Selective and effective oxone-catalysed α-iodination of ketones and 1,3-dicarbonyl compounds in the solid state

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Abstract
Selective α-iodination of ketones and 1,3-dicarbonyl compounds was accomplished in the solid state within a very short reaction time with excellent yields using elemental iodine and Oxone as the catalyst, by grinding in a mortar.

Keywords: Oxone, α-iodination, β-keto esters, iodine, carbonyl compounds

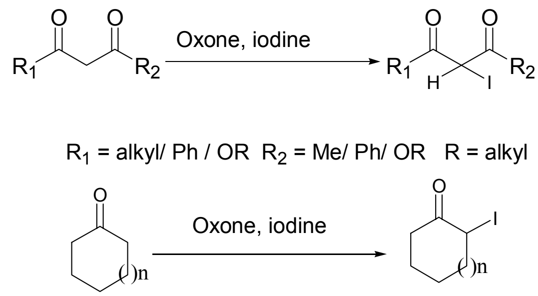
Introduction

Iodo-functionalized organic molecules are versatile intermediates in synthetic organic chemistry, based on their ability to form carbon-carbon bonds and to undergo iodine-metal exchange reactions.[1] Moreover, a considerable number of iodo-substituted molecules possess biological activity and their properties have attracted considerable attention in the medicinal field.[2] Among the variety of methods known for the introduction of iodine atom into a molecule, the most conventional is the use of an oxidizing agent with iodides, iodine or I^+-generating reagents as the source of the iodine atom.[3] Few solvent free iodination methods with microwave irradiation have been reported.[4]

Results and Discussion

In this communication, we report an efficient solvent-free selective α-iodination of ketones and 1,3-diketones, using elemental iodine and a catalytic amount of Oxone, by grinding in a mortar (Scheme 1). There was no requirement for any additives. Oxone is a stable ternary composite of $KHSO_5/KHSO_4$ and K_2SO_4 in 2:1:1 molar ratio and its utility has been established for a variety of organic reactions.[5] Although aromatic iodination using an equimolar amount of oxone and

NH_4I in methanol, at room temperature, has been reported,[6] there are no reports of selective α-iodination of 1,3-dicarbonyl compounds or ketones, using molecular iodine and catalytic Oxone.

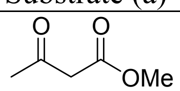
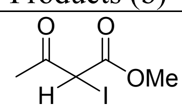
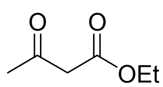
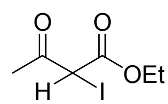
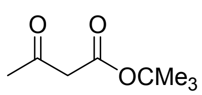
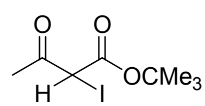
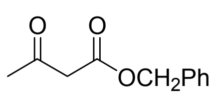
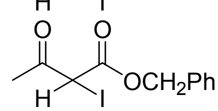
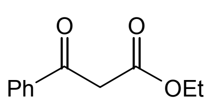
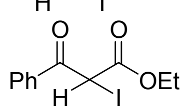
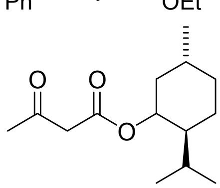
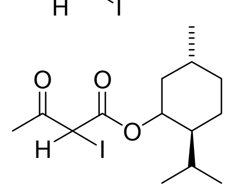


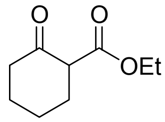
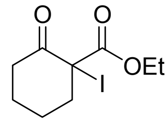
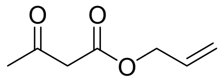
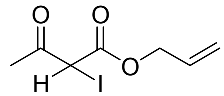
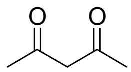
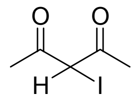
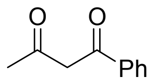
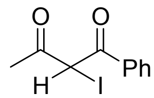
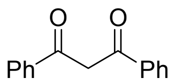
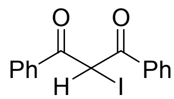
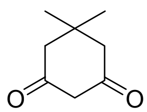
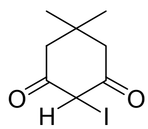
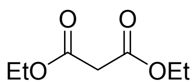
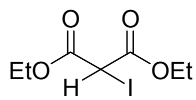
n=5, 6, 12

Scheme 1. Selective α-iodination of 1,3−dicarbonyl and carbonyl compounds.

For the current study, methyl acetoacetate **1a** was taken as the model substrate. Methyl acetoacetate (1 equiv) was mixed with Oxone (0.1 equiv) and molecular iodine (0.5 equiv) and the mixture was ground in a mortar for 1 min. The crude reaction mixture was filtered, dried and analyzed without any further purification. The reaction furnished selectively α-monoiodinated methyl acetoacetate **1b** in excellent yield without the formation of any side products. This result encouraged us to examine other 1,3−dicarbonyl compounds (Table 1).

Table 1. α-Iodination of various β-ketoesters and 1,3-diketones

Entry	Substrate (a)	Products (b)	Time (min)	Yield[a] (%)
1			1	96
2			2	93[3e]
3			2.5	91[4b]
4			3	90
5			3	92[3e]
6			5	85

7			2	93[3e]
8			5	88
9			1	92
10			1.5	94
11			2	95[8a]
12			1	90[8b]
13			4	94[4b]

[a] Isolated yield

The β-keto esters **2a - 6a** reacted smoothly to give α-monoiodinated β-ketoesters. Similarly, the cyclic β-keto ester **7a** also gave the iodinated product **7b**. Reaction of β-keto ester **8a**, which possesses both the active methylene hydrogens together with a carbon-carbon double bond, suffered only α-iodination, without affecting the double bond.

Examination of 1,3-diketones **9a – 12a** showed them also to give mono α-iodinated products in good yields. We note that a ^{13}C carbonyl signal for compound **12b** could not be seen, perhaps due to rapid keto-enol tautomerism. The structure of compound **12b** was confirmed by a single crystal X-ray diffraction study (**Figure 1**).

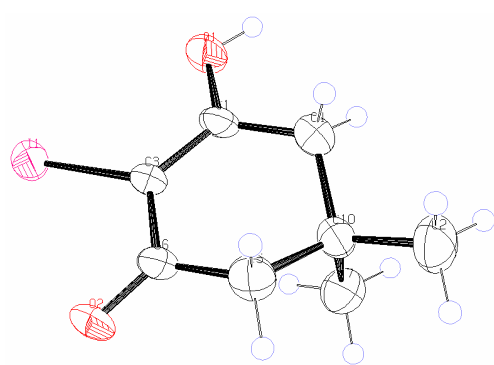
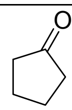
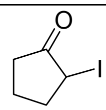
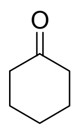
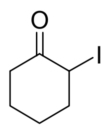
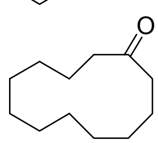
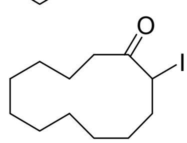
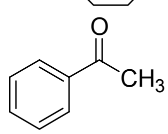
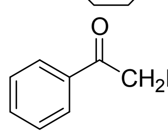
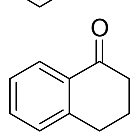
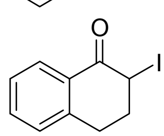


Figure 1. ORTEP plot of α-monoiodo dimedone **12b** with atom numbering scheme

Literature reports[7] reveal the difficulty in iodinating dialkyl malonates. We succeeded in iodinating diethyl malonate **13a** to produce the mono-iodo derivative by increasing the amount of catalyst from 0.1 equiv to 0.25 equiv.

Table 2 summarizes the α-iodination of the ketones **14a – 17a** which furnished exclusively 2-iodo derivatives. For example, cyclopentanone **14a** and cyclohexanone **15a** produced 2-iodocyclopentanone **14b** and 2-iodocyclohexanone **15b** respectively within 1 min in good yields. Cyclododecanone **16a** and acetophenone **17a** underwent the reaction within 2 – 3 min respectively to give **16b** and **17b**. Tetralone **18a** also reacted smoothly to give 2-iodo-1-tetralone.

Table 2. α-Iodination of diketones

Entry	Substrate (a)	Products (b)	Time(min)	Yield[b] (%)
14			1	96
15			1	96
16			2	93
17			3	91
18			3	91

As metal persulfates are known[9] to be activated for oxidation reactions on heating, we suggest that the oxidation of iodine probably involves oxidation induced by the heat and pressure generated in the mortar.

In conclusion, the major advantages of the new method are the introduction of an iodine atom into organic molecules in the absence of an organic co-solvent, complete consumption of iodine, lack of work-up and purification procedure along with the requirement for only a short reaction time. Moreover since iodinated compounds have a tendency to decompose on purification by column chromatography, our procedure overcomes this problem as only monoiodinated products were obtained exclusively.

Experimental Section

General Procedure. Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Some of the β-ketoesters were prepared by reported procedures. Some of the products were characterized by comparison of their spectral (IR, UV, ^{1}H NMR, and ^{13}C NMR) and physical data with the authentic samples.

Typical experimental procedure. Typical experimental procedure: The substrate (1 mmol) was mixed with iodine (0.5 equiv) and Oxone (0.1 equiv) in a mortar and the mixture ground for 1 min. After completion of the reaction as indicated by TLC, the reaction mixture was transferred to a filter paper and extracted with dichloromethane. The extract was evaporated to dryness and the residue analysed without further purification.

Methyl 2-iodo-3-oxobutanoate (1b). Oily liquid, IR (neat): 1738 cm^{-1}. ^{1}H NMR (400 MHz) δ: 2.53 (s,3H), 3.82 (s,3H), 5.02 (s,1H). ^{13}C NMR (100 MHz): δ 24.9, 26.3, 54.0, 167.3, 197.5. Analysis $C_5H_7IO_3$ (242.01): requires C, 24.81%; H, 2.92%. Found C, 25.13%; H, 2.83%.
Ethyl 2-iodo-3-oxobutanoate (2b). Oily liquid, IR (neat):1733 cm^{-1}. ^{1}H NMR (400 MHz) δ: 1.31 (t, 3H, *J* = 7.2 Hz), 2.53 (s, 3H), 4.27 (q, 2H, *J* = 7.2 Hz), 5.00 (s, 1H). ^{13}C NMR (100 MHz): 13.9, 25.7, 26.3, 63.2, 166.9, 197.6 Analysis $C_6H_9IO_3$ (256.04): requires C, 28.15%; H, 3.54% Found C, 27.87%; H, 3.47%.
(1,1-Dimethylethyl) 2-iodo-3-oxobutanoate (3b). Oily liquid, IR (neat): 1731 cm^{-1}. ^{1}H NMR (400 MHz) δ: 1.48 (s,9H), 2.48 (s,3H), 4.91 (s,1H). ^{13}C NMR (100 MHz): 26.2, 27.7 (3C), 28.2, 51.6, 165.7, 197.8. Analysis $C_8H_{13}IO_3$(284.09): requires C, 33.82%; H, 4.61%. Found C, 33.54%; H, 4.54%.
Benzyl 2-iodo-3-oxobutanoate (4b). Oily liquid, IR (neat): 1735 cm^{-1}. ^{1}H NMR (400 MHz) δ: 2.47 (s,3H), 5.08 (s,1H), 5.26 (s,2H), 7.28 (m, 5H). ^{13}C NMR (100 MHz): 24.8, 26.4, 68.8, 128.6 (2C), 128.8 (2C), 133.3,167.4, 197.5. Analysis $C_{11}H_{11}IO_3$ (318.11): requires C, 41.53%; H, 3.49% Found C, 41.25 %; H, 3.58%.
Ethyl 2-iodo-3-oxo-3-phenylpropanoate (5b). Oily liquid, IR (neat): 1675 cm^{-1}. ^{1}H NMR (400 MHz) δ:1.22 (t, 3H, *J* = 7.2 Hz,), 4.24 (q, 2H, *J* = 7.2 Hz), 5.92 (s, 1H), 7.47 (t, 2H, *J* = 7.6 Hz), 7.57 (t,1H, *J* = 7.6 Hz), 7.96 (d, 2H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz): 13.9, 24.2, 63.5, 129.1 (2C), 129.3 (2C), 133.1, 134.3, 166.7, 189.4. Analysis $C_{11}H_{11}IO_3$(318.11): requires C, 41.53%; H, 3.49% Found C, 41.79 %; H, 3.41%.
5-Methyl-2-(1-methylethyl)cyclohexyl 2-iodo-3-oxobutanoate (mixture of two diastereomers) (6b). Viscous oil; IR (neat) : 1731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.77 (d, *J* = 7.6 Hz, 3H), 0.78 (d, *J* = 7.6 Hz, 3H), 0.83-0.93 (m, 12H), 1.00 -1.10 (m, 2H), 1.40-1.51 (m, 4H), 1.65-1.75 (m, 4H), 1.70-1.80 (m, 4H), 2.00-2.20 (m, 4H), 2.53 (s, 6H), 4.74 – 4.78 (m, 2H), 4.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.1, 16.3, 20.7, 20.9, 21.1 (2C), 21.9, 22.2, 23.2, 23.5, 26.0, 26.2, 29.9, 31.3 (2C), 34.0, 34.1, 40.6, 40.9, 46.7, 48.9, 50.3, 75.2 (2C), 166.3 (2C),

200.1 (2C). Analysis $C_{28}H_{46}I_2O_6$(732.48): requires C, 45.91%; H, 6.33% Found C, 45.65%; H, 6.25%.

Ethyl 1-iodo-2-oxocyclohexanecarboxylate (7b). Oily liquid, IR (neat): 1732 cm^{-1}. ^1H NMR (400 MHz) δ:1.29 (t, 3H, *J* = 7.2 Hz), 1.72 (pent, 2H, *J* = 6.8 Hz), 1.79 – 1.85 (m,1H,), 1.97 – 2.02 (m,1H), 2.31 (pent,1H, *J* = 7.2 Hz), 2.48 – 2.56(m,1H) , 2.91 – 2.99 (m, 2H), 4.28 (q, 2H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz): 13.7, 24.6, 27.1, 38.1, 43.1, 53.0, 62.8, 168.9, 199.4. Analysis $C_9H_{13}IO_3$(296.10): requires C, 36.51%; H, 4.43% Found C, 36.78%; H, 4.34%.

2-Propenyl 2-iodo-3-oxobutanoate (8b). Viscous oil; IR (neat) ν:1728, 1648 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 4.69 (d, 2H, *J* = 6.0 Hz), 5.04 (s, 1H), 5.27 (dd, 1H, *J* = 16.0 Hz, *J* = 1.2 Hz), 5.39 (dd, 1H, *J* = 10.2 Hz, *J* = 0.8 Hz), 5.87-5.97 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.3, 26.3, 67.4, 119.5,130.8, 166.4, 197.4. Analysis $C_7H_9IO_3$(268.05): requires C, 31.37%; H, 3.38% Found C, 31.09%; H, 3.30%.

3-Iodopentane-2,4-dione (9b). Viscous oil; IR (neat) ν: 3433, 1733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 6H), 5.03 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.6, 27.5, 33.9, 199.6, 203.5. Analysis $C_5H_7IO_2$(226.00): requires C, 26.57%; H, 3.12% Found C, 26.28%; H, 3.05%.

2-Iodo-1-phenylbutane-1,3-dione (10b). Oily liquid, IR (neat): 1596, 1707 cm^{-1}. ^1H NMR (400 MHz) δ: 2.55 (s,3H), 5.95 (s,1H), 7.49 (t, 2H, *J* = 8.0 Hz), 7.62 (t,1H, *J* = 6.8 Hz), 7.97 (d, 2H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz): 27.2, 32.9, 129.1 (3C), 133.5, 134.4 (2C), 191.3, 198.9. Analysis $C_{10}H_9IO_2$(288.08): requires C, 41.69%; H, 3.15% Found C, 41.98%; H, 3.07%.

2-Iodo-1,3-diphenylpropane-1,3-dione (11b). Crystals, mp: 104 °C (lit[8a] 108 °C), IR (KBr): 1667, 1693 cm^{-1}. ^1H NMR (400 MHz) δ: 6.94 (s,1H), 7.47 (t, 4H, *J* = 8.0 Hz), 7.60 (t, 2H, *J* = 7.2 Hz), 8.09 (d, 4H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz): 34.0, 129.2 (4C), 129.4 (4C), 133.3 (2C), 134.3 (3C), 190.2. Analysis $C_{15}H_{11}IO_2$(350.16): requires C, 51.45%; H, 3.17% Found C, 51.19%; H, 3.10%.

2-Iodo-5,5-dimethylcylohexane-1,3-dione (12b). Crystals, mp: 155 °C (lit[8b] 166 °C), IR (KBr) ν: 3421, 1648 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.11 (s, 6H), 2.45 (s, 2H), 2.57 (s, 2H), 6.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.7 (2C), 32.2, 46.8, 50.1, 76.9. Analysis $C_8H_{11}IO_2$(266.07): requires C, 36.11%; H, 4.17% Found C, 36.35 %; H, 4.09%.

Crystal data

A sample suitable for crystallographic analysis was obtained as colorless plates from MeOH. Data were collected on a Brucker Smart Apex CCD area detector. Ambient temperature: 296(2) K; Radiation wavelength: 0.71073 Å; Radiation type: Mok\a; Completeness to θ= 28.31:88.9%; Cell setting: Orthorhombic; Space group: Pna2(1); Cell length a:13.1696(9) Å, Cell length b:12.3650(8) Å, Cell length c: 5.8531(4) Å; Cell angle α: 90.00°, Cell angle β: 90.00°, Cell angle γ: 90.00°;Cell volume V: 953.13(11); Cell formula units Z: 4; R indices [I>2σ(I)]: R1 = 0.0217, wR2 = 0.0565; R indices [all data]: R1 = 0.0229, wR2 = 0.0571. The structure was refined with SHELXL-97.

Data has been deposited at the Cambridge Crystallographic Data Centre, with deposition number CCDC 651820.

Ethyl-3-ethoxy-2-iodo-3-oxopropanoate (13b). Viscous oil; IR (neat) ν: 1739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, 6H, *J* = 7.2 Hz), 4.25 (q, 4H, *J* = 7.2 Hz), 5.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9 (2C), 16.1, 63.3 (2C), 166.2 (2C). Analysis $C_7H_{11}IO_4$(286.07): requires C, 29.39%; H, 3.88% Found C, 29.12 %; H, 3.94%.

2-Iodocyclopentanone (14b). Viscous oil; IR (neat) ν: 1719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 – 1.49 (m, 2H), 1.62 – 1.70 (m, 2H), 2.44(t, 2H, *J* = 6.2 Hz), 4.06(t, 1H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ:16.4, 25.9, 31.7, 41.5, 201.9. Analysis C_5H_7IO (210.01): requires C, 28.60%; H, 3.36% Found C, 28.45 %; H, 3.24%.

2-Iodocyclohexanone (15b). Viscous oil; IR (neat) ν:1710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 – 1.43 (m, 2H), 1.54 – 1.58 (m, 2H), 1.61 – 1.67 (m, 2H), 2.35(t, 2H, *J* = 6.4 Hz), 4.13(t, 1H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.08, 26.42, 29.23, 32.05, 42.19, 198.01 Analysis C_6H_9IO (224.04): requires C, 32.17%; H, 4.05% Found C, 32.38 %; H, 4.12 %.

2-Iodocyclododecanone (16b). Viscous oil; IR (neat) ν:1721cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29(bs, 14H), 1.68 – 1.75 (m, 2H), 2.46(t, 2H, *J* = 6.4 Hz), 2.98 – 3.0(m, 1H), 3.01 – 3.04(m, 1H), 4.72 (dd, 1H, *J* = 3.2 Hz, *J* = 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.41,22.66, 23.53, 24.29, 24.37, 24.65, 24.81, 25.32, 25.91, 35.19, 40.53, 213.83. Analysis $C_{12}H_{21}IO$ (308.20): requires C, 46.76%; H, 6.87% Found C, 46.89 %; H, 6.93%.

2-Iodo-1-phenylethanone (17b). Viscous oil; IR (neat) ν:1710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.36(s, 2H),7.46 (t, 2H, *J* = 7.2 Hz), 7.57(t, 1H, *J* = 7.6 Hz), 7.96(d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.5, 130.2 (2C), 133.7 (2C), 135.9, 137.8, 190.8. Analysis C_8H_7IO (246.05): requires C, 39.05%; H, 2.87% Found C, 39.22 %; H, 2.94%.

2-Iodo-3,4-dihydro-2*H*-naphthalen-1-one (18b). Viscous oil; IR (neat) ν:1660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18(m, 2H), 2.76 (dd, 1H, *J* = 16.5 Hz, *J* = 4 Hz), 3.06 (m, 1H), 5.01 (t, 1H, *J* = 4), 7.12(dd, 1H, *J* = 8.6 Hz, *J* = 2.7Hz), 7.19(d, 1H, *J* = 8.6 Hz), 7.36 (dd, 1H, *J* = 8.6 Hz, *J* = 2.7 Hz), 7.59(d, 1H, *J* = 2.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 30.9, 31.8, 123.6, 126.4, 127.5, 132.7, 136.4, 137.7, 199.0 Analysis $C_{10}H_9IO$(272.08): requires C, 44.14%; H, 3.33 % Found C, 44.27 %; H, 3.41%.

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