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A novel photoinduced reduction system of low-valent samarium species: reduction of organic halides and chalcogenides, and its application to carbonylation with carbon monoxide

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Abstract—Visible light irradiation is found to enhance the reducing ability of samarium diiodide (SmI_2) dramatically. Organic halides (RCl, RBr, RI) and chalcogenides (RSPh, RSePh, RTePh) are smoothly reduced to the corresponding hydrocarbons by using this $SmI_2-h\nu$ system. The photoactivation can be also applied to ytterbium diiodide (YbI_2) successfully. When the reduction of alkyl chlorides (RCl) by using the $SmI_2-h\nu$ system is conducted under the pressure of carbon monoxide, unsymmetric ketones ($RC(O)CH_2R$) are obtained as carbonylating products. A mechanistic pathway may involve the formation of acylsamarium species ($RC(O)SmI_2$), which undergo dimerization, followed by reduction with SmI_2, leading to the unsymmetric ketones.

1. Introduction

Samarium diiodide (SmI_2) is widely employed as a useful reducing agent in organic synthesis,[1,2] because of its suitable solubility in organic solvent such as THF and appropriate reducing ability. SmI_2 itself acts as a useful single-electron-transfer reagent for various synthetic reactions, for example, C–C bond formation reactions such as Barbier reaction,[3,4] Reformatsky-type reaction,[5] pinacol coupling,[6] ketyl radical-olefin coupling,[7] and medium-size ring formation.[5b,8] Since these reactions proceed under mild conditions, SmI_2 is also available for the synthesis of natural products like taxol analogues,[9] nonadolides,[10] and β-lactams.[11] As can be seen from these synthetic reactions, SmI_2 itself can reduce several functional groups, such as aldehydes, ketones, alkyl bromides or iodides, α,β-unsaturated carbonyl compounds, and epoxides.[12] However, the reduction with SmI_2 alone often requires long period of heating and stirring. Thus, some additives are utilized to enhance the reducing ability of SmI_2. In particular, HMPA (hexamethylphosphoramide) is the most effective activating reagent.[13] Indeed, the reducing ability of SmI_2 is dramatically increased in the presence of HMPA, compared with the SmI_2 single system (SmI_2/THF).

The mechanism of electron transfer by SmI_2 can be explained by inner-sphere and/or outer-sphere processes.[14] The reduction of haloalkanes takes place through the outer-sphere process, whereas the reduction of carbonyl compounds proceeds via the inner-sphere process. In the presence of HMPA, the outer-sphere process is accelerated because of the bulkiness of HMPA. On the other hand, lithium halides are reported to accelerate effectively the inner-sphere electron transfer process.[14]

Besides HMPA, it is known that the use of alcohol,[15] amine,[16] acid or base,[7a,17,18] and water[19] as cosolvents increases the reducing ability of SmI_2. Moreover, the addition of metal reagents like Sm metal,[20] other lanthanoid metals,[21] $FeCl_3$, $Fe(acac)_3$, $Fe(DBM)_3$,[7a,12,22] NiI_2,[23,24] $CrCl_3$,[25] Co derivatives,[26] Cu derivatives,[4a,27] Pd derivatives,[28] Zn–Hg,[29] and Mischmetal[30] are also employed with SmI_2. Some electrochemical data are reported for these SmI_2-additive systems,[14,31] which indicate the relative reducing abilities of these SmI_2-based reduction systems.

Although these SmI_2-based reduction systems involve electron-transfer process from the ground-state of low-valent samarium species, we have recently developed a novel photoinduced reduction system with SmI_2. In this photoinduced system of SmI_2 ($SmI_2-h\nu$), alkyl chlorides,[7b,32–34] selenides, and tosylates[35] are reduced to the corresponding alkanes effectively through the powerful electron-transfer process from an excited state of SmI_2. In addition, the photoinduced carbonylation takes place when

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Keywords: samarium; photoinduced reduction; carbon monoxide; carbonylation; dechlorination; deselenation.

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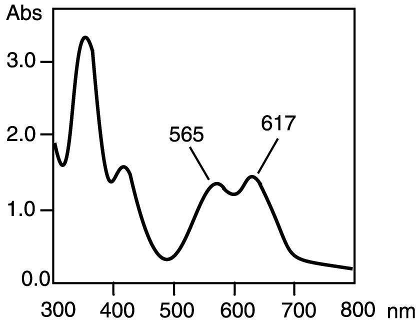


Figure 1. UV–vis. spectrum of SmI_2 in THF (5.0×10^{-4} mol/L).

Table 1. Photoinduced reduction of 1-chlorododecane

$$n\text{-}C_{12}H_{25}Cl \xrightarrow[\text{THF, 40 °C}]{SmI_2 - h\nu} n\text{-}C_{12}H_{26}$$

Entry	Wavelength (nm)	Yield (%)
1	>300	88
2	300–420	Trace
3	>500	91
4	560–800	66
5	>700	Trace
6	Dark	0

Reaction conditions: n-$C_{12}H_{25}I$ (0.15 mmol), SmI_2 (0.33 mmol), THF (1.5 mL), 40°C, 4 h. Irradiation with tungsten lamp (500 W).

the visible light-irradiated reduction of chloroalkanes with SmI_2 is conducted under the pressure of carbon monoxide. In addition to SmI_2, the corresponding ytterbium reagent (YbI_2)[36] is also activated by photoirradiation. Herein we wish to report full details of the photoinduced reduction and reductive carbonylation with SmI_2 and some mechanistic insight into this carbonylation.

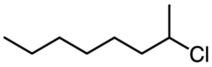
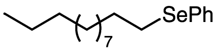
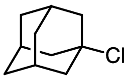
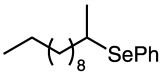
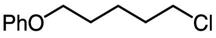
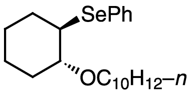
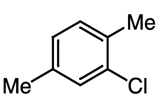
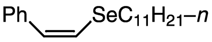
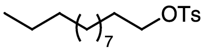
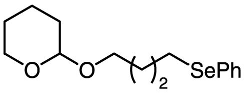
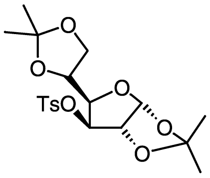
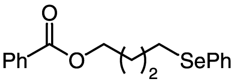
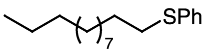
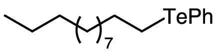
2. Results and discussion

2.1. Photoinduced reduction system of samarium diiodide

A THF solution of SmI_2, which appears deep blue color, exhibits its absorption maximum in the visible region (λ_{max}=565 and 617 nm), which can be assigned as a $4f^6 \rightarrow 4f^5 5d^1$ transition (Fig. 1).[37]

Thus, the irradiation with the light of wavelength in these regions is expected to generate the excited Sm species, which might show different reactivities from the Sm species in the ground state. While the reduction of 1-chlorododecane with SmI_2 alone at 40°C does not proceed at all, the irradiation through Pyrex with a tungsten lamp ($h\nu$>300 nm) enables the efficient reduction of 1-chlorododecane with SmI_2 (Table 1, entry 1). To specify the wavelength effecting the higher reducing power of SmI_2, we examined the photoinduced reduction of 1-chlorododecane with SmI_2 by varying the wavelengths of light (Table 1).[32]

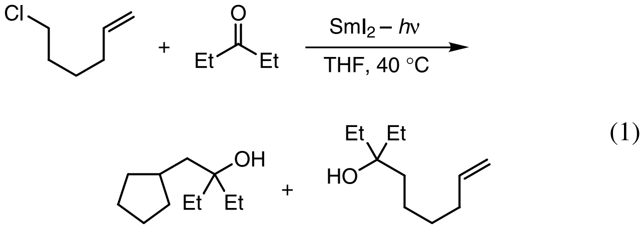
Table 2. Photoinduced reduction of organic chlorides, tosylates, and chalcogenides with SmI_2

Entry	Substrate (R-X)	Yield of R-H (%)	Entry	Substrate (R-X)	Yield of R-H (%)
1		88	8		99
2		86	9		83
3		92	10		84
4		89	11		79 (n-$C_{11}H_{24}$)
5		99	12		84
6		77	13		68
7		59	14		38

Reaction conditions (entries 1–4): RCl (0.15 mmol), SmI_2 (0.33 mmol), THF (1.5 mL), 40°C, 3–9 h. Irradiation with a tungsten lamp (500 W) through Pyrex. (entries 5–14): substrate (0.25 mmol), SmI_2 (2 mmol), THF (10 mL), 67°C (entries 5, 8 and 14: 40°C), 8–16 h (entry 5, 1 h; entry 6, 10 h; entry 7, 30 h). Irradiation with a tungsten lamp (500 W) through Pyrex (entry 8, $h\nu$>400 nm; entry 14, $h\nu$>500 nm).

The reduction does not take place upon irradiation with near UV light (300–420 nm) (entry 2) or the light of wavelength greater than 700 nm (entry 5), whereas the irradiation with the light of wavelength greater than 500 nm successfully induces the desired reduction of n-$C_{12}H_{25}Cl$ (entry 3). Irradiation with the light of wavelength between 560 and 800 nm is also effective for this reduction (entry 4). These results clearly indicate that the light of wavelength between 560 and 700 nm is essential for the activation of SmI_2.

Table 2 represents the results of the photoinduced reduction of group 16 and 17 heteroatom compounds with SmI_2. Secondary alkyl, tertiary alkyl, and aryl chlorides are reduced to the corresponding hydrocarbons efficiently (entries 1, 2, and 4). Although the reduction of dodecyl tosylates with SmI_2 is known to take place in the dark at 67°C for 10 h, the same reduction under photoirradiation conditions proceeds very smoothly even at 40°C for 1 h (entry 5). By using the SmI_2–$h\nu$ system, diacetone-*D*-glucosyl tosylate undergoes detosylation chemoselectively (entry 6). Next, we examined the reduction of organochalcogen compounds, i.e. organic sulfides, selenides, and tellurides, which cannot be reduced by SmI_2 alone.[35] By employing the SmI_2–$h\nu$ systems, C–S, C–Se, and C–Te bond cleavage proceeds, as shown in Table 2 (entries 7–14). In particular, seleno groups can be removed reductively from a variety of organic selenides effectively (entries 8–13). The C(sp^3)–Se bonds of primary and secondary alkyl selenides undergo reductive cleavage smoothly with SmI_2–$h\nu$, whereas the cleavage of C(sp^2)–Se bond does not take place at all (entry 11). β-Alkoxyl selenides that can be obtained easily by the oxyselenation of olefins, are also converted into the corresponding ethers in high yield by using this SmI_2–$h\nu$ system (entry 10). Compared with selenides, the reduction of sulfides proceeds slowly and requires higher temperature (67°C, 30 h), probably due to the higher bond energy of C–S bond (entry 7). In the case of dodecyl phenyl telluride, the cleavage of C–Te bonds occurs at both C(sp^3)–Te and C(sp^2)–Te centers (entry 14).



1 **2**

(1)

In the SmI_2–HMPA system, the first bimolecular rate constants for the reduction of primary alkyl radicals to the corresponding alkylsamarium diiodide is estimated, by using 5-hexenyl radical clock system, to be 0.5–$7.0\times10^6\ M^{-1}\ s^{-1}$.[38] Similarly, we examined the SmI_2-mediated Barbier reaction of 5-hexenyl chloride (0.1 M) with diethyl ketone upon irradiation with visible light (Eq. (1)). Based on the ratio of the cyclic and acyclic Barbier adducts (**1**/**2**=29/71) and the rate constant for the cyclization of 5-hexenyl radical ($4.9\times10^5\ s^{-1}$ at 40°C),[39] the bimolecular rate constant for the photoinduced reduction of primary alkyl radicals with SmI_2 is roughly estimated to be $10^5\ M^{-1}\ s^{-1}$ (at 40°C).[40]

The observed rate constant for the SmI_2–$h\nu$ system is similar as that for the SmI_2-single system (SmI_2–THF). This result requires some comments: the excited SmI_2 has a much more powerful reducing ability, but its concentration in this reaction system is very low. Although the excited SmI_2 can reduce alkyl chloride to generate alkyl radical, the reduction of alkyl radical to alkylsamarium diiodide takes place mainly by the SmI_2 in the ground state, which is present in situ in high concentration.

2.2. Photoinduced reduction system of ytterbium diiodide[36]

Although ytterbium diiodide (YbI_2) can be prepared easily from ytterbium metal and 1,2-diiodoethane in THF similarly to SmI_2, the practical use of YbI_2 in organic synthesis has been limited, because of its lower reducing ability and lower solubility in common organic solvents. YbI_2 exhibits its absorption maximum in near-UV regions (Fig. 2), i.e. λ_{max}=307, 342, and 390 nm, which can be identified as a $4f^{14}\rightarrow4f^{13}5d^1$ transition.[37]

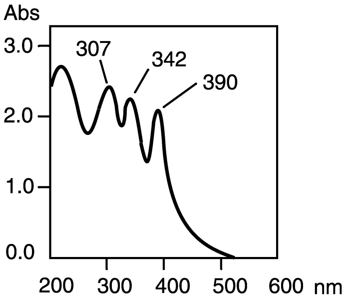


Figure 2. UV–vis. spectrum of YbI_2 in THF (40×10^{-5} mol/L).

Thus, the irradiation with near-UV light leads to the pronounced enhancement of the reducing ability of YbI_2, as shown in Eq. (2).

$$\begin{array}{llll} \text{R-Br} \ + \ \text{YbI}_2 & \xrightarrow[\text{THF, 30 °C}]{h\nu} & \text{R-H} & \\ \text{R} = n\text{-C}_{12}\text{H}_{25} & >300\text{ nm} & 85\% & \\ & 300\sim420\text{ nm} & 60\% & (2) \\ & >500\text{ nm} & \text{trace} & \end{array}$$

Similar conditions can be employed with alkyl iodides and tosylates (entries 1 and 4 in Table 3), but the reduction of dodecyl chloride and dodecyl phenyl selenide gives rise to poor yields of dodecane (entries 3 and 5). The reduction of undecyl α-naphthyl telluride resulted in the formation of both undecane and naphthalene (entry 6). Unambiguously, these results indicate that, upon irradiation with the light of wavelength over 300 nm, YbI_2 exhibits a similar reducing power as that of samarium diiodide itself in THF.

$$\begin{array}{lcl} n\text{-C}_{12}\text{H}_{25}\text{Br} \ + \ \text{Al} & \xrightarrow[\text{THF, 67 °C, 40 h}]{10\text{ mol\% YbI}_2\text{-}h\nu} & n\text{-C}_{12}\text{H}_{26} \\ 1\text{ mmol} \quad 4\text{ mmol} & & 88\% \end{array} \qquad (3)$$

To enhance the synthetic utility of YbI_2–$h\nu$, we further examined the catalytic use of YbI_2 in the reduction of organic bromides. Since the reduction potential of YbI_2 (Yb^{3+}/Yb^{2+}) is estimated to be −1.15 eV, co-reductants bearing a moderate reducing power seem to be suitable for this purpose. Thus, the YbI_2-catalyzed reduction of dodecyl

Table 3. Photoinduced reduction with YbI_2[a]

$$n\text{-}C_{12}H_{25}X + YbI_2 \xrightarrow{h\nu} n\text{-}C_{12}H_{26}$$

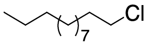
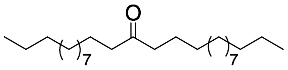
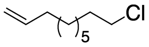
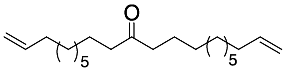
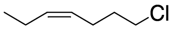
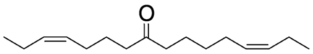
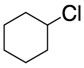
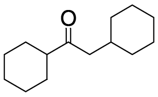
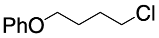
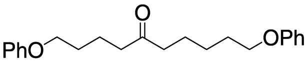
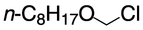
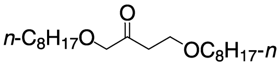
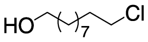
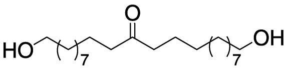
Entry	X	Yield (%)	
		$h\nu$	Dark
1	I	73	4
2	Br	99	Trace
3	Cl	27	No reaction
4	OTs	73	Trace
5	SePh	25	No reaction
6	Te-α-naphthyl[b]	40[c]	7

[a] Substrate (0.5 mmol), YbI_2 (4.0 mmol), THF (20 mL), 60°C, 8 h.

[b] $n\text{-}C_{11}H_{23}TeC_{10}H_7\text{-}\alpha$ is employed.

[c] Both undecane and naphthalene are formed in 40 and 20% yields, respectively.

Table 4. Photoinduced carbonylation of alkyl chlorides with CO and SmI_2

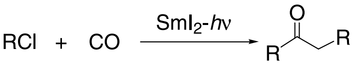
Entry	Chloride	Product	Yield (%)
1			89
2			63
3			61
4			68
5			35
6			8
7			0

RCl (0.5 mmol), CO (50 atm), SmI_2 (4 mmol), THF (20 mL), 50°C, 9 h, $h\nu>400$ nm (Xenon lamp 500 W, filter).

bromide is conducted by using excess amounts of aluminium metal ($Al^{3+}/Al^0=-1.66$ eV) as a co-reductant. The catalytic reaction proceeds successfully, giving dodecane in 88% yield (Eq. (3)). In the absence of a catalytic amount of YbI_2 (or in the dark), the present reduction does not occur at all.

2.3. Photoinduced reductive carbonylation of alkyl chlorides with CO and SmI_2[32]

The present photoinduced reduction of alkyl chlorides (RCl) with SmI_2 proceeds through single-electron transfer processes, and involves the formation of alkyl radical and alkylsamarium species ($R\cdot$ and $RSmI_2$) as key intermediates. Recently, alkylsamarium species are reported to react with isocyanides forming imidoylsamarium species.[41] Furthermore, carbon monoxide, bearing an isoelectronic structure with isocyanide, is known to react with alkyl radicals under high pressure conditions, generating acyl radical species. Thus, we examined the photoirradiated reaction of alkyl chlorides with SmI_2 under the pressure of carbon monoxide. The reaction is conducted by employing a stainless steel autoclave bearing glass windows, through which the photoirradiation is performed. When the reaction of 1-chlorododecane with SmI_2 is carried out under 50 atm of CO upon irradiation with xenon lamp through a filter ($h\nu>400$ nm), the desired carbonylation takes place successfully, providing 89% of dodecyl tridecyl ketone (**3**, $R=n\text{-}C_{12}H_{25}$), which incorporates two dodecyl and two carbon monoxide units (Eq. (4)). In the dark, the same reductive carbonylation does not take place at all.

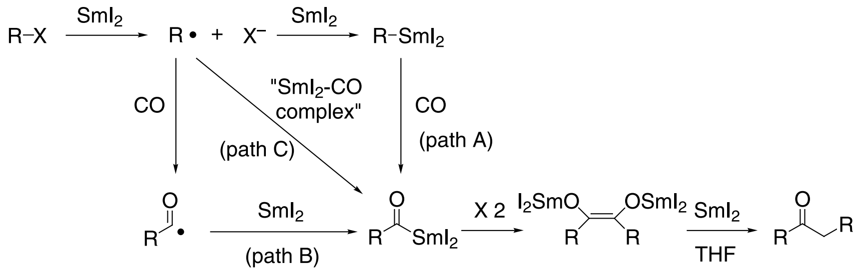


3 (4)

Table 4 represents the results of the photoinduced carbonylation of alkyl chlorides with CO and SmI_2. The carbonylation of alkyl chlorides bearing an olefinic unit proceeds successfully to give the corresponding asymmetrical ketones in good yields (entries 2 and 3). Similarly, secondary alkyl chlorides such as cyclohexyl chloride undergo photoinduced carbonylation to provide the corresponding carbonylated product (entry 4). In contrast, the yields are decreased in the case of ether compounds (entries 5 and 6), and the carbonylation does not take place at all in the case of 10-chloro-1-decanol (entry 7). In these cases, reduction to the corresponding hydrocarbons takes place in preference to the carbonylation. If the carbonylation proceeds via the formation of acyl radical, ether or alcohol compounds might accelerate a second electron transfer, i.e. the reduction of alkyl radical to alkylsamarium species might occur rapidly, in preference to the reaction of alkyl radical with carbon monoxide. Also, in the cases of tertiary alkyl chlorides like 1-adamantyl chloride and aryl chlorides like β-naphthyl chloride, no carbonylation takes place at all (only reduction to the corresponding hydrocarbons occurs).

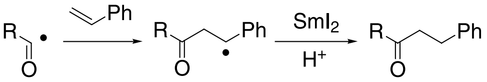
The present photoinduced carbonylation may involve the formation of an acylsamarium species as a key intermediate. Kagan et al. previously reported that the reduction of acyl chlorides by excess amounts of SmI_2 provided the same unsymmetrical ketones through the dimerization of acylsamarium species and the following further reduction.[42]

As to the carbonylation step, several mechanistic pathways can be proposed, as depicted in Scheme 1. The first hypothesis is that alkyl halide is reduced to an alkylsamarium species, which reacts with carbon monoxide to afford an acylsamarium species (path A). Thus, the reaction of an alkylsamarium iodide with pressurized CO was investigated. After 1-chlorododecane was treated with $SmI_2-h\nu$ at room temperature, carbon monoxide was introduced into this solution upon photoirradiation. However, the desired carbonyl compound was not obtained at all, and instead dodecane was formed as a simple reduced product. This result may suggest that acylsamarium iodide ($RC(O)SmI_2$) is not formed by the reaction of an alkylsamarium iodide ($RSmI_2$) with CO. However, another possibility is that $RSmI_2$ is unstable at room temperature and decomposes before the reaction with CO. Therefore, further detailed experiments at lower temperature are required.



Scheme 1. Possible pathways for the carbonylation.

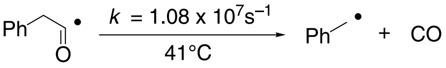
The second hypothesis is that the alkyl radical might directly react with carbon monoxide to afford an acyl radical species, and then the acyl radical undergoes single-electron reduction to provide an acylsamarium species (path B). Ryu and Sonoda reported that acyl radicals are formed when alkyl halides are treated with AIBN and tin hydride under the pressure of carbon monoxide.[43] To elucidate whether this carbonylation involves acyl radical intermediates, we examined the present carbonylation in the presence of excess amounts of alkenes. If an acyl radical is formed, this radical might be trapped by alkenes like styrene, providing the corresponding three-component coupling product.[44] However this type of reaction does not occur (Eq. (5)).



(5)

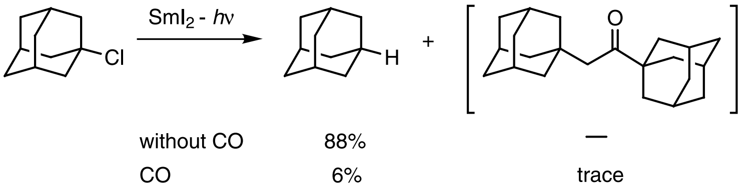
Furthermore, intramolecular trapping of the acyl radical was attempted by using *cis*-4-heptenyl chloride. However, no cyclic compound was detected at all and only asymmetric ketone was obtained in 66% yield (Scheme 2).

One possibility is that the acyl radical formed in this reaction may be reduced to an acylsamarium species very rapidly. In fact, while the rate constant for the decarbonylation of benzylcarbonyl radical is known to be $1.08\times10^7\ \mathrm{s}^{-1}$ (41°C) (Eq. (6)), the reaction of phenylacetyl chloride with SmI_2 does not afford any decarbonylated product.[45] These facts suggest that the reduction of acyl radicals by SmI_2 is much faster than the reduction of usual alkyl radicals.



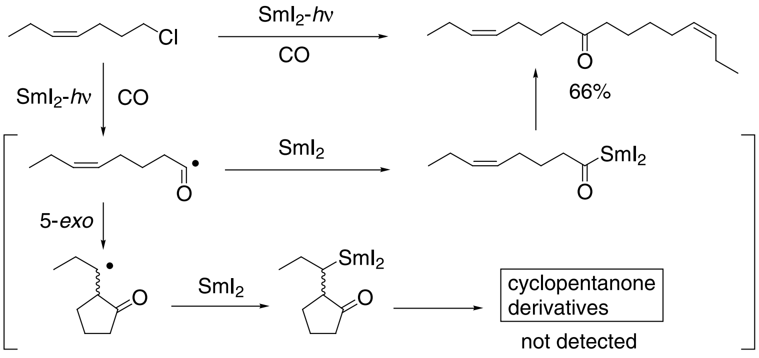
(6)

However, a third possibility cannot be excluded: samarium carbonyl species might be involved (path C). A samarium(0) carbonyl complex was reported previously.[46,47] Intriguingly, the reactivity of SmI_2 in the presence of carbon monoxide is decreased, compared with the reactivity of SmI_2 in the absence of carbon monoxide. For instance, the photoinduced reduction of 1-chloroadamantane with SmI_2 proceeded smoothly in the absence of carbon monoxide to afford adamantane in 88% yield. Under the pressure of carbon monoxide, however, both carbonylation and reduction of chloroadamantane are extremely inhibited: adamantane is obtained only in 6% yield (Eq. (7)).



(7)

A similar phenomenon is also observed with the SmI_2–HMPA system. 1-Chlorododecane is reduced with SmI_2 efficiently in the presence of HMPA, whereas the same reduction using the SmI_2–HMPA system does not take



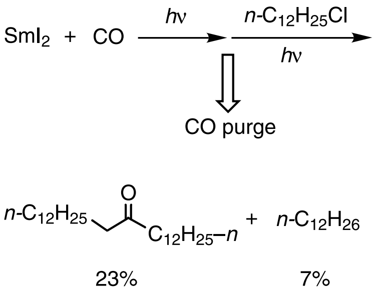
Scheme 2. Photoinduced carbonylation of 4-heptenyl chloride.

place at all in the presence of carbon monoxide (Eq. (8)). These results clearly indicate that carbon monoxide affects the reactivity of SmI_2. Since samarium ions have a high oxophilicity, carbon monoxide might coordinate to the samarium species. This might contribute to the decrease in the reducing ability of SmI_2.

$$\begin{array}{lcl} n\text{-}C_{12}H_{25}Cl & \xrightarrow{SmI_2\text{ - }HMPA} & n\text{-}C_{12}H_{26} \\ & \text{without CO} & >95\% \\ & \text{CO} & \text{trace} \end{array} \qquad (8)$$

Since the reduction of haloalkane is reported to proceed via the outer-sphere process, carbon monoxide retards this process. Similarly, the inner-sphere process might be also reduced. This is strongly supported by the fact that unsymmetrical ketones formed by this carbonylation are not reduced to alcohols or pinacols during the reaction.

A THF solution of SmI_2 in the presence of carbon monoxide is irradiated with visible light, followed by the addition of alkyl chloride after CO release. This reaction affords the unsymmetrical ketone in 23% yield (Eq. (9)). This result suggests the possibility that a samarium carbonyl species generated in situ may act as a carbonylating agent. Thus, we attempted to detect the samarium carbonyl species with an IR spectrometer. After the reaction of SmI_2 with CO (50 atm) upon irradiation with visible-light in the absence of substrates, CO is purged and immediately the IR spectra of the resulting solution is measured. However, no absorbance assigned to a samarium carbonyl species is detected. Even if a samarium carbonyl species is formed, it could exist for only a very short time in the absence of CO.



(9)

3. Conclusion

A novel photoinduced reduction system with SmI_2 has been developed. Irradiation with visible-light dramatically enhances the reducing ability of SmI_2. By using this SmI_2–*hν* system, alkyl chlorides, bromides, sulfides, selenides, tellurides, and tosylates can be reduced efficiently, while the same reduction does not proceed (or requires prolonged reaction time and higher temperature) by use of SmI_2 alone. These findings can be also applied to ytterbium diiodide (YbI_2) in THF. In this case, upon irradiation with near-UV light, YbI_2 exhibits a similar reducing power to that of SmI_2 itself in THF. In these reductions, alkyl radicals and alkylsamarium diiodides might be involved. Thus, when the photoinduced reduction of alkyl chlorides is conducted under the pressure of carbon monoxide, a novel SmI_2-induced carbonylation of alkyl chlorides has occurred to afford the corresponding unsymmetrical ketones in good yields. This carbonylation proceeds via the formation of an acylsamarium species. The synthetic applications of this carbonylation and the elucidation of the precise mechanism for the carbonylation step are now under investigation.

4. Experimental

4.1. General comments

^{1}H NMR spectra were recorded on JEOL JNM-GSX-270 (270 MHz) and JEOL JNM-AL400 (400 MHz) spectrometers using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on JEOL JNM-GSX-270 (68 MHz) and JEOL JNM-AL400 (100 MHz) spectrometers using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} value by using $\delta_{CDCl_3}=76.9$ ppm. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 in the analytical section of Osaka University (Faculty of Engineering). Elemental analyses were also performed there.

Unless otherwise noted, materials were obtained from commercial suppliers and purified by distillation or recrystallization. Tosylates (Table 2, entries 5 and 6) were prepared from the corresponding alcohols by the reaction with tosyl chloride in the presence of DMAP (4-(*N*,*N*-dimethylamino)pyridine).[48] Alkyl phenyl chalcogenides (Table 2, entries 7–9, and 12–14) were obtained by the reaction of phenyllithium (1.8 M in THF, commercially available) with elemental sulfur, selenium, and tellurium (0°C–rt, 1 h), followed by alkylation with the corresponding alkyl halides (rt (or −15°C for entries 12–13), overnight).[49] Vinylic selenide (Table 2, entry 11) was synthesized by the addition of benzeneselenol to phenylacetylene under neutral conditions.[50] β-Hydroxy selenide (Table 2, entry 10) was prepared by the oxyselenation of cyclohexene using phenylselenenyl bromide and 1-decanol. Samarium powder in oil (99.9%) was purchased from High Purity Chemicals, and was used after washing with dry pentane, followed by drying for 4 h under reduced pressure. 1,2-Diiodoethane was purified by washing of its ether solution with sat. sodium thiosulfate, followed by drying under reduced pressure.

4.2. Representative procedure for the photoinduced reduction of organic chlorides and chalcogenides with SmI_2

Representative procedure for the photoinduced reaction of organic chlorides with SmI_2 is as follows: In a 10 mL two-necked flask (Pyrex) was placed under argon atmosphere samarium powder (0.33 mmol), 1,2-diiodoethane (0.33 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (1.5 mL). The mixture was stirred at ambient temperature for 1 h, resulting in the formation of a dark blue solution of SmI_2. After the addition of organic chloride (0.15 mmol) to the solution, the flask was set in a water bath maintained at 40°C and irradiated for 3–9 h using a tungsten lamp (500 W) with stirring. The reduction of aliphatic primary or secondary alkyl chlorides requires *ca*. 3 h, while 6–9 h is essential for the aliphatic tertiary alkyl chlorides and aryl chlorides (e.g. Table 2, entry 1: 3 h; entries 2 and 4: 6 h). After the reaction was complete, the resulting mixture was diluted with diethyl ether, washed with sat. $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided the corresponding hydrocarbons.

The photoinduced reductions of organic chalcogenides with SmI_2 were usually conducted by using excess amounts of SmI_2, in order to complete the reaction in a shorter time:[51] a mixture of chalcogen compound (0.25 mmol) and SmI_2 (2 mmol) in THF (10 mL) was irradiated with a tungsten lamp through Pyrex at 40°C (Table 2, entries 5, 8, and 14) or 67°C (entries 6, 7, and 9–13). As can be seen from the results of the reduction of dodecyl chalcogenides at 40°C, the tosylate and the selenide underwent efficient reduction within 1 h and 8 h, respectively. On the other hand, the reduction of the sulfide required higher temperature and prolonged reaction time (67°C, 30 h). Reaction times (entry) are exemplified as follows: 10 h (entries 6 and 10); 16 h (entry 9); 12 h (entry 11). After similar workups, the purification of the reduced products were performed by preparative TLC (silica gel) (entries 6, 10, 12 and 13). In the cases of hydrocarbons as the product, GC analysis was carried out (entries 5, 7–9, 11, and 14).

To exclude the possibility that the reduction proceeds through the photoinduced generation of carbon radical from the corresponding selenides and tellurides which exhibit their absorption in the near-UV region, the photoirradiation was performed through filters ($h\nu>400$ or 500 nm). The fact that the reaction proceeded smoothly suggests that the reduction does not involve the direct generation of carbon radicals from the selenides and tellurides as the major pathway.

4.3. The photoinduced reduction of 5-hexenyl chloride with SmI_2

5-Hexenyl chloride (0.5 mmol) was added to the THF solution of SmI_2 (1.1 mmol) and the mixture was stirred at 40°C for 4 h. Then, 2-octanone (1.5 mmol) was added and the resulting solution was stirred at 40°C for 4 h. After the reaction was complete, the resulting mixture was diluted with diethyl ether, washed with sat. $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided alcohol (**1**) and (**2**) with the ratio of 29/71. As the rate constant (k_c) for cyclization of 5-hexenyl radicals is $4.19\times10^5\ s^{-1}$ (at 40°C), the bimolecular rate constant for the reduction of R· with SmI_2–$h\nu$ is roughly estimated to be $10^5\ M^{-1}\ s^{-1}$ (at 40°C).

4.4. Representative procedure for the photoinduced reduction with YbI_2

Ytterbium powder in oil (99.9%) was purchased from High Purity Chemicals, and was used after washing with dry pentane, followed by drying 4 h under reduced pressure.

In a 20 mL two-necked flask equipped with a condenser were placed under argon atmosphere ytterbium powder (4.0 mmol), freshly distilled (sodium/benzophenone ketyl) THF (20 mL), and 1,2-diiodoethane (4.0 mmol). Heating of the mixture at 67°C for 1 h with magnetic stirring provided ytterbium diiodide (YbI_2) in THF.

After the addition of substrate (dodecyl iodide, bromide, chloride, tosylate, sulfide, selenide, and telluride) (0.5 mmol) to the YbI_2-THF, the flask was set in a water bath maintained at 60°C and irradiated for 8 h by a tungsten lamp (500 W) with stirring. After the reaction was complete, the resulting mixture was diluted with diethyl ether, washed with sat. $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided dodecane.

4.5. YbI_2-catalyzed reduction of dodecyl bromide with aluminum upon photoirradiation

In a 20 mL two-necked flask equipped with a condenser were placed under argon atmosphere ytterbium powder (0.1 mmol), freshly distilled (sodium/benzophenone ketyl) THF (10 mL), and 1,2-diiodoethane (0.1 mmol). Heating of the mixture at 67°C for 1 h with magnetic stirring provided YbI_2. Dodecyl bromide (1 mmol) and aluminum (4.0 mmol) were added to the YbI_2–THF solution, and stirred at 67°C for 40 h. After the reaction was complete, the resulting mixture was diluted with diethyl ether, washed with sat. $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided the corresponding dodecane.

4.6. Representative procedure for the photoinduced carbonylation of organic chlorides with SmI_2 and CO

Samarium diiodide was prepared, similarly as described above (paragraph 4.2), from samarium powder (4 mmol), 1,2-diiodoethane (4 mmol), and THF (20 mL). The carbonylation was conducted by using a 50 mL stainless steel autoclave equipped with glass windows. In a Pyrex glass tube (length 95 mm; i.d. 25 mm) with a magnetic stirring bar were placed under argon atmosphere alkyl chloride (0.5 mmol) and a solution of samarium diiodide (4 mmol)[51] in THF (20 mL) by syringe technique. The glass tube was immediately inserted into the autoclave, and the apparatus was flushed several times with carbon monoxide and charged with carbon monoxide at 50 atm. The reaction was conducted by irradiating with a xenon lamp (500 W) through a filter ($h\nu>400$ nm) for 9 h upon heating at 50°C. After the reaction was complete, carbon monoxide was purged in a well-ventilated hood. The resulting mixture was poured into 1N 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. NaCl and then 5% NaS_2O_3, and dried over $MgSO_4$. After filtration and evaporation of the solvent, the products were isolated by using column chromatography on silica gel or preparative TLC on silica gel.

4.6.1. 13-Hexacosanone. [Reg. No. 120134-49-8]. White solid; mp 59–61°C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, $J=7.0$ Hz, 6H), 1.26 (br s, 38H), 1.56 (br quint, $J=7.3$ Hz, 4H), 2.38 (t, $J=7.3$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.31, 21.86, 28.41, 23.08, 28.44, 28.51, 28.58, 28.64, 28.81, 30.97, 31.07, 41.94, 210.42; IR (KBr) 2921, 2851, 1705, 1464, 1164, 1068, 908, 733 cm^{-1}; MS (EI), $m/z=330$

(M^+, 2), 211 ($C_{13}H_{27}C(O)^+$, 100), 197 ($C_{12}H_{25}C(O)^+$, 69). Exact mass (M^+) calcd for 380.4018, found 380.4010.

4.6.2. 1,21-Docosadiene-11-one. Pale yellow highly viscous oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.27 (br s, 18H), 1.37 (m, 4H), 1.55 (m, 4H), 2.03 (br q, J=7.6 Hz, 4H), 2.38 (t, J=7.3 Hz, 4H), 4.92 (d, J=11.1 Hz, 2H), 5.01 (d, J=18.6 Hz, 2H), 5.80 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.88, 28.88, 28.91, 29.06, 29.10, 29.24, 29.25, 29.29, 29.35, 29.38, 29.40, 29.41, 33.77, 33.79, 42.80, 42.82, 114.10, 114.12, 139.19, 139.22, 211.74; IR (NaCl) 2921, 2848, 1704, 1643, 1462, 991, 911, 725 cm^{-1}. HRMS calcd for $C_{22}H_{40}O$ 320.3079, found 320.3082.

4.6.3. 3,13-Hexadecadiene-8-one. Highly viscous oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J=7.6 Hz, 6H), 1.31 (m, 2H), 1.60 (m, 4H), 2.02 (m, 8H), 2.42 (t, J=7.6 Hz, 4H), 5.28–5.42 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.28, 20.46, 23.44, 23.69, 26.41, 26.81, 29.30, 42.01, 42.65, 128.07, 128.57, 131.93, 132.51, 211.22; IR (NaCl) 3004, 2962, 2934, 2872, 1712, 1460, 1406, 1371, 1303, 1260, 1069, 796, 712 cm^{-1}; MS (EI), m/z=167 ($M^+-CH_3CH{=}CHCH_2$, 14), 139 ($C_8H_{15}C(O)^+$, 7), 125 ($C_7H_{13}C(O)^+$, 11), 111 ($C_8H_{15}^+$, 26), 97 ($C_7H_{13}^+$, 40). HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2146.

4.6.4. 1,2-Dicyclohexylethanone. [Reg. No. 6713-49-1]. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (br quint, J=10.8 Hz, 2H), 1.27 (m, 10H), 1.67 (m, 4H), 1.78 (br d, J=7.3 Hz, 5H), 2.30 (br d, J=6.8 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.68, 26.10, 26.78, 28.32, 48.41, 51.22, 214.05; IR (NaCl) 2924, 2852, 1706, 1448 cm^{-1}; MS (EI), m/z=208 (M^+, 26), 125 (c-$C_6H_{11}CH_2C(O)^+$, 60), 111 (c-$C_6H_{11}C(O)^+$, 41), 97 (c-$C_6H_{11}CH_2^+$, 100), 83 (c-$C_6H_{11}^+$, 100).

4.7. The attempted photoinduced carbonylation of *n*-dodecyl chloride with SmI_2 and CO in presence of styrene

n-Dodecyl chloride (0.5 mmol) and styrene (2 mmol) were added to the THF solution (20 mL) of SmI_2 (4 mmol), and the mixture was stirred at 50°C for 4 h under the preseure of CO (50 atm) upon irradiation through a filter ($h\nu$>400 nm). Then, the resulting mixture was diluted with Et_2O (50 mL), washed with aqueous saturated $NaHCO_3$, and dried over $MgSO_4$. Filtration and concentration under reduced pressure led to the formation of only 13-hexacosanone (the desired dodecyl phenethyl ketone, generated from the reaction of acyl radical with styrene, was not obtained at all).

4.8. The photoinduced reduction of *n*-dodecyl chloride with SmI_2/THF/HMPA under the pressure of CO

n-Dodecyl chloride (0.5 mmol) was added to the THF solution (20 mL) of SmI_2 (4 mmol) in the presence of HMPA (1 mL) and the mixture was stirred at 50°C for 3 h under the pressure of CO (50 atm). Then, the resulting mixture was diluted with Et_2O (50 mL), washed with aqueous saturated $NaHCO_3$, and dried over $MgSO_4$. Filtration and concentration under reduced pressure led to the recovery of the starting *n*-dodecyl chloride almost quantitatively. In contrast, similar reaction in the absence of CO provided the corresponding dodecane in more than 95% yield.

4.9. The photoinduced reductive carbonylation of *n*-dodecyl chloride with SmI_2 treated with pressurized CO previously

In a 50 mL stainless steel autoclave equipped with glass windows was placed a THF solution (20 mL) of SmI_2 (4 mmol). Carbon monoxide was charged at 50 atm and the photoirradiation through a filter ($h\nu$>400 nm) was conducted at 40°C for 12 h in the absence of the substrate. After CO was purged in a well-ventilated hood, *n*-dodecyl chloride (0.5 mmol) was added to the solution and the resulting solution was stirred at 40°C under argon atmosphere upon photoirradiation. After 9 h, the resulting mixture was diluted with Et_2O (50 mL), washed with aqueous saturated $NaHCO_3$, and dried over $MgSO_4$. The yields of 13-hexacosanone and dodecane (23% and 7% respectively) were determined by GC analysis.

Acknowledgements

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