An Efficient Method for the Synthesis of α-Hydroxyalkyl Aryl Ketones

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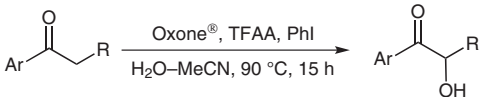
Abstract: Exposure of alkyl aryl ketones to Oxone®/trifluoroacetic anhydride in the presence of a catalytic amount of iodobenzene affords α-hydroxyalkyl aryl ketones in good yield. This method provides an effective and economical entry for the installation of α-hydroxy moieties into ketones and should find wide application in the construction of the α-hydroxy ketone subunit in natural product synthesis.

Key words: Oxone®, hydroxylation, iodobenzene, α-hydroxy ketones

The α-hydroxy carbonyl moiety is a versatile intermediate in the synthesis of many natural products and pharmaceuticals.[1] α-Hydroxy ketones can be prepared in various ways, for example, by the oxidation of preformed enolates and enolate derivatives using various methods including organic peracids,[2] singlet oxygen,[3] osmium tetroxide,[4] lead(IV) salts,[5] and ozonolysis,[6] by the reduction of diketones,[7] and by the oxidation of epoxides and aziridines.[8] There has also been considerable interest in the development of direct methods for the synthesis of α-hydroxy ketones using nontoxic hypervalent iodine reagents;[9] however, stoichiometric amounts of hypervalent iodine reagents are required and equimolecular amounts of iodobenzene are produced as waste in the reaction. To overcome this drawback, Ochiai and co-workers have developed a method for the α-acetoxylation of ketones using only a catalytic amount of iodobenzene.[10] Such a catalytic cycle has not previously been realized, except for electrochemical oxidants.[11] Oxone®, a potassium triple salt containing potassium peroxymonosulfate, is an effective oxidant for numerous transformations.[12] Oxone® has also been demonstrated to oxidize iodoarenes to the hypervalent iodine species.[13] The use of Oxone® as an efficient and mild oxidant has grown rapidly. This is due in part to the stability, ease of transport, nontoxic nature, nonpolluting byproducts, and cost-effectiveness of Oxone®.

In this paper we present the synthesis of α-hydroxyalkyl aryl ketones from alkyl aryl ketones in which Oxone® serves as a terminal oxidant (Scheme 1). Exposure of acetophenone to Oxone® (2.7 equiv)/trifluoroacetic anhydride (7.0 equiv) in the presence of a catalytic amount of iodobenzene (20 mol%) at 90 °C for 15 hours afforded 2-hydroxyacetophenone in 74% yield (Table 1, entry 2). If



Scheme 1

30% aqueous hydrogen peroxide was used to replace part of the Oxone®, no reaction was observed, which showed that Oxone® was not only used as an oxidant but also as a strong acid to induce the enolization of acetophenone (Table 1, entry 7). As water is a stronger nucleophile than trifluoroacetic acid, α-trifluoroacetoxy ketones would not be obtained.[9b,14]

The effect of temperature on the reaction was studied. As shown in Table 1, raising the temperature to 100 °C resulted in a decrease in the yield to 52% (entry 3). Increasing the reaction time to 24 hours did not result in a higher yield (Table 1, entry 4). In this catalytic cycle, iodoarene would be oxidized to the iodine(III) species which reacts with the alkyl aryl ketones to give the α-hydroxyalkyl aryl ketones and iodoarene.[10,15] When acetic anhydride was used instead of trifluoroacetic anhydride, there was a decrease in the yield; this showed that the electron-withdrawing ligand increases the oxidative efficiency of hypervalent iodine reagents (Table 1, entries 2 and 5). If there was no ligand, there was an obvious decrease in the yield (15%) of 2-hydroxyacetophenone (Table 1, entry 6).

Table 1 Oxidation of Acetophenone under Various Conditions[a]

Entry	Temp (°C)	Conversion (%)	Yield[b] (%)
1	70	70	46
2	90	88	74
3	100	73	52
4[c]	90	84	74
5[d]	90	89	67
6[e]	90	30	15
7[f]	90	–	–

[a] Reaction conditions: acetophenone (10 mmol), Oxone® (2.7 equiv), TFAA (7.0 equiv), PhI (0.2 equiv), H_2O–MeCN (1:3, v/v), 15 h.
[b] Isolated yields.
[c] Reaction time: 24 h.
[d] Ac_2O was used instead of TFAA.
[e] TFAA was not used.
[f] Oxone® (1.0 equiv) and 30% aq H_2O_2 (2.7 equiv) were used instead of Oxone® (2.7 equiv).

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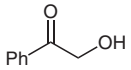
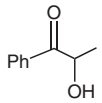
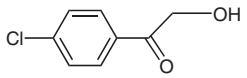
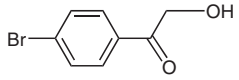
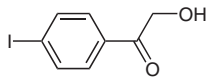
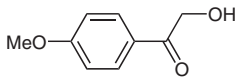
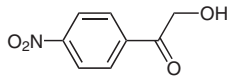
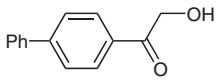
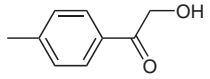
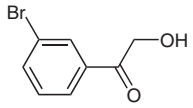
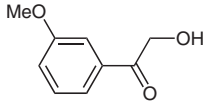
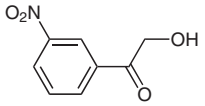
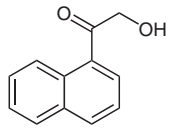
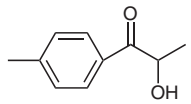
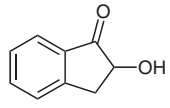
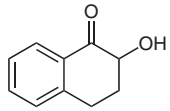
Table 2 α-Hydroxylation of Alkyl Aryl Ketones with Oxone®/Trifluoroacetic Anhydride[a]

Entry	Product	Conversion (%)	Yield[b] (%)
1		88	74
2		80	58
3		91	80
4		91	82
5		93	70
6		79	63
7		70	50
8		86	62
9		76	50
10		89	80
11		78	61
12		73	52
13		75	56
14		88	52
15		81	63
16		76	48

[a] Reaction conditions: ketone (0.3 mmol), Oxone® (2.7 equiv), TFAA (7.0 equiv), PhI (0.2 equiv), H_2O–MeCN (1:3, v/v), 90 °C, 15 h.
[b] Isolated yields.

According to the results in Table 2, when the substituent on the aryl ring in acetophenone was an electron-withdrawing group, a higher yield was obtained than when it was an electron-donating group (Table 2, entries 7–9 and 12). The reaction was also found to be influenced by steric effects; when propiophenone and 1-(naphthalen-1-yl)ethanone were converted into α-hydroxy ketones using this method, the product yield decreased from 74% to 58% and 56%, respectively (Table 2, entries 2 and 13).

In conclusion, the conversion of alkyl aryl ketones into α-hydroxyalkyl aryl ketones using Oxone® and trifluoroacetic anhydride as a terminal oxidant has been accomplished in good yields. The present approach provides an effective and economical entry for the installation of α-hydroxy moieties into ketones and should find wide application in the construction of the α-hydroxy ketone subunit in natural product synthesis.

NMR spectra were recorded on a Mercury 4N-PEG-300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) spectrometer, using $CDCl_3$ or DMSO-d_6 as a solvent and TMS as the internal standard. IR spectra were recorded as KBr pellets or KBr film on a Nicolet Nexus 670 FT IR spectrophotometer. Mass spectra were recorded using the EI method on a HP 5998 mass spectrometer. Melting points are uncorrected.

2-Hydroxyacetophenone; Typical Procedure

A soln of Oxone® (16.6 g, 27 mmol), TFAA (9.8 mL, 70 mmol), and H_2O (50 mL) was stirred at 40 °C for 7 h, and then cooled to r.t. Acetophenone (1.20 g, 10 mmol) and PhI (0.4 g, 2 mmol) in MeCN (150 mL) were added at r.t. The resulting solution was stirred at 90 °C for 15 h (the progress of the reaction was monitored by TLC). Then, CH_2Cl_2 (15 mL) was added. The mixture was neutralized with a cooled 10% aq Na_2CO_3 soln and extracted with CH_2Cl_2 (3 × 70 mL). The combined organic phase was washed with brine (20 mL), dried (anhyd $MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography [silica gel (200–300 mesh), petroleum ether–EtOAc, 8:1] to give 2-hydroxyacetophenone; yield: 1.00 g (74%).

2-Hydroxyacetophenone

White solid; mp 86–89 °C (*n*-hexane).

IR (KBr): 3430, 1683 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.2 Hz, 2 H), 7.66–7.26 (m, 3 H), 4.89 (s, 2 H), 3.52 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 134.3, 133.3, 128.9, 127.7.

MS (EI): *m*/*z* = 136, 105, 77.

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.68; H, 5.80.

2-Hydroxypropiophenone

Colorless liquid.

IR (KBr): 3444, 1685 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.8 Hz, 2 H), 7.66–7.48 (m, 3 H), 5.17 (q, *J* = 7.2 Hz, 1 H), 3.79 (s, 1 H), 1.45 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.3, 133.9, 133.2, 128.8, 128.6, 69.3, 22.2.

MS (EI): *m*/*z* = 150, 122, 105.

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.88; H, 6.74.

4′-Chloro-2-hydroxyacetophenone
White solid; mp 120–123 °C (EtOH).

IR (KBr): 3400, 1680 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 7.92 (d, *J* = 8.6 Hz, 2 H), 7.57 (d, *J* = 8.6 Hz, 2 H), 5.14 (t, *J* = 5.7 Hz, 1 H), 4.75 (d, *J* = 5.7 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 198.3, 138.2, 133.3, 129.6, 128.9, 65.4.

MS (EI): *m*/*z* = 172, 170, 142, 139, 113, 111, 75.

Anal. Calcd for $C_8H_7ClO_2$: C, 56.31; H, 4.14. Found: C, 56.23; H, 3.84.

4′-Bromo-2-hydroxyacetophenone
White solid; mp 118–120 °C (EtOH).

IR (KBr): 3423, 1657 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 7.85 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 5.16 (t, *J* = 5.7 Hz, 1 H), 4.77 (d, *J* = 5.7 Hz, 2 H).

^{13}C NMR (75MHz, DMSO-d_6): δ = 198.0, 133.1, 131.3, 129.1, 126.9, 64.9.

MS (EI): *m*/*z* = 216, 214, 185, 183, 157, 155.

Anal. Calcd for $C_8H_7BrO_2$: C, 44.68; H, 3.28. Found: C, 45.19; H, 3.14.

2-Hydroxy-4′-iodoacetophenone
White solid; mp 140–142 °C (EtOH).

IR (KBr): 3421, 1652 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 7.88 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 4.84 (s, 2 H), 3.43 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 198.8, 137.7, 133.8, 131.1, 129.3, 65.3.

MS (EI): *m*/*z* = 262, 231, 203.

Anal. Calcd for $C_8H_7IO_2$: C, 36.67; H, 2.69. Found: C, 37.18; H, 2.52.

2-Hydroxy-4′-methoxyacetophenone
Pale-yellow solid; mp 104–107 °C (EtOH).

IR (KBr): 3424, 1688 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 7.88 (d, *J* = 8.7 Hz, 2 H), 7.02 (d, *J* = 8.7 Hz, 2 H), 4.94 (t, *J* = 6.0 Hz, 1 H), 4.71 (d, *J* = 6.0 Hz, 2 H), 3.82 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 198.1, 163.9, 130.5, 128.1, 114.7, 65.7, 56.2.

MS (EI): *m*/*z* = 166, 135, 107, 92.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.13; H, 5.98.

2-Hydroxy-4′-nitroacetophenone
Yellow solid; mp 138–140 °C (EtOH).

IR (KBr): 3422, 1658 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.33 (d, *J* = 8.4 Hz, 2 H), 8.14 (d, *J* = 8.4 Hz, 2 H), 5.31 (t, *J* = 5.7 Hz, 1 H), 4.84 (d, *J* = 5.7 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 198.2, 149.5, 138.9, 128.6, 123.4, 65.4.

MS (EI): *m*/*z* = 181, 150, 122.

Anal. Calcd for $C_8H_7NO_4$: C, 53.04; H, 3.89. Found: C, 53.16; H, 3.74.

2-Hydroxy-4′-phenylacetophenone
Pale-yellow solid; mp 125–127 °C (EtOH).

IR (KBr): 3418, 1684 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.63 (q, *J* = 7.8 Hz, 2 H), 7.50–7.26 (m, 3 H), 4.92 (d, *J* = 8.4 Hz, 2 H), 3.55 (t, *J* = 4.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.9, 147.0, 139.5, 132.0, 129.0, 128.5, 128.3, 127.6, 127.3, 65.4.

MS (EI): *m*/*z* = 212, 181, 152.

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 80.01; H, 5.55.

2-Hydroxy-4′-methylacetophenone
Light-yellow solid; mp 81–83 °C (EtOH).

IR (KBr): 3434, 1682 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 4.86 (s, 2 H), 3.57 (s, 1 H), 2.44 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.9, 145.4, 130.2, 129.6, 127.8, 65.3, 21.8.

MS (EI): *m*/*z* = 150, 119.

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.56.

3′-Bromo-2-hydroxyacetophenone
White solid; mp 104–106 °C (EtOH).

IR (KBr): 3426, 1660 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.05 (s, 1 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.49 (dd, *J* = 7.5, 7.8 Hz, 1 H), 5.21 (t, *J* = 4.8 Hz, 1 H), 4.79 (d, *J* = 4.8 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 198.3, 136.7, 136.0, 131.1, 130.2, 126.7, 122.2, 65.5.

MS (EI): *m*/*z* = 216, 214, 185, 183, 157, 155.

Anal. Calcd for $C_8H_7BrO_2$: C, 44.68; H, 3.28. Found: C, 45.10; H, 3.12.

2-Hydroxy-3′-methoxyacetophenone
Colorless solid; mp 49–51 °C (EtOH).

IR (KBr): 3428, 1685 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.37 (m, 3 H), 7.17 (d, *J* = 8.1 Hz, 1 H), 4.91 (s, 2 H), 3.87 (s, 3 H), 3.56 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 159.9, 134.5, 129.9, 120.6, 120.1, 111.9, 65.5, 55.4.

MS (EI): *m*/*z* = 166, 135, 107, 92.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.11; H, 5.91.

2-Hydroxy-3′-nitroacetophenone
Light-yellow solid; mp 69–70 °C (EtOH).

IR (KBr): 3422, 1656 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.59 (s, 1 H), 8.43 (d, *J* = 8.1 Hz, 1 H), 8.32 (d, *J* = 7.5 Hz, 1 H), 7.80 (dd, *J* = 8.1, 7.5 Hz, 1 H), 5.33 (s, 1 H), 4.85 (s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 197.9, 148.0, 135.8, 134.0, 130.6, 127.5, 122.1, 65.8.

MS (EI): *m*/*z* = 181, 150, 122.

Anal. Calcd for $C_8H_7NO_4$: C, 53.04; H, 3.89. Found: C, 53.06; H, 3.79.

2-Hydroxy-1-(naphthalen-1-yl)ethanone
Yellow oil.

IR (KBr): 3413, 1648 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 8.7 Hz, 1 H), 8.11–7.88 (m, 3 H), 7.70–7.50 (m, 3 H), 4.93 (s, 3 H), 3.74 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.2, 134.5, 133.9, 130.7, 130.3, 128.7, 128.6, 128.4, 126.8, 125.5, 124.3, 66.6.

MS (EI): *m*/*z* = 186, 155, 127.

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.56; H, 5.20.

2-Hydroxy-4′-methylpropiophenone
Colorless solid; mp 47–49 °C (*n*-hexane).

IR (KBr): 3430, 1680 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 5.13 (q, *J* = 6.6 Hz, 1 H), 3.82 (s, 1 H), 2.43 (s, 3 H), 1.44 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.9, 145.0, 130.7, 129.5, 128.8, 69.1, 22.4.

MS (EI): *m*/*z* = 164, 149, 119, 91.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.21; H, 7.21.

2-Hydroxyindan-1-one
Colorless solid; mp 79–82 °C (*n*-hexane).

IR (KBr): 3144, 1719 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.5 Hz, 1 H), 7.66–7.61 (m, 1 H), 7.47–7.37 (m, 2 H), 4.55 (dd, *J* = 4.8, 8.1 Hz, 1 H), 3.58 (dd, *J* = 8.1, 16.5 Hz, 1 H), 3.04 (s, 1 H), 3.02 (dd, *J* = 4.8, 16.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.5, 150.9, 135.8, 133.9, 128.0, 126.8, 124.4, 74.2, 35.1.

MS (EI): *m*/*z* = 148, 119, 91.

Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.01; H, 5.21.

2-Hydroxy-1-tetralone
Pale-yellow oil.

IR (KBr): 3476, 1685 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 1 H), 7.56–7.32 (m, 2 H), 7.28 (d, *J* = 6.9 Hz, 1 H), 4.39 (dd, *J* = 6.0, 13.5 Hz, 1 H), 3.92 (s, 1 H), 3.23–2.99 (m, 2 H), 2.59–2.49 (m, 1 H), 2.13–1.97 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.6, 144.3, 134.2, 130.4, 128.9, 127.6, 12.9, 73.8, 31.8, 27.7.

MS (EI): *m*/*z* = 162, 144, 133, 118, 103, 90, 77.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.13; H, 6.10.

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