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# Intermolecular Couplization and Cyclization of Chalcones Promoted by Samarium in DMF

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**Abstract:** Under mild and neutral conditions, reductive coupling-cyclization of chalcones was promoted by samarium metal with an activator in DMF to afford products in good to excellent yields. The reaction is regioselective over the competitive carbon-carbon double-bond reduction and stereocontrolled.

Keywords: Chalcones, cycntanols, DMF, samarium

In recent decades, the expansion of synthetic methodology to lanthanide metals including samarium reagents bloomed as a result of their particular application to the synthesis of natural products.<sup>[1]</sup> Moreover, by virtue of samarium's potential in synthetic chemistry, various original means were adopted to try many organic reactions based on its excellent reduction–coupling ability, and a lot of useful reactions have been developed in the course of these attempts lately.<sup>[2]</sup>

Carbon–carbon bond formation is the essence of organic synthesis, and the reductive dimerization of carbonyl derivatives is one of the most valuable methods for establishing carbon–carbon bonds. In a general fashion, the carbonyl derivatives are aldehydes, ketones, carboxylic esters, acid chlorides, or imines.<sup>[3]</sup> Recently, samarium(II) iodide–induced

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reductive cyclodimerization of  $\alpha,\beta$ -unsatuated ketones has been reported.<sup>[4]</sup> Although samarium diiodide is a very useful reducing reagent, there are some drawbacks when it is used as a reductant, such as its sensitivity to air and moisture and difficult storage. Because of consideration of atom economy, its application in organic synthesis is, to some extent, limited. Presently, the direct use of metallic samarium as a reducing agent in organic transformations has attracted the attention of a great many organic chemists.<sup>[5]</sup> To improve the activity of metallic samarium, some additives are needed.<sup>[6]</sup> THF has been one of the most favorite reaction media in organic reactions presented by samarium,<sup>[1,5,7]</sup> whereas we have explored some drastically interesting characteristics of metallic samarium as a reducing agent when N,N-dimethylformamide (DMF) was used as the solvent.<sup>[8]</sup>

Here we report that when DMF is used as a solvent instead of THF, metallic samarium, with iodine or TMSCl as an activator, can promote the reductive cyclization of chalcones, affording cycntanols in good yields at room temperature (Scheme 1).

Table 1 summarized the results of the cyclization reactions of various substrates. Comparing to the results when TMSCl was used as the activator (entries 17–20), the yields were relatively higher when  $I_2$  was used, but longer reaction time was required (entries 1, 3, 4, 10). Among all the results, the yields of the products also depended on the electronic effect of the substituents. According to the results shown in Table 1, when the substrates were attached with extraordinarily electron-donating groups (entries 2, 7, 9, 12) such as methoxyl or furyl either on Ar or Ar', the yields of products were lowered and longer reaction time was needed. On the other hand, when the electron-drawing ability of substituents strengthened, especially on Ar', the corresponding yield decreased markedly (entries 6, 11, 13, 15, 16).

The IR spectra show the infrared absorption of the arylcarbonyls of products are much less than normal value (most of them are less than  $1640 \text{ cm}^{-1}$ ; see the Experimental section), which indicates a hydrogen



Entry	Ar	Ar'	Time (h)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	3	82 ( <b>2</b> a)
2	2-Furyl	$C_6H_5$	4	62 ( <b>2b</b> )
3	$4-CH_3C_6H_4$	$C_6H_5$	3.5	95 ( <b>2c</b> )
4	$4-ClC_6H_4$	$C_6H_5$	3.5	95 ( <b>2d</b> )
5	$C_6H_5$	$4-CH_3C_6H_4$	4	81 ( <b>2e</b> )
6	$C_6H_5$	$4-ClC_6H_4$	4.5	68 ( <b>2f</b> )
7	$C_6H_5$	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	5	66 ( <b>2g</b> )
8	$4-CH_3C_6H_4$	$4-CH_3C_6H_4$	3	80 ( <b>2h</b> )
9	$4-CH_3C_6H_4$	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4	66 ( <b>2i</b> )
10	$4-ClC_6H_4$	$4-CH_3C_6H_4$	3	90 ( <b>2</b> j)
11	$4-CH_3C_6H_4$	$4-ClC_6H_4$	3	75 ( <b>2k</b> )
12	$4-ClC_6H_4$	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4	62 ( <b>2l</b> )
13	$C_6H_5$	$4-FC_6H_4$	4	32 ( <b>2</b> m)
14	$C_6H_5$	$C_6H_5CH = CH -$	3	34 ( <b>2n</b> )
15	$4-ClC_6H_4$	$4-ClC_6H_4$	4	b
16	$4-C_6H_4$	$4-NO_2C_6H_5$	3.5	b
17	$4-CH_3C_6H_4$	$C_6H_5$	2	83 $(2c)^{c}$
18	$4-ClC_6H_4$	$C_6H_5$	2	80 ( <b>2d</b> ) <sup>c</sup>
19	$4-CH_3C_6H_4$	$4-ClC_6H_4$	2	74 ( <b>2k</b> ) <sup>c</sup>
20	$C_6H_5$	$C_6H_5$	2	66 ( <b>2a</b> ) <sup>c</sup>

Table 1. Coupling-cyclization of chalcones promoted by samarium metal in DMF

<sup>a</sup>Isolated yields, based on substrates.

<sup>b</sup>A complicated mixture was afforded.

<sup>c</sup>TMSCl was used instead of I<sub>2</sub>.

bond may exist between the carbonyl and the vicinal hydroxyl; therefore, a cis-configuration I should be presented, possibly resulting from the coordination of samarium during the reaction process (II).<sup>[4]</sup>

In conclusion, the use of metallic samarium was successful for the reaction type of couplization and cyclization that would typically have employed  $SmI_2$ . This reaction provides useful products from readily obtainable starting materials in good yields.

### EXPERIMENTAL

### General

All <sup>1</sup>H NMR spectra were recorded on a Bruker AV 500 spectrometer with TMS as the internal standard. Chemical shifts are expressed in parts per million (ppm), and J values are given in hertz (Hz). Infrared (IR)

spectra were run on a Nicolet FT-IR Magna-750 spectrometer. Elemental analyses were performed on a Vario-ELIII equipment. Single-crystal X-ray diffraction were performed on NONIUS-CAD4. Melting points are uncorrected. All the reactions in this article were performed under a nitrogen atmosphere. DMF was redistilled over calcium hydride before use.

## Typical Procedure for the Sm/Cat. I<sub>2</sub> System–Promoted Reductive Cyclization of Chalcones

A chalcone (2 mmol) was added to a mixture of Sm powder (2 mmol) and iodine (0.01 mmol) in DMF (10 mL) at room temperature with magnetic stirring under a nitrogen atmosphere. The reaction was monitored by thin-layer chromatography (TLC). After being stirred for a given time (Table 1), the reaction was quenched with dilute HCl (0.1 mol/L, 5 mL), and the mixture was extracted with ethyl acetate ( $3 \times 15 \text{ mL}$ ). The organic phase was washed with saturated brine (15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed under reduced pressure to give the crude product, which was isolated by silica-gel chromatography using ethyl acetate and cyclohexane (1:5) as eluant.

### Data

(2-Hydroxy-2,4,5-triphenylcyclopentyl)(phenyl)methanone (2a)

White solid, mp 190–192 °C (lit.<sup>[4]</sup> 192–194 °C);  $\nu_{max}/cm^{-1}$  (KBr): 3437 (OH), 3028, 2923, 1641 (C=O);  $\delta_{\rm H}$  (acetone): 2.48 (dd, 1 H), 3.10 (dd, 1 H), 3.96 (dd, 1 H), 4.23 (t, 1 H), 4.85 (d, 1 H), 5.17 (s, 1 H), 7.01–7.03 (m, 1 H), 7.04–7.20 (m, 6 H), 7.24–7.30 (m, 4 H), 7.37–7.45 (m, 5 H), 7.62–7.65 (m, 2 H), 7.72–7.75 (m, 2 H). <sup>13</sup>C NMR  $\delta$  (acetone): 202.7, 147.0, 144.7, 141.1, 138.2, 133.4, 128.63, 128.61, 126.55, 128.44, 128.34, 128.29, 127.0, 126.6, 125.6, 83.7, 64.3, 58.6, 53.3, 51.9. Anal. calcd. for C<sub>30</sub>H<sub>26</sub>O<sub>2</sub>: C, 86.09; H, 6.26. Found: C, 86.46; H, 6.27.

(4,5-Di(furan-2-yl)-2-hydroxy-2-phenylcyclopentyl)(phenyl)methanone (2b)

White solid, mp 134–135 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3456 (OH), 3057, 2983, 2869, 1660 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.50 (dd, 1 H), 2.76 (dd, 1 H), 3.94 (m, 1 H), 4.23 (dd, 1 H), 4.59 (d, 1 H), 5.16 (S, 1 H), 5.93–6.28 (m, 4 H),

### Samarium-Promoted Reactions of Chalcones

7.15–7.53 (m, 12 H). Anal. calcd. for  $C_{26}H_{22}O_4$ : C, 78.37; H, 5.57. Found: C, 78.50; H, 5.54.

(2-Hydroxy-2-phenyl-4,5-dip-tolylcyclopentyl)(phenyl)methanone (2c)

White solid, mp 188–190 °C (lit.<sup>[4]</sup> 188–190 °C);  $\nu_{max}/cm^{-1}$  (KBr): 3434 (OH), 3023, 2920, 1639 (C=O);  $\delta_{\rm H}$  (DMSO): 2.12 (s, 3 H), 2.22 (s, 3 H), 2.30 (dd, 1 H), 2.90 (dd, 1 H), 3.71 (dd, 1 H), 4.17 (t, 1 H), 4.41 (d, 1 H), 5.56 (s, 1 H), 6.92–6.94 (m, 2 H), 7.04–7.11 (m, 4 H), 7.16–7.20 (m, 3 H), 7.22–7.27 (m, 6 H), 7.32–7.34 (m, 1 H), 7.56–7.58 (m, 2 H). Anal. calcd. for  $C_{32}H_{30}O_2$ : C, 86.06; H, 6.77. Found: C, 86.12; H, 6.78.

(4,5-Bis(4-chlorophenyl)-2-hydroxy-2-phenylcyclopentyl)(phenyl) methanone (**2d**)

White solid, mp 187–189 °C (lit.<sup>[4]</sup> 192–194 °C);  $\nu_{max}/cm^{-1}$  (KBr): 3435 (OH), 3045, 2935, 1636 (C=O);  $\delta_{\rm H}$  (DMSO): 2.34 (dd, 1 H), 2.95 (dd, 1 H), 3.77 (dd, 1 H), 4.18 (t, 1 H), 4.46 (d, 1 H), 5.68 (s, 1 H), 7.07–7.10 (m, 2 H), 7.15–7.18 (m, 1 H), 7.21–7.27 (m, 6 H), 7.31–7.38 (m, 7 H), 7.55–7.57 (m, 2 H). Anal. calcd. for C<sub>30</sub>H<sub>24</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 73.92; H, 4.96. Found: C, 73.89; H, 4.95.

(2-Hydroxy-4,5-diphenyl-2-p-tolylcyclopentyl)(p-tolyl)methanone (2e)

White solid, mp 172–174 °C (lit.<sup>[4]</sup> 170–171.5 °C);  $\nu_{max}/cm^{-1}$  (KBr): 3453 (OH), 3027, 2970, 1637 (C=O);  $\delta_{\rm H}$  (acetone): 2.18 (s, 3 H), 2.19 (s, 3 H), 2.37 (dd, 1 H), 2.98 (dd, 1 H), 3.87 (m, 1 H), 4.12 (t, 1 H), 4.80 (d, 1 H), 5.21 (s, 1 H), 6.95–6.97 (m, 3 H), 7.03–7.10 (m, 5 H), 7.17–7.19 (m, 2 H), 7.29–7.31 (m, 2 H), 7.36–7.38 (m, 2 H), 7.44–7.46 (m, 2 H), 7.56–7.58 (m, 2 H). <sup>13</sup>C NMR  $\delta$  (acetone): 203.8, 146.0, 145.6, 144.9, 142.1, 137.3, 136.7, 130.1, 129.9, 129.8, 129.6, 129.5, 129.4, 129.3, 127.9, 127.5, 126.5, 85.0, 64.6, 60.4, 53.9, 52.8, 21.9, 21.4. Anal. calcd. for  $C_{32}H_{30}O_2$ : C, 86.06; H, 6.77. Found: C, 86.01; H, 6.79.

(4-Chlorophenyl)(2-(4-chlorophenyl)-2-hydroxy-4,5-diphenylcyclopentyl)methanone (**2f**)

White solid, mp 163–165 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3449 (OH), 3060, 2926, 1642 (C=O);  $\delta_{\rm H}$  (acetone): 2.43 (dd, 1 H), 3.03 (dd, 1 H), 3.88 (dd, 1 H), 4.19 (t, 1 H), 4.72 (d, 1 H), 5.14 (s, 1 H), 6.98–7.00 (m, 1 H), 7.08–7.10

(m, 3 H), 7.16–7.19 (m, 4 H), 7.23–7.25 (m, 2 H), 7.31–7.36 (m, 4 H), 7.46–7.48 (m, 2 H), 7.67–7.69 (m, 2 H). Anal. calcd. for  $C_{30}H_{24}Cl_2O_2$ : C, 73.92; H, 4.96. Found: C, 73.88; H, 4.95.

(2-Hydroxy-2-(4-methoxyphenyl)-4,5-diphenylcyclopentyl) (4-methoxyphenyl)meth-anone (**2g**)

White solid, mp 144–145 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3424 (OH), 3027, 2933, 1632 (C=O);  $\delta_{\rm H}$  (acetone): 2.36 (dd, 1 H), 2.99 (dd, 1 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 3.86 (m, 1 H), 4.12 (t, 1 H), 4.79 (d, 1 H), 5.35 (s, 1 H), 6.69–6.70 (m, 2 H), 6.79–6.81 (m, 2 H), 6.95–6.97 (m, 1 H), 7.09–7.40 (m, 9 H), 7.59–7.63 (m, 4 H). Anal. calcd. for C<sub>32</sub>H<sub>30</sub>O<sub>4</sub>: C, 80.31; H, 6.32. Found: C, 80.26; H, 6.35.

(2-Hydroxy-2,4,5-trip-tolylcyclopentyl)(p-tolyl)methanone (2h)

White solid, mp 180–182 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3433 (OH), 3024, 2920, 1634 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.18 (s, 3 H), 2.27 (s, 3 H), 2.28 (s, 3 H), 2.29 (s, 3 H), 2.51 (dd, 1 H), 2.94 (dd, 1 H), 3.70 (m, 1 H), 4.04 (t, 1 H), 4.47 (d, 1 H), 5.27 (s, 1 H), 6.90–6.92 (m, 2 H), 6.96–6.98 (m, 2 H), 7.03–7.10 (m, 6 H), 7.28–7.30 (m, 2 H), 7.36–7.38 (m, 2 H), 7.43–7.45 (m, 2 H). Anal. calcd. for C<sub>34</sub>H<sub>34</sub>O<sub>2</sub>: C, 86.04; H, 7.22. Found: C, 86.20; H, 7.24.

(2-Hydroxy-2-(4-methoxyphenyl)-4,5-di-*p*-tolylcyclopentyl) (4-methoxyphenyl)meth-anone (**2i**)

White solid, mp 129–131 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3428 (OH), 3007, 2932, 1631 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.19 (s, 3 H), 2.29 (s, 3 H), 2.51 (dd, 1 H), 2.92 (dd, 1 H), 3.68 (m, 1 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 4.04 (t, 1 H), 4.41 (d, 1 H), 5.40 (s, 1 H), 6.64–6.66 (m, 2 H), 6.81–6.82 (m, 2 H), 6.91–6.93 (m, 1 H), 7.03–7.07 (m, 5 H), 7.28–7.30 (m, 2 H), 7.47–7.49 (m, 4 H). Anal. calcd. for  $C_{34}H_{34}O_4$ : C, 80.60; H, 6.76. Found: C, 80.85; H, 6.80.

(4,5-Bis(4-chlorophenyl)-2-hydroxy-2-*p*-tolylcyclopentyl)(*p*-tolyl) methanone (**2j**)

White solid, mp 112–114 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3449 (OH), 3032, 2924, 1636 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.28 (s, 3 H), 2.30 (s, 3 H), 2.48 (dd, 1 H), 2.52 (dd, 1 H), 3.62 (m, 1 H), 3.99 (t, 1 H), 4.47 (d, 1 H), 5.27 (s, 1 H),

7.00–7.01 (m, 2 H), 7.06–7.11 (m, 6 H), 7.22–7.23 (m, 2 H), 7.32–7.33 (m, 2 H), 7.37–7.39 (m, 2 H), 7.43–7.45 (m, 2 H). Anal. calcd. for  $C_{32}H_{28}Cl_2O_2$ : C, 74.56; H, 5.48. Found: C, 74.44; H, 5.46.

(4-Chlorophenyl)(2-(4-chlorophenyl)-2-hydroxy-4,5-di-*p*-tolylcyclopentyl)methanone (**2k**)

White solid, mp 177–179 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3443 (OH), 3024, 2921, 1642 (C=O);  $\delta_{H}$ (CDCl<sub>3</sub>): 2.16 (s, 3 H), 2.25 (s, 3 H), 2.48 (dd, 1 H), 2.87 (dd, 1 H), 3.70 (m, 1 H), 3.99 (t, 1 H), 4.33 (d, 1 H), 5.17 (s, 1 H), 6.89–6.91 (m, 2 H), 6.99–7.04 (m, 6 H), 7.11–7.13 (m, 2 H), 7.23–7.26 (m, 2 H), 7.31–7.33 (m, 2 H), 7.44–7.46 (m, 2 H). Anal. calcd. for  $C_{32}H_{28}Cl_2O_2$ : C, 74.56; H, 5.48. Found: C, 74.68; H, 5.50.

(4,5-Bis(4-chlorophenyl)-2-hydroxy-2-(4-methoxyphenyl)cyclopentyl) (4-methoxyph-enyl)methanone (**2**I)

White solid, mp 166–168 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3452 (OH), 3026, 2931, 1633 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.50 (dd, 1 H), 2.93 (dd, 1 H), 3.62 (m, 1 H), 3.76 (s, 3 H), 3.78 (s, 3 H), 3.99 (t, 1 H), 4.43 (d, 1 H), 5.37 (s, 1 H), 6.67–6.68 (m, 2 H), 6.81–6.83 (m, 2 H), 7.07–7.12 (m, 4 H), 7.23–7.26 (m, 2 H), 7.30–7.32 (m, 2 H), 7.45–7.47 (m, 4 H). Anal. calcd. for  $C_{32}H_{28}Cl_2O_4$ : C, 70.20; H, 5.16. Found: C, 70.31; H, 5.19.

(4-Fluorophenyl)(2-(4-fluorophenyl)-2-hydroxy-4,5-diphenylcyclopentyl)methanone (**2m**)

White solid, mp 232–233 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3396 (OH), 3088, 2976, 1643 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.49 (dd, 1 H), 2.84 (dd, 1 H), 3.50 (m, 1 H), 3.99 (t, 1 H), 4.44 (d, 1 H), 5.10 (s, 1 H), 6.74–6.76 (m, 2 H), 6.94–6.96 (m, 2 H), 7.04–7.11 (m, 4 H), 7.18–7.32 (m, 7 H), 7.59–7.61 (m, 1 H), 7.72–7.74 (m, 2 H). Anal. calcd. for C<sub>30</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>: C, 79.28; H, 5.32. Found: C, 79.32; H, 5.29.

(*E*)-1-(2-Hydroxy-4,5-diphenyl-2-(*E*)-styrylcyclopentyl)-3-phenylprop-2-en-1-one (**2n**)

White solid, mp 214–216 °C;  $\nu_{max}/cm^{-1}$  (KBr): 3416 (OH), 3123, 3066, 2946, 1640 (C=O);  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 2.30 (dd, 1 H), 2.72 (dd, 1 H), 3.58

(m, 1 H), 3.65 (d, 1 H), 3.85 (dd, 1 H), 5.04 (s, 1 H), 6.22 (d, 1 H, J = 16 Hz), 6.39 (d, 1 H, J = 16 Hz), 6.79 (d, 1 H, J = 16 Hz), 7.13–7.36 (m, 21 H). Anal. calcd. for C<sub>34</sub>H<sub>30</sub>O<sub>2</sub>: C, 86.77; H, 6.43. Found: C, 86.67; H, 6.44.

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