

# New Generation Method for a Samarium(II) Equivalent: $\text{Me}_3\text{SiX}$ ( $\text{X} = \text{Br}$ and $\text{I}$ )/Sm-Assisted Intermolecular Carbon-Carbon Bond Forming Reactions for Carbonyl Compounds

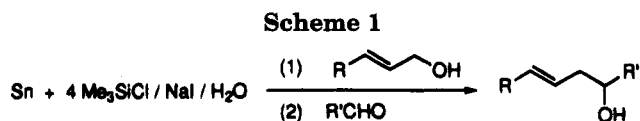
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Samarium(II) species can be efficiently generated in situ from a reaction between elemental samarium and chlorotrimethylsilane ( $\text{Me}_3\text{SiCl}$ )/sodium iodide ( $\text{NaI}$ ) reagent or bromotrimethylsilane ( $\text{Me}_3\text{SiBr}$ ) in acetonitrile. The reductive coupling reaction of carbonyl compounds was achieved by the action of Sm(II) reagent thus generated from Sm/ $\text{Me}_3\text{SiCl}$ /NaI or Sm/ $\text{Me}_3\text{SiBr}$  to give the corresponding pinacol products in moderate to high yields. The samarium(II) reagent induced the intermolecular coupling reaction of  $\alpha,\beta$ -unsaturated esters with carbonyl compounds or imines followed by intramolecular cyclization to form the corresponding  $\gamma$ -lactones or  $\gamma$ -lactams in moderate yields. The reaction of  $\alpha$ -bromo esters with carbonyl compounds using the Sm(II) species, generated from the Sm/ $\text{Me}_3\text{SiX}$  system, led to the corresponding  $\beta$ -hydroxy esters in 52–95% yields.

Recently lanthanide metals, lanthanide metal salts, and organolanthanide compounds have been widely employed as useful reagents or catalysts in organic synthesis.<sup>1</sup> Since pioneering studies by Kagan and co-workers demonstrated the particular effectiveness of samarium(II) diiodide ( $\text{SmI}_2$ ) as a strong one-electron transfer reducing agent,<sup>2</sup> the utilization of  $\text{SmI}_2$  reagent in synthetic organic chemistry has been dramatically documented, (e.g., the deoxygenation of sulfoxides<sup>3</sup> and epoxides,<sup>4</sup> the reduction of organohalo compounds,<sup>2,5</sup> the homocoupling of allylic or benzylic halides,<sup>6</sup> acid chlorides,<sup>7</sup> carbonyl compounds,<sup>8</sup> the Barbier reaction,<sup>9</sup> and the Reformatsky reaction,<sup>10</sup> etc.). Although samarium(II) diiodide ( $\text{SmI}_2$ ) is usually prepared from metallic



samarium and 1,2-diiodoethane,<sup>2</sup> diiodomethane,<sup>11</sup> or molecular iodide<sup>12</sup> in THF, an alternative route to a samarium(II) equivalent is desired to extend the scope of the samarium species in organic synthesis.

Previously we have shown that elemental tin reacts with allylic alcohols in the presence of iodotrimethylsilane ( $\text{Me}_3\text{SiI}$ ) derived from chlorotrimethylsilane and sodium iodide ( $\text{Me}_3\text{SiCl}/\text{NaI}$ ) to form an allylic iodotin species, which subsequently undergoes the  $\alpha$ -selective coupling reaction with aldehydes to give the corresponding homoallylic alcohols in good yields under ambient conditions (Scheme 1).<sup>13</sup> In addition, the extension of this method to samarium in place of tin provides a new general route to samarium(II) species.<sup>14</sup>

In this paper, we would like to report further details of a new approach for the generation of Sm(II) species by the reaction of samarium metal with  $\text{Me}_3\text{SiCl}/\text{NaI}$  or  $\text{Me}_3\text{SiBr}$  and the intermolecular carbon-carbon bond construction reactions of carbonyl compounds using the Sm(II) species thus generated.

## Results and Discussion

**(1) Generation of Sm(II) Species from Sm/ $\text{Me}_3\text{SiCl}$ /NaI and Sm/ $\text{Me}_3\text{SiBr}$ .** To a solution of sodium iodide in dry acetonitrile was added chlorotrimethylsilane fol-

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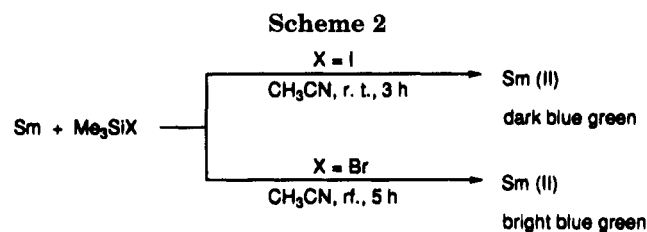
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lowed by samarium grains under nitrogen atmosphere at room temperature. The mixture was stirred for 3 h at room temperature. Samarium was gradually dissolved in acetonitrile and the color of the solution changed to dark green, which was quite similar to the THF solution of samarium(II) diiodide obtained by Kagan's method. A similar result was obtained by using Sm and Me<sub>3</sub>SiI in place of Me<sub>3</sub>SiCl/NaI. Thus it was found that a samarium(II) equivalent is prepared with ease upon the treatment of samarium metal with Me<sub>3</sub>SiCl/NaI or Me<sub>3</sub>SiI in acetonitrile under mild conditions. The samarium(II) species can be also generated by the treatment of metallic samarium with Me<sub>3</sub>SiBr. However, samarium metal should be allowed to react with Me<sub>3</sub>SiBr in refluxing acetonitrile, because of the sluggishness of the generation of samarium(II) species. When THF was employed in place of CH<sub>3</sub>CN as a solvent, samarium reacted readily with Me<sub>3</sub>SiX (X = I and Br) to generate the samarium(II) species.



The synthetic potential of the samarium(II) species thus generated was examined by carrying out the dehalogenation of α-halocarbonyl compounds. Dechlorination of 2-chlorocyclohexanone to cyclohexanone was successfully achieved by the Sm(II) obtained by treating samarium with Me<sub>3</sub>SiX. These results show that the Sm(II) equivalent can be easily generated by allowing samarium to react with Me<sub>3</sub>SiX in CH<sub>3</sub>CN or THF (Scheme 2). The Sm(II) thus prepared was applied to a wide variety of coupling reactions.

**(2) Use of the Sm/Me<sub>3</sub>SiCl/NaI or Sm/Me<sub>3</sub>SiBr System for the Reductive Coupling of Acetophenone.** The reductive coupling of carbonyl compounds is known as one of the notable reactions accomplished by samarium(II) diiodide.<sup>8</sup> The coupling reaction of acetophenone could be accomplished by the Sm/Me<sub>3</sub>SiCl/NaI and Sm/Me<sub>3</sub>SiBr systems.<sup>15</sup>

Treatment of acetophenone (1) (2 mmol) with Me<sub>3</sub>SiCl/NaI/Sm (6 mmol/6 mmol/2 mmol) reagent at room temperature for 0.25 h, followed by protonation with 1 M HCl, gave 2,3-diphenyl-2,3-butanediol (2), a reductive coupling product, which consisted of about a 1:1 ratio of *meso* and *dl* isomers in 72% yield (run 4 in Table 1).<sup>16</sup> This result showed that the Sm(II) species generated from Sm/Me<sub>3</sub>SiCl/NaI system in CH<sub>3</sub>CN possesses a reactivity similar to that of SmI<sub>2</sub>, obtained by Kagan's method. To establish the proper conditions where the Sm(II) species is favorably generated by this method, samarium was allowed to react with Me<sub>3</sub>SiCl/NaI reagent under several reaction conditions, and the reaction of the resulting samarium species with 1 was examined. The

(15) Recently Yb/TMSBr-promoted homocoupling reaction of aliphatic ketones and α,β-unsaturated carbonyl compounds has been reported by Y. Fujiwara et al. See: Taniguchi, Y.; Nakahashi, M.; Kuno, T.; Tsuno, M.; Makioka, Y.; Fujiwara, Y. *Tetrahedron Lett.* **1994**, *35*, 4111.

(16) The ratio of *meso* and *dl* isomers was determined by <sup>1</sup>H NMR. See: Agahiglam, H.; Moraveck, J. F.; Gauthier, H. *Can. J. Chem.* **1963**, *41*, 194.

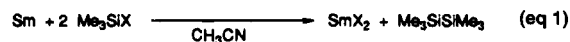
**Table 1. Reductive Couplings of Acetophenone Using the Me<sub>3</sub>SiCl/NaI/Sm System under Various Reaction Conditions**

run	Me <sub>3</sub> SiCl / NaI / Sm	solvent	temp. °C	yield, % <sup>a, b</sup>
1	4 / 4 / 0	CH <sub>3</sub> CN	r. t.	0
2	2 / 2 / 2	CH <sub>3</sub> CN	r. t.	11
3	4 / 4 / 2	CH <sub>3</sub> CN	r. t.	50
4	6 / 6 / 2	CH <sub>3</sub> CN	r. t.	72
5	6 / 6 / 2	THF	r. t.	14
6	6 / 6 / 2	C <sub>6</sub> H <sub>6</sub>	r. t.	13
7	6 / 6 / 2	CH <sub>3</sub> CN	0	49
8	6 / 6 / 2	CH <sub>3</sub> CN	reflux	0
9 <sup>c</sup>	4 / 0 / 2	CH <sub>3</sub> CN	r. t.	52 (13) <sup>d</sup>

<sup>a</sup> Based on acetophenone. <sup>b</sup> GLC yields. <sup>c</sup> Me<sub>3</sub>SiBr was used instead of Me<sub>3</sub>SiCl/NaI reagent. <sup>d</sup> The number in parenthesis is the yield of [PhC(OSiMe<sub>3</sub>)CH<sub>3</sub>]<sub>2</sub>.

results are shown in Table 1. The yield of 2 was markedly affected by the ratio of Me<sub>3</sub>SiCl/NaI reagent to samarium metal (runs 1–4). The reaction of 1 with Me<sub>3</sub>SiCl/NaI/Sm (4 mmol/4 mmol/2 mmol) gave 2 in unsatisfactory yield (50%) (run 3).<sup>17</sup> However, the reductive coupling reaction was found to be satisfactorily achieved by the use of 3 equiv of Me<sub>3</sub>SiCl/NaI with respect to samarium in acetonitrile (run 4). Unfortunately, it is uncertain that undesired reactions are induced when THF was employed instead of CH<sub>3</sub>CN (run 5). In the reaction of α-halo carbonyl compounds with Sm(II) species generated in CH<sub>3</sub>CN and THF, the dehalogenation is achieved in higher conversion by the Sm(II) species prepared in THF.<sup>14</sup> It seems that the Sm(II) species prepared in THF is more reactive than that prepared in CH<sub>3</sub>CN. Pinacol product 2 was obtained in 72% yield at room temperature, but the yield of 2 was considerably decreased at 0 °C (runs 4 and 7). Under refluxing temperature, many byproducts were formed (run 8). It was found that the Sm(II) species generated from samarium and Me<sub>3</sub>SiBr in place of Me<sub>3</sub>SiCl/NaI undergoes the reductive coupling reaction of 1 to 2 (run 9). Recently, Kagan has reported that SmBr<sub>2</sub>, which can be prepared by the reduction of SmBr<sub>3</sub> with Li metal, is an efficient reagent for the pinacol coupling reaction of carbonyl compounds.<sup>18</sup>

(17) It was expected that Sm(II) species and hexamethyldisilane (Me<sub>3</sub>SiSiMe<sub>3</sub>) are generated in situ from the reaction of 2 equiv of Me<sub>3</sub>SiCl/NaI or Me<sub>3</sub>SiBr with samarium metal (eq 1). In a stoichiometric reaction of Sm and Me<sub>3</sub>SiCl/NaI (1:2) to produce Sm(II) species, a part of the samarium metal remains unreacted in the reaction system. Furthermore, we have examined the isolation of silicon species in this reaction by using several organosilicon compounds such as Me<sub>2</sub>PhSiCl. However, we have not obtained a definite evidence to support the formation of disilanes from this system. At present, we are unable to confirm the structure of the Sm(II) equivalent generated from the Sm/Me<sub>3</sub>SiX system.



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**Table 2. Reductive Coupling of Various Carbonyl Compounds**

run	substrate	product	yield, % <sup>a, b</sup>
1			72
2 <sup>c</sup>	(1)		52 (13) <sup>d</sup>
3 <sup>e</sup>			79
4 <sup>e</sup>			40
5 <sup>e</sup>			27
6 <sup>f</sup>			28
7 <sup>f, g</sup>	(10)	(11)	67
8 <sup>f, h</sup>	(10)	(11)	67

<sup>a</sup> Based on carbonyl compound. <sup>b</sup> GLC yields. <sup>c</sup> Quenched by NaOH. <sup>d</sup> The number in parenthesis is the yield of diol. <sup>e</sup> 15 h. <sup>f</sup> 0.5 h. <sup>g</sup> HMPA (1 mL) was added. <sup>h</sup> Me<sub>3</sub>SiBr was used instead of Me<sub>3</sub>SiCl/NaI reagent.

**(3) Reductive Coupling Reaction of Various Carbonyl Compounds.** In order to ascertain the potential of the samarium(II) obtained by this method, various carbonyl compounds were reacted with Sm/Me<sub>3</sub>SiCl/NaI and Sm/Me<sub>3</sub>SiBr reagents under the same reaction conditions as described in run 4 or 9 in Table 1 (Table 2). The reaction of acetophenone **1** with Sm/Me<sub>3</sub>SiCl/NaI, followed by quenching with protons produced reductive coupling product **2**. However, treatment of **1** with Sm/Me<sub>3</sub>SiCl/NaI followed by quenching with a base gave pinacol compound bearing a trimethylsilyloxy group, **3**, together with a small amount of **2** (run 2). Although the pinacol coupling of cyclohexanone (**4**) required a longer reaction time, bicyclohexane-1,1'-diol (**5**) was afforded in good yield (run 3). Cyclopentanone (**6**) and 2-hexanone (**8**) were also converted into the corresponding pinacols in moderate yields (runs 4 and 5). Benzaldehyde (**10**) produced no coupling product under the same reaction conditions, but hydrobenzoin (**11**) was obtained in 67% yield when HMPA was added to the reaction system (runs 6 and 7). Using the Sm/Me<sub>3</sub>SiBr system, **10** was successfully converted into **11** even without HMPA (run 8).

**(4) Preparation of  $\gamma$ -Lactones and  $\gamma$ -Lactams.**  $\gamma$ -Lactones are biologically interesting products, and useful synthetic methods based on coupling reactions have been reported: (i) manganese(II) or chromium(IV) salt assisted the radical oxidative coupling of olefins with carboxylic acids,<sup>19</sup> (ii) radical coupling of stannyl  $\alpha$ -iodo esters with olefins,<sup>20</sup> (iii) addition of metal ester homoenolates to carbonyl compounds,<sup>21</sup> (iv) reductive coupling reaction of  $\alpha,\beta$ -unsaturated esters and carbonyl compounds by electrolytic methods,<sup>22</sup> zinc,<sup>23</sup> or zinc-

chlorotrimethylsilane reagent.<sup>24</sup> Recently Fukuzawa and co-workers demonstrated a convenient one-pot synthetic method for  $\gamma$ -lactones by the coupling reaction of  $\alpha,\beta$ -unsaturated esters with carbonyl compounds in the presence of SmI<sub>2</sub>.<sup>25</sup> In order to test the broad utilization of Sm(II) species generated from Sm/Me<sub>3</sub>SiCl/NaI and Sm/Me<sub>3</sub>SiBr systems in organic synthesis, we examined the coupling reaction of  $\alpha,\beta$ -unsaturated esters with carbonyl compounds.

The reaction of cyclohexanone (**4**) with methyl acrylate (**12**) assisted by in situ generated Sm(II) species from Sm metal and Me<sub>3</sub>SiCl/NaI or Me<sub>3</sub>SiBr reagent in acetonitrile, containing 2-propanol as the proton source, gave the corresponding spiro lactone **13** in 53 or 49% yield, respectively (Scheme 3). Particularly impressive is the fact that the Sm(II) species assisted the coupling reaction of **12** with imines such as *N*-cyclohexylidene 1-propanamine (**14**) or *N*-propylidene 1-octanamine (**16**), followed by intramolecular cyclization under mild conditions to form the corresponding  $\gamma$ -lactams in fair yields (Schemes 4 and 5). When Me<sub>3</sub>SiCl/NaI reagent was replaced by Me<sub>3</sub>SiBr, the yield of lactam was improved (Scheme 5).

**(5) Coupling Reaction of Carbonyl Compounds with Organo halo Compounds.** Zinc metal is most often utilized in the Reformatsky reaction; however, there are inherent problems in this method, e.g., the necessity of a longer reaction time and higher reaction temperature resulted in the formation of various byproducts such as  $\alpha,\beta$ -unsaturated esters or self-condensation products of the carbonyl substrates.

Results from previous studies of the SmI<sub>2</sub>-mediated intramolecular Reformatsky reactions show that this strategy is an efficient synthetic method for the construction of medium and large ring lactones.<sup>10</sup> As for the intermolecular Reformatsky reaction, there is only one example in Kagan's report.<sup>2</sup> Hence, the scope and limitation of the SmI<sub>2</sub>-mediated Reformatsky reaction is not understood. Thus, we have investigated the coupling reaction of carbonyl compounds with  $\alpha$ -bromo esters by the Sm/Me<sub>3</sub>SiCl/NaI system. Results are provided in Table 3. The reaction of ethyl bromoacetate (**18**) with cyclohexanone (**4**) was conducted under the influence of Sm(II) species, giving coupling product **19** in 75% yield without formation of 1,2-diacetates (run 1).<sup>25</sup> The coupling of **18** with aromatic ketone (**2**), acyclic ketone (**21**), and aliphatic aldehyde (**23**) afforded the corresponding  $\beta$ -hydroxy esters in 50–94% yields (runs 2–4).

In addition, the Sm(II) species thus generated induced the Barbier reaction of allylic iodide (**25**) and octanal (**23**) to form homoallylic alcohol **26** in 80% yield (Scheme 6).

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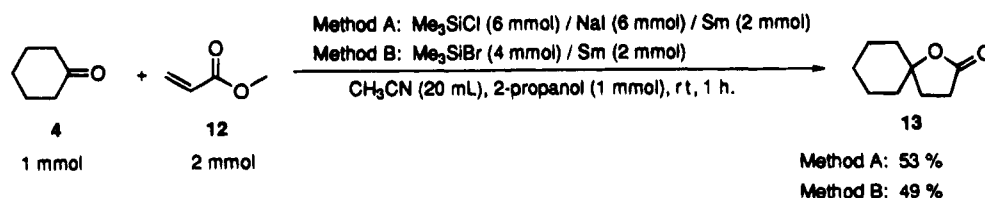
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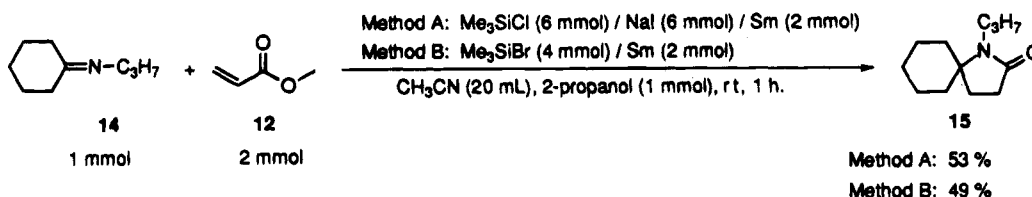
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(26) Recently it has been reported that the SmI<sub>2</sub>-assisted coupling reaction of  $\alpha$ -halo esters gave the corresponding 1,2-diacetates derivatives in good yields.<sup>27</sup>

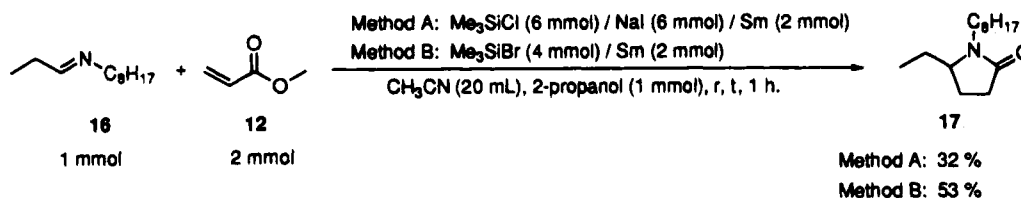
## Scheme 3



## Scheme 4



## Scheme 5

Table 3. Reformatsky Reaction with the  $\text{Me}_3\text{SiCl}/\text{NaI}/\text{Sm}$  System

run	substrate	product	yield, % <sup>a, b</sup>
1			7 <sup>f</sup>
2			50 <sup>c</sup>
3			72
4			94

<sup>a</sup> Based on ketones. <sup>b</sup> GLC yields. <sup>c</sup> Pinacol (12%) was formed.

The reactions described in this publication show that  $\text{Me}_3\text{SiCl}/\text{NaI}$  and  $\text{Me}_3\text{SiBr}$  are efficient reagents for the generation of  $\text{Sm}(\text{II})$  equivalents from samarium metal. The scope of the reactivity of the  $\text{Sm}(\text{II})$  species, generated very easily from the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  and  $\text{Sm}/\text{Me}_3\text{SiBr}$  systems, is not fully established. Nevertheless, results described in this paper led us to hope that this method will permit in situ generation of  $\text{Sm}(\text{II})$  species at the desired reducing potential suited for each reaction, because the reactivity of the  $\text{Sm}(\text{II})$  can be controlled by choosing the kind of X or R of the  $\text{R}_n\text{SiX}_{4-n}$  allowed to react with samarium metal.

## Experimental Section

**General Procedure.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR were measured at 400 and 100 MHz, respectively, in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as the internal standard. Infrared spectra (IR) were measured using

a  $\text{NaCl}$  plate. GLC analyses were performed with a flame ionization detector using a 0.2 mm  $\times$  25 m capillary column (OV-1). HPLC purification was conducted with JAIGEL-H (20 mm  $\times$  600 mm, 3.5 mL/min). Elemental samarium, carbonyl compounds, methyl acrylate, ethyl bromoacetate, and 1-iodo-2-propene were purchased from commercial sources and used without purification. Acetonitrile, THF, and benzene were commercially available and distilled prior to use. Imines were synthesized by the reaction of a carbonyl compound with an amine following the usual procedure.

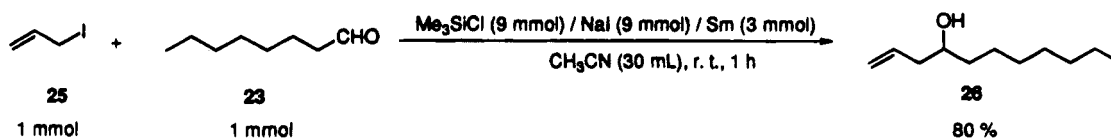
**Generation Method for  $\text{Sm}(\text{II})$  Species from the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  System.** To an acetonitrile or THF (20 mL) solution of  $\text{NaI}$  (0.9 g, 6 mmol) was added  $\text{Me}_3\text{SiCl}$  (0.76 mL, 6 mmol) under nitrogen atmosphere at room temperature. Metallic samarium (0.3 g, 2 mg atom) was added to the resulting solution and the mixture was stirred for 3 h at room temperature to form a suspended dark green solution.

**Generation Method for  $\text{Sm}(\text{II})$  Species from the  $\text{Sm}/\text{Me}_3\text{SiBr}$  System.** Samarium powder (0.3 g, 2 mg atom) and 20 mL of  $\text{CH}_3\text{CN}$  or THF were placed in a reaction flask.  $\text{Me}_3\text{SiBr}$  (0.53 mL, 4 mmol) was slowly added, and the contents of the flask were stirred for 5 h at reflux temperature under nitrogen atmosphere to form a suspended blue green solution.

**General Procedure for the Reductive Dehalogenation of 2-Chlorocyclohexanone by the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  System.** To an acetonitrile (20 mL) solution of  $\text{NaI}$  (0.9 g, 6 mmol) was added  $\text{Me}_3\text{SiCl}$  (0.76 mL, 6 mmol) under nitrogen atmosphere at room temperature. Metallic samarium (0.3 g, 2 mg atom) was added to the resulting solution, and the mixture was stirred for 3 h at room temperature to form a suspended dark green solution. After addition of the 2-chlorocyclohexanone (1 mmol) in methanol (1 mL), the solution was stirred for 0.5 h at ambient temperature, quenched with 1 M  $\text{HCl}$  (20 mL), and extracted with diethyl ether (50 mL  $\times$  4). The combined extracts were washed with sodium bisulfite solution (100 mL  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$  and analyzed by GLC. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with hexane/ $\text{AcOEt}$  (10:1 v/v) as eluant to give cyclohexanone. Cyclohexanone was identified by comparison of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of an authentic sample.

**General Procedure for the Reductive Dehalogenation of 2-Chlorocyclohexanone by the  $\text{Sm}/\text{Me}_3\text{SiBr}$  System.** Samarium powder (0.3 g, 2 mg atom) and 20 mL of  $\text{CH}_3\text{CN}$

Scheme 6



were placed in a reaction flask.  $\text{Me}_3\text{SiBr}$  (0.53 mL, 4 mmol) was slowly added and the contents of the flask were stirred for 5 h at reflux temperature under nitrogen atmosphere. 2-Chlorocyclohexanone (1 mmol) in MeOH (1 mL) was added to the resulting solution and the solution was stirred for 0.5 h at ambient temperature. The same workup described for the general procedure for the reductive dehalogenation of 2-chlorocyclohexanone by the  $\text{Me}_3\text{SiCl}/\text{NaI}/\text{Sm}$  system was carried out, and the resulting extracts were analyzed by GLC.

**General Procedure for the Reductive Coupling of Carbonyl Compounds by the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  System.** An acetonitrile solution of Sm(II) species was prepared by the same procedure described for the generation method for Sm(II) species from the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  system. To the  $\text{CH}_3\text{CN}$  (20 mL) solution of Sm(II) (2 mmol) was added a solution of carbonyl compound (2 mmol). The solution was stirred for 0.25–15 h at ambient temperature, quenched with 1 M HCl (20 mL), and extracted with diethyl ether (50 mL  $\times$  4). The combined extracts were washed with sodium bisulfite solution (100 mL  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$  and analyzed by GLC. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with hexane/AcOEt (5:1 v/v) as eluant to give the corresponding pinacol product. Pinacol products (**2**,<sup>8c</sup> **5**,<sup>27</sup> **7**,<sup>28</sup> and **11**<sup>8c</sup>) were identified by comparison of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra and GLC retention times with authentic samples. Pinacol **9** was identified by comparison of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of an authentic sample prepared by the reaction of 2-heptanone with THF solution of  $\text{SmI}_2$ , which was generated by Kagan's method.<sup>2</sup>

**9:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  0.93 (t,  $J = 7.0$  Hz, 6H), 1.15 (d,  $J = 3.3$  Hz, 6H), 1.30–1.58 (m, 12H), 1.91 (brs, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  14.2, 20.7, 21.1, 23.5, 26.0, 26.1, 35.6, 36.0, 77.2; IR (NaCl) 939, 1024, 1143, 1378, 1467, 2871, 2956, 3450  $\text{cm}^{-1}$ .

**General Procedure for the Reductive Coupling of Carbonyl Compounds by the  $\text{Sm}/\text{Me}_3\text{SiBr}$  System.** An acetonitrile solution of Sm(II) species was prepared by the same procedure described for the generation method for Sm(II) species from the  $\text{Sm}/\text{Me}_3\text{SiBr}$  system. The carbonyl compound (2 mmol) was added to the  $\text{CH}_3\text{CN}$  (20 mL) solution of Sm(II) (2 mmol) and the solution was stirred for 0.25–0.5 h at ambient temperature. The same workup described for the general procedure for the reductive coupling of carbonyl compounds by the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  system was carried out, and the resulting extracts were analyzed by GLC.

**Typical Procedure for the Synthesis of 3.** Acetophenone (**1**) was allowed to react with Sm(II) under the same reaction conditions as described in the general procedure for the reductive coupling of carbonyl compounds by the  $\text{Me}_3\text{SiCl}/\text{NaI}/\text{Sm}$  system. The solution was stirred for 0.25 h at ambient temperature, quenched with 5 M NaOH (10 mL), and extracted with diethyl ether (50 mL  $\times$  4). The combined extracts were washed with sodium bisulfite solution (100 mL  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$  and analyzed by GLC using an internal standard. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with hexane/AcOEt (5:1 v/v) as eluant to give **3** in 52% yield.

**3** (mixture of *meso* and *dl* isomers):  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  0.06 (s, 9H), 1.68 (s, 3H), 6.80–7.02 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  2.0, 2.2, 23.7, 24.1, 81.3, 82.0, 125.8, 125.9, 126.2, 126.6, 127.8, 128.0, 145.2, 146.1; IR (NaCl) 626, 700,

755, 842, 989, 1028, 1075, 1148, 1251, 1366, 1445, 2957  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{44}\text{O}_2\text{Si}_2$ : C, 68.34; H, 8.86. Found: C, 68.23; H, 9.15.

**Typical Procedure for the Synthesis of  $\gamma$ -Lactone.** An acetonitrile solution of Sm(II) species was prepared by the same procedure described for the generation method for Sm(II) species from the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  or  $\text{Sm}/\text{Me}_3\text{SiBr}$  system. To the  $\text{CH}_3\text{CN}$  (20 mL) solution of Sm(II) (2 mmol) was added a solution of methyl acrylate (**12**) (2 mmol), cyclohexanone (**4**) (1 mmol), and 2-propanol (1 mmol) in  $\text{CH}_3\text{CN}$  (3 mL), and the reaction mixture was stirred at room temperature for 1 h. The same workup described for the general procedure for the reductive coupling of carbonyl compounds was carried out, and the resulting extracts were purified by HPLC with  $\text{CHCl}_3$  as eluant giving **13** in 49 or 53% yield. **13** was identified by the comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of literature values.<sup>23</sup>

**General Procedure for the Synthesis of  $\gamma$ -Lactams.** An acetonitrile solution of Sm(II) species was prepared by the same procedure described for the generation method for Sm(II) species from the  $\text{Sm}/\text{Me}_3\text{SiCl}/\text{NaI}$  or  $\text{Sm}/\text{Me}_3\text{SiBr}$  system. To the  $\text{CH}_3\text{CN}$  (20 mL) solution of Sm(II) (2 mmol) was added a solution of  $\alpha,\beta$ -unsaturated ester (2 mmol), imine (1 mmol), and 2-propanol (1 mmol) in  $\text{CH}_3\text{CN}$  (3 mL). The solution was stirred for 1 h at ambient temperature, quenched with water (10 mL), and extracted with diethyl ether (50 mL  $\times$  4). The combined extracts were washed with sodium bisulfite solution (100 mL  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$  and analyzed by GLC using an internal standard. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by HPLC with  $\text{CHCl}_3$  as eluant to give the corresponding  $\delta$ -lactam.

**15:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  0.91 (t,  $J = 7.7$  Hz, 3H), 1.34–1.75 (m, 12H), 1.88 (t,  $J = 7.7$  Hz, 2H), 2.33 (t,  $J = 7.7$  Hz, 2H), 3.03–3.07 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  11.6, 23.0, 25.1, 29.0, 29.4, 35.3, 41.3, 64.0, 174.6; IR (NaCl) 1409, 1436, 1682, 2858, 2932  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{21}\text{NO}$ : C, 73.80; H, 10.84. Found: C, 73.54; H 10.93.

**17:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  0.88 (t,  $J = 7.3$  Hz, 3H), 0.89 (t,  $J = 7.0$  Hz, 3H), 1.20–1.47 (m, 12H), 1.61–1.78 (m, 2H), 2.08–2.16 (m, 2H), 2.28–2.47 (m, 2H), 2.83–2.90 (m, 2H), 3.52–3.67 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  8.9, 14.4, 22.9, 23.7, 26.0, 27.3, 27.6, 29.5, 29.6, 30.7, 32.0, 40.4, 58.7, 175.1; IR (NaCl) 753, 1422, 1462, 1689, 2857, 2927  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{27}\text{NO}$ : C, 74.61; H, 12.08. Found: C 74.87, H 11.98.

**General Procedure for the  $\beta$ -Hydroxy Esters.** To a  $\text{CH}_3\text{CN}$  (30 mL) solution of Sm(II) (3 mmol) was added a solution of ethyl bromoacetate (**18**) (2 mmol) and ketone (1 mmol) in  $\text{CH}_3\text{CN}$  (3 mL), and the reaction mixture was stirred at room temperature for 1 h. The same workup described for the reductive coupling of carbonyl compounds was carried out, and the resulting extracts were purified by column chromatography on silica gel ( $n\text{-C}_6\text{H}_{14}/\text{AcOEt} = 9/1$ ) giving the corresponding  $\beta$ -hydroxy ester.  $\beta$ -Hydroxy esters **19**,<sup>29</sup> **20**,<sup>30</sup> and **24**<sup>30</sup> were identified by comparison of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of authentic samples. **22** was identified by comparison of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of an authentic sample prepared by the reaction of ethyl bromoacetate (**18**) and 3-pentanone (**26**) in the presence of zinc dust.

**22:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  0.89 (t,  $J = 7.0$  Hz, 6H), 1.28 (t,  $J = 7.3$  Hz, 3H), 1.52 (q,  $J = 7.3$  Hz, 2H), 1.53 (q,  $J = 7.3$  Hz, 2H), 2.45 (s, 2H), 3.45 (s, 1H), 4.18 (q,  $J = 7.0$  Hz, 2H);

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$^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$  7.9, 14.2, 31.1, 42.2, 60.6, 73.3, 173.3; IR (NaCl) 1031, 1138, 1197, 1372, 1715, 2941, 2971, 3315  $\text{cm}^{-1}$ .

**General Procedure for the Barbier Reaction.** To a  $\text{CH}_3\text{CN}$  (30 mL) solution of Sm(II) (3 mmol) was added a solution of 1-iodo-2-propene (**25**) (1 mmol) and octanal (**23**) (1 mmol) in  $\text{CH}_3\text{CN}$  (3 mL), and the reaction mixture was stirred at room temperature for 1 h. The same workup described for the general procedure for the reductive coupling of carbonyl compounds was carried out, and the resulting extracts were purified by column chromatography on silica gel with hexane/AcOEt (10:1 v/v) as eluant giving 1-undecen-4-ol (**26**) in 80% yield. **26** was identified by the comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra with those of literature values.<sup>13</sup>

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**Supplementary Material Available:** Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all compounds (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.