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Trichlorolanthanoid ($LnCl_3$)/Zn Catalyzed Cyclodimerization of Chalcone

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The trichlorolanthanoid ($LnCl_3$)/Zn system has been found to cause cyclodimerization of chalcone to give cyclopentanol derivatives (**1** and **2**) in both high yields and selectivities (**1**/**2** ratio) compared with the reaction by Yb metal alone. Of trichlorolanthanoids the chlorides of Yb and Eu or Sm showed maximum yields and selectivities (**1**/**2**).

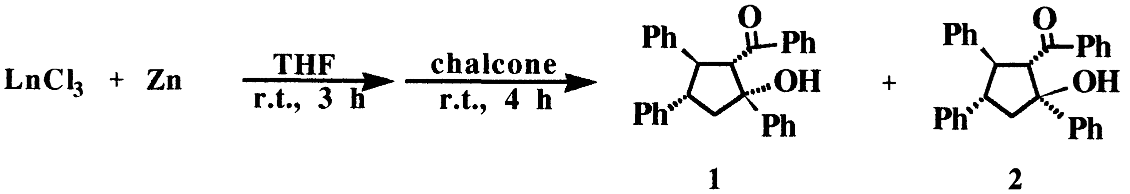
In previous paper, we reported cyclodimerization of α,β-unsaturated carbonyl compounds by Yb metal, to give cyclopentanol derivatives regio- and stereo-selectively.1) This reaction proceeds via a radical enolate formed by electron transfer from Yb metal to the carbonyl compounds due to a strong reducing potential of the metal. We thought that the reaction should be also caused by lower-valent Yb species other than Yb metal itself, and found that the $LnCl_3$/Zn system brings about the reaction. In this communication, we would like to report these results.2)

First, we investigated stoichiometric reactions of chalcone and $LnCl_3$ using Zn powder as a reducing agent. Table 1 summarizes the typical results of the reaction with various $LnCl_3$.

As can be seen from the table, the $LnCl_3$/Zn system gives higher total yields of ($1R^*,2S^*,4S^*$)-2-benzoyl-1,3,4-triphenylcyclopentanol (**1**) and its stereoisomer (**2**) (Run 1 vs. 2 and 7) or higher selectivities (**1**/**2** ratio) (Run 1 vs. 3, 4, 5, 6, and 7) than the case of the reaction with Yb metal.3) The total yield of **1** plus **2** and the selectivity (**1**/**2**) of the reaction of chalcone with all rare earth trichlorides ($LnCl_3$) except for the case of radioactive $PmCl_3$ were plotted in Fig. 1.

Interestingly enough, the figure shows that the maximum yield and selectivity are obtained by the chlorides of Yb and Eu or Sm whose electronic configurationa are stable, filled f^{14} (Yb^{2+}), half filled f^7 (Eu^{2+}) or f^6 (Sm^{2+}). This result seems to indicate that the reaction is caused by Ln(II) species.4,5) The possible mechanism is shown in Scheme 1. $YbCl_3$ is

Table 1. $LnCl_3/Zn$ Promoted cyclodimerization of chalcone[a)]



Run	$LnCl_3$	Product 1	:	Product 2	Yield/%[b)] 1 + 2
1	–[c)]	71	:	29	95[d)]
2	$ScCl_3$	72	:	28	96[d)]
3	YCl_3	98	:	2	95
4	$LaCl_3$	82	:	18	63[e)]
5	$SmCl_3$	84	:	16	72
6	$EuCl_3$[f)]	96	:	4	67
7	$YbCl_3$	90	:	10	98

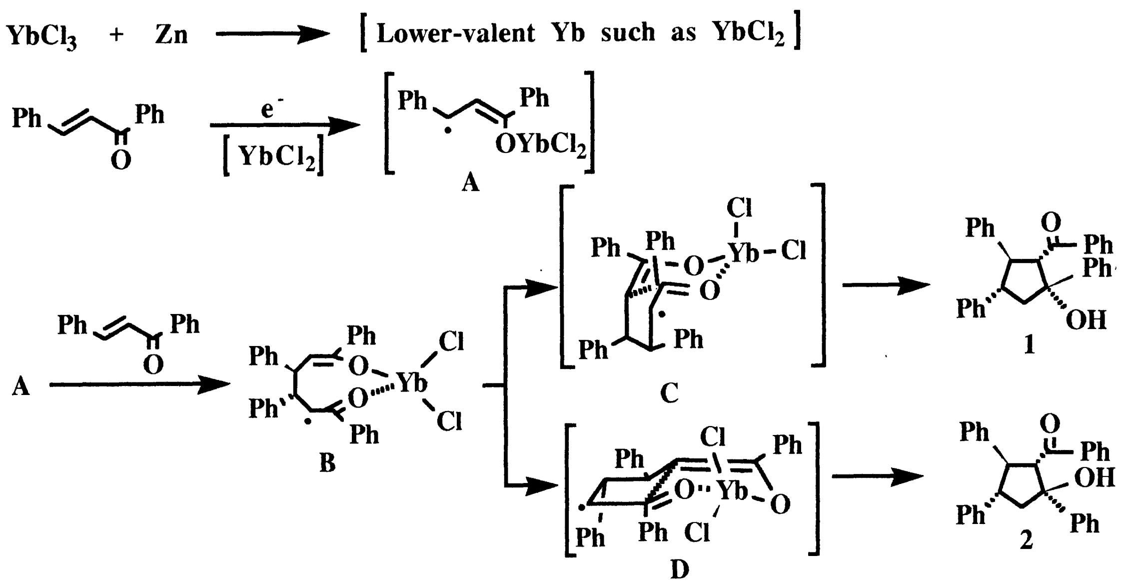
a) $LnCl_3$ 1 mmol, Zn powder 1.5 mmol, THF 4 ml, then chalcone 1 mmol, THF 3 ml. b) HPLC yield based on chalcone. c) Yb metal (1 mmol) used instead of $YbCl_3$. d) Benzylacetophenone was also formed in 2% yield. e) Benzylacetophenone was also formed in 9% yield. f) Reaction time is 69 h.

Table 2. $LnCl_3/Zn$ Catalyzed cyclodimerization of chalcone[a)]

Run	$LnCl_3$ (mmol)	Product 1	:	Product 2	Yield/%[b)] 1 + 2
1	$YbCl_3$ (0.1)	81	:	19	75 (350)
2	$YbCl_3$ (0.1)[c)]	90	:	10	62 (308)
3	$EuCl_3$ (0.1)[d)]	95	:	5	85 (426)[e)]
4	$EuCl_3$ (0.05)[f)]	96	:	4	92 (920)[e)]
5	$EuCl_3$ (0.01)[g)]	89	:	11	71 (3500)[h)]

a) Zn 1.5 mmol, THF 4 ml, r.t., 3 h, then chalcone 1 mmol, THF 3 ml, r.t., 4 h. b) HPLC yield based on chalcone and numbers in parentheses are based on $LnCl_3$. c) Aging time: 5 min. Reaction time: 100 h. d) Reaction time: 54 h. e) Benzylacetophenone and 1,3-diphenyl-2-propyn-1-one were also formed in 1% yield each. f) Reaction time: 95 h. g) Reaction time: 60 h. h) Benzylacetophenone and 1,3-diphenyl-2-propyn-1-one were also formed in 8 and 4% yields, respectively.

reduced by Zn to give low-valent species such as $YbCl_2$. Then, electron transfer from $YbCl_2$ to chalcone results in the formation of radical enolate



Scheme 1.

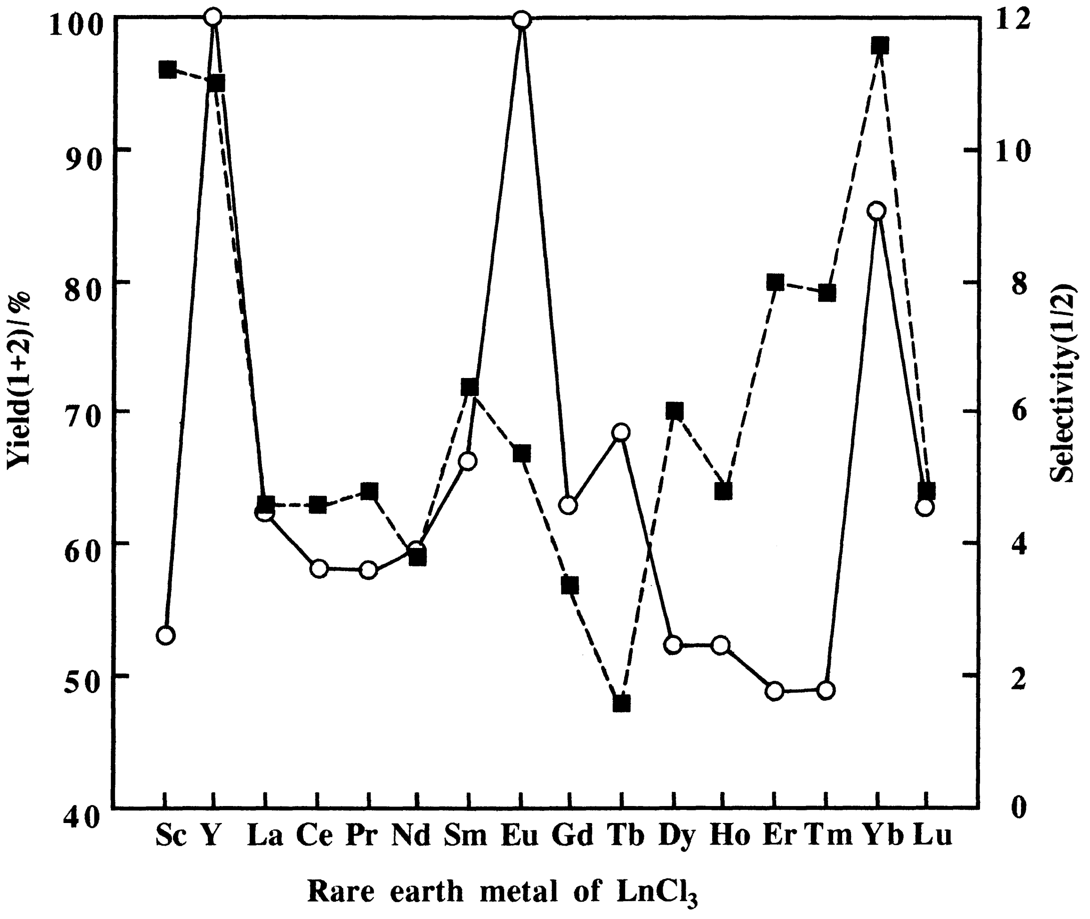


Fig. 1. $LnCl_3/Zn$ Promoted cyclodimerization of chalcone. The reaction was carried out as in Table 1. ■ : Total yield (**1**+**2**). ○ : Selectivity (**1**/**2**). Selectivities 49 and 24 for Y and Eu, respectively are plotted on the point 12 for the sake of clarity.

A which adds to chalcone to form **B**. Intermediate **B** would be transformed to **1** and **2** through a stable chair form transition state **C** and a less stable boat form **D**, respectively. The reason why the $LnCl_3/Zn$ system gives higher selectivity of **1** than Yb metal does, would be attributed to the ease with which the rigid, monomeric 6-membered ring **C** is formed because of less crowded ligand (Cl) on Yb, whereas in the case of Yb metal alone, two or three enolates would attach to the metal, which disturbs the formation of 6-membered transition states.

Finally we investigated the catalytic reaction using the $YbCl_3/Zn$ and $EuCl_3/Zn$ systems and chalcone as a substrate.6) Table 2 summarizes the results and the data in the table show that the reaction proceeds catalytically with respect to $LnCl_3$, to give cyclopentanol (**1**) in both good yield and selectivity.

In summary, we have found that the all trichlorolanthanoids ($LnCl_3$)/Zn systems except for $PmCl_3$ catalyze the cyclodimerization of chalcone to give cyclopentanol derivatives in both good yield and product selectivity.

The mechanism of the catalytic reaction and extention of substrates are under investigation.

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References

1) K. Takaki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku, and Y. Fujiwara, *J. Chem. Soc., Chem. Commun.*, **1990**, 516.

2) K. Nagase, F. Beppu, K. Tanaka, and Y. Fujiwara, 61st National Meeting of the Chemical Society of Japan, Yokohama, March 1991, Abstr. II, No. 1C440.

3) Zn powder alone also causes the reaction, but the low yield (34%) and selectivity (58:42) are obtained.

4) N. Mine, Y. Fujiwara, and H. Taniguchi, *Chem. Lett.*, **1986**, 357.

5) The reason of high reactivity and selectivity in the reaction with YCl_3 which has no f-electrons, is not obvious.

6) A typical procedure is as follows. A mixture of anhydrous $YbCl_3$ (0.1 m mol) and Zn powder (1.5 mmol) in THF (4 ml) was stirred at room temperature for 3 h under nitrogen. The color of the suspension became green. Then, chalcone (1 mmol) in THF (3 ml) was added and the mixture was stirred at room temperature for 4 h under nitrogen. The reaction was quenched with dil. HCl and the organic layer was extracted with ether. After usual work-up, the products were separated by column chromatography (silica gel).

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