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A novel photoinduced reduction of haloalkanes with rare earth metals

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Abstract

By using a series of rare earth metals, the reduction of 1-iodododecane has been investigated in detail. Fine powdered europium metal (ca. 20 mesh) is found to exhibit an excellent reducing ability toward the reduction of 1-iodododecane in the dark, providing the corresponding reduction and reductive coupling products ($^{n}C_{12}H_{26}$ and $^{n}C_{24}H_{50}$) in 54 and 18% yields, respectively. Under identical conditions, however, some other fine powdered rare earth metals, i.e., Y, Pr, Gd, Dy, and Er, indicate no reducing ability toward the reduction of 1-iodododecane. Interestingly, cerium, neodymium, samarium, and europium metals have been revealed to work as useful reducing agents for the reduction of 1-iodododecane upon irradiation through Pyrex with a xenon lamp ($h\nu > 300$ nm).

Keywords: Europium; Reduction; Haloalkane; Photoirradiation; Rare earth metal

1. Introduction

The chemistry of lanthanoid compounds has been growing in recent years, and many synthetically useful applications of lanthanoid compounds have been developed based on the characteristic features of rare earths [1]. Among these, the reductions and reductive transformations using divalent lanthanoid halides such as SmI_2 have been widely utilized in organic synthesis [2]. Compared with divalent lanthanoid compounds, however, the use of zero-valent lanthanoid metals themselves directly in organic synthesis has been largely unexplored [3]. This is most probably due to their heterogeneous nature in organic solvents and lower reactivities compared with divalent lanthanoid halides. Contrary to this, we have revealed that fine powdered europium metal has an excellent reducing ability toward haloalkanes, and more interestingly that the photoirradiation with a xenon lamp through Pyrex dramatically accelerates the reduction of haloalkanes with zero-valent rare earth metals, i.e., cerium, neodymium, samarium, and europium metals.

2. Experimental

2.1. General comments

Gas chromatography (GC) spectra were recorded on Shimadzu GC-14A instrument equipped with a flame-ionizing detector and equipped using a capillary column (0.25 mm × 30 m). A xenon lamp by Ushio Optical Modulex (SX-UI500XQ) was employed.

Unless otherwise noted, the materials were obtained from commercial supplies and purified by distillation. The rare earth powders purchased from commercial sources (40 mesh, 99.9% in mineral oil) were used after washing with dry *n*-pentane to remove the mineral oil, followed by drying for 3 h under reduced pressure. Europium powder was not available from companies. Therefore, we purchased europium ingot (99.9%) in oil and was used after powderization in a grove box under a nitrogen atmosphere. Similarly, fine-powdered Y, Pr, Dy, and Er metals were also prepared

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from their ingot. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl under a nitrogen atmosphere, prior to use. 1-Iodododecane was used without purification.

2.2. *Reduction of 1-iodododecane with fine powdered europium metal in the dark*

In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed Eu powder (1.0 mmol) and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under a nitrogen atmosphere. To the THF solution involving Eu metal was added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and *n*-tetradecane (0.2 mmol, as an internal standard for gas chromatography analysis) in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. To quench the reaction, the flask was exposed to air. Aqueous saturated $NaHCO_3$ (40 mL) was added to the reaction mixture, and the products were extracted with MTBE (*t*-butyl methyl ether) or diethyl ether (20 mL three times). The combined extracts were dried over anhydrous $MgSO_4$, and filtered off. The resulting ethereal solution was analyzed by GC, which indicated the formation of $^nC_{12}H_{26}$ (54%), $^nC_{24}H_{50}$ (18%), and $^nC_{12}H_{24}$ (2%).

2.3. *Photoinduced reduction of 1-iodododecane with neodymium metal in THF*

In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed Nd powder (1.0 mmol) and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under a nitrogen atmosphere. To the THF solution involving Nd metal was added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and *n*-tetradecane as an internal standard (0.2 mmol) in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. Irradiation through Pyrex with a xenon lamp (500 W) was performed during the reaction. To quench the reaction, the flask was exposed to air. Aqueous saturated $NaHCO_3$ (40 mL) was added to the reaction mixture, and the products were extracted with MTBE or Et_2O (20 mL three times). The combined extracts were dried over anhydrous $MgSO_4$, and filtered off. The resulting ethereal solution was analyzed by GC, which indicated the formation of $^nC_{12}H_{26}$ (67%), $^nC_{24}H_{50}$ (20%), and $^nC_{12}H_{24}$ (3%).

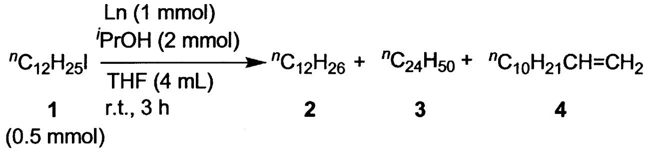
2.4. *Photoinduced reduction of 1-iodododecane with europium metal at −23 °C*

In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed Eu powder (1.0 mmol) and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under a nitrogen atmosphere. To the THF solution involving Eu metal was added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and *n*-tetradecane as an internal standard (0.2 mmol) in THF (2 mL) for 1 h at −23 °C, and the reaction was continued for additional 2 h. Irradiation through Pyrex with a xenon lamp (500 W) was performed during the reaction. To quench the reaction, the flask was exposed to air. Aqueous saturated $NaHCO_3$ (40 mL) was added to the reaction mixture, and the products were extracted with MTBE or Et_2O (20 mL three times). The combined extracts were dried over anhydrous $MgSO_4$, and filtered off. The resulting ethereal solution was analyzed by GC, which indicated the formation of $^nC_{12}H_{26}$ (82%), $^nC_{24}H_{50}$ (10%), and $^nC_{12}H_{24}$ (trace).

3. Results and discussion

3.1. *Reduction of 1-iodododecane with rare earth metals in the dark*

To elucidate the reducing ability of rare earth metals toward the reductive dehalogenation of haloalkanes, we selected 1-iodododecane as a model substrate and examined the reduction using a series of rare earth metals in THF. Except europium, high-grade lanthanoid powders (40 mesh) are commercially available. Thus, the reduction of 1-iodododecane was attempted by employing these commercially available powders without further activation, but the desired reduction did not proceed at all. As to europium metal, we filed Eu ingot to powder (ca. 20 mesh) in a grove box under a nitrogen atmosphere and directly utilized for the reduction of 1-iodododecane. Surprisingly, the desired reduction took place successfully, providing dodecane (**2**), tetracosane (**3**), and dodecene (**4**) in 54, 18, and 2%, respectively, as can be seen from Eq. (1) and Fig. 1.

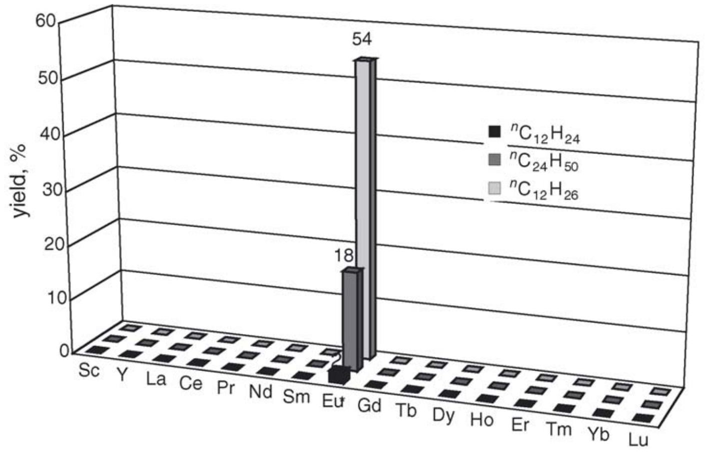


$$\underset{\substack{\mathbf{1}\\(0.5\ \text{mmol})}}{^nC_{12}H_{25}I} \xrightarrow[\substack{\text{THF (4 mL)}\\ \text{r.t., 3 h}}]{\substack{\text{Ln (1 mmol)}\\ ^i\text{PrOH (2 mmol)}}} \underset{\mathbf{2}}{^nC_{12}H_{26}} + \underset{\mathbf{3}}{^nC_{24}H_{50}} + \underset{\mathbf{4}}{^nC_{10}H_{21}CH{=}CH_2} \quad (1)$$

To clarify whether the reducing ability observed in the case of europium powder depends on the preparation method of lanthanoid powders, we next examined the same reduction of 1-iodododecane by using some other rare earth powders prepared by the same procedure in the case of europium. We prepared fine powders (ca. 20 mesh) of Y, Pr, Gd, Dy, and Er from their ingot in a grove box under a nitrogen atmosphere, and then examined the reduction of 1-iodododecane. However, the desired reduction did not occur at all in the dark. These results suggest that europium metal has an excellent reducing ability compared with other rare earth metals examined. This might be associated with the fact that europium metals easily undergo air-oxidation compared with other rare earth metals.

3.2. *Photoinduced reduction of 1-iodododecane with rare earth metals*

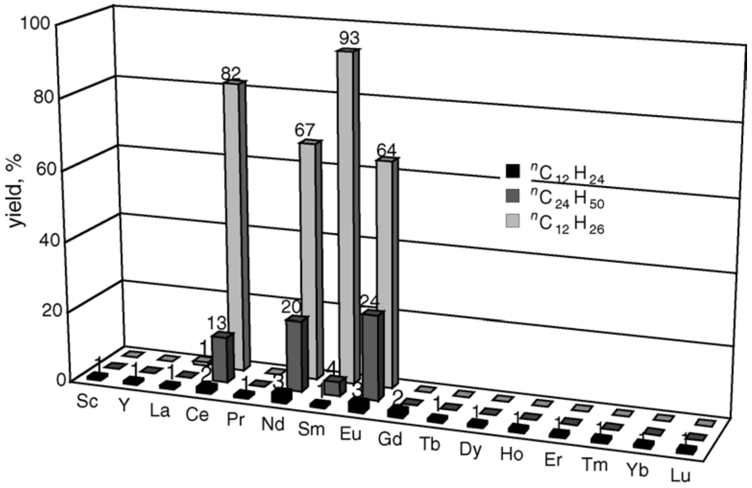
Recently, we have developed a novel photoinduced reduction system of samarium diiodide: visible-light irradiation



	Sc	Y*	La	Ce	Pr*	Nd	Sm	Eu*	Gd*	Tb	Dy*	Ho	Er*	Tm	Yb	Lu
■	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0
▨	0	0	0	0	0	0	0	18	0	0	0	0	0	0	0	0
□	0	0	0	0	0	0	0	54	0	0	0	0	0	0	0	0

(*ca. 20 mesh)

Fig. 1. Reduction of 1-iodododecane with Ln metals (40 mesh) in the dark.

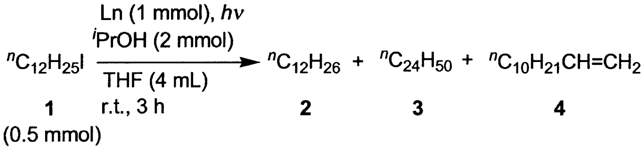


	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
■	1	1	1	2	1	3	1	3	2	1	1	1	1	1	1	1
▨	0	0	0	13	0	20	4	24	0	0	0	0	0	0	0	0
□	0	0	1	82	0	67	93	64	0	0	0	0	0	0	0	0

Fig. 2. Photoinduced reduction of 1-iodododecane with Ln metals.

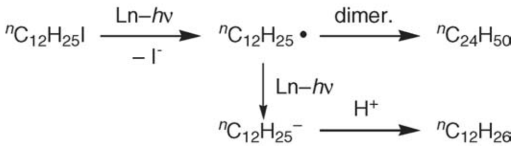
leads to the excitation of SmI_2, which makes it possible to attain an excellent electron-transfer to organic compounds such as organic halides and chalcogenides, etc. [4]. Although the reaction of 1-iodododecane with a series of rare earth metals did not proceed at all in the dark, as described in Section 3.1, the reaction solution indicates the change of color, which suggests the formation of small amounts of soluble lanthanoid(II) species in THF.

Thus, we examined the reduction of 1-iodododecane using a series of rare earth metals upon irradiation through Pyrex with a xenon lamp, and the results are summarized in Eq. (2) and Fig. 2.



$$\underset{\substack{\mathbf{1}\\(0.5\ \text{mmol})}}{{}^{n}C_{12}H_{25}I} \xrightarrow[\substack{\text{THF (4 mL)}\\ \text{r.t., 3 h}}]{\substack{\text{Ln (1 mmol), } h\nu\\ {}^{i}\text{PrOH (2 mmol)}}} \underset{\mathbf{2}}{{}^{n}C_{12}H_{26}} + \underset{\mathbf{3}}{{}^{n}C_{24}H_{50}} + \underset{\mathbf{4}}{{}^{n}C_{10}H_{21}CH{=}CH_2} \quad (2)$$

Very interestingly, lighter metals such as Ce, Nd, Sm [5], and Eu exhibit good reducing abilities toward the deiodation of 1-iodododecane under photoirradiation conditions. On the other hand, heavy rare earth metals indicate no reducing ability even upon photoirradiation.



Scheme 1. A possible reaction pathway for reduction.

Table 1
Reduction of 1-iodododecane by use of Eu reagents

Entry	Temperature (°C)		Yield (%)[a]			
			$C_{12}H_{26}$	$C_{24}H_{50}$	$C_{12}H_{24}$	$C_{12}H_{25}I$
1	10	Dark	58	23	2	8
2	−23	Dark	4	Trace	0	95
3	−23	hν	82	10	Trace	5

[a] Determined by GC.

A possible reaction pathway for this reduction is shown in Scheme 1. Most probably, the reduction may proceed via the single-electron transfer from rare earth metal to 1-iodododecane generating dodecyl radical. Further reduction of dodecyl radical with rare earth species leads to dodecyllanthanoid iodide, which is protonated with water during workups. On the other hand, dimerization of dodecyl radicals affords tetracosane.

In the case of samarium, the product selectivity to give dodecane is higher compared with the cases of other rare earth metals. This is probably because the solubility of samarium diiodide in THF is superior to other divalent rare earth species: dodecyl radical intermediate formed in situ may be immediately reduced by the homogeneous low-valent samarium species (SmI_2) in THF.

In the case of europium metal, photoirradiation clearly accelerated the reduction of 1-iodododecane, although the product ratio of **2**/**3** was similar to that in the dark. The influence of the photoirradiation on the reduction can be understood by the results of the reduction at lower temperature (see Table 1). At lower temperature (−23 °C), photoirradiation is effective for the reduction of 1-iodododecane. In the dark, the conversion of the reduction dramatically decreased as dropping the reaction temperatures (entries 1 and 2). Even at −23 °C, however, the reduction proceeded efficiently under photoirradiation conditions (entry 3).

4. Conclusions

In conclusion, we have revealed that europium metal can be employed as an excellent reducing agent for the reduction of iodoalkanes. Furthermore, it has been found that the photoinduced reduction of 1-iodododecane with several lighter rare earth metals such as cerium, neodymium, samarium, and europium takes place successfully. In this reaction, the reaction solution indicates the following color, i.e., Ce (ocher), Nd (gray), Sm (blue), and Eu (dark green), and therefore, the corresponding divalent species are formed in situ. The photoirradiation may activate the divalent species, although the precise mechanism requires further detailed investigations.

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