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Reduction of Organic Halides with Lanthanum Metal: A Novel Generation Method of Alkyl Radicals

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Results of the reaction of alkyl halides with lanthanum metal have been shown. The reduction of alkyl iodide with 1/3 equiv of lanthanum metal efficiently proceeded to give the corresponding reductive dimerized products along with the formation of reduction and dehydroiodination products. In the case of alkyl bromides and chlorides, the reaction did not proceed under the same reaction conditions as that of alkyl iodides; however, the reaction was dramatically promoted by the addition of a catalytic amount of iodine. A reaction pathway including alkyl radicals was suggested.

Introduction

Recently, the utilization of lanthanoid metal salts and organolanthanoid compounds as synthetic reagents in organic synthesis has been steadily increasing due to their unique chemical properties.[1] Although the use of an unstable lanthanoid species, which were generated in situ by the reaction of alkyl halides with low-valent lanthanoid compounds such as SmI_2, as a versatile reagent has been shown,[2] the reaction of alkyl halides with lanthanoid metals and the utilization of the intermediates prepared by the reaction have received considerably less attention in organic synthesis.[3] Almost thirty years ago, Evans showed that alkyl lanthanoid species (RLnX: Ln = Sm, Yb, and Eu) were easily formed by the treatment of lanthanoid metals such as samarium, ytterbium, and europium with alkyl iodide.[3a,b] Subsequently, Fujiwara[4] and Beletskaya[5] investigated the utilization of PhLnX (Ln = Sm, Eu, Yb, and Ce) species in organic synthesis, which were generated in situ by the reaction of PhI with lanthanoid metal, and showed some unique reactivity of these species toward various electrophiles. The synthesis and characterization of various lanthanoid(II) alkyl and aryl compounds (Ln = Sm, Eu, and Yb) were also recently reported.[6] However, to the best of our knowledge, there are no reports on the reaction of alkyl halides with the other lanthanoid metals and the utilization of the intermediates prepared by the reaction in organic synthesis.

We have recently investigated the direct use of lanthanum metal in organic reactions and showed that the

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[1] For recent reviews, see: (a) Kagan, H. B. *New J. Chem.* **1990**, *14*, 453. Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943. (b) Molander, G. A.; *Chem. Rev.* **1992**, *92*, 29. Kobayashi, S. *Synlett* **1994**, 689. (c) Kamochi, Y.; Kubo, T. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 285. (d) Imamoto, T. In *Lanthanides in Organic Synthesis*; Academic Press: New York, 1994. (e) Matsuda, Y. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 987. (f) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (g) Ito, Y.; Fujiwara, Y.; Yamamoto, T. In *Kikan Kagaku Sousetu; Organic Synthesis by Means of Lanthanoids No. 37*; Gakkai Press Center, 1998. (h) Kobayashi, S. In *Lanthanide: Chemistry and Use in Organic Synthesis*; Springer-Verlag: Berlin, Herdelberg, 1999. (i) Steel, P. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2727, and references therein.

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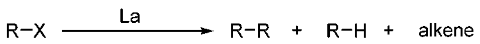
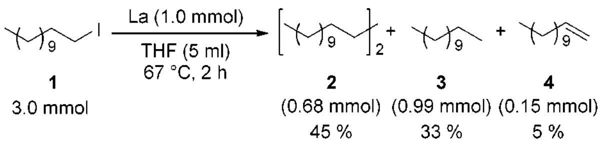
Scheme 1



Scheme 2



reductive dimerization of carbonyl compounds or imine compounds was assisted by the lanthanum metal to give the corresponding *vic*-diols or *vic*-diamines.[7] In connection with a study on the direct use of lanthanum metal in organic synthesis, we found that the generation of alkyl radicals from alkyl halides was accompanied by the efficient transfer of available electrons from the lanthanum metal (Scheme 1).

Results and Discussion

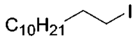
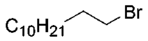
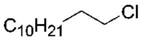
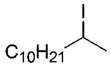
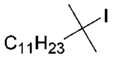
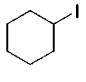
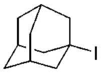
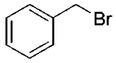
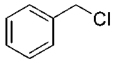
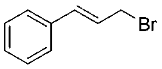
When a stoichiometric amount of lanthanum metal was treated with 1-iodododecane (**1**) in THF solution, the color of the reaction solution gradually changed to dark gray. Workup by quenching the reaction with aqueous HCl gave tetracosane (**2**), a reductive dimerization product, in 70% yield along with the formation of dodecane (**3**) (18%) and dodecene (**4**) (6%). For the reduction of organic compounds using lanthanum metal as the reducing agent, the efficient utilization of three electrons, which may be supplied during the change from the zerovalent metal to the stable trivalent ion, is expected. To determine the possibility of the efficient use of several electrons present in a zerovalent lanthanum metal, **1** was next allowed to react with the 1/3 equiv of lanthanum metal and it was found that a mixture of **2** (45%), **3** (33%), and **4** (5%) was formed in the reaction (Scheme 2). These yields clearly proved that about 2.5 e including the lanthanum metal was efficiently utilized in reduction of 1-iodododecane. To understand the reactivity of other lanthanoid metals toward alkyl halides, various lanthanoid metals were treated with 1-iodododecane (**1**), and the results of this series of experiments are summarized in Table 1. After the quenching with aqueous HCl, the yields of products were determined by GC. In the case of cerium, praseodymium, neodymium, and europium, **2** was mainly formed. In contrast, the use of samarium metal, which is known to form the alkyl samarium intermediates (RSmI),[2,3b−d] and gadolinium led to the predominant formation of dodecane (**3**), a reduction product of **1**. The other lanthanoid metals did not show high reactivity in the reaction of **1**.

Table 1. Reaction of 1-Iodododecane with Lanthanoid Metals[a]

		yield (%)[b]		
entry	lanthanoid metal	**2**	**3**	**4**
1	lanthanum	64	24	6
2	cerium	53	26	5
3	praseodymium	55	31	4
4	neodymium	56	33	5
5	samarium	2	49	10
6	europium	59	27	4
7	gadolinium	23	40	4
8	terbium	8	4	trace
9	dysprosium	15	19	1
10	holmium	5	3	trace
11	erbium	15	15	4
12	thulium	5	4	trace
13	ytterbium	39	27	3
14	lutetium	2	trace	trace

[a] Reaction conditions: 1-iodododecane (2.0 mmol) and Ln (1.0 mmol) in THF (5 mL) at 67 °C for 2 h. [b]GC yield.

Table 2. Reaction of Various Organic Halides with Lanthanum Metal[a]

entry	R-X	yield (%)[b]		
		R-R	R-H	Alkene
1		64 (45)	24 (33)	6 (5)
2[c]		60	23	8
3[c]		4	9	trace
4		50[d] (40)	33 (30)	19[e] (15)
5		13 (13)	42 (39)	40[f] (38)
6		45 (33)	27 (27)	18 (14)
7		57 (40)	36 (31)	-
8		83 (85)	2 (3)	-
9[c]		77	6	-
10		84[g] (73)	4 (3)	-

[a] Reaction conditions: R−X (2.0 mmol) and La (1.0 mmol) in THF (5 mL) at 67 °C for 2 h. [b] GC yield. The number in parentheses shows the yield in the presence of 1/3 equiv of La.[c] I_2 (0.2 mmol) was added. [d] *Dl*/*meso* = 52:48. [e] 1-Dodecene/2-dodecene = 60:40. [f] 2-Methyl-1-tridecene/2-methyl-2-tridecene = 83:17. [g] 1,6-Diphenyl-1,5-hexadiene/1,4-diphenyl-1,5-hexadiene/3,4-diphenyl-1,5-hexadiene = 33:48:19.

Next, various alkyl halides were allowed to react with 1/3 and 1/2 equiv of lanthanum metal, and results are shown in Table 2. Although 2-iodododecane and iodoadamantane mainly formed the coupling products, for 2-methyl-2-iodododecane, the yield of the dimerized product was low due to the predominant formation of the reduction (42%) and dehydroiodination (40%) products. The reductive dimerization of benzyl bromide and cinnamyl bromide with lanthanum metal efficiently proceeded to give dimerized products. The reaction of chloro- and bromododecane and benzyl chloride did not proceed under the same reaction conditions as that of the iodododecane; however, the reaction of these compounds was promoted by the addition of a catalytic amount of iodine (20 mol %).[8,9]

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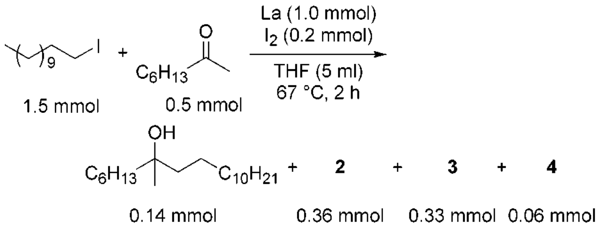
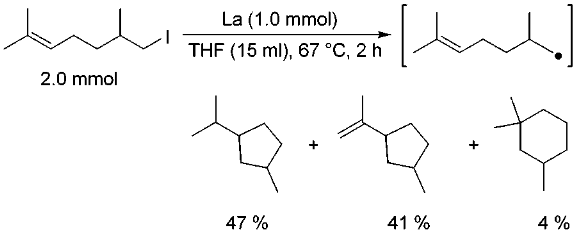
(8) We have already shown that the addition of a catalytic amount of iodine dramatically enhanced the reductive dimerization of carbonyl compounds or imines with lanthanum metal. See ref 7.

Scheme 3



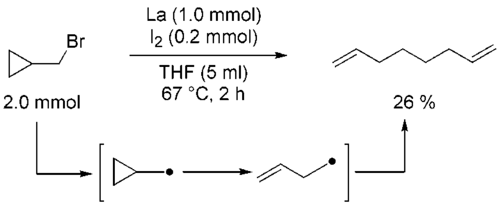
Scheme 4



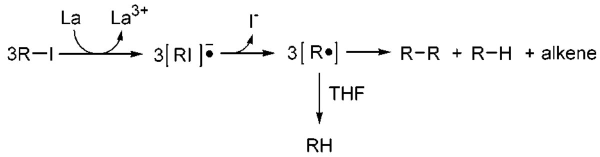
To better understand the intermediates in the reaction of alkyl halides with lanthanum metal, the reaction was quenched with DCl/D_2O instead of HCl/H_2O; however, the corresponding C-deuterated products were not obtained. Although Barbier-type reaction of RI with carbonyl compounds in the presence of lanthanum metal was examined, the dimerized product (**2**) was obtained in 48% yield and the yield of the Barbier-type reaction product was low (Scheme 3).[2c] Then, we speculated that the coupling product arose by the initial formation of the alkyl radical, followed by coupling of the alkyl radical. When 7-iodo-2,6-dimethyl-2-heptene (**11**) was used as an alkyl halide, the 5-exo-cyclized products, 1-isopropyl-3-methyl- and 1-isopropenyl-3-methylcyclopentane, were obtained in 47 and 41% yields, respectively, along with a small amount of the 6-endo-cyclized product, 1,1,3-trimethylcyclohexane (4%) (Scheme 4).[10] In addition, in the case of cyclopropylmethyl bromide, the reductive dimerization was accomplished via the ring opening of the cyclopropylmethyl radical to give 1,7-octadiene (Scheme 5).[11]

From these results, the reaction pathway including alkyl radicals by the reaction of alkyl halides with lanthanum metal is strongly suggested (Scheme 6). The one-electron transfer from lanthanum metal or low-valent lanthanum species to alkyl halides, followed by the elimination of the iodine anion, forms alkyl radicals.[12] The alkyl radicals were coupled to form the reductive dimerized products. On the other hand, the disproportionation and/or the absorption of hydrogen from THF used as a solvent by alkyl radicals led to the formation of alkanes and alkenes.[13]

Scheme 5



Scheme 6. Possible Pathway of the Reaction of RI with La Metal



In summary, we found that the treatment of alkyl halides with lanthanum metal is a novel generation method of alkyl radicals. In addition, the efficient utilization of electrons from lanthanum metal was successfully achieved during this reaction. The application of alkyl radicals generated by the reaction of alkyl halides with lanthanum metal in organic synthesis is now progress.

Experimental Section

Instruments. ${}^1H$ and ${}^{13}C$ NMR spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer using $CDCl_3$ as a solvent with tetramethylsilane as the internal standard. FT-IR spectra were obtained on a Perkin-Elmer Model PARAGON 1000 spectrophotometer. Mass spectra were measured on a Shimadzu Model QP-5050A instrument. Gas chromatography (GC) was carried out on a Shimadzu GC-14A instrument equipped with a flame-ionizing detector and using a capillary column (Hicap-CBP-1-S25-025, 0.25 mm × 25 m).

Reagents. Praseodymium, neodymium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and lutetium powder (−20 mesh), organic halides, and iodine were commercially available high-grade products and were used without purification. Lanthanum, cerium, samarium, europium, and ytterbium were commercially available high-grade products and were used after powderization. 7-Iodo-2,6-dimethyl-2-heptene was prepared by the reaction of 2,6-dimethyl-5-heptene-1-ol with I_2 in the presence of PPh_3 and imidazole. 2-Iodo-2-methyltridecane was synthesized by iodination of 2-methyl-2-tridecanol with LiI in aqueous HI (55%). The other reagents and solvents were purified by the usual methods before use.

General Procedure for the Reaction of Organic Halides with Lanthanum Metal. Lanthanum powder (139 mg, 1 mmol) was placed in a two-necked flask. THF (5 mL) and organic halide (1−3 mmol) were added to the flask, and the mixture was stirred at 67 °C for 2 h under a nitrogen atmosphere. The color of the solution gradually changed to dark gray. After the reaction, aqueous HCl (1 M, 5 mL) was added to the reaction mixture, and the mixture was extracted with *n*-hexane (20 mL × 5). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated. Purification of the residue by HPLC afforded the corresponding reductive dimerization, reduction, and dehydrohalogenation products. Products were characterized by

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(9) In the reaction that used ytterbium or samarium metal, it was also disclosed that various reactions were promoted by the addition of a catalytic amount of methyl iodide or iodine; however, the mechanism of the effect of methyl iodide or iodine was not explained in these manuscripts: (a) Hou, Z.; Takamine, K.; Aoki, O.; Shiraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 6077. (b) Yanada, R.; Bessho, K.; Yanada, K. *Synlett* **1995**, 443. (c) Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271. (d) Yanada, R.; Negoro, N.; Okaniwa, M.; Miwa, Y.; Taga, T.; Yanada, K.; Fujita, T. *Synlett* **1999**, 537. (e) Wang, L.; Zhou, L.; Zhang, Y. *Synlett* **1999**, 1065. (f) Talukdar, S.; Fang, J.-M. *J. Org. Chem.* **2001**, *66*, 330.

(10) It is well-known that substituted 5-hexenyl radicals rapidly cyclized in a highly regioselective 5-exo fashion to form the corresponding cyclopentylmethyl radicals: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

(11) Ingold reported that the cyclopropyl radical was rapidly rearranged to homoallyl radical ($k^{25 °C} = 1.3 \times 10^3\ s^{-1}$): Effio, A.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

(12) On the reaction of alkyl halides with SmI_2, the alkyl radicals, which were formed by the reduction of alkyl halides with SmI_2, are rapidly reduced by SmI_2 in THF/HMPA to form alkyl samarium reagents ($RSmI_2$). See refs 2c and 2d.

(13) At the present time, in the formation of alkenes, possibilities including the β-hydrogen elimination of organolanthanum species cannot be rigorously ruled out.

comparison of their spectral data (^{1}H and ^{13}C NMR and IR) with those of authentic samples (2-methyl-1-tridecene,[14] 2-methyl-2-tridecene,[14] 1,6-diphenyl-1,5-hexadiene,[15] 1,4-diphenyl-1,5-hexadiene,[15] and 3,4-diphenyl-1,5-hexadiene[15]). 2-Methyltridecane, 11,12-Dimethyltricosane, 12,12,13,13-tetramethyltetracosane, and 1,1′-biadamantane were characterized by comparison of their spectra data with those of samples prepared by hydrogenation of 2-methyl-2-tridecene[16] or by the reductive coupling of 2-iodododecane, 2-iodo-2-methyltridecane, and 1-iodoadamantane with sodium.[17]

General Procedure for the Reaction of Organic Halides with Lanthanum Metal in the Presence of a Catalytic Amount of Iodine. Lanthanum powder (139 mg, 1 mmol) and iodine (51 mg, 0.2 mmol) were placed in a two-necked flask. THF (5 mL) and organic halide (1−3 mmol) were added to the flask, and the mixture was stirred at 67 °C for 2 h under a nitrogen atmosphere. After the reaction, the same workup as that of the reaction of alkyl halides with lanthanum metal in the absence of a catalytic amount of iodine was carried out.

Reaction of 1-Iodododecane with Lanthanum Metal in the Presence of 2-Octanone. Lanthanum powder (139 mg, 1 mmol), iodine (51 mg, 0.2 mmol), 1-iodododecane (444 mg, 1.5 mmol), and 2-octanone (64 mg, 0.5 mmol) in THF (5 mL) solution was stirred at 67 °C for 2 h. The reaction was quenched with aqueous HCl (1 M, 5 mL), and the mixture was extracted with diisopropyl ether (20 mL × 5). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated. Purification of the residue by HPLC afforded the corresponding alcohol, reductive dimerization, reduction, and dehydrohalogenation products. Products were characterized by comparison of their spectral data (^{1}H and ^{13}C NMR and IR) with those of authentic sample prepared by the reaction of 2-octanone with n-$C_{12}H_{25}MgBr$.

Reaction of 7-Iodo-2,6-dimethyl-2-heptene (11) with Lanthanum Metal. A THF (5 mL) solution of 7-iodo-2,6-dimethyl-2-heptene (**11**) (476 mg, 2.0 mmol) and lanthanum powder (139 mg, 1 mmol) were added to the flask, and the mixture was stirred at 67 °C for 2 h under a nitrogen atmosphere. The color of the solution gradually changed to dark gray. After the reaction, aqueous HCl (1 M, 5 mL) was added to the reaction mixture and the mixture was extracted with diethyl ether (20 mL × 5). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated. Purification of the residue by HPLC afforded the corresponding cyclized products.

Reaction of Cyclopropylmethyl Bromide with Lanthanum Metal. Lanthanum powder (139 mg, 1 mmol) and iodine (51 mg, 0.2 mmol) were placed in a two-necked flask. THF (5 mL) and cyclopropylmethyl bromide (270 mg, 2.0 mmol) were added to the flask, and the mixture was stirred at 67 °C for 2 h under a nitrogen atmosphere. The color of the solution gradually changed to dark gray. After the reaction, aqueous HCl (1 M, 5 mL) was added to the reaction mixture and the mixture was extracted with diisopropyl ether (20 mL × 5). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated. Purification of the residue by HPLC afforded 1,7-octadiene.

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Supporting Information Available: Spectra (^{1}H and ^{13}C NMR and IR) for all coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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