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Enhanced Reducing Ability by the Combination of SmI_2 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_2 with Sm metal. The reducing ability of this Sm/SmI_2 mixed reagent is superior to that of SmI_2 or Sm metal used independently.

Samarium diiodide (SmI_2) is widely employed as a useful one-electron reducing agent for various functional groups including carbonyl groups such as aldehydes and ketones.[1] Although it can not reduce amides by itself, we have recently disclosed that combination of samarium metal with equimolar or catalytic amounts of SmI_2 attains the efficient reductive coupling of amides to give *vic*-diaminoalkenes.[2] This finding led us to examine whether the Sm/SmI_2 reagent has a similar pronounced effect on the reduction of haloalkanes.

The reduction of bromo- and iodoalkanes with SmI_2 is reported to require long period of heating at THF reflux (*e.g.*, n-$C_{12}H_{25}Br$, 2 d, 82%; n-$C_{12}H_{25}I$, 6 h, 95%).[3] Upon coexisting SmI_2 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_2 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_2. Since SmI_2 in the presence of HMPA is reported to reduce chloroalkanes efficiently in refluxing THF,[4] the order of reducing ability is estimated tentatively as SmI_2/HMPA > Sm/SmI_2 > SmI_2. The difference of reactivity between bromides and chlorides toward Sm/SmI_2 enabled selective reduction of 1-bromo-6-chlorohexane (**1c**) to n-hexyl chloride (r.t., 20 h, 68%).

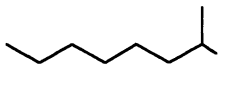
We have also taken a close look at the reduction of haloalkanes by independent use of Sm metal. Reduction

Table 1. Reduction of 1-Halododecanes with Samarium Reagents[a]

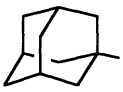
n-$C_{12}H_{25}X$ $\xrightarrow[\text{2-propanol, THF}]{\text{Sm reagent}}$ n-$C_{12}H_{26}$

R-X	Conditions	Yield of dodecane[b] Sm / SmI_2[c]	SmI_2[d]	Sm[e]	Sm / cat. SmI_2[f]
n-$C_{12}H_{25}I$	(r.t., 45 min)	88%	trace	72%	96%
	(-23 °C, 1 h)	64%		0%	82%
n-$C_{12}H_{25}Br$	(r.t., 4 h)	78%	trace	0%	95%
n-$C_{12}H_{25}Cl$	(67 °C, 20 h)	30%	10%	0%	

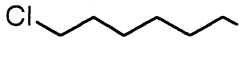
a) n-$C_{12}H_{25}X$ (0.5 mmol), 2-propanol (2.0 mmol). b) Determined by GLC. c) Sm (0.5 mmol), SmI_2 (1.1 mmol), THF (11 mL). d) SmI_2 (1.1 mmol), THF (11 mL). e) Sm (0.5 mmol), THF (5 mL). f) Sm (1.0 mmol), SmI_2 (0.1 mmol), THF (1 mL). Compared with Sm/SmI_2, higher yields of n-$C_{12}H_{26}$ were observed in the case using Sm /cat.SmI_2, because the reduction by Sm/cat.SmI_2 was conducted with higher concentration of substrates.



(1a)



(1b)

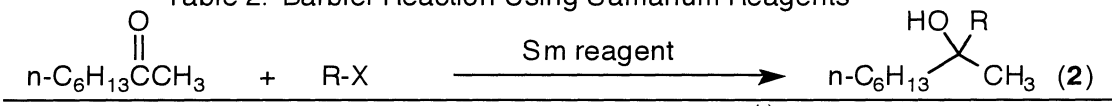


(1c)

of n-$C_{12}H_{25}I$ with Sm metal proceeded at room temperature as well as Sm/SmI_2 and resulted in the formation of n-$C_{12}H_{26}$ (72%) along with n-$C_{24}H_{50}$ (12%). On the other hand, no reaction was recognized with Sm alone at -23 ℃, whereas Sm/SmI_2 could reduce n-$C_{12}H_{25}I$ even at -23 ℃ (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 ℃,[5] the positive result with Sm alone at room temperature may be rationalized by assuming the formation of catalytic amounts of SmI_2 *via* the generation and decomposition of n-$C_{12}H_{25}SmI$ (*i.e.*, R-I + Sm → RSmI; RSmI + R-I → SmI_2 + R-R). Thus, SmI_2 formed at the initial stage may catalyze the reduction of n-$C_{12}H_{25}I$ with Sm. Indeed, in the presence of catalytic amounts of SmI_2, n-$C_{12}H_{25}I$ was reduced with Sm even at -23 ℃.

With these results mentioned above in hand, we developed a Barbier reaction using Sm/SmI_2. Longer reaction time and heating at 67 ℃ are essential for the Barbier reaction using SmI_2 alone,[3,6] whereas Sm/SmI_2 was operative at room temperature as depicted in Table 2. Interestingly, Sm metal itself can be an attractive alternative to this Sm/SmI_2 system for the Barbier reaction using iodoalkanes.[7]

Table 2. Barbier Reaction Using Samarium Reagents[a]



(2)

		Yield of 2[b]			
R-X	Conditions	Sm / SmI_2[c]	SmI_2[d]	Sm[e]	Sm / cat. SmI_2[f]
n-C_4H_9I	(r.t., 1 h)	96%	trace	91%	78% (2.5 h)
n-C_4H_9Br	(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_2 (1.6 mmol), THF (16 mL). d) SmI_2 (1.5 mmol), THF (15 mL). e) Sm (1.5 mmol), THF (10 mL). f) Sm (1.0 mmol), SmI_2 (0.1 mmol), THF (1 mL).

In general, SmI_2 is prepared by the reaction of Sm metal with diiodoethane in THF and is utilized as a THF solution of pure SmI_2 by removing unreacted Sm metal.[3] In some cases, however, it appears that SmI_2 prepared in THF is directly employed without removal of excess Sm metal. Our results suggest that thus formed "SmI_2" should be distinguished carefully from pure SmI_2. Investigations are underway to further demonstrate the reduction reactions using Sm/SmI_2 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_2/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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