Journal of Alloys and Compounds 408–412 (2006) 437–440

Journal of ALLOYS AND COMPOUNDS

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A highly efficient reduction of group 14 heteroatom-chlorine single bonds by using samarium diiodide-mediated reaction systems

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Received 29 July 2004; received in revised form 8 December 2004; accepted 8 December 2004
Available online 27 June 2005

Abstract

The reduction of group 14 heteroatom-chlorine single bonds by using samarium diiodide-mediated reduction systems in tetrahydrofuran has been investigated in detail. When the reduction of chlorostannanes and chlorogermanes are conducted by employing excess amounts of samarium diiodide (4 equiv.) at the THF refluxing temperature, the corresponding distannanes and digermanes are obtained in good yields, respectively. By the combination with magnesium metal or samarium metal, a novel samarium diiodide-catalyzed reduction of chlorostannanes and chlorogermanes takes place successfully. In contrast, the reduction of chlorosilanes with SmI_2 in THF does not occur at all, because the silylative ring-opening of THF with silyl iodode (formed in situ from chlorosilanes and SmI_2) proceeds in preference to the desired reduction of chlorosilanes.

Keywords: Samarium diiodide; Reductive dimerization; Chlorostannane; Chlorogermane; Chlorosilane

1. Introduction

The reductive coupling of chlorosilanes, chlorogermanes, and chlorostannanes is one of the most important synthetic methods for the construction of Si–Si, Ge–Ge, and Sn–Sn linkages, and alkali metals and related low-valent metals are usually employed as the reducing agents for this purpose [1]. However, these reactions often suffer from further reductions of functional groups on side-chains and great difficulty in controlling the reactions, because these low-valent metals bear powerful reducing abilities and are generally insoluble in organic solvents.

Samarium diiodide (SmI_2) is widely employed as a useful single-electron reducing agent in organic synthesis, because of its adequate reducing ability and suitable solubility in organic solvent such as THF [2]. Although samarium diiodide itself can reduce aldehydes, ketones, alkyl bromides, and iodides, the reduction often requires long period of heating and stirring. To employ the potential reducing ability of low-valent samarium species, therefore, several unique methods have been developed recently, which include tuning ligands [3], combination with other metals [4], and photoexcitation [5]. Recently, we have developed new reduction systems by the combination of samarium diiodide and samarium metal or magnesium metal, which are effective for the reduction of carbon–halogen single bonds of organic halides [6,4(b)–(d)]. Along our continuing interest about the reduction of group 14 element-halogen linkages, we report here a novel samarium diiodide-catalyzed reduction of group 14 heteroatom-halogen single bonds in the presence of samarium metal or magnesium metal (Eq. (1)) [4(a),7].

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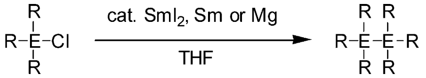
doi:10.1016/j.jallcom.2004.12.085



$$R_3E{-}Cl \xrightarrow[\text{THF}]{\text{cat. SmI}_2\text{, Sm or Mg}} R_3E{-}ER_3$$

(E = Sn, Ge) (1)

2. Experimental

2.1. Samarium diiodide-catalyzed reduction of chlorostannanes with magnesium metal

Samarium powder in oil (99.9%) was purchased from High Purity Chemical Co., Ltd., and was used after washing with dry *n*-pentane, followed by drying for 4 h under the reduced pressure. 1,2-Diiodoethane was purified by washing its ether solution with sat. sodium thiosulfate, followed by drying under the reduced pressure. Representative procedure for the reductive dimerization of chlorostannanes with cat. SmI_2/Mg-mixed system is as follows: In a 20 mL two-necked flask with a magnetic stirring bar was placed under an argon atmosphere magnesium metal (commercially available for Grignard synthesis, 6 mmol) and then the reaction vessel was heated with a heat gun under the reduced pressure. After cooling to room temperature, the flask was filled with argon, and samarium powder (0.3 mmol) and 1,2-diiodoethane (0.3 mmol) were added in this order into the flask. Freshly distilled (sodium/benzophenone ketyl) tetrahydrofuran (THF, 3 mL) was added to the mixture by syringe technique. The mixture was stirred at ambient temperature for about 30 min, resulting in the formation of a dark blue solution of SmI_2 in THF (cat. SmI_2/Mg-mixed system). After the addition of chlorostannanes (1 mmol) to the solution, the reaction mixture was stirred for 24 h. The resulting mixture was poured into 1.5N hydrochloric acid (30 mL), and the products were extracted with diethyl ether (30 mL × 3). The combined extracts were washed each two times with sat. $NaHCO_3$ aq. (30 mL) and then sat. NaCl aq. (30 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the products were purified by recycling preparative HPLC (Japan Analytical Industry, Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) with $CHCl_3$ as an eluent.

2.2. Samarium diiodide-catalyzed reduction of chlorogermanes with samarium metal

After drying with a heat gun under the reduced pressure, samarium powder (1 mmol) and 1,2-diiodoethane (0.3 mmol) were added under an argon atmosphere in a 20 mL two-necked flask with a magnetic stirring bar. Then, freshly distilled (sodium/benzophenone ketyl) THF (3 mL) was added to the mixture. The mixture was stirred at ambient temperature for 30 min, resulting in the formation of a dark blue solution of SmI_2 in THF (cat. SmI_2/Sm-mixed system). After the addition of chlorotriethylgermane (1 mmol) to the solution, the reaction mixture was stirred for 24 h. The resulting mixture was poured into 1.5N hydrochloric acid (30 mL), and the products were extracted with diethyl ether (30 mL × 3). The combined extracts were washed each two times with sat. $NaHCO_3$ aq. (30 mL) and then sat. NaCl aq. (30 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the products were purified by recycling preparative HPLC (Japan Analytical Industry, Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) with $CHCl_3$ as eluent.

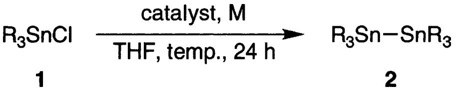
3. Results and discussion

3.1. Samarium diiodide-catalyzed reduction of chlorostannanes

Table 1 shows the results of the reduction of chlorostannanes (**1**) with samarium diiodide in the presence (or absence) of magnesium metal (or samarium metal). By using excess amounts of samarium diiodide (4 equiv.) at the THF refluxing temperature for 8 h, chloro(tri-*n*-butyl)stannane could be reduced by SmI_2 itself (entry 1). However the same reduction did not proceed at room temperature for 24 h.

We previously reported that the combination of SmI_2 and Sm metal extensively enhanced the reducing ability of samarium reagents compared with those of their single systems. Thus, the reduction of $^nBu_3SnCl$ by employing a Sm/SmI_2-

Table 1
Reductive dimerization of chlorostannanes

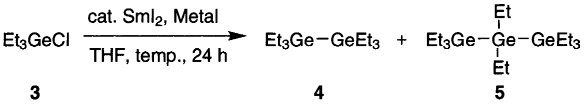


$$\underset{\mathbf{1}}{R_3SnCl} \xrightarrow[\text{THF, temp., 24 h}]{\text{catalyst, M}} \underset{\mathbf{2}}{R_3Sn{-}SnR_3}$$

Entry	*R*	Cat. (equiv.)	M (equiv.)	Temperature	Yield[a] (%)	
					2	**1**
1[b]	^{n}Bu	SmI_2 (4.0)	–	Reflux	76	21
2	^{n}Bu	SmI_2 (0.3)	Sm (0.7)	r.t.	85	3
3	^{n}Bu	SmI_2 (0.3)	Mg (6.0)	r.t.	82	Trace
4	^{n}Bu	–	Mg (6.0)	r.t.	No reaction	
5	^{n}Bu	Cp_2TiCl_2 (0.3)	Mg (6.0)	r.t.	No reaction	
6	Ph	SmI_2 (0.3)	Mg (6.0)	r.t.	58	Trace

[a] Isolated yield.
[b] 8 h.

Table 2
Catalytic reductive dimerization of a chlorotriethylgermane



$$\underset{\mathbf{3}}{Et_3GeCl} \xrightarrow[\text{THF, temp., 24 h}]{\text{cat. SmI}_2\text{, Metal}} \underset{\mathbf{4}}{Et_3Ge{-}GeEt_3} + \underset{\mathbf{5}}{Et_3Ge{-}\overset{Et}{\underset{Et}{Ge}}{-}GeEt_3}$$

Entry	SmI_2 (equiv.)	Metal (equiv.)	Temperature	Yield[a] (%)	
				4	**5**
1	1.0	–	r.t	No reaction	
2	6.0	–	Reflux	84	Trace
3	0.3	Sm (0.7)	r.t	73	5
4	–	Sm (0.7)	r.t	No reaction	
5	0.3	Mg (6.0)	r.t	74	6
6	–	Mg (6.0)	r.t.	No reaction	

[a] Isolated yield.

mixed system was examined, which successfully provided the distannane (**2**) in good yields even at room temperature (entry 2).

More remarkable is the observation that magnesium metal ($Mg^{2+}/Mg = -2.37$ V), which has a reducing power similar to that of samarium metal ($Sm^{3+}/Sm = -2.41$ V), also effected the reductive coupling of $^{n}Bu_3SnCl$ in the presence of catalytic amounts of SmI_2 (entry 3). In the absence of SmI_2 or in the presence of Cp_2TiCl_2, the reduction of $^{n}Bu_3SnCl$ with magnesium metal did not proceed at all (entries 4 and 5, respectively). Thus, SmI_2 is essential for this reductive coupling of $^{n}Bu_3SnCl$. Chlorotriphenylstannane also underwent reductive coupling by use of a cat. SmI_2/Mg-mixed system (entry 6). The same reduction also proceeded by using a cat. SmI_2/Sm-mixed system (62%, r.t., 24 h).

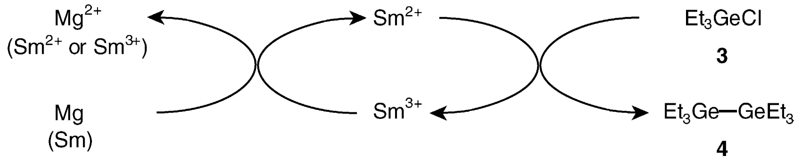
3.2. *Samarium diiodide-catalyzed reduction of chlorogermanes*

The results of the reduction of chlorotriethylgermane (**3**) with samarium diiodide and related reducing agents are shown in Table 2. As can be seen from entries 1 and 2, an equimolar amount of samarium diiodide could not reduce chlorotriethylgermane (**3**) at room temperature, whereas the use of excess amounts of SmI_2 in refluxing THF led to the reductive dimerization efficiently, providing the corresponding digermane (**4**) in good yield. In the presence of samarium metal or magnesium metal, however, the reductive coupling using a catalytic amount of SmI_2 took place efficiently even at room temperature (entries 3 and 5). Noteworthy is that small amounts of the corresponding trigermane (**5**) was obtained in both reactions. In the absence of SmI_2, neither samarium metal nor magnesium metal could work at room temperature for the reductive dimerization of Et_3GeCl (**3**) (entries 4 and 6).

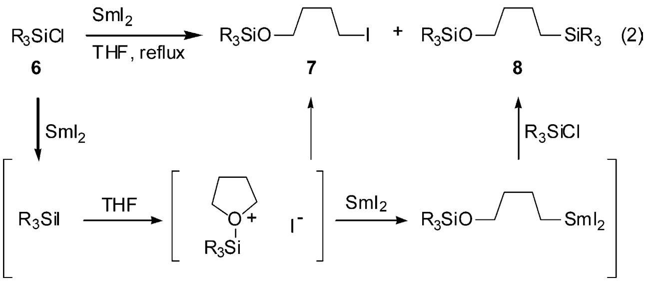
A possible catalytic cycle for the present SmI_2/Sm or Mg-mixed system is shown in Scheme 1. Chlorotriethylgermane (**3**) undergoes single-electron transfer from Sm(II) species to give the corresponding digermane (**4**) and thus the formed Sm(III) species is reduced by samarium metal or magnesium metal to regenerate Sm(II) species in situ. However, the reduction of chlorogermane (**3**) in the presence of samarium metal or magnesium metal gave the reduced products in good yields (entries 3 and 5), whereas the same reduction using only SmI_2 did not proceed at all (entry 1). These facts are in conflict with the possible pathway (Scheme 1), where samarium metal and magnesium metal are used only for the reduction of Sm(III) species to Sm(II) species. On the other hand, we previously suggested that Sm(I) species is formed as a powerful reducing agent by the proportionation between Sm(II) species and samarium metal [4(a),(b)]. To elucidate the presence of Sm(I) species in the this reduction system, especially, SmI_2/Mg-mixed system, further detailed mechanistic experiments are required.

3.3. *Attempted reduction of chlorosilanes with samarium diiodide in THF*

Similarly as the samarium diiodide-mediated reduction of chlorostannanes and chlorogermanes, the reductive coupling of chlorosilanes (**6**) was examined. However, the desired disilanes (R_3SiSiR_3) were not obtained at all, and instead silylative ring-opening products of THF (**7** and **8**) were formed as the main products (Eq. (2)).



Scheme 1.



A possible reaction pathway for the formation of **7** and **8** is shown in Eq. (2), which may include the following: (i) the reaction of chlorosilane (**6**) with SmI_2 generates in situ silyl iodide, which is well-known as a powerful silylating reagent for cyclic ethers [8]; (ii) silylative ring-opening of THF provides **7**; (iii) further reduction of **7** with SmI_2 leads to **8**.

4. Conclusions

We have developed a samarium diiodide-catalyzed reductive coupling of chlorostannanes and chlorogermanes by the combination of samarium metal or magnesium metal, which provides a useful tool to distannanes and digermanes. In contrast, the samarium diiodide-mediated reduction of chlorosilanes failed, because in situ formed silyl iodide worked as a silylating reagent for THF. Further detailed investigations of the reductive coupling of chlorosilanes are now underway.

Acknowledgements

We wish to express our sincerest gratitude to Professor Toshikazu Hirao for his helpful suggestions. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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