Photoinduced Reduction and Carbonylation of **Organic Chlorides with Samarium Diiodide**

Akiya Ogawa,* Yukihito Sumino, Taizoh Nanke, Syoji Ohya, Noboru Sonoda,* and Toshikazu Hirao

Department of Applied Chemistry, Faculty of Engineering Osaka University, Suita, Osaka 565, Japan

Received September 5, 1996

Herein we report that the irradiation with visible light enhances the reducing ability of samarium diiodide. While samarium diiodide1 is well-known to reduce organic bromides and iodides to the corresponding hydrocarbons efficiently,² the reduction of organic chlorides with SmI₂ alone is difficult. In fact, the reduction of organic chlorides with SmI2 requires excess amounts of HMPA.³ In marked contrast to this, irradiation of the reaction mixture through Pyrex with a tungsten lamp enables the efficient reduction of organic chlorides with SmI2 even in the absence of HMPA (eq 1).4,5

$$n-C_{12}H_{25}CI + Sml_2 \xrightarrow{hv} n-C_{12}H_{26} (1)$$

2.2 equiv. hv > 300 nm 88%
dark 0%

Figure 1 shows the UV-vis spectrum of SmI₂ in THF. To specify the wavelength effecting the higher reducing power of SmI₂, we examined the photoinduced reduction of 1-chlorododecane with SmI₂ by varying the wavelengths of light (Table 1). While the reduction did not take place for irradiation with near UV light (300-420 nm) (entry 1) or the light of wavelength greater than 700 nm (entry 4), irradiation with the light of wavelength between 560 and 800 nm led to the successful reduction of 1-chlorododecane (entry 3). These results clearly indicate that SmI2 was activated by irradiating with the light of wavelength between 560 and 700 nm.⁶

The procedure can be employed with a variety of organic chlorides such as secondary and tertiary alkyl chlorides and aromatic chlorides, as represented in entries 5-11 of Table 1. When the photoinduced reduction of o-chlorophenyl allyl ether (1) with SmI_2 was conducted in the presence of diethyl ketone, a cyclic ether (2) was produced in 72% yield (eq 2). The formation of 2 can be accounted for by the following processes, $^{7-9}$ i.e., 5-exo cyclization of the aryl radical 3, followed by reduction

(2) Girard, P.; Namy, J. L.; Kagan, H. B. J. Am. Chem. Soc. 1980, 102, 2693.

(3) (a) Inanaga, J.; Ishikawa, M.; Yamaguchi, M. Chem. Lett. 1987, 1485. (b) Inanaga, J. Rev. Heteroat. Chem. 1990, 3, 75.

(4) Recently, we have developed that the Sm/SmI2 mixed reagent exhibits higher reducing abilities in the reduction of alkyl bromides and iodides, compared with those SmI₂ or Sm metal used independently. However, the Sm/SmI_2 reagent was not effective for the reduction of alkyl chlorides. (a) Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. J.
Am. Chem. Soc. 1992, 114, 8729. (b) Ogawa, A.; Nanke, T.; Takami, N.;
Sumino, Y.; Ryu, I.; Sonoda, N. Chem. Lett. 1994, 379.
(5) Imamoto, T.; Tawarayama, Y.; Kusumoto, T.; Yokoyama, M. J.
Synth. Org. Chem. Jpn. 1984, 42, 143.

Synth. Org. Chem. Jph. 1964, 42, 145. (6) The absorbance of SmI₂ ($\lambda_{max} = 565$ and 617 nm) is identified as a $4f^6 \rightarrow 4f^55d^1$ transition: (a) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. J. Chem. Soc. A **1971**, 1931. (b) Namy, J. L.; Girard, P.; Kagan, H. B. N. J. Chim. **1981**, 5, 479. (c) Okaue, Y.; Isobe, T. Inorg. Chem. Acta **1988**, 144, 142. A reservible reduction activuty micht invutue a circle alternative 144, 143. A possible reduction pathway might involve a single-electron transfer from photoexcited SmI2 species to organic chlorides.

(7) (a) Molander, G. A.; Harring, L. S. J. Org. Chem. 1990, 55, 6171.
(b) Molander, G. A.; Kenny, C. J. Org. Chem. 1991, 56, 1439.



Figure 1. UV-vis spectrum of SmI₂ in THF (5.0 \times 10⁻⁴ mol/L).

Table 1. Photoinduced Reduction of Organic Chlorides with SmI₂^a Sml...h

	RCI —		•	- RH
entry	chloride (R-Cl)			ield of R-H, %
1	n-C12H25CI	hv:	300~420 n	m trace
2			> 500 nm	91
3			560~800 ni	m 66
4			>700 nm	trace
5	\sim	\sim	/	88
		ċ	1	
6	A	\int_{c}	I	86
7	PhO	\sim	_CI	92
8	Me	∲с	51	89
9	MeO-	<u>}</u> -		83
10		\sim	α - Cl	79
11		~ <u>~</u> 0	β - Cl	86

^a RCl (0.15 mmol), SmI₂ (0.33 mmol), THF (1.5 mL), 40 °C, 3-9 h, hv; tungsten lamp (500 W), Pyrex.



with SmI2 and the subsequent addition of alkylsamarium species 4 to diethyl ketone. Similarly, the photoinitiated reduction of chloroalkanes with SmI₂ may proceed via the formation of alkyl radicals and alkylsamarium species.

Recently, a series of synthetic reactions have been developed on the basis of the carbonylation of carbon radicals with carbon monoxide.¹⁰ It may be expected that, in the photoinduced

⁽¹⁾ For reviews concerning SmI2, see: (a) Kagan, H. B.; Namy, J. L. Tetrahedron 1986, 42, 6573. (b) Kagan, H. B. New J. Chem. 1990, 14, 453. (c) Molander, G. A. In Comprehensive Organic Synthesis; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 1.9, p 251. (d) Soderquist, J. A. Aldrichimica Acta 1991, 24, 15. (e) Molander, G. A. Chem. Rev. 1992, 92, 29. (f) Molander, G. A. Org. React. 1994, 46, 211. (g) Imamoto, T. Lanthanides in Organic Synthesis; Academic Press: London, 1994; pp 21-62. (h) Molander, G. A.; Harris, C. R. Chem. Rev. 1996, 96, 307

^{(8) (}a) Curran, D. P.; Fevig, T. L.; Totleben, M. J. Synlett **1990**, 773. (b) Totleben, M. J.; Curran, D. P.; Wipf, P. J. Org. Chem. **1992**, 57, 1740. (c) Curran, D. P.; Totleben, M. J. J. Am. Chem. Soc. **1992**, 114, 6050. (d) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. Synlett **1992**, 943.

⁽⁹⁾ Inanaga, J.; Ujikawa, O.; Yamaguchi, M. Tetrahedron Lett. 1991, 32, 1737.

 ^{(10) (}a) Ryu, I.; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. J. Am. Chem. Soc. 1990, 112, 1295. (b) Ryu, I.; Yamazaki, H.; Kusano, K.; Ogawa, A.; Sonoda, N. J. Am. Chem. Soc. 1991, 113, 8558. (c) Ryu, I.; Yamazaki, H.; Kusano, K.; Chem. Soc. 1991, 113, 8558. H.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1993**, *115*, 1187. (d) Tsunoi, S.; Ryu, I.; Fukushima, H.; Tanaka, M.; Komatsu, M.; Sonoda,

Table 2. Photoinduced Carbonylation of Alkyl Chlorides with CO and SmI2^a



^a RCl (0.5 mmol), CO (50 atm), SmI₂ (4 mmol), THF (20 mL), 50 °C, 9 h, $h\nu > 400$ nm (xenon lamp 500 W, filter).

reduction of alkyl chlorides with SmI₂, the copresence of carbon monoxide leads to a novel carbonylation involving alkyl radicals (or alkylsamarium species) as key intermediates. Thus, we examined the photoinitiated reaction of alkyl chlorides with SmI2 in the presence of carbon monoxide.^{11,12} When the reaction of 1-chlorododecane with SmI2 was carried out under the pressure of carbon monoxide (50 atm) upon irradiation with a xenon lamp through a filter $(h\nu > 400 \text{ nm})$,¹³ carbonylation of 1-chlorododecane took place successfully, giving 89% of dodecyl tridecyl ketone (5, $R = n-C_{12}H_{25}$), which incorporated two dodecyl and two carbon monoxide units (eq 3 and entry 1 in Table 2). On the other hand, no carbonylation took place in the dark.

RCI + CO
$$\xrightarrow{\text{Sml}_2-\text{hv}}$$
 $\underset{R \neq 5}{\overset{O}{\text{sml}}}$ (3)

Table 2 represents the results of the photoinduced carbonylation of alkyl chlorides with CO and SmI₂. The carbonylation of alkyl chlorides bearing an olefinic unit proceeded successfully to give the corresponding asymmetrical ketones in good yields (entries 2 and 3). Similarly, secondary alkyl chlorides such as cyclohexyl chloride underwent photoinduced carbonylation to provide the products consisting of two alkyl and two carbon monoxide units (entry 4). With tertiary alkyl chlorides like 1-adamantyl chloride and aryl chlorides like β -naphthyl chloride, however, no carbonylation took place at all (only reduction to the corresponding hydrocarbons occurred).

Recently, Kagan et al. reported that the reaction of acyl chlorides with SmI₂ generated acylsamarium species, which underwent dimerization to give asymmetrical ketones in the presence of excess amounts of SmI2.14 In fact, the reaction of

(13) The photoinduced carbonylation was conducted by using a stainless steel autoclave bearing glass windows. For the detailed experimental procedure, see the Supporting Information. (14) (a) Girard, P.; Couffignal, R.; Kagan, H. B. *Tetrahedron Lett.* **1981**,

F.; Kagan, H. B. J. Org. Chem. 1991, 56, 3118. (f) Namy, J. L.; Colomb, M.; Kagan, H. B. Tetrahedron Lett. 1994, 35, 1723.



chlorides with SmI₂ afforded α -ketols.^{14e} Therefore, these results suggest that the photoinduced carbonylation with SmI₂ included the formation of acylsamarium species (as a key intermediate), which may dimerize to give asymmetrical ketones. As to the carbonylation step, the following two mechanistic pathways can be proposed: The first postulates the reaction of alkyl radical with CO to give acyl radical, which undergoes further reduction with excess SmI₂ to acylsamarium species. The second includes the reaction of alkylsamarium with CO.15 However, the second mechanistic pathway can be ruled out easily by the fact that the photoinduced reaction of an alkylsamarium (n-C12H25SmI2) with CO (50 atm) at 40 °C did not afford the desired carbonylated product at all. In order to clarify the formation of acyl radicals in this carbonylation, several attempts to capture acyl radicals with olefins were performed, but no trace of addition products could be detected.¹⁷ In addition, in the carbonylation of 4-heptenyl chloride (entry 3 in Table 2), any product derived from 5-exo cyclization of the acyl radical was not detected. Moreover, the present carbonylation could proceed even under the atmospheric pressure of CO,¹⁸ while the radical carbonylation usually requires higher pressures of CO.¹⁰ However, these observations can be explained if the electron transfer from SmI₂ to acyl radicals is extremely fast.¹⁹ We are currently examining the application of this photoinduced new reduction system with SmI₂ to different classes of substrates, as well as clarifying the precise mechanism of this carbonylation.

Acknowledgment. This research was supported in part by a Grantin-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" no.08220243 from the Ministry of Education, Science, and Culture, Japan. We thank Dr. Ilhyong Ryu for helpful suggestion and advice concerning the carbonylation reactions.

Supporting Information Available: Experimental details and ¹H NMR spectra (8 pages). See any current masthead page for ordering and Internet access instructions.

JA963117P

N. Synlett 1995, 1249. (e) Ryu, I.; Muraoka, H.; Kambe, N.; Komatsu, M.; Sonoda, N. J. Org. Chem. 1996, 61, 6396. (f) Ryu, I.; Sonoda, N.; Curran, D. P. Chem. Rev. 1996, 96, 177. (g) Ryu, I.; Sonoda, N. Angew. Chem., Int. Ed. Engl. 1996, 35, 1050 and references cited therein.

⁽¹¹⁾ For the reactions of divalent organosamarium complexes with CO, See: (a) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J.
L. J. Am. Chem. Soc. 1985, 107, 3728. (b) Evans, W. J.; Grate, J. W.;
Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. J. Am. Chem. Soc. 1986, 108, 1722. (c) Evans, W. J. Polyhedron 1987, 6, 803. (d) Evans, W. J.; Drummond, D. K. J. Am. Chem. Soc. 1988, 110, 2772. (e) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. J. Am. Chem. Soc. 1988, 110, 4983.
 (12) Collin, J.; Kagan, H. B. Tetrahedron Lett. 1988, 29, 6097.

⁽¹⁵⁾ The third hypothesis suggests that the alkyl radical reacts with samarium carbonyl species¹⁶ to give acylsamarium species directly. Thus, we attempted to detect samarium carbonyl species with IR spectrometer: After the reaction of SmI₂ with CO (50 atm) upon visible light irradiation (in the absence of substrates), CO was purged and immediately IR spectra of the resulting solution was measured. However, no absorbance assigned to samarium carbonyl species was detected.

⁽¹⁶⁾ For a carbonyl complex of samarium, see: Kolobova, N. E.; Suleimanov, G. Z.; Kazimirchuk, E. I.; Khandozhko, V. N.; Mekhdiev, R. Yu.; Lokshin, B. V.; Ezernitskaya, M. G.; Beletskaya, I. P. Izv. Akad. Nauk SSSR, Ser. Khim. 1985, 2833.

⁽¹⁷⁾ The tin radical-mediated carbonylation of alkyl iodides with CO in the copresence of excess styrene proceeds *via* the capture of acyl radicals with styrene: Ryu, I.; Kusano, K.; Yamazaki, H.; Sonoda, N. J. Org. Chem. 1991, 56, 5003.

⁽¹⁸⁾ The photoinduced reaction of 1-dodecyl chloride (0.5 mmol) with SmI₂ (4 mmol) and CO (1 atm) in THF (20 mL) at 50 °C for 6 h provided 39% of dodecyl tridecyl ketone and 52% of n-dodecane.

⁽¹⁹⁾ The rate constants for the reaction of primary alkyl radicals with Sml₂ in THF/HMPA are reported to be 5×10^5 to 7×10^6 M⁻¹ s⁻¹ (Hasegawa, E.; Curran, D. P. *Tetrahedron Lett.* **1993**, *34*, 1717). While the rate constant for the decarbonylation of PhCH2CO• is known to be 1.08 $\times 10^7 \text{ s}^{-1}$ (41 °C), the reaction of phenylacetyl chloride with SmI₂ did not give any decarbonylated product.^{14b} This suggests that the reduction of acyl radicals by SmI_2 is much faster than that of primary alkyl radicals.