Cyclodimerization of α,β-Unsaturated Ketones Catalyzed by Lanthanoid Tri-2-propoxides

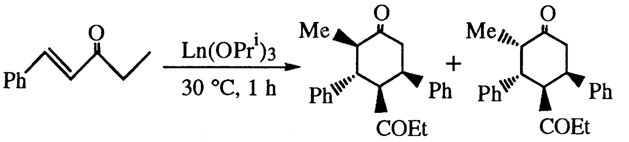
Tamon Okano,* Katsutoshi Ohno, and Jitsuo Kiji
Department of Materials Science, Faculty of Engineering, Tottori University, Tottori 680

(Received September 6, 1996)

α,β-Unsaturated ketones are cyclodimerized by the catalysis of lanthanoid tri-2-propoxides into substituted cycohexanones in good yields. The catalytic activity of the lanthanoids is fairly superior to those of the sodium or aluminum propoxides.

The catalysis of lanthanoid compounds has recently attracted considerable attention because of their remarkable reactivities.[1] Though the lanthanoid alkoxides are relatively still unfamiliar among the lanthanoid compounds, several reactions in which the alkoxides exhibit high ractivities or selectivities have been reported.[2] However, reactions peculiar to the lanthanoid alkoxides have rarely been known. Here we will report a novel cyclodimerizaton of α,β-unsaturated ketones in the presence of lanthanoid tri-2-propxides.

Treatment of 1-phenyl-1-penten-3-one with Yb(OPr^i)$_3$[3] (5 mol%) in benzene at 30 °C for 1 h afforded oily product, crystallization of which from cyclohexane gave crystals of γ-2-methyl-*t*-3,*c*-5-diphenyl-*c*-propionylcyclohexan-1-one (**1a**)[4] in a 51% yield. Another isomer, γ-2-methyl-*c*-3,*t*-5-diphenyl-*t*-propionylcyclohexan-1-one (**1b**),[4] was isolated from the residual oil by column chromatography on silica in a 16% yield. By means of HPLC and ^{1}H NMR, the original yields of **1a** and **1b** were estimated to be 64 and 27%, respectively (Table 1).



trans-isomer (**1a**) *cis*-isomer (**1b**)

The reaction at 20 °C for 20 min was almost equal to the above reaction in the yield of **1**, suggesting that the cyclodimerization is very fast. However, the two reactions totally differed in the ratio of **1a** to **1b**. This fact indicates that the dominant product of this reaction is **1b**, which gradually isomerized into **1a**. In fact, treatment of **1b** with Yb(OPr^i)$_3$ (5 mol%) in benzene at 30°C for 1 h gave a mixture of **1a** and **1b** (**1a** : **1b** = 74 : 26).

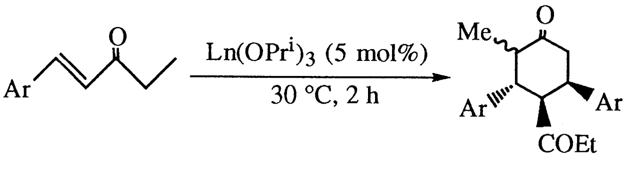
Other lanthanoid tri-2-propoxides were also catalytically active for the cyclodimerization. However, the yields of the reactions with Gd(OPr^i)$_3$ and La(OPr^i)$_3$ at 20°C for 20 min were lower than that of the corresponding reaction with Yb(OPr^i)$_3$. In contrast with the lanthanoids, sodium 2-propoxide which is a strong base was catalytically inefficient at the low temperature, and the reactions at elevated temperatures gave mostly polymeric products. Aluminum and titanium propoxides, which are considered to be more acidic than the lanthanoid propoxides, showed poor activities.

Table 1. Cyclodimrization of trans-PhCH=CHCOCH$_2$CH$_3$

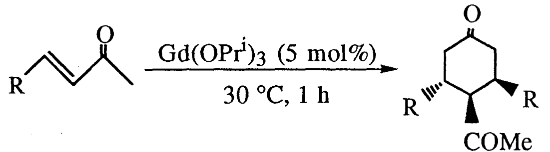
Catalyst	Conditions[a]	Yield/% of **1** (**1a**:**1b**)[b]
Y(OPr^i)$_3$	30 °C 1 h	95 (69:31)
Yb(OPr^i)$_3$	30 °C 1 h	91 (70:30)
Yb(OPr^i)$_3$	20 °C 20 min	90 (35:65)
Gd(OPr^i)$_3$	30 °C 1 h	85 (72:28)
Gd(OPr^i)$_3$	20 °C 20 min	62 (67:33)
Nd(OPr^i)$_3$	30 °C 1 h	78 (74:26)
La(OPr^i)$_3$	20 °C 20 min	51 (57:42)
Na OPr^i	60 °C 1 h	25 (73:27)
Mg(OPr^i)$_2$	30 °C 1 h	5
Al(OPr^i)$_3$	60 °C 1 h	15 (52:48)
Ti(OPr^i)$_4$	30 °C 1 h	trace

[a]The mixture of 1-phenyl-1-penten-3-one (2 mmol) and M(OPr^i)$_n$ (0.1 mmol) in benzene (2 cm^3) was stirred. [b]The yield and the ratio were determined by HPLC (Inertsil SIL) and ^{1}H NMR using *p*-di-*t*-butylbenzene as an internal standard.

The catalytic cyclodimerization of various α,β-unsaturated ketones was also achieved under the mild conditions. 1-(*p*-Anisyl) and 1-(2-furyl)-1-penten-3-ones afforded the corresponding cyclohexanones in considerable yields. Methyl ketones such as 4-phenyl-3-buten-2-one and 3-hepten-2-one gave the cyclohexanones which did not contain any other stereo isomers. However, the yields were not high, and polymer-like products were formed. On the other hand, isopropyl ketones

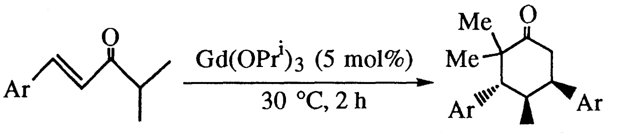


Ar = 2-Furyl Ln = Gd Yield 60% (*trans*:*cis*=65:35)
p-MeOC$_6$H$_4$ Yb 71% (*trans*:*cis*=83:17)



R = Ph Yield 36%
n-Pr 15%

gave the cyclohexanones without serious amounts of byproducts.



Ar = Ph Yield 82%
2-Furyl 53%

We consider that the following two reaction pathways are possible for the cyclodimerization (Figure 1). The key intermediate in both paths is a lanthanoid dienolate. Path A is a double Michael reaction based on the basic properties of the lanthanoid propoxides. The double Michael addition using special bases and reaction conditions is known.[5] Path B is a Diels-Alder reaction based on the fact that the heavy lanthanoids having a stronger Lewis acidity than the light lanthanoids are catalytically more active. Having no direct evidence for the determination of the path, we consider that the coordination of the oxygen atom of the carbonyl group to the lanthanoid is very important for the effective annulation.

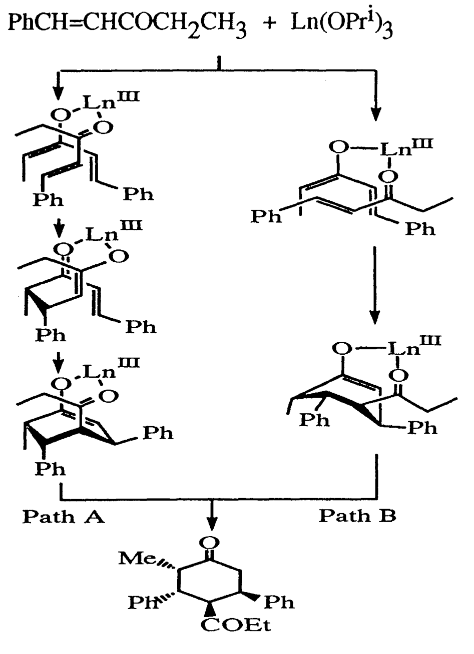


Figure 1. Possible mechanisms for the cyclodimerization.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 06241107 from The Ministry of Education, Science and Culture.

References and Notes

1 For reviews, see: J. A. Molander, *Chem. Rev.*, **92**, 29 (1992); T. Imamoto, *Rev. Heteroat. Chem.*, **3**, 87 (1990); W. J. Evans, *Adv. Organomet. Chem.*, **24**, 131 (1985).

2 M. Meguro, N. Asao, and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1995**, 1021; T. Okano, K. Miyamoto, and J. Kiji, *Chem. Lett.*, **1995**, 246; H. Sasai, T. Arai, Y. Satow, K. N. Houk, and N. Shibasaki, *J. Am. Chem. Soc.*, **117**, 6194 (1995); C. F. de Graauw, J. A. Peters, H. van Bekkum, and J. Huskens, *Synthesis*, **1994**, 1007; H. Ohno, A. Mori, and S. Inoue, *Chem. Lett.*, **1993**, 975; T. Okano, Y. Hayashizaki, and J. Kiji, *Bull. Chem. Soc. Jpn.*, **66**, 1863 (1993); H. Sasai, T. Suzuki, S. Arai, T. Arai, and M. Shibasaki, *J. Am. Chem. Soc.*, **114**, 4418 (1992); T. Okano, K. Ohno, and J. Kiji, *Chem. Express*, **7**, 393 (1992).

3 The lanthanoid tri-2-propoxides were prepared from metal shavings and 2-propanol, and recrystallized from a mixture of toluene and 2-propanol. See: T. Okano, M. Matsuoka, M. Kinoshita, and J. Kiji, *Nippon Kagaku Kaishi*, **1993**, 487.

4 **1a**: mp 135 °C; ^{1}H NMR (270 MHz, in CDCl$_3$ at 30 °C) δ 0.51 (3H, t, J= 7.1 Hz), 0.92 (3H, d, J= 6.6 Hz), 1.53 (1H, m), 1.71 (1H, m), 2.78 (1H, dq, J= 12.1 Hz), 2.81 (1H, dd, J= 16.4 and 5.4 Hz), 3.09 (1H, dd, J= 8.1 Hz), 3.20 (1H, dd, J= 10.0 Hz), 3.63 (1H, dd, J= 10.0 Hz), 3.84 (1H, ddd). **1b**: mp 118 °C; ^{1}H NMR (270 MHz, in CDCl$_3$ at 30 °C) δ 0.70 (3H, d, J= 7.1 Hz), 0.90 (3H, t, J= 6.8 Hz), 1.83 (1H, m), 2.37 (1H, m), 2.64 (1H, dd, J= 14.2 and 4.6 Hz), 3.22 (1H, dq, J= 12.1 Hz), 3.37 (1H and 1H, m), 3.55 (1H, ddd, J= 3.8 and 4.9 Hz), 3.71 (1H, dd).

5 H. Hagiwara, *Yuki Gosei Kagaku Kyokai Shi*, **50**, 713 (1992).