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High-Yielding Oxidation of β-Hydroxyketones to β-Diketones Using *o*-Iodoxybenzoic Acid

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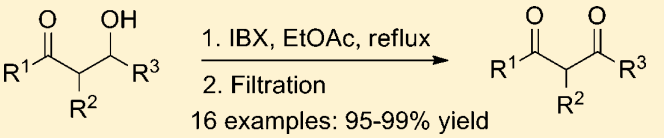
Supporting Information

ABSTRACT: The oxidation of β-hydroxyketones to β-diketones was systematically investigated. *o*-Iodoxybenzoic acid (IBX) was found to be efficient, operationally easy, and superior to other common oxidants. The reaction is suitable for milligram- to gram-scale oxidations.



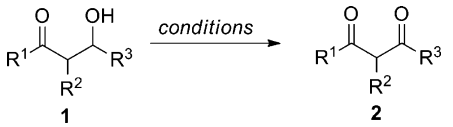
Beta-diketones are reactants in many venerable time-honored C−C bond forming reactions, including the Knoevenagel condensation,[1] the Tsuji−Trost reaction,[2] and the DeMayo reaction.[3] Despite the importance of the β-diketone function in the literature, relatively few reports describe its production from the corresponding β-hydroxyketone. A notable exception is the systematic study of Smith and Levenberg describing the Swern-type oxidation of β-hydroxyketones.[4] Therein, they found that the DMSO-based oxidations gave superior yields compared with Cr(VI) oxidations. Another oxidant known to oxidize β-hydroxyketones is the Dess−Martin periodinane (DMP),[5] and high reaction yields have been observed.[6]

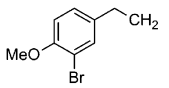
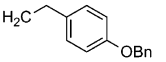
Recently, we required the oxidation of β-hydroxyketone **1a** to the corresponding β-diketone **2a** (Table 1, entry 1).[7] We found that **1a** was oxidized under Swern conditions[8] to give **2a**; however, the yield was 35%. DMP oxidation gave the desired diketone in 40% yield. Attempts to buffer the potentially acidic reaction conditions, conducting the experiment at lower temperatures, or limiting the oxidant to precisely 1.0 equiv did not result in improvement of yield. Oxidation using Ley's conditions (TPAP/NMO) gave only a trace amount of **2a**.[9] Ultimately, we found that the oxidation of **1a** with *o*-iodoxybenzoic acid (IBX)[10,11] using the conditions described by Finney was high-yielding and remarkably convenient.[12,13] The reaction mixture is simply filtered to remove the oxidant and concentrated to give **2a** in near-quantitative yield.

Several disparate examples of the IBX-promoted oxidation of β-hydroxyketones to form β-diketones appear in the literature,[14,15] but in relatively few cases[15] do the diketones have acidic α-protons. Additionally, IBX is known to promote oxidation of 1,3-diols to β-ketoaldehydes, presumably via β-hydroxyketone intermediates.[16,17] We decided to undertake a systematic study of this transformation; our results are described herein.

We began with a comparison of reaction yields using Swern, DMP, and IBX oxidations on a variety of different β-hydroxyketones (Table 1). The starting β-hydroxyketones were prepared as described elsewhere.[18] In all cases, IBX showed clean, near-quantitative conversion to the corresponding diketone. In all cases, only a single product was detectable by TLC, ^{1}H NMR, or ^{13}C NMR of the crude reaction mixture. With benzylic alcohols (Table 1, entries 2 and 4), aliphatic alcohols (Table 1, entries 3, 5 and 6), and cyclic substrates (Table 1, entry 4), we found IBX to be superior to both Swern and DMP oxidations. The oxidation was performed on a

Table 1. Comparison of Different Oxidants for β-Diketone Formation



entry	product	R^1	R^2	R^3	Yield (%) Swern[a]	DMP[b]	IBX[c]
1	**2a**		H		35	40	95
2	**2b**	Ph	H	Ph	52	42	99
3	**2c**	Ph	H	Me	74	42	98
4	**2d**	-$(CH_2)_4$-		*p*-$C_6H_4NO_2$[d]	91	75	98[e]
5	**2e**	Ph	H	*i*-Bu	63	40	99
6	**2f**	Ph	Cl	*n*-Pr[f]	69	38	96

[a]Swern: 1.2 equiv of $(COCl)_2$, 2.4 equiv of DMSO, 5.4 equiv of Et_3N, CH_2Cl_2 (0.15 M), −78 °C. [b]DMP: 2.0 equiv of Dess−Martin periodinane, 4.0 equiv of $NaHCO_3$, CH_2Cl_2 (0.10 M), rt. [c]IBX: 3.0 equiv of *o*-iodoxybenzoic acid, EtOAc (0.14 M), 77 °C. [d]Substrate is the *anti*-diastereomer. [e]Reaction performed on 8.6 mmol (2.1 g) scale. [f]Substrate is the *syn*-diastereomer.

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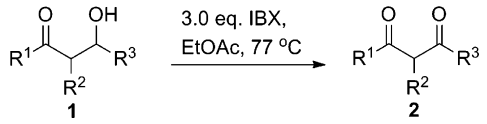
multiple-gram (8.6 mmol) scale with no observed loss in yield (Table 1, entry 4). Both *syn*- and *anti*-β-hydroxyketones were smoothly oxidized to the corresponding β-diketones (Table 1, entries 6 and 4, respectively). Additionally, we were delighted to find that chlorine substitution is tolerated in the IBX-mediated oxidation (Table 1, entry 6).

We next investigated the IBX oxidation using a variety of aldol-type substrates.[18] As seen in Table 2, every substrate gave near-quantitative yield of the expected diketone product. Aryl and alkyl substitution was widely tolerated, as was substitution at the α-position of the hydroxyketone. Acyclic and cyclic β-hydroxyketones were all productive substrates. *Syn*- and *anti*-aldol diastereomers were well tolerated. Even α-iodo-substrates[19] oxidized smoothly to give the corresponding diketones (Table 2, entries 9 and 10). The pure α-iodo-β-diketone products decomposed with half-lives of several hours, which demonstrates the mild nature of these conditions.

Table 2. β-Diketone Synthesis



entry	product	R^1	R^2	R^3	yield (%)
1	**2g**	Me	H	*p*-$C_6H_4NO_2$	99
2	**2h**	$-(CH_2)_4-$		*p*-C_6H_4Cl[a]	99
3	**2i**	Me	H	*o*-C_6H_4Cl	99
4	**2c**	Me	H	Ph	99
5	**2j**	Et	Me	*n*-Hept[b]	96
6	**2k**	*n*-Pr	Et	*n*-Pr[b]	99
7	**2l**	Ph	Me	*n*-Pr[b]	97
8	**2m**	Ph	Me	Ph[b]	99
9	**2n**	Me	I	Ph[a]	97
10	**2o**	Ph	I	Ph[a]	99

[a]Substrate is the *anti* diastereomer. [b]Substrate is the *syn* diastereomer.

The structural similarity of IBX with DMP caused us to wonder why the chemical yield of oxidation with IBX was superior. We attribute this observation to two distinct factors. First, β-diketones may decompose upon purification by standard column chromatography. In the reaction from Table 1, entry 5, IBX provides clean oxidation to form **2e**. The purification procedure involves rapid filtration of the crude reaction mixture through a small plug of silica gel to remove the heterogeneous oxidant and concentration of the filtrate to deliver pure **2e** (Figure 1a). In the case of Swern and DMP oxidations, the reaction mixtures contain byproducts that require further purification (Figure 1b and c, respectively). In our hands, subjection of β-diketones to standard column chromatography always results in production of new compounds (TLC, NMR) and a corresponding loss of mass balance.

Second, the IBX conditions promote selective oxidation of β-hydroxyketones over β-diketones, but DMP does not. In the oxidation of **1e** to **2e** with DMP, prior to complete conversion, the reaction mixture contains **2e** as well as various byproducts (TLC, NMR). Furthermore, subjection of pure β-diketone **2e** to DMP for 30 min results in formation of new compounds by NMR (Figure 1d).[20] Finally, subjection of **2e** to the standard IBX reaction conditions results in no reaction.[21]

In conclusion, despite the ubiquity of β-hydroxyketones, no systematic study of their oxidation to β-diketones using IBX has appeared. We found that IBX is a superior oxidant for this transformation. The reaction gives quantitative yields for a wide range of starting materials, including α-halo-β-hydroxyketones. The superiority of IBX likely results from ease of purification of the reaction mixtures and its ability to selectively oxidize β-hydroxyketones in the presence of the product β-diketones.

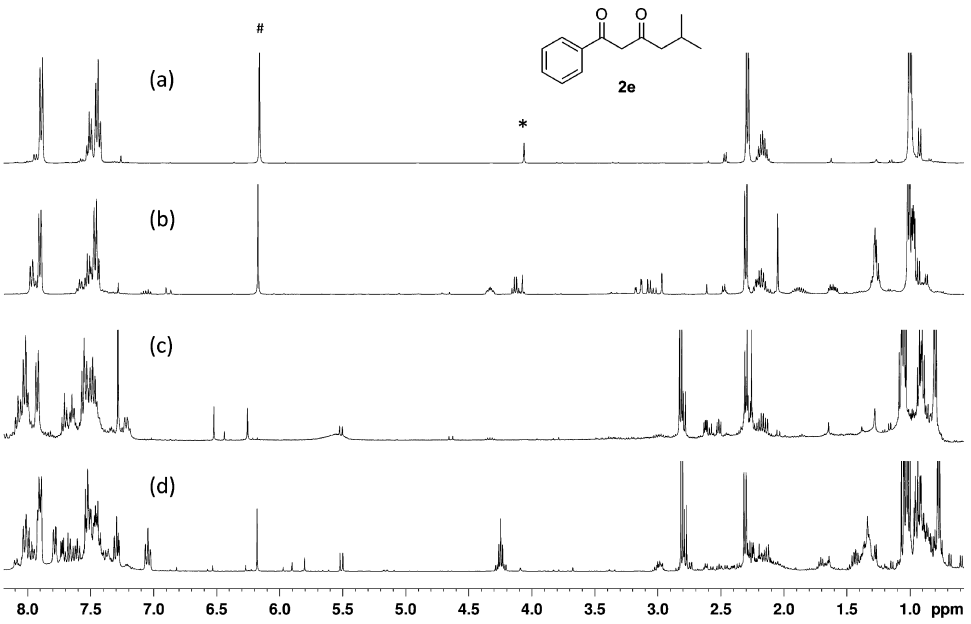


Figure 1. ^{1}H NMR data of reaction mixtures. (a) Product **2e** from IBX oxidation after simple filtration. (b) Product **2e** from Swern oxidation after aqueous workup. (c) Product **2e** from DMP oxidation after aqueous workup. (d) Reaction mixture after subjection of pure **2e** to DMP for 30 min and aqueous workup. (∗) α-Methylene protons (keto form). (#) α-Methyne proton (enol form).

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EXPERIMENTAL SECTION

Swern Oxidation General Procedure (Entry 2, Table 1). To a solution of DMSO (341 μL, 2.29 mmol) in CH_2Cl_2 (6.0 mL) at −78 °C was added $(COCl)_2$ (99 μL, 1.15 mmol) dropwise. After 15 min, a solution of β-hydroxyketone (216 mg, 0.956 mmol) in CH_2Cl_2 (0.37 mL) was added, and the mixture was stirred for 30 min. Et_3N (718 μL, 5.16 mmol) was added, and the mixture was allowed to warm to rt. The reaction mixture was diluted with hexanes (10 mL) and poured into a separatory funnel containing saturated aqueous $NaHCO_3$ (10 mL). The layers were separated, and the organic layer was washed with additional $NaHCO_3$ solution (3 × 10 mL). The combined aqueous layers were extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated to give the crude reaction mixture. This mixture was purified by flash column chromatography (4:1 hexanes/EtOAc) to give **2b** (112 mg, 0.497 mmol, 52%).

Dess−Martin Oxidation General Procedure (Entry 2, Table 1). To a solution of β-hydroxyketone (23.5 mg, 0.104 mmol) in CH_2Cl_2 (1.04 mL) at rt were sequentially added $NaHCO_3$ (34.9 mg, 0.416 mmol) and the Dess−Martin periodinane (88.2 mg, 0.208 mmol). The reaction mixture was stirred until complete consumption of the starting material was observed (TLC). The reaction mixture was diluted with CH_2Cl_2 (5 mL) and poured into a separatory funnel containing a 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated to give the crude reaction mixture. This mixture was purified by flash column chromatography (4:1 hexanes/EtOAc) to give **2b** (10 mg, 0.045 mmol, 42%).

IBX Oxidation General Procedure (Entry 2, Table 1). To a solution of β-hydroxyketone (100 mg, 0.442 mmol) in EtOAc (3.2 mL) at rt was added IBX (371 mg, 1.33 mmol). The reaction mixture was heated to 77 °C until complete consumption of the starting material was observed (TLC, approximately 3−12 h). The reaction mixture was allowed to cool to rt, filtered through a small pad (1−2 cm) of silica, and concentrated to give pure **2b** (98 mg, 0.438 mmol, 99%).

1-(4-(Benzyloxy)phenyl)-7-(3-bromo-4-methoxyphenyl)-heptane-3,5-dione. 2a: R_f 0.45 (3:1 hexanes/EtOAc); IR (thin film) 3025, 2921, 1728, 1717, 1603, 1249 cm^{-1}; (exists as a 2:1 ratio of enol/keto tautomers; data is for the enol tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 15.4 (br s, 1H), 7.45−6.80 (m, 12 H), 5.42 (s, 1 H), 5.04 (s, 2 H), 3.86 (s, 3 H), 2.85 (m, 4 H), 2.56 (m, 4 H); (data is for the keto/enol mixture) ^{13}C NMR (100 MHz, $CDCl_3$) δ *C* 203.2, 202.8, 193.0, 192.8, 157.2, 154.3, 137.1, 134.3, 134.1, 132.9, 132.7, 111.5; *C*H 133.0, 129.24, 129.20, 128.5, 128.3, 128.2, 127.9, 127.4, 114.9, 111.9, 99.7; CH_2 69.9, 57.5, 45.3, 45.0, 40.1, 39.9, 30.7, 30.2, 28.5, 28.0; CH_3 56.2; HRMS (CI) calcd for $C_{27}H_{27}BrO_4$ $[M^+]$ 494.1093, found 494.1100.

1,3-Diphenylpropane-1,3-dione. 2b: R_f 0.71 (3:1 hexanes/EtOAc); IR (thin film) 3058, 2922, 1593, 1527, 1478, 1299 cm^{-1}; (exists as the enol tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 16.9 (br s, 1 H), 8.00 (m, 4 H), 7.57 (t, *J* = 7 Hz, 2 H), 7.50 (t, *J* = 8 Hz, 4 H), 6.91 (s, 1 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 185.7, 135.4; *C*H 132.4, 128.6, 127.1, 93.0; HRMS (CI) calcd for $C_{15}H_{13}O_2$ [M + H] 225.0916, found 225.0911.

1-Phenylbutane-1,3-dione. 2c: R_f 0.65 (3:1 hexanes/EtOAc); IR (thin film) 1602, 1276 cm^{-1}; (exists as the enol tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 16.2 (br s, 1 H), 7.86 (d, *J* = 8 Hz, 2 H), 7.49 (t, *J* = 7 Hz, 1 H), 7.42 (t, *J* = 7 Hz, 2 H), 6.16 (s, 1 H), 2.17 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 193.8, 183.3, 134.8; *C*H 132.3, 128.6, 127.0, 96.7; CH_3 25.9; HRMS (CI) calcd for $C_{10}H_{11}O_2$ [M + H] 163.0759, found 163.0755.

2-(4-Nitrobenzoyl)cyclohexanone. 2d: R_f 0.71 (2:1 hexanes/EtOAc); IR (thin film) 3107, 2933, 2867, 1696, 1674, 1603, 1516, 1397, 1342 cm^{-1}; (exists as the keto tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9 Hz, 2 H), 8.00 (d, *J* = 8 Hz, 2 H), 4.36 (dd, *J* = 10, 6 Hz, 1 H), 2.51 (app t, *J* = 6 Hz, 2 H), 2.34−2.14 (m, 2 H), 2.04 (m, 2 H), 1.91−1.71 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, HSQC) δ *C* 208.0, 196.3, 150.2, 141.1; *C*H 129.4, 123.8, 59.2; CH_2 42.4, 29.5, 27.2, 23.3; HRMS (CI) calcd for $C_{13}H_{14}NO_4$ [M + H] 248.0923, found 248.0927.

5-Methyl-1-phenylhexane-1,3-dione. 2e: R_f 0.73 (4:1 hexanes/EtOAc); IR (thin film) 3063, 2954, 1604 cm^{-1}; (exists as the enol tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 16.3 (br s, 1 H), 7.89 (d, *J* = 8 Hz, 2 H), 7.51 (t, *J* = 7 Hz, 1 H), 7.44 (t, *J* = 8 Hz, 2 H), 6.16 (s, 1 H), 2.29 (d, *J* = 7 Hz, 2 H), 2.17 (sept, *J* = 6 Hz, 1 H), 1.00 (d, *J* = 6 Hz, 6 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 195.6, 184.2, 135.2; *C*H 132.2, 128.6, 127.0, 96.8, 26.5; CH_2 48.2; CH_3 22.6; HRMS (CI) calcd for $C_{13}H_{17}O_2$ [M + H] 205.1229, found 205.1226.

2-Chloro-1-phenylhexane-1,3-dione. 2f: R_f 0.50 (4:1 hexanes/EtOAc); IR (thin film) 2965, 1723, 1686, 1596, 1449, 1288 cm^{-1}; (exists as a 2.6:1 ratio of keto/enol tautomers; data is for the keto tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7 Hz, 2 H), 7.60 (t, *J* = 7 Hz, 1 H), 7.48 (m, 2 H), 5.61 (s, 1 H), 2.73 (m, 2 H), 1.61 (pent, *J* = 7 Hz, 2 H), 0.89 (t, *J* = 7 Hz, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 200.8, 189.9, 133.7; *C*H 134.5, 129.4, 129.0, 64.4; CH_2 40.9, 16.9; CH_3 13.4; HRMS (CI) calcd for $C_{12}H_{14}ClO_2$ [M + H] 225.0682, found 225.0679.

1-(4-Nitrophenyl)butane-1,3-dione. 2g: R_f 0.85 (2:1 hexanes/EtOAc); IR (thin film) 3107, 1734, 1696, 1587, 1527, 1342; (exists as the enol tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 15.9 (br s, 1 H), 8.29 (d, *J* = 9 Hz, 2 H), 8.02 (d, *J* = 9 Hz, 2 H), 6.23 (s, 1 H), 2.26 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 196.3, 179.0, 149.7, 140.3; *C*H 127.8, 123.8, 98.0; CH_3 26.5; HRMS (CI) calcd for $C_{10}H_{10}NO_4$ [M + H] 208.0610, found 208.0608.

2-(4-Chlorobenzoyl)cyclohexanone. 2h: R_f 0.65 (2:1 hexanes/EtOAc); IR (thin film) 2938, 1713, 1680, 1593, 1081; (exists as a 1.3:1 ratio of keto/enol tautomers; data is for the keto tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6 Hz, 2 H), 7.41 (d, *J* = 6 Hz, 2 H), 4.31 (ddd, *J* = 9, 6, 1 Hz, 1 H), 2.54−1.25 (m, 8 H); (data is for the keto/enol mixture) ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 208.5, 196.3, 189.94, 189.88, 139.7, 136.5, 135.7, 134.8, 107.02; *C*H 129.9, 129.1, 128.9,128.4, 58.8; CH_2 42.3, 32.7, 29.8, 27.2, 26.4, 23.3, 23.1, 21.7; HRMS (CI) calcd for $C_{13}H_{14}ClO_2$ [M + H] 237.0682, found 237.0680.

1-(2-Chlorophenyl)butane-1,3-dione. 2i: R_f 0.53 (4:1 hexanes/EtOAc); IR (thin film) 3063, 1729, 1609, 1424, 1293; (exists as the enol tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 15.7 (br s, 1 H), 7.58 (dd, *J* = 8, 2 Hz, 1 H), 7.43 (dd, *J* = 8, 1 Hz, 1 H), 7.37 (td, *J* = 8, 2 Hz, 1 H), 7.33 (td, *J* = 8, 1 Hz, 1 H), 6.05 (s, 1 H), 2.19 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC, DEPT) δ *C* 192.8, 184.6, 135.5, 131.7; *C*H 131.6, 130.6, 130.0, 126.9, 101.9; CH_3 25.5; HRMS (CI) calcd for $C_{10}H_{10}ClO_2$ [M + H] 197.0369, found 197.0364.

4-Methyldodecane-3,5-dione. 2j: R_f 0.58 (6:1 hexanes/EtOAc); IR (thin film) 2922, 1723, 1702, 1598, 1457; (exists as a 4.2:1 ratio of keto/enol tautomers; data is for the keto tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 3.68 (q, *J* = 7 Hz, 1 H), 2.53−2.42 (m, 4 H), 1.30 (d, *J* = 7 Hz, 3 H), 1.29−1.21 (m, 10 H), 1.04 (t, *J* = 7 Hz, 3 H), 0.87 (m, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 207.9, 207.5; *C*H 60.62; CH_2 41.5, 34.7, 31.6, 29.0, 23.4, 22.6; CH_3 14.1, 12.8, 7.6; HRMS (CI) calcd for $C_{13}H_{25}O_2$ [M + H] 213.1855, found 213.1848.

5-Ethylnonane-4,6-dione. 2k: R_f 0.64 (4:1 hexanes/EtOAc); IR (thin film) 2965, 1723, 1696, 1462 cm^{-1}; (exists as a 10:1 ratio of keto/enol tautomers; data is for the keto tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 3.55 (t, *J* = 7 Hz, 1 H), 2.42 (m, 4 H), 1.86 (pent, *J* = 7 Hz, 2 H), 1.57 (sext, *J* = 7 Hz, 4 H), 0.88 (t, *J* = 7 Hz, 6 H), 0.87 (t, *J* = 7 Hz, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 206.6; *C*H 69.6; CH_2 43.8, 21.7, 16.8; CH_3 13.6, 12.2; HRMS (CI) calcd for $C_{11}H_{21}O_2$ [M + H] 185.1542, found 185.1545.

2-Methyl-1-phenylhexane-1,3-dione. 2l: R_f 0.56 (4:1 hexanes/EtOAc); IR (thin film) 3058, 2960, 1712, 1669, 1440 cm^{-1}; (exists as the keto tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7 Hz, 2 H), 7.55 (t, *J* = 8 Hz, 1 H), 7.44 (t, *J* = 8 Hz, 2 H), 4.47 (q, *J* = 7 Hz, 1 H), 2.46 (dt, *J* = 17, 7 Hz, 1 H), 2.34 (dt, *J* = 17, 7 Hz, 1 H), 1.52 (m, 2 H), 1.40 (d, *J* = 7 Hz, 3 H), 0.80 (t, *J* = 7 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, HSQC) δ *C* 206.9, 197.3, 136.0; *C*H 133.5, 128.7, 128.5,

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56.0; CH_2 42.4, 16.8; CH_3 13.43, 13.37; HRMS (CI) calcd for $C_{13}H_{17}O_2$ [M + H] 205.1229, found 205.1236.

2-Methyl-1,3-diphenylpropane-1,3-dione. 2m: R_f 0.50 (4:1 hexanes/EtOAc); IR (thin film) 3058, 2932, 1696, 1669, 966 cm^{-1}; (exists as the keto tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8 Hz, 4 H), 7.55 (t, J = 7 Hz, 2 H), 7.44 (t, J = 8 Hz, 4 H), 5.29 (q, J = 7 Hz, 1 H), 1.59 (d, J = 7 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, HSQC) δ *C* 197.1, 135.5; *C*H 133.4, 128.8, 128.4, 50.8; CH_3 14.3; HRMS (CI) calcd for $C_{16}H_{15}O_2$ [M + H] 239.1072, found 239.1075.

2-Iodo-1-phenylbutane-1,3-dione. 2n: R_f 0.58 (4:1 hexanes/EtOAc); IR (thin film) 2382, 1707, 1671, 1223 cm^{-1}; (exists as the keto tautomer) ^1H NMR (700 MHz, $CDCl_3$) δ 7.96 (d, J = 8 Hz, 2 H), 7.61 (t, J = 8 Hz, 1 H), 7.47 (t, J = 8 Hz, 2 H), 5.98 (s, 1 H), 2.54 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$, HSQC) δ *C* 198.7, 191.0, 133.3; *C*H 134.3, 129.03, 128.95, 32.6; CH_3 26.9; HRMS (CI) calcd for $C_{10}H_9IO_2$ [M^+] 287.9648, found 287.9650.

2-Iodo-1,3-diphenylpropane-1,3-dione. 2o: R_f 0.48 (4:1 hexanes/EtOAc); IR (thin film) 3063, 1696, 1663, 1288 cm^{-1}; (exists as the keto tautomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 4 H), 7.59 (t, J = 7 Hz, 2 H), 7.46 (t, J = 8 Hz, 4 H), 6.96 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, HSQC) δ *C* 190.0, 133.2; *C*H 134.1, 129.2, 129.0, 33.7; HRMS (CI) calcd for $C_{15}H_{12}IO_2$ [M + H] 350.9882, found 350.9896.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all β-diketone products. This material is available free of charge via the Internet at http://pubs.acs.org.

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