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Dehalogenation of *o*-dihalogen substituted arenes and α,α′-dihalogen substituted *o*-xylenes with lanthanum metal

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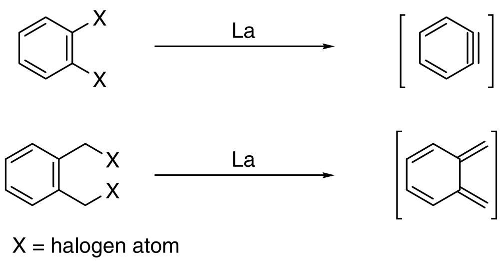
Dedicated to Professor Noboru Sonoda on the occasion of his 70th birthday.

Abstract—It was found that lanthanum metal caused the dehalogenation of *o*-dihalogen substituted arenes and α,α′-dihalogen substituted *o*-xylenes to generate the corresponding benzynes and *o*-quinodimethanes. When *o*-dihalogen substituted arenes were allowed to react with lanthanum metal in the presence of dienes, the Diels–Alder products between benzyne and dienes were formed in moderate to good yields. Similarly, the Diels–Alder adducts of *o*-quinodimethane with dienophiles were obtained, in the reaction of α,α′-dibromo-*o*-xylenes with lanthanum metal in the presence of dienophiles.

1. Introduction

The use of lanthanoid salts and organolanthanoid compounds in organic synthesis has been steadily increasing in recent years.[1] Although there are many reports on the use of di-, tri- and tetravalent lanthanoid compounds in organic synthesis, the direct use of lanthanoid metal are very limited. The direct use of lanthanoid metal such as Ce,[2] Sm[3] and Yb[4] in organic synthesis has been recently shown, there are few reports on the direct use of the other lanthanoid metals. We have recently investigated the direct use of lanthanum metal in organic synthesis and found that the reductive dimerization of alkyl halides was undertaken by lanthanum metal giving the corresponding dimerized alkanes.[5] In this reaction, the reaction pathway including the formation of alkyl radical intermediate, which was formed by one-electron transfer from lanthanum metal to alkyl halide followed by elimination of halogen anion, was suggested. From the proposal of the reaction pathway in the reaction of alkyl halides, in the reduction of *o*-dihalogen substituted arenes and α,α′-dihalogen substituted *o*-xylenes, the generation of benzyne and *o*-quinodimethane is expected to occur via the electron transfer from lanthanum metal to these compounds followed by elimination of halogen anion (Scheme 1). The full results on the reaction of *o*-dihalogen substituted arenes and α,α′-dihalogen substituted *o*-xylenes with lanthanum metal are shown in this paper.[6]



Scheme 1.

2. Results and discussion

2.1. Reaction of *α*-dihalogen substituted arenes

The intra- and intermolecular cycloaddition of benzyne are important methods for the synthesis of bicyclic compounds in organic synthesis.[7] Many methods for the generation of benzyne have been developed since Wittig reported a generation of benzyne by the reaction of *o*-dihalogen substituted arenes with lithium metal.[8] However, these methods have some problems in the case of actual use as follows: (i) a use of strong base, (ii) a treatment of explosive intermediate, and (iii) use of the starting materials prepared by multi-step procedures. Thus, there is an increasing interest in the convenient generation method of benzyne. Then, generation of benzyne by the treatment of *o*-dihalogen substituted arenes with lanthanoid metal was firstly examined. In order to know the reactivity of lanthanoid metals, 1-chloro-2-iodobenzene (**1a**) was allowed to treat with various lanthanoid metals in the presence of furan (30 equiv.) at 25°C for 4 h, and these results are shown in

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Keywords: lanthanum; *o*-dihalogen substituted arenes; α,α′-dihalogen substituted *o*-xylenes.

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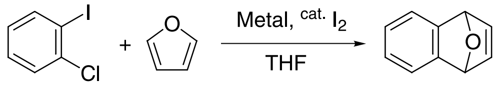
Table 1. Effect of lanthanoid metal



1a **2a**

Entry	Metal	Yield (%)[a]	Entry	Metal	Yield (%)[a]
1	La	100	8	Tb	0
2	Ce	89	9	Dy	0
3	Pr	77	10	Ho	0
4	Nd	59	11	Er	0
5	Sm	Trace	12	Tm	0
6	Eu	0	13	Yb	54
7	Gd	0	14	Lu	0

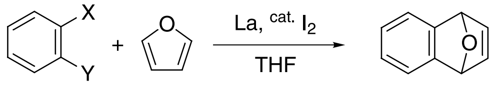
Reaction conditions: **1a** (1.0 mmol), metal (1.0 mmol), furan (30 mmol), I_2 (0.04 mmol) and THF (10 ml) at 25°C for 4 h.

[a] GC yield.

Table 1.[9] The treatment of **1a** with an equimolar amount of lanthanum metal in the presence of an excess amount of furan (30 equiv.) and a catalytic amount of iodine gave 1,4-dihydro-1,4-epoxynaphthalene (**2a**), the Diels–Alder adduct between benzyne and furan, in almost quantitative yield (entry 1). Although the reaction efficiently proceeded at lower reaction temperature (0°C: 100%), the reaction did not occur in the absence of iodide.[10,13] The use of Ce, Pr, Nd, and Yb metal led to the formation of **2a**; however, the yield of **2a** was decreased. In the case of samarium metal, which is widely used in organic synthesis, the yield of **2a** was very low owing to the formation of various complex products. In the reaction of other lanthanoid metals, the reaction did not proceed, and **1a** was recovered. To understand the scope and limitation of generation of benzyne by the reduction of *o*-dihalogen substituted arenes with lanthanum metal, 1-fluoro- (**1b**), 1-bromo-2-iodobenzene (**1c**), and 1,2-diio-dobenzene (**1d**) instead of **1a** was reacted with lanthanum metal in the presence of furan, and the results are shown in Table 2. For every *o*-halogen substituted iodobenzenes, the Diels–Alder adduct **2a** was obtained in moderate yields; however, the yields of **2a** were slightly decreased compared with that of **1a**, owing to the formation of fluoro-, bromo- and iodobenzene, reductive deiodination products, as by products. In the case of 1,2-dibromobenzene (**1e**), the reaction did not occur and starting material was recovered.

Next, *o*-halogen substituted iodobenzene was allowed to react with lanthanum metal in the presence of 2-methylfuran or cyclopentadiene. For the reaction of 1-chloro-2-iodobenzene (**1a**), the Diels–Alder addition products were formed in moderate yields; however, the yields of the Diels–Alder adducts were improved by the use of 1-bromo-2-iodobenzene (**1c**) instead of **1a** (Scheme 2). In the case of isoprene, the yield of coupling product was low owing to the formation of various complex products. Similarly, various arynes were successfully generated by the reduction of 1-chloro-2-iodobenzenes, 1,2-, 1,3-, 1,4-dichloro-6-iodobenzene, 1,2,4-trichloro-5-iodobenzene 4-chloro-3-iodotoluene, and 4-chloro-3-iodoanisole, with lanthanum metal, and the corresponding 1,4-dihydro-1,4-epoxynaphthalenes were obtained in relatively high yields

Table 2. The reaction of various 1,2-dihalogeno-benzenes

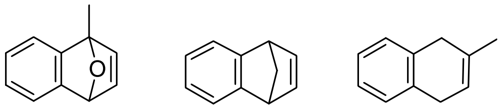


1 **2a**

Entry	X	Y		Yield (%)[a]
1	F	I	(**1b**)	80
2	Cl	I	(**1a**)	100
3	Br	I	(**1c**)	87
4	I	I	(**1d**)	82
5	Br	Br	(**1e**)	Trace

Reaction conditions: 1,2-halobenzene (1.0 mmol), furan (30 mmol), La (1.0 mmol), I_2 (0.04 mmol) and THF (10 ml) at 25°C for 4 h.

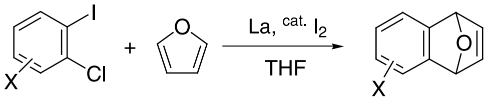
[a] GC yield.



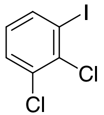
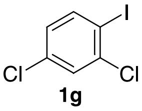
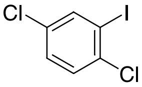
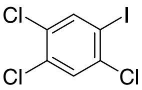
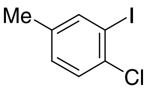
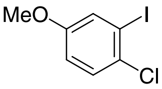
2b 65 % **2c** 100 % **2d** 23 %

Scheme 2. Reaction of 1-bromo-2-iodobenzene with various dienes.

Table 3. The reaction of various 1-chloro-2-iodo-benzene derivatives

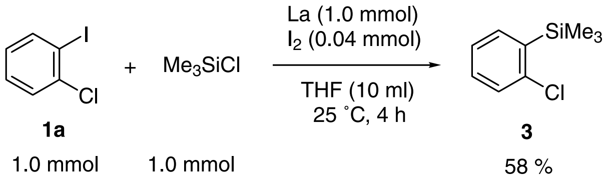


1 **2**

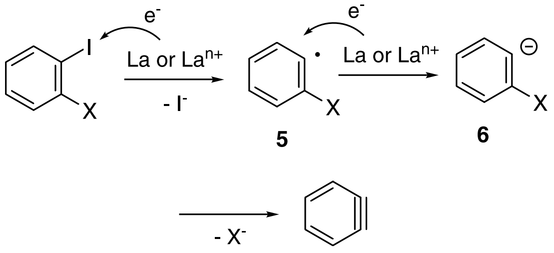
Entry	Substrate	Yield (%)[a]
1	 **1f**	**2f** (55)
2	 **1g**	**2g** (44)
3	 **1h**	**2g** (60)
4	 **1i**	**2i** (29)
5	 **1j**	**2j** (47)
6	 **1k**	**2k** (48)

Reaction conditions: substrate (1.0 mmol), furan (30 mmol), La (1.0 mmol), I_2 (0.04 mmol) and THF (10 ml) at 25°C for 4 h.

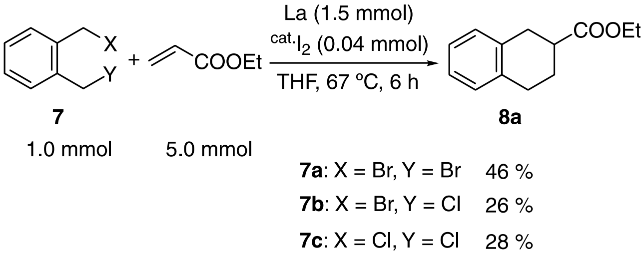
[a] GC yield.



Scheme 3.



Scheme 5. Plausible reaction path.



Scheme 6.

(Table 3). In these reactions, reductive deiodinated products were obtained as byproducts.

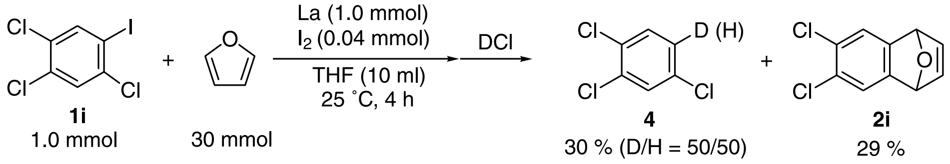
In order to get some information on the reaction pathway for the generation of benzyne, the treatment of 1-chloro-2-iodobenzene (**1a**) with lanthanum metal in the presence of trimethylchlorosilane was carried out. In the reaction, 1-chloro-2-trimethylsilylbenzene (**3**) was obtained in 58% yield (Scheme 3). In addition, the reaction of 1,2,4-trichloro-5-iodobenzene (**1i**) with furan in the presence of lanthanum metal followed by quenching with DCl/D_2O instead of HCl/H_2O gave a deuterated trichlorobenzene (**4**) (Scheme 4).[15]

At the present time, while the reaction pathway for the generation of benzyne is not shown in detail, these results suggest that benzyne is generated via *o*-substituted phenyl anion as an intermediate (Scheme 5). Transfer of electron from lanthanum metal or low-valent lanthanum species to 1,2-dihalogen substituted benzenes, elimination of iodine anion followed by another one electron transfer from lanthanum metal or low-valent lanthanum species to **5** forms the corresponding phenyl anion species (**6**). Although we cannot get a clear evidence for clarify the reasons why the yield of **2a** was affected by lanthanoid metals used, it was suggested that the oxidative-reduction potential of lanthanoid elements played an important role in this step (Table 1). In fact, the decrease in the oxidative-reduction potential of lanthanoid elements led to the decrease in the yield of **2a**.[16] The halogen anion was easily eliminated from **6** to form the corresponding benzyne intermediate. In the case of 1,2-dihalogeno benzenes having electron-withdrawing group, it seems likely that elimination of the halogen anion from **6** was suppressed owing to the increase in stability of the *o*-substituted phenyl anion giving the deiodination product after the work-up of the aqueous HCl. Furthermore, the yields of **2a** was explained by the elimination ability of halogen anion from **6**.

2.2. Reaction of α,α′-dihalogen substituted *o*-xylenes

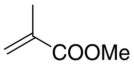
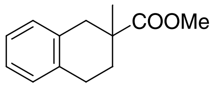
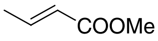
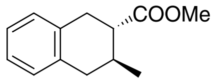
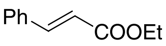
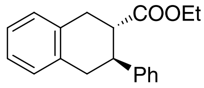
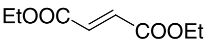
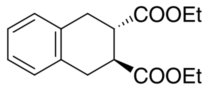
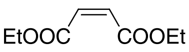
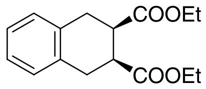
Since Cava and his co-worker first recognized the intermediacy of *o*-quinodimethane, a variety of methods for the generation of *o*-quinodimethane intermediates have been developed,[17] and their characterization, structure and chemical reactivity have been thoroughly studied.[22] Recently, there has been an increasing interest in utilization of *o*-quinodimethane as a synthetic intermediate. The Diels–Alder reaction of various dienophiles with the highly reactive diene, *o*-quinodimethane, stereoselectively proceeds leading to the successful preparation of polycyclic compounds such as steroids, alkaloids, terperoids and some antibiotics.

Then if the reductive dehalogenation of α,α′-dihalogen substituted *o*-xylenes can be similarly proceeded by lanthanum metal to that of *o*-dihalogen substituted arenes, generation of *o*-quinodimethane is expected to occur. The generation of *o*-quinodimethane by the reductive dehalogenation of bis(halomethyl)benzene with lanthanum was next examined. When 1,2-bis(bromomethyl)benzene (**7a**) was treated with lanthanum metal (1.5 equiv.) in the presence of an excess amount of ethyl acrylate (5 equiv.) at 67°C for 6 h, ethyl-1,2,3,4-tetrahydro-2-naphthalene carboxylate (**8a**), the Diels–Alder adduct of *o*-quinodimethane and ethyl acrylate, was obtained in 46% yield. 1-(Bromomethyl)-2-(chloromethyl)benzene (**7b**) and 1,2-bis(chloromethyl)benzene (**7c**) instead of **7a** were allowed to react with lanthanum metal in the presence of ethyl acrylate, and the results were shown in Scheme 6. The coupling product was obtained for each 1,2-bis(halomethyl)benzene, however, the yields of **8a** were decreased compared with that of **7a**. 1,2-Bis(bromomethyl)benzene (**7a**) was treated with lanthanum metal in the presence of electron-withdrawing groups substituted alkenes, and the results were shown in Table 4. The reaction of methyl methacrylate, α-methyl substituted unsaturated ester, led to produce the corresponding coupling product in moderate yield. In the reaction, the coupling reaction proceeded steroselectively. When **7a** was allowed to react with ethyl



Scheme 4.

Table 4. The reaction of **7a** various alkenes

Entry	Alkene	Product	Yield (%)[a]
1		 **8b**	47
2		 **8c**	33
3[b]		 **8d**	34
4[c]		 **8e**	52
5[c]		 **8f**	55

Reaction conditions: **7a** (1.0 mmol), alkene (5.0 mmol), La (1.5 mmol), I_2 (0.04 mmol) and THF (10 ml) at 67°C for 6 h.

[a] GC yield.

[b] La (2.0 mmol) and alkene (10.0 mmol) were used.

[c] La (5.0 mmol) and alkene (10.0 mmol) were used.

trans-cinnamate or diethyl fumalate, corresponding *trans*-products were obtained in moderate yield (entries 3 and 4). In the case of *cis*-alkene, stereoselective reaction of **7a** with diethyl maleate similarly occurred to give *cis*-product (entry 5).

3. Conclusion

In summary, we found that the treatment of *o*-dihalogen substituted arenes with lanthanum metal is a new generation method of benzyne. Similarly, the generation of *o*-quinodimethanes was successfully achieved by the dehalogenation of α,α'-dihalogen substituted *o*-xylenes with lanthanum metal.

4. Experimental

4.1. Instruments

^1H and ^{13}C NMR spectra were recorded on a 400 and 99.5 MHz spectrometer using $CDCl_3$ as a solvent with tetramethylsilane as the internal standard. IR spectra were recorded on a FT-IR spectrophotometer. Gas chromatography (GC) was carried out on a flame ionizing detector-equipped instrument and using a capillary column (0.25 mm×25 m). HPLC separation was performed on recycling preparative HPLC equipped with 20 mm×600 mm and 20 mm×600 mm columns.

4.2. Reagents

1-Fluoro-2-iodo-, 1-chloro-2-iodo-, 1-bromo-2- iodo-, 1,3-dichloro-4-iodo, 1,4-dichloro-2-iodo, and 1,2-dichloro-3-iodobenzene, α,α'-Dihalo-*o*-xylene, alkene, iodine and lanthanum metal were commercially available high-grade products and were used without purification. Lanthanum metal was used after powderization. The other reagents and solvents were purified by the usual methods before use.

4.3. General procedure of synthesis of 1-chloro-2-iodobenzene derivatives

Sodium nitrite (7.8 mmol) dissolved in sulfuric acid (3.4 ml) was added to acetic acid (6 ml) solution of 2-chlroaniline derivative (6.0 mmol) at 0°C and stirred for 40 min. The reaction mixture was added to sodium iodide (28.5 mmol) of water (18 ml) and stirred at 60°C for 1 h. The reaction was neutralized with aqueous NaOH and extracted with chloroform. The organic solution was washed with aqueous sodium thiosulfate and water. The organic layer was dried over $MgSO_4$. The solution was filtered, and the filtrate was concentrated. Purification of residue by column chromatography on silica gel (*n*-hexane–ethyl acetate (19:1)) afforded 1-chloro-2-iodobenzene derivatives.

4.4. General procedure of reaction of *o*-dihalogen substituted benzenes with diene in the presence of lanthanum metal

Lanthanum powder (139 mg, 1.0 mmol) and iodine (10 mg, 0.04 mmol) were placed in a round-bottomed flask. Tetrahydrofuran (10 ml), diene (30 mmol) and *o*-dihalogen substituted benzene were added into the flask, and the mixture was stirred at 25°C for 4 h under nitrogen atmosphere. The reaction was quenched with aqueous HCl (5%), and the mixture was extracted with diisopropylether (10 ml×3). The organic layer was washed with aqueous sodium thiosulfate and dried over $MgSO_4$. The solution was filtered, and the filtrate was concentrated. Purification of residue by column chromatography on silica gel afforded the corresponding naphthalene derivatives. Products were characterized by comparison of their spectral data (^1H and ^{13}C NMR and IR) with those of authentic samples (**2a**,[23] **2b**,[23] **2c**,[24] **2f**,[25] **2g**,[26] **2i**,[27] **2j**[23] and **2g**[28]).

4.4.1. Reaction of 1-chloro-2-iodobenzene with trimethylsilyl chloride in the presence of lanthanum metal. Lanthanum powder (139 mg, 1.0 mmol) and iodine (10 mg, 0.04 mmol) were placed in a round-bottomed flask. Tetrahydrofuran (10 ml), trimethylsilyl chloride (108 mg, 1.0 mmol) and 1-chloro-2-iodobenzene (238 mg, 1.0 mmol) were added into the flask, and the mixture was stirred at 25°C for 4 h under nitrogen atmosphere. After reaction was completed, aqueous HCl (5%) was added until residual lanthanum salt was disappeared. Extraction of the resulting solution with three portions of 10 ml diisopropylether, and washing of organic layer with sodium thiosulfate aqueous solution were carried out. And the resulting solution was dried over magnesium sulfate. Evaporation of solvent and purification of the residue by column chromatography on silica gel afforded the 1-chloro-2-trimethylsilylbenzene (**3**). Product (**3**) was characterized by comparison of the spectral data (^1H and ^{13}C NMR and IR) with that of authentic sample.[29]

4.4.2. Reaction of 1,2,4-trichloro-5-iodobenzene (1i) with furan in the presence of lanthanum metal: the formation of 1,2,4-trichloro-5-deuteriobenzene (4) by quenching with D_2O. Lanthanum powder (139 mg, 1.0 mmol) and iodine (10 mg, 0.04 mmol) were placed in a round-bottomed flask. Tetrahydrofuran (10 ml), furan (2.04 g, 30 mmol) and 1,2,4-trichloro-5-iodobenzene (307 mg, 1.0 mmol) were added into the flask, and the mixture was stirred at 25°C for 4 h under nitrogen atmosphere. The reaction was quenched with DCl/D_2O (5%), and the mixture was extracted with diisopropylether (10 ml×3). The organic layer was washed with aqueous sodium thiosulfate and dried over $MgSO_4$. The solution was filtered, and the filtrate was concentrated. Purification of residue by column chromatography on silica gel afforded 1,2,4-trichloro-5-deuteriobenzene, 1,2,4-trichlorobenzene and the corresponding naphthalene derivative.

1,2,4-Trichloro-5-deuteriobenzene: ^{1}H NMR δ 7.382 (s, 1H), 7.461 (s, 1H); ^{13}C NMR δ 128.22, 130.53, 131.24, 131.34 (t), 131.85, 131.97.

4.5. General procedure of reaction of 1,2-bis(bromomethyl)benzene (7a) with alkene in the presence of lanthanum metal

Lanthanum powder (208 mg, 1.5 mmol) and iodine (10 mg, 0.04 mmol) were placed in a three-necked flask. Tetrahydrofuran (10 ml), alkene (5.0 mmol) and *o*-bis(bromomethyl)benzene (263 mg, 1.0 mmol) were added into the flask, and the mixture was stirred at 67°C for 6 h under nitrogen atmosphere. The reaction was quenched with aqueous HCl (5%), and the mixture was extracted with diisopropylether (10 ml×3). The organic layer was washed with aqueous sodium thiosulfate and dried over $MgSO_4$. The solution was filtered, and the filtrate was concentrated. Purification of residue by column chromatography on silica gel afforded the corresponding naphthalene derivatives. Products were characterized by comparison of their spectral data (^{1}H and ^{13}C NMR and IR) with those of authentic samples (**8b**,[30] **8c**,[30] **8e**,[31] and **8f**[31]).

4.5.1. Compound 8d. ^{1}H NMR δ 0.91 (t, J=7.2 Hz, 3H), 2.98–3.14 (m, 4H), 3.18–3.23 (m, 2H), 3.87(q, J=7.2 Hz, 2H), 7.09–7.33 (m, 9H); ^{13}C NMR δ 13.9, 33.1, 37.5, 43.8, 46.9, 60.2, 126.0, 126.7, 127.4, 128.3, 128.6, 134.2, 135.5, 143.3, 174.5; IR 700, 747, 1024, 1175, 1729, 2926, 2979, 3026, 3061 cm^{-1}.

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References

1. For recent reviews: (a) Kagan, H. B. *New J. Chem.* **1990**, *14*, 453. (b) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943. (c) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (d) Kobayashi, S. *Synlett* **1994**, 689. (e) Kamochi, Y.; Kubo, T. *J. Synth. Org. Chem. Jpn* **1994**, *52*, 285. (f) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic: New York, 1994. (g) Matsuda, F. *J. Synth. Org. Chem. Jpn* **1995**, *53*, 987. (h) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (i) Ito, Y.; Fujiwara, Y.; Yamamoto, T. *Kikan Kagaku Sousetu. Organic Synthesis by Means of Lanthanoids No. 37*; Gakkai, 1998. (j) Kobayashi, S. *Lanthanide: Chemistry and Use in Organic Synthesis*; Springer: Berlin, 1999. (k) Steel, P. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2727. and references cited therein.
2. (a) Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353. (b) Fukuzawa, S.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Chem. Commun.* **1986**, 475. (c) Fukuzawa, S.; Sumimoto, N.; Fujinami, T.; Sakai, S. *J. Org. Chem.* **1990**, *55*, 1328.
3. (a) Yanada, R.; Bessho, K.; Yanada, K. *Chem. Lett.* **1994**, 1279. (b) Yanada, R.; Bessho, K.; Yanada, K. *Synlett* **1995**, 443. (c) Yanada, R.; Bessho, K.; Yanada, K. *Synlett* **1995**, 1261. (d) Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1996**, *37*, 9313. (e) Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271. (f) Ding, Z.-B.; Wu, S.-H. *Youji Huaxue* **1997**, *17*, 165. (g) Wang, L.; Zhang, Y. *Tetrahedron* **1998**, *54*, 11129.
4. (a) Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353. (b) Fukuzawa, S.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Chem. Commun.* **1986**, 475. (c) Fukuzawa, S.; Sumimoto, N.; Fujinami, T.; Sakai, S. *J. Org. Chem.* **1990**, *55*, 1328.
5. Nishino, T.; Watanabe, T.; Okada, M.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 966.
6. Kawabata, H.; Nishino, T.; Nishiyama, Y.; Sonoda, N. *Tetrahedron Lett.* **2002**, *43*, 4911.
7. (a) Kaelin D. K., Jr.; Lopez, O. D.; Martin, S. F. *J. Am. Chem. Soc.* **2001**, *123*, 6937. (b) Knight, D. W.; Little, P. B. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2343. and references cited therein.
8. (a) Wittig, G.; Pohmer, L. *Angew. Chem.* **1960**, *72*, 564. (b) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334. (c) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674. (d) Kitamura, T.; Fukatsu, N.; Fujiwara, Y. *J. Org. Chem.* **1998**, *63*, 8579. (e) Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983. (f) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967. (g) Gilchrist, T. L. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chlichester, 1983; Chapter 11. (h) Hart, H. *The Chemistry of Triple-bonded Functional Groups, Supplement C2*; Patai, S., Ed.; Willey: Chichester, 1994; Chapter 18. (i) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211. and reference cited therein.
9. Lanthanum metal was commercially available high-grade product and was used after powderization (ca. −40 mesh).
10. We have already shown that the addition of a catalytic amount of iodine dramatically enhanced the reductive dimerization of carbonyl compounds[11] or imine[12] with lanthanum metal.
11. Nishino, T.; Nishiyama, Y.; Sonoda, N. *Heteroat. Chem.* **2000**, *11*, 81.
12. Nishino, T.; Nishiyama, Y.; Sonoda, N. *Heteroat. Chem.* **2002**, *13*, 131.
13. In the reaction used ytterbium or samarium metal, it was 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.[14].

14. (a) Hou, Z.; Tamamine, K.; Aoki, O.; Shiraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 6077. (b) Yanada, R.; Negoro, N.; Okaniwa, M.; Taga, T.; Yanada, K.; Fujita, T. *Synlett* **1999**, 537. (c) Wang, L.; Zhou, L.; Zhang, Y. *Synlett* **1999**, 1065. (d) Taluldar, S.; Fang, J.-M. *J. Org. Chem.* **2001**, *66*, 330.
15. At present, the formation pathway of 1,2,4-trichlorobenzene has not been explained; however, it was suggested that 1,2,4-trichlorobenzene was formed by the hydrogen abstraction of the phenyl radical, which was generated in situ by the one-electron transfer from lanthanum metal to 1,2,4-trichloro-5-iodobenzene (**1i**) followed by the elimination of I^-, from THF as a solvent.
16. Marks, T. J. *Prog. Inorg. Chem.* **1978**, *25*, 51.
17. Novel sequences based on 1,4-elimination of complementary bis(benzyl) substituents,[18] cheletropic eliminations,[19] photo-enolizations[20] or fragmentation of benzocyclobutenes[21] have been used to generate *o*-quinodimethane.
18. (a) Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 751. (b) Rubottom, G. M.; Wey, J. E. *Synth. Commun.* **1984**, *14*, 507. (c) Inaba, S.; Wehmeyer, R. M.; Forkner, M. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 339. (d) Schiess, P. *Thermochim. Acta* **1987**, *112*, 31 and references cited therein.
19. (a) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (b) Jung, F.; Molin, M.; Van Den Dlzen, R.; Durst, T. *J. Am. Chem. Soc.* **1974**, *96*, 935. (c) Durst, T.; Tetreault-Ryan, L. *Tetrahedron Lett.* **1978**, 2353. (d) Charlton, J. L. *Can. J. Chem.* **1985**, *64*, 723 and references cited therein.
20. (a) Jung, M. E.; Lowe, J. A. *J. Org. Chem.* **1977**, *42*, 2371. (b) Krohn, K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 790. (c) Krohn, K.; Rieger, H.; Broser, E.; Schiess, P.; Chen, S.; Strubin, T. *Liebigs Ann. Chem.* **1988**, 943. (d) Coll, G.; Costa, A.; Deya, P. M.; Flexas, F.; Rotger, C.; Saa, J. M. *J. Org. Chem.* **1992**, *57*, 6222. (e) Kessar, S. V.; Mankotia, A. K. S.; Agnihotri, K. R. *J. Chem. Soc., Chem. Commun.* **1993**, 598 and references cited therein.
21. (a) Jensen, F.; Coleman, W. E. *J. Am. Chem. Soc.* **1958**, *80*, 6149. (b) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401. (c) Franck, R. W.; John, T. V.; Olejniczak, K. *J. Am. Chem. Soc.* **1982**, *104*, 1106. (d) Jung, M. E.; Lam, P. Y.-S.; Mansuri, M.; Spettz, L. M. *J. Org. Chem.* **1985**, *50*, 1087. (e) Wong, H. N. C.; Lan, K.-L.; Tam, D. F. *Top. Curr. Chem.* **1986**, *133*, 124. (f) Macdonald, D. I.; Durst, T. *J. Org. Chem.* **1986**, *51*, 4750. (g) Allen, J. G.; Hentemann, M. F.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 571 and references cited therein.
22. (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (b) Martín, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237. (c) Segura, J. L.; Martín, N. *Chem. Rev.* **1999**, *99*, 3199 and references cited therein.
23. Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674.
24. Reinecke, M. G.; Newson, J. G.; Chen, L.-J. *J. Am. Chem. Soc.* **1981**, *103*, 2760.
25. Effenberger, F.; Daub, W. *Chem. Ber.* **1991**, *124*, 2113.
26. Caster, K. C.; Keck, C. G.; Walls, R. D. *J. Org. Chem.* **2001**, *66*, 2932.
27. Raymo, F.; Kohnke, F. H.; Cardullo, F.; Girreser, U.; Stoddart, J. F. *Tetrahedron* **1992**, *48*, 6827.
28. Giles, R. G. F.; Hughes, A. B.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1581.
29. Deffieux, D.; Bordeau, M.; Biran, C.; Dunogues, J. *Organometallics* **1994**, *13*, 2415.
30. Eru, E.; Hawkes, G. E.; Utley, J. H. P.; Wyatt, P. B. *Tetrahedron* **1995**, *51*, 3033.
31. Inaba, S.; Wehmeyer, R. M.; Forker, M. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 339.