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Deoxygenative Dimerization of Benzylic and Allylic Alcohols, and Their Ethers and Esters Using Lanthanum Metal and Chlorotrimethylsilane in the Presence of a Catalytic Amount of Iodine and Copper(I) Iodide

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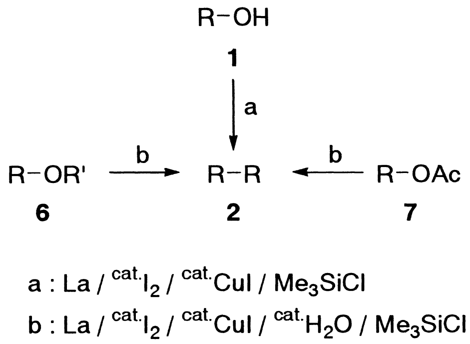
Benzylic and allylic alcohols were deoxygenatively dimerized by a treatment with lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine, giving the corresponding coupling products, alkanes, in moderate-to-good yields. This dimerization reaction was dramatically accelerated by the addition of a catalytic amount of copper(I) iodide. Similarly, ethers and esters were deoxygenatively dimerized by La/Me_3SiCl/$^{cat.}I_2$/$^{cat.}$CuI system in the presence of a catalytic amount of H_2O.

The development of new synthetic reactions using lanthanoid metal salts and organolanthanoid compounds has been steadily increasing in organic chemistry.[1] In contrast to many reports available concerning the reduction of organic compounds with low-valent lanthanoid compounds, such as samarium diiodide,[2] there are limited examples concerning the direct use of lanthanoid metals as the reducing reagent.[3] We recently succeeded in the direct use of lanthanum metal on the reduction of carbonyl compounds, imines, and alkyl and aryl halides.[4] We found that benzylic and allylic alcohols were deoxygenatively dimerized by a treatment with lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine. Furthermore, it was clarified that the reaction was dramatically accelerated by the addition of a catalytic amount of copper(I) iodide. We also found that this reaction system was applicable to the deoxygenative dimerization of ethers and esters. Significant features of these reactions are as follows: (i) the formation of alkyl iodide as an intermediate with a catalytic amount of iodine, (ii) the generation of active zerovalent copper as a catalyst of a coupling reaction, and (iii) lanthanum playing a double role: as a generator of iodination reagent, iodotrimethylsilane, and as a reducing reagent of alkyl iodide and/or copper(I) iodide. This paper discloses the full results of the deoxygenative dimerization of alcohols, ethers, and esters with lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine and copper(I) iodide in detail (Scheme 1).[5]



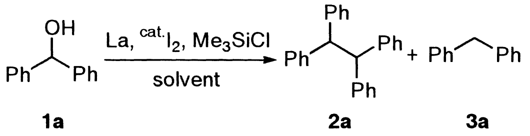
Scheme 1.

Results and Discussion

Deoxygenative Dimerization of Alcohols. The reductive coupling of alkyl halides to the corresponding alkanes is a useful method for constructing carbon-carbon bonds. Although reductive coupling can be accomplished with various reagents,[6] there are some disadvantages for the utilization of alkyl halides as a starting material: (i) an instability of tertiary iodides, (ii) a lachrymatory property of some halides, such as benzylic bromide, and (iii) the requirement of an excess or stoichiometric amount of halogenation reagent for the synthesis of alkyl halides. Many alcohols can be purchased from commercial sources, and easily synthesized from various organic compounds, and alkyl halides are generally synthesized by the substitution reaction of alcohols and their derivatives.[7] Consequently, the development of a deoxygenative dimerization method of alcohols has attracted much attention; however, there are few reports on the transformation. To the best of our knowledge, low-valent titanium[8] and niobium[9] compounds prepared by the reduction of metal halides are limited reagents for the deoxygenative dimerization of alcohols. During the course of the study on the direct use of zerovalent lanthanum metal in organic synthesis, we found that some alcohols easily underwent deoxygenative dimerization to give the corresponding hydrocarbons (Table 1).

When benzhydrol (**1a**) was treated with lanthanum metal and chlorotrimethylsilane (2 equiv) in the presence of a catalytic amount of iodine in THF as a solvent at 25 °C for 8 h, 1,1,2,2-tetraphenylethane (**2a**), the deoxygenative dimerized product of **1a**, was obtained along with diphenylmethane (entry 4). The reaction did not take place in the absence of iodine or chlorotrimethylsilane (entries 1–3). The use of acetonitrile as a solvent led to an increase in the conversion of **1a** and the

Table 1. Deoxygenative Dimerization of Benzhydrol with Lanthanum Metal[a)]



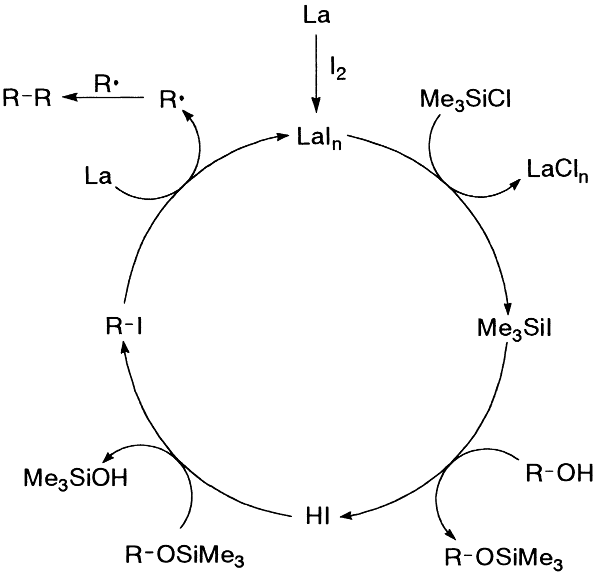
Entry	I$_2$ mmol	Me$_3$SiCl mmol	Add.	Solv.	Time h	Yield/(%)[b)] 2a	3a
1	—	—	—	THF	8	0	0
2	0.2	—	—	THF	8	0	0
3	—	2.0	—	THF	8	0	2
4	0.2	2.0	—	THF	8	6	27
5	0.2	2.0	—	CH$_3$CN	8	51	33
6[c)]	0.2	2.0	—	CH$_3$CN	1	54	35
7	0.2	2.0	CuI[d)]	CH$_3$CN	10 min	87	13
8[e)]	0.2	2.0	CuI[d)]	CH$_3$CN	8	0	0
9[f)]	0.2	2.0	CuI[d)]	CH$_3$CN	10 min	3	4

a) Reaction conditions: **1a** (1.0 mmol), La (1.0 mmol), and solvent (3.0 mL). b) GC yield. c) 82 °C. d) CuI (0.2 mmol) was added. e) La was not used. f) Mg was used instead of La.

Table 2. Effect of Metal Halides on the Deoxygenative Dimerization of **1a**[a)]

Entry	Metal Halide	Temp. (°C)	Yield/(%)[b)] **2a**	**3a**
1	—	82	54	35
2[c)]	CuI	25	87	13
3	CuBr	25	88	8
4	CuCl	25	91	7
5	CuBr$_2$	25	96	4
6	AgI	25	85	14
7	NiI$_2$	25	91	4
8	PbI$_2$	25	84	15
9	CoI$_2$	25	99	1
10	FeI$_2$	25	87	5
11	ZnI$_2$	82	68	13
12	TiI$_4$	82	58	24
13	MnI$_2$	82	59	18

a) Reaction conditions: **1a** (1.0 mmol), La (1.0 mmol), Me$_3$SiCl (2.0 mmol), I$_2$ (0.2 mmol), metal halide (0.2 mmol), and CH$_3$CN (3.0 mL) for 1 h. b) GC yields. c) 10 min.

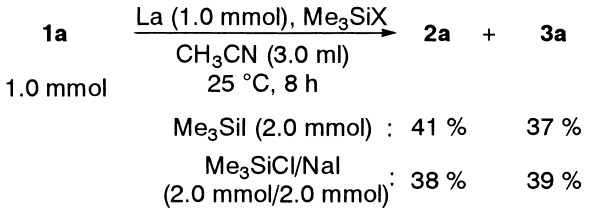


Scheme 2. A possible reaction path.

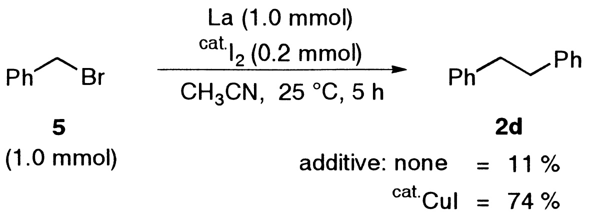
yield of **2a** (entry 5). For the reaction at higher temperature (82 °C), the reaction was promoted, however, the selectivity of **2a** was not affected by the reaction temperature (entry 6). It is interesting to note that the deoxygenative dimerization reaction was dramatically accelerated by the addition of a catalytic amount of metal halides. When **1a** was treated with lanthanum metal in the presence of chlorotrimethylsilane (2 equiv), a catalytic amount of iodine (0.2 equiv), and copper(I) iodide (0.2 equiv) in acetonitrile at 25 °C, **1a** was completely consumed within 10 min, and **2a** was obtained in 87% yield (entry 7). When magnesium metal was used as a reducing reagent instead of lanthanum metal, **2a** and **3a** were hardly produced (entry 9). The effect of various metal halides on the reaction of **1a** was examined; the results are given in Table 2. The other copper halides, and silver, nickel, lead, cobalt, and iron iodides showed catalytic activity for the reaction of **1a**; however, in the case of zinc, titanium, and manganese iodides, no improvement of the selectivity and yield was observed.

A preparative method of iodotrimethylsilane by a halogen exchange reaction of chlorotrimethylsilane with magnesium iodide (MgI$_2$) has been developed by Krüerke.[10] It was already known that the treatment of alcohols with iodotrimethylsilane, which was generated in situ by a reaction of chlorotrimethylsilane with sodium iodide in acetonitrile, gave the corresponding alkyl iodides in good yields.[11,12] We have recently shown that alkyl iodides were reductively coupled by lanthanum metal, giving the corresponding alkanes.[4c] Based on the results described above, a possible reaction pathway involving the formation of alkyl iodide is suggested, as shown in Scheme 2. The first step involves the generation of iodotrimethylsilane by a halogen-exchange reaction of chlorotrimethylsilane with lanthanum iodide, which is generated in situ by the reaction of lanthanum metal with iodine. Iodotrimethylsilane reacts with alcohol, forming the corresponding alkyl iodide. In the absence of copper(I) iodide, in situ generated alkyl iodide is reductively coupled by lanthanum metal, giving the corresponding symmetrical alkane, and subsequently lanthanum iodide species (LaI$_n$) is regenerated. Thus, the reaction does not require an excess or stoichiometric amount of iodination reagent despite the formation of alkyl iodide as an intermediate. In order to confirm the possibility of an intermediacy of iodotrimethylsilane generated in situ by the reaction of lanthanum metal, iodine, and chlorotrimethylsilane, iodotrimethylsilane or the equivalent, mixture of sodium iodide and chlorotrimethylsilane, was examined independently in the reaction of **1a**. As shown in Scheme 3, the treatment of **1a** with lanthanum metal and iodotrimethylsilane or sodium iodide/chlorotrimethylsilane gave the dimerization product without using iodine (cf. Table 1, entry 3).

It was found that the deoxygenative dimerization of alcohols

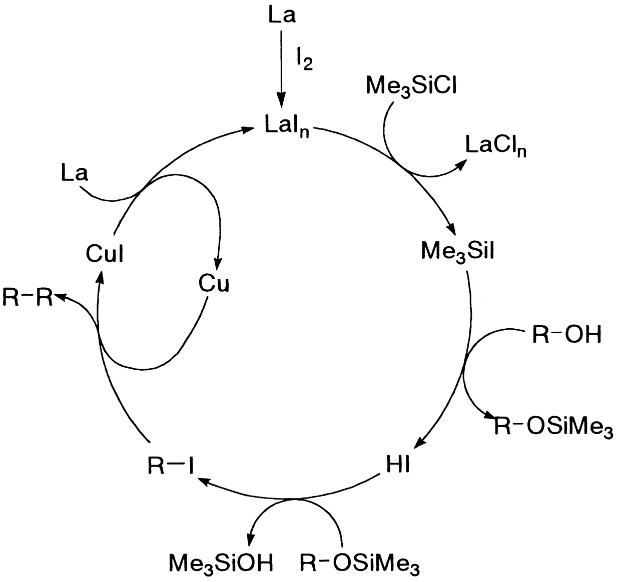


Scheme 3.



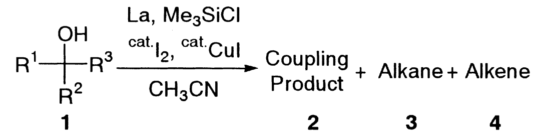
Scheme 4.

was markedly accelerated by the addition of a catalytic amount of copper(I) iodide. In order to obtain further information on the role of copper(I) iodide, the reaction of benzyl bromide (**5**) with lanthanum metal was examined in the presence or absence of copper(I) iodide. The treatment of **5** with lanthanum metal in the presence of a catalytic amount of iodine and copper(I) iodide (0.2 equiv) in acetonitrile as a solvent at 25 °C for 5 h gave 1,2-diphenylethane (**2d**) in 74% yield; however, in the absence of copper(I) iodide, the reaction proceeded extremely slow (11%) (Scheme 4). It had already been known that the activated zerovalent metal generated in situ by the reduction of metal halide with reducing reagent shows a higher reducing ability than that of a commercially available zerovalent metal.[13] Ebert et al. reported that benzylic and allylic halides were reduced by activated copper generated by the reduction of copper salt with lithium naphthalenide, giving the reductive coupling products within a few minutes in good yields.[14] In fact, when copper(I) iodide was treated with an equal molar amount of lanthanum metal in acetonitrile as a solvent at 25 °C for 15 min, lanthanum metal was gradually dissolved, giving a dark-brown suspension. Subsequently, the addition of benzyl bromide (**5**) to the solution produced 1,2-diphenylethane (**2d**) within 1 h in 70% yield.[15] These results suggest that the activated zerovalent copper plays an important role in the reductive dimerization of in situ generated alkyl iodide. Therefore, the deoxygenative dimerization of alcohol appears to occur through the reaction pathway via the reduction of alkyl iodide with activated copper generated by the reduction of copper(I) iodide with lanthanum metal (Scheme 5). For the other metal iodides bearing a large oxidation-reduction potential, it is proposed that metal halides were reduced by lanthanum species to produce the corresponding activated zerovalent metal, which acts as a reducing agent in the reactions (Table 2, entries 6–10).[16]



Scheme 5. A possible path of the reaction of alcohols in the presence of a catalytic amount of CuI.

Table 3. Deoxygenative Dimerization of Various Alcohols with La Metal[a)]

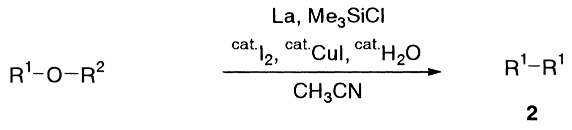


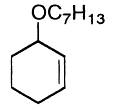
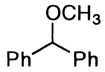
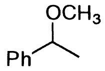
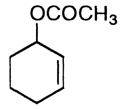
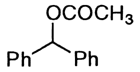
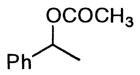
Entry	1	R^1	R^2	R^3	Yield/%[b)]		
					2	3	4
1	**1b**	C_6H_5	CH_3	CH_3	54	13	29
2[c)]	**1b**				29	6	36
3	**1c**	C_6H_5	CH_3	H	72[d)]	11	6
4[c)]	**1c**				54	11	7
5	**1d**	C_6H_5	H	H	42	15	—
6	**1e**	*p*-CH_3O-C_6H_4	H	H	67	5	—
7	**1f**	*p*-CH_3-C_6H_4	H	H	59	10	—
8	**1g**	*p*-Cl-C_6H_4	H	H	34	18	—
9	**1h**	*p*-CN-C_6H_4	H	H	0	0	—
10	**1i**	C_6H_5CH=CH	H	H	(71)[e)]	n.q.[f)]	n.q.[f)]
11	**1j**	—CH=CH—$(CH_2)_3$—		H	75[g)]	n.q.[f)]	n.q.[f)]
12	**1k**	$C_{11}H_{23}$	CH_3	CH_3	trace	(46)	(23)[h)]
13	**1l**	$C_{10}H_{21}$	CH_3	H	trace	trace	trace
14	**1m**	$C_{11}H_{23}$	H	H	trace	trace	trace

a) Reaction conditions: alcohol (1.0 mmol), La (1.0 mmol), Me_3SiCl (2.0 mmol), I_2 (0.2 mmol), CuI (0.2 mmol), and CH_3CN (3.0 mL) at 82 °C for 1 h. b) GC yield. The number on parenthesis indicated isolated yield. c) CoI_2 was used instead of CuI. d) Dl: meso = 50:50. Determined by ^1H NMR. e) 1,6-Diphenyl-1,5-hexadiene:1,4-diphenyl-1,5-hexadiene:3,4-diphenyl-1,5-hexadiene = 32:49:19. f) Not quantified. g) Dl:meso = 50:50. Determined by ^1H NMR. h) 2-Methyl-2-tridecene:2-methyl-1-tridecene = 88:12.

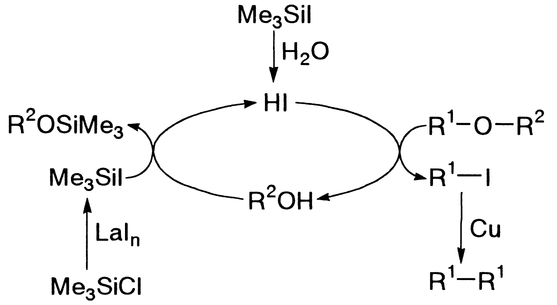
In order to develop applications of this reaction, various alcohols were treated with lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine and copper(I) iodide in acetonitrile solvent as the solvent (Table 3). The reaction of α-methylbenzyl alcohol (**1c**) efficiently proceeded, giving 2,3-diphenylbutane (**2c**) in 72% yield (entry 3). Similarly, benzyl alcohol (**1d**) was deoxygenatively dimerized under the same reaction conditions as that of **1a** to give 1,2-diphenylethane (**2d**) in 42% yield (entry 5). Methoxy, methyl, and chloro substituted benzyl alcohols gave the corresponding 1,2-diarylethanes in moderate yields; however, the deoxygenative dimerization of 4-cyanobenzyl alcohol did not proceed (entries 6–9). In the case of tertiary alcohol (**1b**), the yield of the deoxygenative dimerization product (**2b**) was slightly decreased due to an increase in the yield of 2-phenylpropene (**4b**) as a byproduct (entry 1). The use of cobalt(II) iodide instead of copper(I) iodide led to a decrease in the yield of the coupling product, despite the good result for the coupling of **1a** (entries 2 and 4). This method can be applied to allylic alcohols to form 1,5-dienes. The reaction of 2-cyclohexene-1-ol (**1j**) with lanthanum metal afforded 3,3′-bicyclohexenyl (**2j**) in 75% yield (entry 11). Similar treatment of cinnamyl alcohol (**1i**) produced a mixture of three isomers of 1,5-hexadienes in 71% yield (entry 10). In contrast to benzylic and allylic alcohols, the reaction of tertiary aliphatic alcohols, 2-methyl-2-tridecanol, resulted in the formation of a deoxygenation product and dehydration products in preference to a dimerization product (entry 12). In the case of primary and secondary aliphatic alcohols, the expected dimerization reactions did not occur, and trimethylsilyl ethers were obtained in almost quantitative yields (entries 13 and 14). The explanation is that the reaction of aliphatic silyl ether with hydrogen iodide is slower than that of benzylic and allylic silyl ether.[17] As a result, the iodination and following coupling reaction are probably suppressed due to the consumption of hydrogen iodide by the competing reaction, which is a reaction of hydrogen iodide with lanthanum metal.[18]

Table 4. Deoxygenative Dimerization of Ethers and Esters with La Metal[a)]



Entry	Substrate		Product	Yield(%)[b)]
1[c)]		**6j**	**2j**	62
2		**6j**	**2j**	81[d)]
3		**6a**	**2a**	65
4		**6c**	**2c**	54[e)]
5		**7j**	**2j**	57[d)]
6		**7a**	**2a**	85
7		**7c**	**2c**	44[e)]

a) Reaction conditions: substrate (1.0 mmol), La (1.0 mmol), Me_3SiCl (2.0 mmol), I_2 (0.2 mmol), CuI (0.2 mmol), H_2O (2.0 mmol), and CH_3CN (3.0 mL) at 82 °C for 1 h. b) GC yield. c) H_2O was not added. d) Dl: meso = 50:50. Determined by ^1H NMR. e) Dl: meso = 50:50. Determined by GC.



R^1 = benzyl or allyl, R^2 = alkyl or acetyl

Scheme 6.

Deoxygenative Dimerization of Ethers and Esters. In the deoxygenative dimerization of alcohols with the $La/Me_3SiCl/^{cat.}I_2/^{cat.}CuI$ system, the reaction pathway was suggested to involve the conversion of alcohols into the corresponding alkyl iodides. Since it was already disclosed that ethers and esters were efficiently converted to alkyl iodides by a treatment with iodotrimethylsilane or hydrogen iodide,[19] it is expected that the deoxygenative dimerization of ethers and esters may take place by treatment with $La/Me_3SiCl/^{cat.}I_2/^{cat.}CuI$. The deoxygenative dimerization of 3-heptyloxycyclohexen (**6j**) gave 3,3′-bicyclohexenyl (**2j**), but the yield of **2j** was lower than that of cyclohexenol (**1j**) (Table 4, entry 1). The yield of **2j** was improved by the addition of a catalytic amount of H_2O to the reaction mixture (entry 2). Various ethers and esters were also deoxygenatively dimerized by a treatment with lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine, copper(I) iodide, and H_2O (Table 4). It has been already shown that the reaction of iodotrimethylsilane or sodium iodide/chlorotrimethylsilane with H_2O is an efficient in situ generation method of hydrogen iodide.[20] Then, it was suggested that the generation of alkyl iodide from ethers or esters was accelerated by hydrogen iodide, which was generated by the reaction of Me_3SiI with H_2O. In the case of the deoxygenative dimerization of **6j**, heptyloxytrimethylsilane was obtained as a byproduct. From these results, the following reaction pathway is suggested for the reaction of ethers. At first, hydrogen iodide is generated by the reaction of iodotrimethylsilane with H_2O, and then the reaction of ether with hydrogen iodide takes place to yield alkyl iodide. The iodide is reductively dimerized by zerovalent copper to afford the coupling product and alcohol. The generated alcohol reacts with iodotrimethylsilane, giving the corresponding silyl ether and regenerating hydrogen iodide. Hence, the reaction was efficiently accelerated even when a catalytic amount of H_2O was added (Scheme 6).

Conclusions

In summary, we found that alcohols were deoxygenatively dimerized by the treatment of lanthanum metal and chlorotrimethylsilane in the presence of a catalytic amount of iodine. The reaction was dramatically accelerated by the addition of a catalytic amount of copper(I) iodide. Similarly, ethers and esters were deoxygenatively dimerized by using the $La/Me_3SiCl/^{cat.}I_2/^{cat.}CuI$ system in the presence of a small amount of water, giving the corresponding dimerization products. The key features of this approach were firstly the formation of alkyl iodide as an intermediate with a catalytic amount of iodine, and secondary the generation of active zerovalent copper as a coupling reagent. These features were linked to each other by lanthanum, which played a doubly important role as a generator of an iodination reagent and a reducing reagent of copper(I) iodide, to constitute the catalytic cycle.

Experimental

Instruments. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-400 (400 and 99.5 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 using a capillary column (Hicap-CBP-1-S25-025, 0.25 mm × 25 m). HPLC separation was performed on recycling preparative HPLC (Japan Analytical Industry Co., Ltd. LC-908) equipped with JAIGEL-1H (20 mm × 600 mm) and JAIGEL-2H (20 mm × 600 mm) columns and an RI detector.

Reagents. Alcohols (**1e**, **1g**, and **1h**) were synthesized by reduction of the corresponding aldehydes with $NaBH_4$. 2-Methyl-2-tridecanol (**1l**) was synthesized by the reaction of ethyl dodecanoate with MeMgI. Ethers (**6**) were prepared by the reaction of the corresponding alcohols (**1**) with alkyl iodide in the presence of sodium hydride. Esters (**7**) were prepared by the reaction of sodium alkoxide with acetyl chloride. The other alcohols, iodine, metal halides, and chlorotrimethylsilane were commercially available high-grade products, and were used without purification. Lanthanum metal was a commercially available high-grade product, and was used after powderization. The other reagents and solvents were purified by the usual methods before use.

Deoxygenative Coupling of Benzhydrol (1a) with Lanthanum Metal. Lanthanum powder (139 mg, 1.0 mmol) and iodine (51 mg, 0.2 mmol) were placed in a round-bottomed flask. CH_3CN (3 mL) and benzhydrol (184 mg , 1.0 mmol) were added to the flask. Then, chlorotrimethylsilane (217 mg, 2.0 mmol) was added, and the mixture was stirred at 25 °C for 8 h under a nitrogen atmosphere. The color of the solution gradually changed to gray. After the reaction, aq HCl was added to the reaction mixture and extracted with benzene. 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 1,1,2,2-tetraphenylethane (**2a**) and diphenylmethane (**3a**). The products were characterized by comparing their spectral data (^1H- and ^{13}C NMR and IR) with those of authentic samples. The GC yields were determined by the internal standard method.

1,1,2,2-Tetraphenylethane (2a).[21] ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 (s, 2H), 6.97–7.21 (m, 20H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 56.3, 125.8, 128.1, 128.5, 143.4; IR (KBr) 3079, 3022, 2890, 1595, 1490, 1447, 1070, 1028, 744, 684 cm^{-1}.

Diphenylmethane (3a). ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 2H), 7.16–7.29 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 41.9, 126.0, 128.4, 128.9, 141.0; IR (neat) 3061, 3026, 2907, 1599, 1493, 1451, 1076, 1029, 735, 689 cm^{-1}.

General Procedure of the Deoxygenative Coupling of Alcohols (1) Using Lanthanum Metal in the Presence of Copper(I) Iodide. After lanthanum powder (139 mg, 1.0 mmol), iodine (51 mg, 0.2 mmol), and copper(I) iodide (36 mg, 0.2 mmol) were placed in a three-necked flask, CH_3CN (3 mL) and alcohol (1.0 mmol) were added. Then, chlorotrimethylsilane (217 mg, 2.0 mmol) was added, and the mixture was stirred at 82 °C for 1 h under a nitrogen atmosphere. After the reaction, aq HCl was added to the reaction mixture and extracted with benzene. 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 deoxygenative dimerization, deoxygenation, and dehydration products. Products were characterized by comparing their spectral data (^1H- and ^{13}C NMR and IR) with those of authentic samples. The GC yields were determined by the internal-standard method.

2,3-Dimethyl-2,3-diphenylbutane (2b):[22] ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 12H), 7.05–7.18 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 25.2, 43.6, 125.3, 126.5, 128.5, 146.7; IR (KBr) 3025, 2967, 2890, 1601, 1483, 1450, 1370, 1159, 1079, 1027, 758, 698 cm^{-1}.

2,3-Diphenylbutane (2c) (Mixture of *meso* and *dl* Isomers):[23] ^1H NMR (400 MHz, $CDCl_3$) δ 0.99–1.04 (m, 3H), 1.25–1.30 (m, 3H), 2.70–2.82 (m, 1H), 2.91–3.03 (m, 1H), 6.99–7.32 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 18.0, 21.0, 46.5, 47.2 125.6, 125.9, 127.5, 127.6, 128.1, 145.7, 146.3; IR ($CHCl_3$) 3060, 3025, 2987, 2925, 1601, 1483, 1450, 1370, 1159, 1079, 1027, 758, 699 cm^{-1}.

1,2-Diphenylethane (2d): ^1H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 4H), 7.16–7.29 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 38.1, 126.0, 128.5, 128.6, 141.9; IR (neat) 3062, 2927, 2925, 2858, 1601, 1494, 1453, 1218, 1067, 1029, 755, 698 cm^{-1}.

1,2-Bis(4-methoxybenzene)ethane (2e):[24] ^1H NMR (400 MHz, $CDCl_3$) δ 2.81 (s, 4H), 3.76 (s, 6H), 6.79–7.07 (m, 8H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 37.2, 55.2, 113.6, 129.2, 133.8, 157.6; IR (KBr) 2963, 2914, 2849, 1609, 1509, 1242, 1029, 831, 721 cm^{-1}.

1,2-Bis(4-methylbenzene)ethane (2f):[25] ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 6H), 2.84 (s, 4H), 7.06 (s, 8H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 21.0, 37.6, 128.1, 128.8, 135.1, 138.7; IR (KBr) 3001, 2915, 2854, 1512, 1452, 1142, 1098, 1042, 811 cm^{-1}.

1,2-Bis(4-chlorobenzene)ethane (2g):[25] ^1H NMR (400 MHz, $CDCl_3$) δ 2.84 (s, 4H), 7.02–7.23 (m, 8H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 37.0, 128.3, 129.7, 131.6, 139.5; IR (KBr) 2924, 2859, 1488, 1087, 1013, 823, 791 cm^{-1}.

Mixture of 1,6-Diphenyl-1,5-hexadiene (2i–a), 1,4-Diphenyl-1,5-hexadiene (2i–b), and 3,4-Diphenyl-1,5-hexadiene (2i–c):[26] ^1H NMR (400 MHz, $CDCl_3$) δ 2.34–2.41 (m, 1.3H, allylic CH_2 of **2i–a**), 2.57–2.69 (m, 1.0H, allylic CH_2 of **2i–b**), 3.37–3.45 (m, 0.5H, benzylic CH of **2i–b**), 3.57–3.55 (m, 0.4H, benzylic CH of **2i–c**), 4.78–6.44 (m, 5H), 7.01–7.34 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 32.9, 39.0, 49.9, 55.4, 114.5, 115.6, 125.8, 125.9, 126.2, 126.2, 126.8, 127.5, 127.9, 128.0, 128.2, 128.3, 128.3, 128.4, 129.8, 130.2, 131.2, 137.5, 137.5, 139.9, 141.3, 142.3, 143.5; IR (neat) 3080, 3059, 3025, 2921, 2841, 1599, 1493, 1449, 964, 911, 743, 699 cm^{-1}.

3,3′-Bicyclohexenyl (2j) (mixture of *meso* and *dl* Isomers):[27] ^1H NMR (400 MHz, $CDCl_3$) δ 1.31–2.13 (m, 14H), 5.53–5.73 (m, 4H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 22.2, 22.3, 25.4, 25.9, 26.0, 40.1, 127.4, 127.7, 128.0, 128.1, 130.1, 130.2, 130.3, 130.4, 130.4, 130.5, 130.6; IR (neat) 3016, 2926, 2857, 2835, 1446, 1141, 898, 722 cm^{-1}.

Deoxygenative Coupling of 1a Using Lanthanum Metal and Iodotrimethylsilane. Lanthanum powder (139 mg, 1.0 mmol) was placed in a round-bottomed flask. CH_3CN (3 mL) and **1a** (184 mg, 1.0 mmol) were added to the flask. Then, iodotrimethylsilane (400 mg, 2.0 mmol) was added, and the mixture was stirred at 25 °C for 8 h under a nitrogen atmosphere. After the reaction, a similar work-up to that of the deoxygenative coupling of alcohols using lanthanum metal was carried out.

Deoxygenative Coupling of 1a Using Lanthanum Metal, Sodium Iodide, and Chlorotrimethylsilane. Lanthanum powder (139 mg, 1.0 mmol) and sodium iodide (300 mg, 2.0 mmol) were placed in a round-bottomed flask. CH_3CN (3 mL) and **1a** (184 mg, 1.0 mmol) were added to the flask. Then, chlorotrimethylsilane (217 mg, 2.0 mmol) was added, and the mixture was stirred at 25 °C for 8 h under a nitrogen atmosphere. After the reaction, a similar work-up to that of the deoxygenative coupling of alcohols using lanthanum metal was carried out. The GC yields were determined by the internal-standard method.

Reductive Coupling of Benzyl Bromide (5) with Lanthanum Metal. Lanthanum powder (139 mg, 1.0 mmol) and iodine (51 mg, 0.2 mmol) were placed in a round-bottomed flask. CH_3CN (3 mL) and **5** (171 mg, 1.0 mmol) were added to the flask. The mixture was then stirred at 25 °C for 5 h under a nitrogen atmosphere. After the reaction, a similar work-up to that of the deoxygenative coupling of alcohols using lanthanum metal was carried out. The GC yields were determined by the internal-standard method.

Reductive Coupling of 5 with Lanthanum Metal in the Presence of Copper(I) Iodide. After lanthanum powder (139 mg, 1.0 mmol), iodine (51 mg, 0.2 mmol), and copper(I) iodide (36 mg, 0.2 mmol) were placed in a round-bottomed flask, CH_3CN (3 mL) and **5** (171 mg, 1.0 mmol) were added. The mixture was then stirred at 25 °C for 5 h under a nitrogen atmosphere. After the reaction, a similar work-up to that of the deoxygenative coupling of alcohols using lanthanum metal was carried out. The GC yields were determined by the internal-standard method.

General Procedure of the Deoxygenative Coupling of Ethers (6) or Esters (7). After lanthanum powder (139 mg, 1.0 mmol), iodine (51 mg, 0.2 mmol), and copper(I) iodide (36 mg, 0.2 mmol) were placed in a three-necked flask, CH_3CN (3 mL), ether or ester (1.0 mmol) and H_2O (4 mg, 0.2 mmol) were added. Then, chlorotrimethylsilane (217 mg, 2.0 mmol) was added, and the mixture was stirred at 82 °C for 1 h under a nitrogen atmosphere. The color of the solution gradually changed to gray. After the reaction, a similar work-up to that of the deoxygenative coupling of alcohols using lanthanum metal was carried out. The GC yields were determined by the internal-standard method.

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