Ar}]{\begin{array}{c} m\text{-CPBA (1.4)} \\ \text{PhI (0.1), H}_2\text{O (5)} \end{array}} \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{CH}_2-\text{OAc} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{Me}-\text{C}-\text{O}-\text{Ph} \end{array} $				
entry	acid	(equiv)	α -acetoxyacetophenone (%) ^b	phenyl acetate (%) ^c
1	BF ₃ -Et ₂ O	-	-	18
2	BF ₃ -Et ₂ O	(1)	21	11
3	BF ₃ -Et ₂ O	(3)	84	-
4	BF ₃ -Et ₂ O	(5)	88	-
5	Yb(OTf) ₃	(3)	39	-
6	Sc(OTf) ₃	(3)	6	-
7	CF ₃ SO ₃ H	(3)	44	-
8	HBf ₄ -Me ₂ O	(3)	41	-

^a Reaction conditions: acetophenone (0.25 M) in acetic acid, *m*-CPBA (1.4 equiv), H₂O (5 equiv), and iodobenzene (0.1 equiv) at 25–30 °C for 24 h under argon. ^b GC yields. ^c ¹H NMR yields.

Table S2. Substituent Effects of Iodobenzene^a

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{Me} \end{array} \xrightarrow[\text{AcOH, 25-30 } ^\circ\text{C, 24 h, Ar}]{\begin{array}{c} m\text{-CPBA (2), BF}_3\text{-Et}_2\text{O (3)} \\ \text{Arl (0.1), H}_2\text{O (5)} \end{array}} \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{CH}_2-\text{OAc} \end{array} $		
entry	Arl	α -acetoxyacetophenone (%) ^b
1	<i>p</i> -MeOC ₆ H ₄ I	67
2	<i>p</i> -MeC ₆ H ₄ I	84
3	PhI	84
4	<i>p</i> -ClC ₆ H ₄ I	81
5	<i>p</i> -NO ₂ C ₆ H ₄ I	58

^a Reaction conditions: acetophenone (0.25 M) in acetic acid, *m*-CPBA (2 equiv), H₂O (5 equiv), BF₃-Et₂O (3 equiv), and iodoarene (0.1 equiv) at 25–30 °C for 24 h under argon. ^b GC yields.

General Information. IR spectra were recorded on Perkin Elmer 1720 FT-IR spectrometers. ¹H NMR spectra were obtained on a JEOL JNM-AL300 or JNM-AL400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me₄Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer.

General Procedure for Catalytic α-Acetoxylation of Ketones with *m*-Chloroperbenzoic Acid. A Typical Example (Table 2, Entry 1): 3-Acetoxy-4-heptanone. *m*-Chloroperbenzoic acid (72% purity, 101 mg, 0.42 mmol) was dried under vacuum for 1 h at room temperature. To a stirred solution of *m*-CPBA in acetic acid (0.82 mL) was added water (19 mg, 1.1 mmol), 4-heptanone (24 mg, 0.21 mmol), iodobenzene (4.3 mg, 0.021 mmol), and then boron trifluoride-diethyl etherate (distilled from CaH₂ under argon, 89 mg, 0.63 mmol) at room temperature under argon and the mixture was stirred for 20 h. Water (1 mL) and diethyl ether (5 mL) was added and the organic phase was analyzed by GC using a capillary column of FFS ULBON HR-1 (0.25 mm x 50 m, 70 °C, decane as an internal standard): 3-acetoxy-4-heptanone (79%). The mixture was neutralized with a cooled 10% aqueous sodium carbonate solution and extracted with diethyl ether three times. The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at 0 °C under an aspirator vacuum to give an oil, which was purified by silica gel column chromatography using hexane-diethyl ether (6:1) to give 3-acetoxy-4-heptanone (16.8 mg, 46%):¹ IR (film) 2968, 2879, 1745, 1730, 1459, 1374, 1235 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.95 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.55–2.32 (m, 2H), 2.15 (s, 3H), 1.92–1.55 (m, 4H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); MS *m/z* (relative intensity) 172 (0.3, M⁺), 129 (15), 101 (20), 71 (100).

4-Acetoxy-5-nonanone:² IR (film) 2961, 2874, 1745, 1730, 1466, 1374, 1231 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.01 (dd, *J* = 7.5, 5.3 Hz, 1H), 2.56–2.34 (m, 2H), 2.14 (s, 3H), 1.78–1.65 (m, 2H), 1.61–1.51 (m, 2H), 1.48–1.25 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); MS *m/z* (relative intensity) 200 (10, M⁺), 159 (27), 115 (43), 85 (100), 83 (23), 57 (82).

5-Acetoxy-6-undecanone: IR (film) 2958, 2864, 1745, 1731, 1467, 1374, 1234 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.99 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.55–2.33 (m, 2H), 2.14 (s, 3H), 1.82–1.53 (m, 4H), 1.44–1.21 (m, 8H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.6 Hz, 3H); MS *m/z* (relative intensity) 228 (0.1, M⁺), 129 (10), 99 (100), 71 (38).

α-Acetoxy-*p*-fluoroacetophenone:³ IR (film) 3077, 2939, 1747, 1704, 1600, 1508, 1416, 1375, 1220, 1160, 972, 833 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 2H), 5.30 (s, 2H), 2.23 (s, 3H); MS *m/z* (relative intensity) 196 (4, M⁺), 123 (100), 95 (22), 75 (10).

α-Acetoxy-*p*-chloroacetophenone:⁴ IR (KBr) 3072, 2982, 2940, 1742, 1698, 1593, 1425, 1241, 1087, 975, 823, 729, 648 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 5.30 (s, 2H), 2.24 (s, 3H); MS *m/z* (relative intensity) 212 (2, M⁺), 141 (38), 139 (100), 113 (9), 111 (27).

α-Acetoxy-*p*-bromoacetophenone:⁵ IR (KBr) 2989, 2951, 1746, 1694, 1586, 1431, 1380, 1226, 1000, 971, 816, 715 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* =

8.4 Hz, 2H), 5.29 (s, 2H), 2.23 (s, 3H); MS m/z (relative intensity) 258 (11), 256 (11, M^+), 185 (99), 183 (100), 157 (18), 155(18), 76 (12), 75 (10).

α -Acetoxy-*p*-iodoacetophenone:⁵ IR (KBr) 1747, 1702, 1606, 1523, 1220 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 5.28 (s, 2H), 2.22 (s, 3H); MS m/z (relative intensity) 304 (10, M^+), 231 (100), 202 (16).

α -Acetoxypropiophenone:⁶ IR (CHCl_3) 3018, 2944, 2833, 1736, 1698, 1598, 1450, 1374 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.7$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.48 (dd, $J = 7.7$, 7.3 Hz, 2H), 5.97 (q, $J = 7.1$ Hz, 1H), 2.16 (s, 3H), 1.53 (d, $J = 7.1$ Hz, 3H); MS m/z (relative intensity) 192 (0.2, M^+), 149 (5), 132 (7), 105 (100), 77 (36).

2-Acetoxy-1-phenyl-1-pentanone:⁷ IR (film) 3063, 2963, 2875, 1746, 1696, 1598, 1449, 1234, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.7$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48 (dd, $J = 7.7$, 7.4 Hz, 2H), 5.88 (dd, $J = 7.4$, 5.4 Hz, 1H), 2.16 (s, 3H), 1.87–1.80 (m, 2H), 1.57–1.41 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); MS m/z (relative intensity) 220 (0.1, M^+), 178 (5), 160 (5), 105 (100), 77 (25).

2-Acetoxy-1-cyclopropylethanone:⁸ IR (film) 3012, 2931, 1751, 1718, 1395, 1232, 1051, 1022, 894 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.83 (s, 2H), 2.18 (s, 3H), 1.98–1.90 (m, 1H), 1.17–1.10 (m, 2H), 1.03–0.94 (m, 2H); MS m/z (relative intensity) 142 (0.3, M^+), 112 (2), 83 (7), 69 (100).

Ethyl α -Acetoxybenzoylacetate:⁹ IR (film) 3064, 2984, 2940, 1750, 1695, 1598, 1449, 1373, 1225, 1095, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (br d, $J = 7.8$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.50 (dd, $J = 7.8$, 7.2 Hz, 2H), 6.33 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.23 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H); MS m/z (relative intensity) 250 (1, M^+), 205 (2), 105 (100), 77 (62).

3-Acetoxy-2-undecanone:¹⁰ IR (film) 2926, 2856, 1746, 1466, 1434, 1374, 1240 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.98 (dd, $J = 8.1$, 4.4 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 1.83–1.66 (m, 2H), 1.44–1.22 (m, 12H), 0.88 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 228 (0.1, M^+), 185 (5), 125 (56), 116 (41), 83 (39), 69(100).

1-Acetoxy-2-undecanone:¹¹ IR (CHCl_3) 2928, 2856, 1748, 1732, 1466, 1376 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 4.65 (s, 2H), 2.41 (t, $J = 7.6$ Hz, 2H), 2.17 (s, 3H), 1.67–1.55 (m, 2H), 1.35–1.20 (12H), 0.88 (t, $J = 6.5$ Hz, 3H); MS m/z (relative intensity) 228 (0.2, M^+), 186 (10), 155 (72), 116 (26), 85 (45), 71 (100).

4-Acetoxy-3-octanone: IR (film) 2958, 2873, 1741, 1732, 1462, 1375, 1238 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.01 (dd, $J = 7.7$, 4.4 Hz, 1H), 2.61–2.35 (m, 2H), 2.14 (s, 3H), 1.84–1.64 (m, 2H), 1.43–1.23 (m, 4H), 1.07 (t, $J = 7.3$ Hz, 3H) 0.96–0.84 (m, 3H).

2-Acetoxy-3-octanone: IR (film) 2958, 2935, 2873, 1745, 1730, 1458, 1371, 1236 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.08 (q, $J = 7.2$ Hz, 1H), 2.57–2.36 (m, 2H), 2.14 (s, 3H), 1.65–1.53 (m,

2H), 1.42–1.20 (m, 4H), 1.39 (d, $J = 7.2$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H).

4-Acetoxy-3-dodecanone: IR (film) 2927, 2856, 1745, 1732, 1461, 1374, 1237 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.01 (dd, $J = 8.1, 4.4$ Hz, 1H), 2.59–2.38 (m, 2H), 2.14 (s, 3H), 1.82–1.64 (m, 2H), 1.44–1.20 (m, 12H), 1.07 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 242 (0.2, M^+), 130 (8), 125 (17), 83 (10), 69 (25), 57 (100).

2-Acetoxy-3-dodecanone:¹² IR (film) 2926, 2855, 1746, 1731, 1457, 1372, 1236 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.08 (q, $J = 7.0$ Hz, 1H), 2.56–2.36 (m, 2H), 2.14 (s, 3H), 1.65–1.52 (m, 2H), 1.39 (d, $J = 7.0$ Hz, 3H), 1.35–1.20 (12H), 0.88 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 242 (0.1, M^+), 200 (7), 155 (100), 130 (12), 85 (37), 71 (78), 57 (89).

1-Acetoxy-4,4-dimethyl-2-pentanone: IR (film) 2956, 1753, 1732, 1371, 1232, 1063 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.62 (s, 2H), 2.28 (s, 2H), 2.18 (s, 3H), 1.04 (s, 9H); MS m/z (relative intensity) 112 (5), 99 (26), 71 (11), 57 (100). Anal. Calcd for $\text{C}_9\text{H}_{16}\text{O}_3 \cdot 1/4\text{H}_2\text{O}$: C, 61.17; H, 9.41. Found: C, 61.12; H, 9.05.

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