



# A novel lanthanum metal-assisted reaction of diaryl ketones and electrophiles



Rui Umeda, Masashi Ninomiya, Toshiaki Nishino, Makoto Kishida, Shunsuke Toiya, Tomoki Saito, Yutaka Nishiyama\*, Noboru Sonoda

Department of Chemistry and Material Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

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## ABSTRACT

A novel and efficient lanthanum metal-assisted carbon-carbon bond formation of diaryl ketones and various electrophiles, such as carbonyl compounds, esters, nitriles, and epoxides, has been developed. When diaryl ketones were allowed to react with dialkyl ketones in the presence of lanthanum metal and a catalytic amount of iodine, the cross pinacol coupling reaction proceeded to give the corresponding unsymmetrical 1,2-diols in moderate to good yields.  $\alpha$ -Hydroxy ketones were prepared by the lanthanum metal-assisted reaction of diaryl ketones with esters or nitriles, followed by hydrolysis with aq. HCl. It is interesting to note that for the epoxides, the coupling reaction proceeded via the Meinwald rearrangement of epoxides to give the corresponding 1,2-diols.

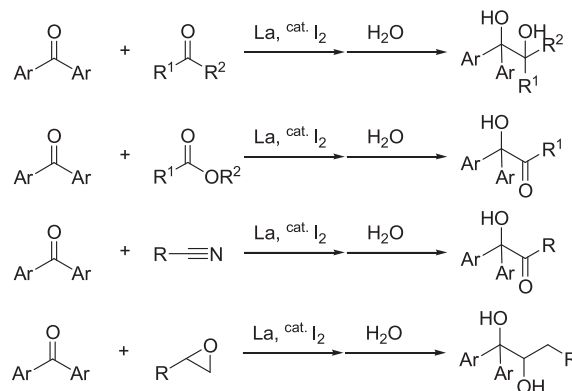
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## 1. Introduction

The utilization of lanthanoid metal salts and organolanthanoid compounds as synthetic reagents or catalysts in organic synthesis has been steadily increasing due to their unique chemical properties. In particular, low-valent, trivalent, and tetravalent lanthanoid compounds have been widely used in organic reactions.<sup>1</sup> On the hand, although it is expected that zero-valent lanthanoid metals bear a potential reducing ability could be used as the reducing agent in organic synthesis, the direct use of lanthanoid metals in organic synthesis is still rare due to their low solubility in an organic solvent or to their instability under aerobic conditions.<sup>2–5</sup>

We have recently succeeded in the direct use of lanthanum metal as a reagent in the presence of a catalytic amount of iodine in organic synthesis.<sup>6</sup> During the course of our study on the direct use of lanthanum metal in organic synthesis, it was found that various electrophiles were efficiently introduced onto the carbonyl carbon of diaryl ketones in the presence of lanthanum metal and a catalytic amount of iodine.<sup>7</sup> When diaryl ketones were treated with dialkyl ketones in the presence of lanthanum metal and a catalytic amount of iodine, the corresponding unsymmetrical 1,2-diols, the cross pinacol coupling products, were formed in moderate to good yields.<sup>10,11</sup> For the reaction of nitriles<sup>12</sup> and esters,<sup>13</sup>  $\alpha$ -hydroxy

ketones were obtained. It is interesting to note that for the epoxides, the coupling reaction proceeded via the Meinwald rearrangement of epoxides to give the corresponding 1,2-diols (Scheme 1).<sup>14</sup> Fujiwara et al. have already reported ytterbium metal promoted the cross-coupling reaction of diaryl ketones with a various electrophiles to give the corresponding products.<sup>4a–c</sup> However, in the case of Yb, two-step procedures (time integration<sup>15</sup>), including (i) the reaction of diaryl ketones with Yb metal and (ii) the addition of electrophiles to the resulting solution of (i), were used on the reaction. On the other hand, in the case of La metal, the cross pinacol coupling products were formed in good yields by a simple



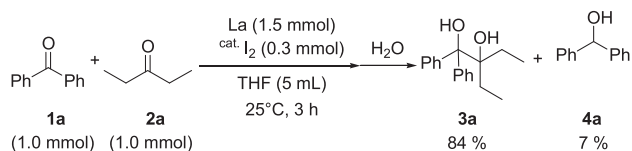
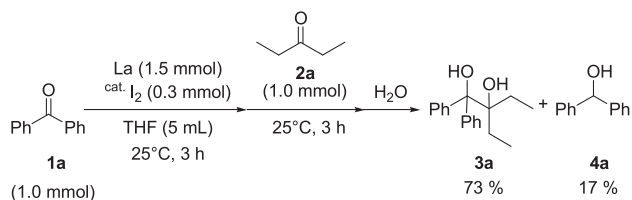
Scheme 1.

\* Corresponding author. Tel.: +81 6 6368 0902; fax: +81 6 6339 4026; e-mail address: [nishiya@kansai-u.ac.jp](mailto:nishiya@kansai-u.ac.jp) (Y. Nishiyama).

procedure. Furthermore, in the case of epoxide, it is interesting to note that the reaction proceeded via the Meinwald rearrangement of epoxides.

## 2. Results and discussion

When benzophenone (**1a**) was allowed to react with lanthanum metal in a presence of a catalytic amount of iodine in THF solvent at 25 °C, the solution initially showed a ketyl-like blue color that gradually turned brown. After stirring for 3 h, 3-pentanone (**2a**) was added to the resulting solution, and the solution was stirred for additional 3 h. Subsequent hydrolysis of the reaction mixture with aq HCl formed 2-ethyl-1,1-diphenyl-1,2-butanediol (**3a**), a cross-coupling product between **1** and **2**, in 73% yield along with benzhydrol (**4a**), the reduction product of **1a** (17%) (Scheme 2). This cross-coupling reaction could be conducted by a convenient one-step procedure (time and space integration<sup>15</sup>). As shown in Scheme 3, in the case of the one-pot procedure (time and space integration), cross-coupling between **1a** and **2a** produced a higher selectivity than that of the two-step procedures (time integration), and the yield of **3a** had increased to 84%.



To elucidate the scope and limitation of the lanthanum metal-assisted coupling reaction of diaryl ketones and carbonyl compounds, various diaryl ketones were treated with carbonyl compounds in the presence of lanthanum metal and a catalytic amount of iodine, and these results are shown in Table 1. The coupling of 4-methyl-, 3-methyl-, 4-methoxy-, 4,4'-dimethyl-, and 4,4'-dimethoxybenzophenone, in which the electron donating group was substituted on the aromatic ring, gave the corresponding unsymmetrical 1,2-diols **3b,c,d,g,h** in 67–90% yield (entries 2, 3, 5, 8, and 9). In the case of 4-chloro- and 4,4'-dichlorobenzophenones bearing an electron withdrawing group, the yields of the corresponding unsymmetrical 1,2-diols were significantly decreased (entries 6 and 10). For the sterically hindered diaryl ketone, such as 2-methylbenzophenone, the cross-coupling product was not obtained at all (entry 4). 2-Ethyl-1-(2-naphthyl)-1-phenyl-1,2-butanediol (**3f**) was obtained in 74% yield by the reaction between 2-naphthyl phenyl ketone and 3-pentanone (entry 7). When cyclohexanone was used as an aliphatic ketone instead of **2a**, the cross pinacol coupling reaction also proceeded to form 1,2-diol **3j** in 47% yield (entry 13). In the case of a sterically hindered dialkyl ketone, such as 2,4-dimethyl-3-pentanone, the coupling reaction did not proceed at all and benzhydrol (**4a**), the reduction product of **1a**, was formed in 87% yield (entry 12). For the reaction of 3-methyl-2-butanone and acetophenone, the yields of the cross-coupling products decreased, however, the product

**Table 1**

La-assisted reaction of diaryl ketones with carbonyl compounds<sup>a</sup>

Entry	Diaryl ketone	Carbonyl compound	Yield <sup>b</sup> (%)
1			<b>3a</b> 84
2			<b>3b</b> 67
3			<b>3c</b> 90
4			Trace
5 <sup>c</sup>			<b>3d</b> 90
6			<b>3e</b> 37
7			<b>3f</b> 74
8			<b>3g</b> 74
9			<b>3h</b> 74
10			trace
11 <sup>d</sup>			<b>3i</b> 61
12 <sup>d,e</sup>			<b>4a</b> 87
13			<b>3j</b> 47
14 <sup>f</sup>			<b>3k</b> 44
15 <sup>e</sup>			<b>4a</b> 64

<sup>a</sup> Reaction conditions: La (1.5 mmol), diaryl ketone (1.0 mmol), carbonyl compound (1.0 mmol), I<sub>2</sub> (0.3 mmol), THF (5 mL) at 25 °C for 3 h.

<sup>b</sup> Isolated yield.

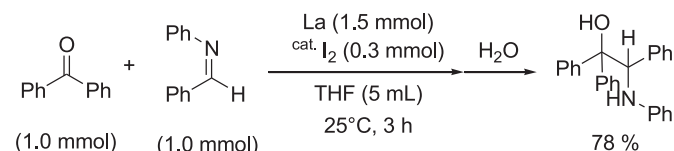
<sup>c</sup> 3-Pentanone (2.0 mmol) was used.

<sup>d</sup> At 67 °C for 9 h.

<sup>e</sup> The yield of benzhydrol.

<sup>f</sup> At 67 °C for 15 h.

yields **3i,k** were improved by extending the reaction time at a higher reaction temperature (67 °C) (entries 11 and 14). In the case of benzaldehyde, **4a** was formed in 64% yield along with the formation of various complicated by-products (entry 15). When an imine was used as the electrophile instead of carbonyl compounds,  $\alpha$ -amino alcohol was also synthesized by this protocol (Scheme 4).<sup>16,17</sup>



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