# Facile Deoxygenation of Dicarbonyl Compounds Using a Samarium Diiodide–Additive System

Yasuko KAMOCHI,* Tadahiro KUDO, Toshinobu MASUDA, and Akira TAKADATE

*Daiichi College of Pharmaceutical Sciences; 22–1 Tamagawa-cho, Minami-ku, Fukuoka 815–8511, Japan.*

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**The reduction of $\alpha$- and $\beta$-dicarbonyl compounds was investigated with samarium diiodide in the presence of additive. Diketones and ketocarboxylic acids were easily reduced at room temperature to give the mono-alcohols in good to excellent yield, and ketoester afforded the saturated ester as the major product in moderate yield. These reductions containing the reductive deoxygenation can be rapidly performed under the facile and mild conditions by this method.**

**Key words** samarium diiodide; reductive deoxygenation; $\alpha$-dicarbonyl compound; $\beta$-dicarbonyl compound; mono-ketone; mono-alcohol

Samarium diiodide ($SmI_2$) has been used as a versatile reagent for synthetic organic chemistry due to its unique characteristics.[1—5] The single-electron donor ability of $SmI_2$ is strongly affected by the nature of the ligands around $Sm^{2+}$. Generally, it can be expected to facilitate the release of an electron from a metal ion when sufficient electrons are supplied from ligands around the metal ion. Therefore, the reducing ability can be greatly enhanced by the coordination of additive to $SmI_2$.

In a previous paper,[6] we reported that a variety of organic functionalities such as carboxylic acids, esters, amides, nitriles, phenols and pyridines were rapidly reduced to the corresponding products with the $SmI_2$–additive system. In fact, the marked effects of additives such as base,[7—11] acid[12] and water[13,14] were observed in the reduction of organic compounds with $SmI_2$.

A few reducing reagents have been reported for the deoxygenation of diketones, such as Zn–Hg/HCl,[15,16] Zn–Hg/HI,[17] Zn/AcOH[18] and $LiAlH_4$.[19] Regarding the deoxygenation of $\alpha$-oxygenated esters, $SmI_2$–MeOH and $SmI_2$–HMPA–pivalic acid systems have also been described.[20—22] However, little has been reported on the deoxygenation of $\alpha$- and $\beta$-diketones with $SmI_2$. The present paper deals with the facile reductive deoxygenation of $\alpha$- or $\beta$-diketones, ketocarboxylic acids, and their derivatives. As shown in Table 1, in order to compare the reducing abilities of $SmI_2$–additive systems towards dicarbonyl compounds, we first attempted the reduction of benzil with a variety of $SmI_2$–additive systems (Runs 1—8). The reductive deoxygenation with $SmI_2$ in the absence of additive did not proceed with high efficiency (Runs 1, 2). However, as might be expected, the same reactions of $\alpha$-diketones were rapidly performed with $SmI_2$ in the presence of an additive such as $H_2O$, $H_3PO_4$ or KOH. Among the systems tested, benzil was rapidly reduced with the $SmI_2$–$H_2O$ (Run 4) or 50% KOH (Run 8) system at room temperature to give 1,2-diphenylethanol, in good yield, accompanied by deoxybenzoin. Because it could be performed under extremely mild conditions, the reductive deoxygenation reactions of some $\alpha$-diketones were examined using the $SmI_2$–$H_2O$ system (Runs 9—14). The $\alpha$-diketones tested were rapidly reduced to the corresponding mono-alcohols at high yields, and the formyl group of phenylglyoxal was particularly easily converted into a methyl group with this system to give 1-phenylethanol in excellent yield (Run 9). The reduction of 1,2-diketoacenaphthene by this system afforded acenaphthenol as a major product along with acenaphthylene and acenaphthene (Run 14).

Also, as shown in Tables 2 and 3, the reactions of ketocarboxylic acids and their derivatives with this system were carried out under similar conditions.

In the reduction reactions of $\alpha$-ketocarboxylic acids and ester, reductive deoxygenation with the $SmI_2$–KOH system proceeded more smoothly than with the other systems. In addition, the reduction of carboxyl functionality was advanced more effectively than ester functionality with this system (Table 2). This is believed to be because the single-electron transfer from $Sm^{2+}$ to substrate is easy to become cause by coordination of substrate to $Sm^{2+}$. Accordingly, because the ketocarboxylic acid generates a carboxylate ion in the presence of KOH, its coordination ability increases compared with ester. Furthermore, the single-electron donor ability of $Sm^{2+}$ can be greatly enhanced by the addition of a base and hence the reduction of ketocarboxylic acid has been facilitated by this system. Actually, ketocarboxylic acids gave mono-alcohols in high yields (Runs 5, 6). However, in the reduction of ketoester, saturated ester was obtained as a main product under the same reaction conditions in moderate yields (Runs 9—11).

Interestingly, on the reaction of $\alpha$-ketonitrile, benzoyl cyanide was reduced by this system to yield benzaldehyde with reductive elimination of the cyano group under similar conditions (Table 3).

In the similar reduction of $\beta$-diketones, the result of the reductions was almost the same as for $\alpha$-diketones. As shown in Table 4, the reductive deoxygenation of these compounds also proceeded with $SmI_2$–additive systems at room temperature to afford the corresponding mono-alcohols and mono-ketones along with the bis-alcohols. Mono-alcohols were obtained with the $SmI_2$–$H_2O$ system in good to excellent yields (Runs 1, 2, 5—7).

On the other hand, in the reaction of $\beta$-ketocarboxylic acid and ester, the yields of deoxygenated products were generally unsatisfactory (Table 5).

The deoxygenation of $\gamma$-carbonyl compounds did not proceed using this system, and the reduction product was the bis-alcohol. For example, cyclohexane-1,4-dione was imme-

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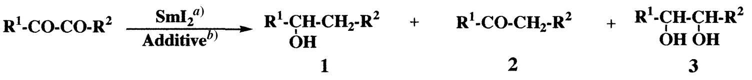
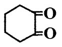
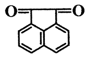
* To whom correspondence should be addressed. e-mail: kamochi@daiichi-cps.ac.jp

Table 1. Reduction of $\alpha$-Diketones

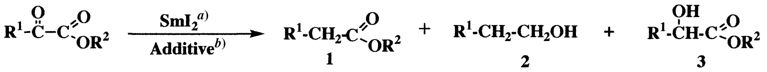


$$R^1\text{-CO-CO-}R^2 \xrightarrow[\text{Additive}^{b)}]{\text{SmI}_2{}^{a)}} \underset{\mathbf{1}}{R^1\text{-}\underset{OH}{CH}\text{-CH}_2\text{-}R^2} + \underset{\mathbf{2}}{R^1\text{-CO-CH}_2\text{-}R^2} + \underset{\mathbf{3}}{R^1\text{-}\underset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}R^2}$$

| Run | Substrate | | $SmI_2$ (eq mol) | Additive (ml) | Time (min) | Product (%) | | |
|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | | | | **1** | **2** | **3** |
| 1 | Ph | Ph | 4 | None | 110 | | 9[c] | |
| 2 | Ph | Ph | 8 | None | 200 | Trace | 16[d] | |
| 3 | Ph | Ph | 4 | $H_2O$ (0.5) | 1 | 9 | 49 | 5 |
| 4 | Ph | Ph | 8 | $H_2O$ (1) | 1.5 | 85 | 11 | 3 |
| 5 | Ph | Ph | 4 | 85% $H_3PO_4$ (0.5) | <3 s | 29 | 36 | 4 |
| 6 | Ph | Ph | 8 | 85% $H_3PO_4$ (1) | 3 s | 34 | 45 | 9 |
| 7 | Ph | Ph | 4 | 50% KOH (0.5) | 3 s | 29 | 53 | Trace |
| 8 | Ph | Ph | 8 | 50% KOH (1) | 1 | 87 | 12 | Trace |
| 9 | Ph | H | 8 | $H_2O$ (1) | 5 | 92 | 3 | |
| 10 | Me | Me | 8 | $H_2O$ (1) | 12 | 89 | 8 | 2 |
| 11 | Ph | Me | 8 | $H_2O$ (1) | 10 | 79[e] | 7[f] | 3 |
| 12 | *i*-Bu | Me | 8 | $H_2O$ (1) | 9 | 51[g] | 15[h] | Trace |
| 13 |  | | 6 | $H_2O$ (0.75) | 12 | 94 | 4 | |
| 14 |  | | 8 | $H_2O$ (1) | 10 s | 41[i] | | |

*a*) 0.1 M solution in THF. *b*) Additive was added to a solution of substrate (0.5 mmol) and $SmI_2$ in THF at room temperature under argon. *c*) By-product; PhCOCH(OH)Ph 25%. *d*) By-product; PhCOCH(OH)Ph 38%. *e*) By-product; $PhCH_2CH(OH)Me$ 6%. *f*) By-product; $PhCH_2COMe$ 3%. *g*) By-product; *i*-$BuCH_2CH(OH)Me$ 21%. *h*) By-product; *i*-$BuCH_2COMe$ 5%. *i*) By-product;  23% and  26%.

Table 2. Reduction of $\alpha$-Ketocarboxylic Acids and Ester

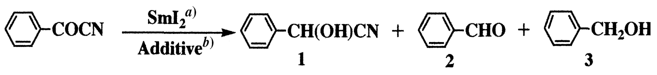


$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}C\overset{O}{\underset{OR^2}{\lessdot}} \xrightarrow[\text{Additive}^{b)}]{\text{SmI}_2{}^{a)}} \underset{\mathbf{1}}{R^1\text{-CH}_2\text{-}C\overset{O}{\underset{OR^2}{\lessdot}}} + \underset{\mathbf{2}}{R^1\text{-CH}_2\text{-CH}_2\text{OH}} + \underset{\mathbf{3}}{R^1\text{-}\overset{OH}{CH}\text{-}C\overset{O}{\underset{OR^2}{\lessdot}}}$$

| Run | $R^1$ | $R^2$ | $SmI_2$ (eq mol) | Additive (ml) | Time (min) | Product yield (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | **1** | **2** | **3** |
| 1 | Phenyl | H | 4 | $H_2O$ (0.5) | 12 | 16 | | 66 |
| 2 | Phenyl | H | 4 | 85% $H_3PO_4$ (1) | <3 s | 25 | | 32 |
| 3 | Phenyl | H | 4 | 50% KOH (0.5) | 8 | 28 | 36 | Trace |
| 4 | Phenyl | H | 6 | 50% KOH (1) | 13 | 18 | 71 | |
| 5 | Phenyl | H | 8 | 50% KOH (1.5) | 21 | 2 | 95 | |
| 6 | Benzyl | H | 8 | 50% KOH (1.5) | 30 | 2 | 88 | |
| 7 | Phenyl | Me | 4 | $H_2O$ (0.5) | 1 | 23 | | 34 |
| 8 | Phenyl | Me | 4 | 85% $H_3PO_4$ (1) | 0.2 | 43 | | 41 |
| 9 | Phenyl | Me | 4 | 50% KOH (0.5) | 0.8 | 58 | 8 | 3 |
| 10 | Phenyl | Me | 6 | 50% KOH (1) | 3 | 65 | 15 | |
| 11 | Phenyl | Me | 8 | 50% KOH (1.5) | 15 | 76 | 23 | |

*a*) 0.1 M solution in THF. *b*) Additive was added to a solution of substrate (0.5 mmol) and $SmI_2$ in THF at room temperature under argon.

Table 3. Reduction of Benzoylcyanide



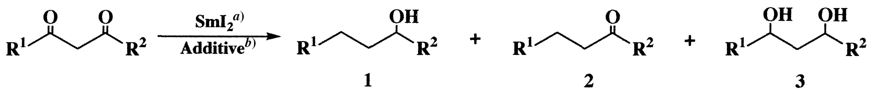
| Run | $SmI_2$ (eq mol) | Additive (ml) | Time (s) | Product yield (%) | | |
|---|---|---|---|---|---|---|
| | | | | **1** | **2** | **3** |
| 1 | 2 | $H_2O$ (0.5) | 15 | 1 | 41 | |
| 2 | 4 | $H_2O$ (1) | 120 | | 36 | 28 |
| 3 | 6 | $H_2O$ (1.5) | 100 | | 53 | 46 |
| 4 | 2 | 85% $H_3PO_4$ (1) | 17 | 5 | 40 | |
| 5 | 2 | 50% KOH (0.25) | 60 | 3 | 43 | |

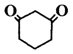
*a*) 0.1 M solution in THF. *b*) Additive was added to a solution of substrate (0.5 mmol) and $SmI_2$ in THF at room temperature under argon.

diately reduced with the $SmI_2$ (4 eq mol)–$H_2O$ system to give 1,4-cyclohexanediol in a quantitative yield (>99%).

These reductions have arisen because of the characteristics of $SmI_2$, such as its high coordination number, high affinity with oxygen atoms, and high reduction potential. As described above, it was revealed that the addition of additives accelerated the single-electron-donating ability of $Sm^{2+}$. Additives may play an important role in these reductions since these reductions in the absence of an additive afforded the deoxygenated products at a low yield. Thus, it can be assumed that $SmI_2$ first forms the coordination bond with the substrates, following which the additives act as ligands with the Sm atom in these complexes. Consequently, as shown in Chart 1, it is believed that these reactions proceed through the formation of the enol by the promoted elimination of

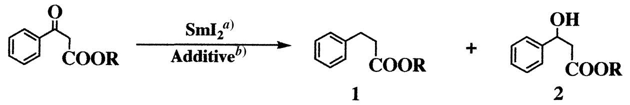
Table 4. Reduction of $\beta$-Diketones



| Run | Substrate | | $SmI_2$ (eq mol) | Additive (ml) | Time (min) | Product (%) | | |
|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | | | | **1** | **2** | **3** |
| 1 | Ph | Ph | 4 | $H_2O$ (0.5) | 3 | 86 | 11 | Trace |
| 2 | Ph | Ph | 8 | $H_2O$ (1) | 4 | 93 | 2 | 4 |
| 3 | Ph | Ph | 8 | 85% $H_3PO_4$ (0.5) | 3 s | 34 | 3 | 9 |
| 4 | Ph | Ph | 8 | 50% KOH (0.5) | 6 | 75[c] | | 11 |
| 5 | Ph | Me | 8 | $H_2O$ (1) | 8 | 95 | | 3 |
| 6 | Me | Me | 8 | $H_2O$ (1) | 8.5 | 78 | 6 | 6 |
| 7 |  | | 8 | $H_2O$ (1) | 10 | 88 | 5 | 5 |

*a*) 0.1 M solution in THF. *b*) Additive was added to a solution of substrate (0.5 mmol) and $SmI_2$ in THF at room temperature under argon. *c*) By-product; $PhCOCH_2CH(OH)Ph$ 12%.

Table 5. Reduction of $\beta$-Ketocarboxylic Acid and Ester



| Run | R | $SmI_2$ (eq mol) | Additive (ml) | Time (min) | Yield (%) | |
|---|---|---|---|---|---|---|
| | | | | | **1** | **2** |
| 1 | H | 8 | $H_2O$ (1.5) | 38 | 11 | 88 |
| 2 | H | 8 | 50% KOH (1.5) | 4 | 68[c] | 2 |
| 3 | Et | 4 | $H_2O$ (0.5) | 10 s | 7 | 80 |
| 4 | Et | 4 | 85% $H_3PO_4$ (0.5) | 3 s | 6 | 61 |
| 5 | Et | 4 | 50% KOH (0.5) | 2 | 9 | 76 |
| 6 | Et | 6 | 50% KOH (1) | 3 | 23 | 62 |
| 7 | Et | 8 | 50% KOH (1.5) | 5 | 46 | 52 |

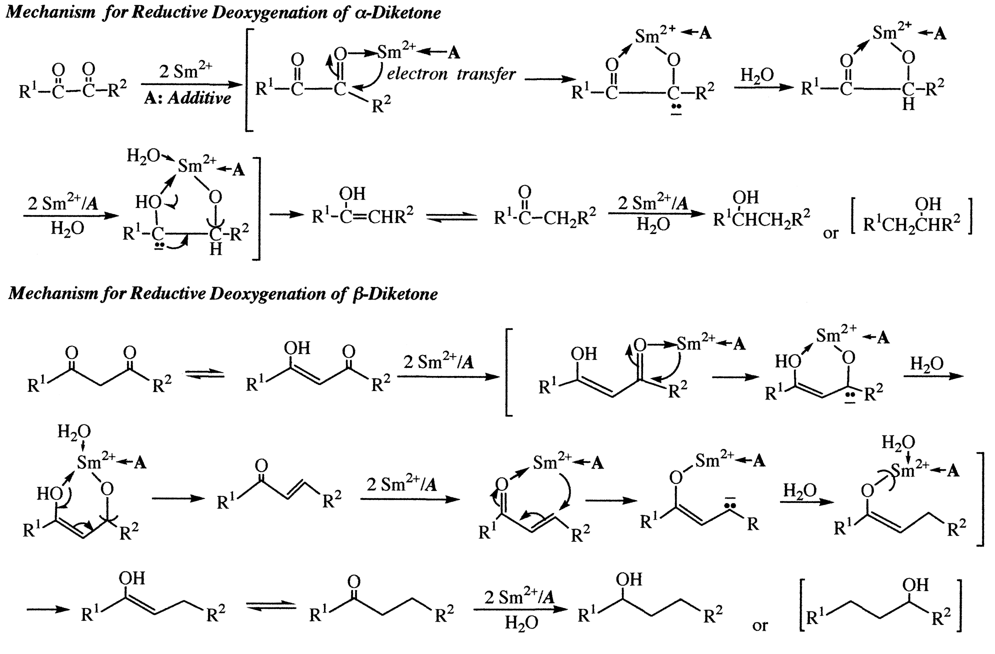
*a*) 0.1 M solution in THF. *b*) Additive was added to a solution of substrate (0.5 mmol) and $SmI_2$ in THF at room temperature under argon. *c*) By-product; $PhCH_2CH_2H_2OH$ 28%.

oxygenated functional groups rather than the rapid protonation in the carbanion. A possible mechanism is proposed in Chart 1.

It is noteworthy that the present method can be used for the conversion of $\alpha$- or $\beta$-dicarbonyl compounds to mono-alcohols or mono-ketones by the facile reduction that takes place with extreme ease under essentially neutral conditions as a $SmI_2$–$H_2O$ system at room temperature. Therefore, these deoxygenations with this system may provide a useful and simple route in synthetic chemistry.

## Experimental

IR spectra were measured in Nujol mulls or as liquid films with a JASCO A-100 (Nihon Bunko) infrared spectrophotometer. MS and GC-MS spectra were recorded on JMS-D100 and JMS AX505W mass spectrometers, respectively. GC analyses were performed with a CBP5-S50-050 (50 m, 0.33 mm, Shimadzu) capillary column connected to a Shimadzu GC-14A gas chromatograph. Gas chromatography-Fourier transform infrared spectrometry (GC-FTIR) was performed with a CBP5-S50-050 (50 m, 0.33 mm, Shimadzu) capillary column connected to a Shimadzu GC-17A-IRG 8000


Mechanism for Reductive Deoxygenation of α-Diketone

Mechanism for Reductive Deoxygenation of β-Diketone

Chart 1

spectrometer. $^1$H-NMR spectra were recorded on the JEOL FX90-Q spectrometer (Nihon Denshi). Products were characterized by comparison with authentic samples and with their IR, GC, GC-MS, GC-FTIR, and/or NMR spectra. Commercial THF solutions of $SmI_2$ (0.1 M, Aldrich) were used throughout this work, and all of the reactions were carried out at room temperature under argon with magnetic stirring.

**General Procedure for the Reduction of Dicarbonyl Compound with $SmI_2$–Additives System** A solution of 0.5 mmol of substrate dissolved in 1 ml of tetrahydrofuran (THF) was added to a solution of 0.1 M $SmI_2$ in THF with the aid of a syringe, followed by the immediate addition of each additive such as KOH, $H_2O$ and $H_3PO_4$. After the reaction mixture turned to grayish-white or yellow-green, 10% HCl or saturated $NaHCO_3$ for neutralization and $H_2O$ was added respectively, and the mixture stirred at room temperature for 10 min. The THF layer was separated and the residue was extracted twice with ether. The combined organic extracts were washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel or neutral alumina). The reduction products were characterized with the spectral data of authentic sample based on comparisons of their GC, GC/MS, IR and GC-FTIR spectra. The results and reaction conditions are listed in the respective tables.

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