

Enhanced Reducing Ability by the Combination of SmI<sub>2</sub> and Sm Metal in the Reduction of Alkyl Halides

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Reduction of alkyl bromides and iodides easily takes place under mild conditions by the use of a reaction system combining SmI<sub>2</sub> with Sm metal. The reducing ability of this Sm/SmI<sub>2</sub> mixed reagent is superior to that of SmI<sub>2</sub> or Sm metal used independently.

Samarium diiodide (SmI<sub>2</sub>) is widely employed as a useful one-electron reducing agent for various functional groups including carbonyl groups such as aldehydes and ketones.<sup>1)</sup> Although it can not reduce amides by itself, we have recently disclosed that combination of samarium metal with equimolar or catalytic amounts of SmI<sub>2</sub> attains the efficient reductive coupling of amides to give *vic*-diaminoalkenes.<sup>2)</sup> This finding led us to examine whether the Sm/SmI<sub>2</sub> reagent has a similar pronounced effect on the reduction of haloalkanes.

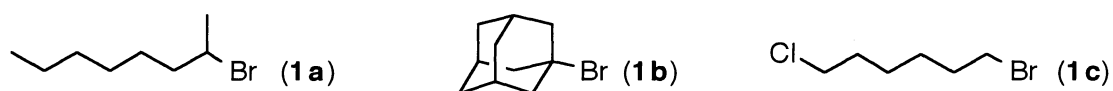
The reduction of bromo- and iodoalkanes with SmI<sub>2</sub> is reported to require long period of heating at THF reflux (*e.g.*, n-C<sub>12</sub>H<sub>25</sub>Br, 2 d, 82%; n-C<sub>12</sub>H<sub>25</sub>I, 6 h, 95%).<sup>3)</sup> Upon coexisting SmI<sub>2</sub> with Sm metal, however, the reduction of 1-bromo- and 1-iodoalkanes took place smoothly even at room temperature as indicated in Table 1. Likewise, Sm/SmI<sub>2</sub> is effective for the reduction of secondary and tertiary alkyl bromides (*e.g.*, **1a**, r.t., 5 h, 78%; **1b**, r.t., 15 h, 95% (for conditions, see ref. c in Table 1)). Contrary to this, lower yields were observed in the reduction of chloroalkanes with Sm/SmI<sub>2</sub>. Since SmI<sub>2</sub> in the presence of HMPA is reported to reduce chloroalkanes efficiently in refluxing THF,<sup>4)</sup> the order of reducing ability is estimated tentatively as SmI<sub>2</sub>/HMPA > Sm/SmI<sub>2</sub> > SmI<sub>2</sub>. The difference of reactivity between bromides and chlorides toward Sm/SmI<sub>2</sub> enabled selective reduction of 1-bromo-6-chlorohexane (**1c**) to n-hexyl chloride (r.t., 20 h, 68%).

We have also taken a close look at the reduction of haloalkanes by independent use of Sm metal. Reduction

Table 1. Reduction of 1-Halododecanes with Samarium Reagents<sup>a)</sup>

n-C <sub>12</sub> H <sub>25</sub> X		Sm reagent 2-propanol, THF		n-C <sub>12</sub> H <sub>26</sub>	
R-X	Conditions	Sm / SmI <sub>2</sub> <sup>c)</sup>	Yield of dodecane <sup>b)</sup> SmI <sub>2</sub> <sup>d)</sup>	Sm <sup>e)</sup>	Sm / cat. SmI <sub>2</sub> <sup>f)</sup>
n-C <sub>12</sub> H <sub>25</sub> I	(r.t., 45 min)	88%	trace	72%	96%
	(-23 °C, 1 h)	64%		0%	82%
n-C <sub>12</sub> H <sub>25</sub> Br	(r.t., 4 h)	78%	trace	0%	95%
n-C <sub>12</sub> H <sub>25</sub> Cl	(67 °C, 20 h)	30%	10%	0%	

a) n-C<sub>12</sub>H<sub>25</sub>X (0.5 mmol), 2-propanol (2.0 mmol). b) Determined by GLC. c) Sm (0.5 mmol), SmI<sub>2</sub> (1.1 mmol), THF (11 mL). d) SmI<sub>2</sub> (1.1 mmol), THF (11 mL). e) Sm (0.5 mmol), THF (5 mL). f) Sm (1.0 mmol), SmI<sub>2</sub> (0.1 mmol), THF (1 mL). Compared with Sm/SmI<sub>2</sub>, higher yields of n-C<sub>12</sub>H<sub>26</sub> were observed in the case using Sm/cat. SmI<sub>2</sub>, because the reduction by Sm/cat. SmI<sub>2</sub> was conducted with higher concentration of substrates.



of  $n\text{-C}_{12}\text{H}_{25}\text{I}$  with Sm metal proceeded at room temperature as well as Sm/SmI<sub>2</sub> and resulted in the formation of  $n\text{-C}_{12}\text{H}_{26}$  (72%) along with  $n\text{-C}_{24}\text{H}_{50}$  (12%). On the other hand, no reaction was recognized with Sm alone at  $-23\text{ }^{\circ}\text{C}$ , whereas Sm/SmI<sub>2</sub> could reduce  $n\text{-C}_{12}\text{H}_{25}\text{I}$  even at  $-23\text{ }^{\circ}\text{C}$  (Table 1). The observed temperature dependence of R-I/Sm system may require some comments. In light of Evans' report presenting that oxidative addition of iodoalkanes to Sm occurred at room temperature but hardly proceeded at  $-20\text{ }^{\circ}\text{C}$ ,<sup>5)</sup> the positive result with Sm alone at room temperature may be rationalized by assuming the formation of catalytic amounts of SmI<sub>2</sub> via the generation and decomposition of  $n\text{-C}_{12}\text{H}_{25}\text{SmI}$  (*i.e.*,  $\text{R-I} + \text{Sm} \rightarrow \text{RSmI}$ ;  $\text{RSmI} + \text{R-I} \rightarrow \text{SmI}_2 + \text{R-R}$ ). Thus, SmI<sub>2</sub> formed at the initial stage may catalyze the reduction of  $n\text{-C}_{12}\text{H}_{25}\text{I}$  with Sm. Indeed, in the presence of catalytic amounts of SmI<sub>2</sub>,  $n\text{-C}_{12}\text{H}_{25}\text{I}$  was reduced with Sm even at  $-23\text{ }^{\circ}\text{C}$ .

With these results mentioned above in hand, we developed a Barbier reaction using Sm/SmI<sub>2</sub>. Longer reaction time and heating at  $67\text{ }^{\circ}\text{C}$  are essential for the Barbier reaction using SmI<sub>2</sub> alone,<sup>3,6)</sup> whereas Sm/SmI<sub>2</sub> was operative at room temperature as depicted in Table 2. Interestingly, Sm metal itself can be an attractive alternative to this Sm/SmI<sub>2</sub> system for the Barbier reaction using iodoalkanes.<sup>7)</sup>

Table 2. Barbier Reaction Using Samarium Reagents<sup>a)</sup>

$n\text{-C}_6\text{H}_{13}\text{C}(=\text{O})\text{CH}_3$ + R-X		Sm reagent		$n\text{-C}_6\text{H}_{13}\text{C}(\text{OH})(\text{R})\text{CH}_3$ ( <b>2</b> )		
R-X	Conditions	Sm / SmI <sub>2</sub> <sup>c)</sup>	Yield of <b>2</b> <sup>b)</sup> SmI <sub>2</sub> <sup>d)</sup>	Sm <sup>e)</sup>	Sm / cat. SmI <sub>2</sub> <sup>f)</sup>	
$n\text{-C}_4\text{H}_9\text{I}$	(r.t., 1 h)	96%	trace	91%	78% (2.5 h)	
$n\text{-C}_4\text{H}_9\text{Br}$	(r.t., 2 h)	76%	trace	0%	10% (5 h)	

a) RX (1.5 mmol), 2-octanone (0.5 mmol). b) GLC yield. c) Sm (0.5 mmol), SmI<sub>2</sub> (1.6 mmol), THF (16 mL). d) SmI<sub>2</sub> (1.5 mmol), THF (15 mL). e) Sm (1.5 mmol), THF (10 mL). f) Sm (1.0 mmol), SmI<sub>2</sub> (0.1 mmol), THF (1 mL).

In general, SmI<sub>2</sub> is prepared by the reaction of Sm metal with diiodoethane in THF and is utilized as a THF solution of pure SmI<sub>2</sub> by removing unreacted Sm metal.<sup>3)</sup> In some cases, however, it appears that SmI<sub>2</sub> prepared in THF is directly employed without removal of excess Sm metal. Our results suggest that thus formed "SmI<sub>2</sub>" should be distinguished carefully from pure SmI<sub>2</sub>. Investigations are underway to further demonstrate the reduction reactions using Sm/SmI<sub>2</sub> and elucidate the mechanistic aspects.

#### References

- 1) H. B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1986); G. A. Molander, *Chem. Rev.*, **92**, 29 (1992).
- 2) A. Ogawa, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe, and N. Sonoda, *J. Am. Chem. Soc.*, **114**, 8729 (1992).
- 3) P. Girard, J. L. Namy, and H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).
- 4) J. Inanaga, M. Ishikawa, and M. Yamaguchi, *Chem. Lett.*, **1987**, 1485.
- 5) D. F. Evans, G. V. Fazakerley, and R. F. Phillips, *J. Chem. Soc. (A)*, **1971**, 1931.
- 6) SmI<sub>2</sub>/HMPA is used for this purpose, see: K. Otsubo, K. Kawamura, J. Inanaga, and M. Yamaguchi, *Chem. Lett.*, **1987**, 1487; D. P. Curran, T. L. Fevig, C. P. Jasperse, and M. J. Totleben, *Synlett*, **1992**, 943.
- 7) G. A. Molander and J. B. Etter, *J. Org. Chem.*, **51**, 1778 (1986).

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