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Meerwein-Ponndorf-Verley Reduction of Ketones and Aldehydes Catalyzed by Lanthanide Tri-2-propoxides

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Lanthanide tri-2-propoxides, $Ln(i\text{-}PrO)_3$ (Ln=Nd, Eu, Gd, Dy, Er, Tm, Yb), are very efficient for the catalytic Meerwein-Ponndorf-Verley reduction. The catalytic activity of $Gd(i\text{-}PrO)_3$ is about 10^3 times as high as that of $Al(i\text{-}PrO)_3$. Compared with $Gd(i\text{-}PrO)_3$, $Yb(i\text{-}PrO)_3$ is less active for the reduction of ketones but is efficient for that of aldehydes.

In the organic syntheses using lanthanides, although many of the reactions resemble the reaction patterns of Groups IA and IIA elements,$^{1)}$ few reactions are similer to those of Group IIIA.$^{2,3)}$ We have investigated the reactions of lanthanides analogous to those of Group IIIA, and found that lanthanide tri-2-propoxides act as catalysts for Meerwein-Ponndorf-Verley(MPV) reduction which is a typical reaction of aluminium alkoxides. Recently Kagan and coworkers reported that $SmI_2(t\text{-}BuO)$ is able to act as a catalyst for the MPV reduction.$^{3)}$ The lanthanide tri-2-propoxides are not only comparable with $Al(i\text{-}PrO)_3$ in reactivity, but also are easy to be prepared. This paper deals with the reactivity and applicability of some lanthanide tri-2-propoxides in the MPV reduction.

$$\text{RCOR'} \quad + \quad \text{2-Propanol} \quad \xrightarrow{Ln(i\text{-}PrO)_3} \quad \text{RCH(OH)R'} \quad + \quad \text{Acetone}$$

The lanthanide tri-2-propoxides, $Ln(i\text{-}PrO)_3$ (Ln=Nd, Gd, Dy, Er, Yb) were prepared by refluxing 2-propanol suspensions of metal turnings in the presence of mercuric chloride (1 mol% to Ln).$^{4,5)}$ The other propoxides, $Eu(i\text{-}PrO)_3$ and $Tm(i\text{-}PrO)_3$, were prepared from anhydrous $LnCl_3$ and sodium 2-propoxide.$^{4,6)}$ The purification of each compound was accomplished by recrystallization from benzene

Table 1. Catalytic Activities of Some Lanthanide Tri-2-propoxides(Ln(i-PrO)$_3$) in the Meerwein-Ponndorf-Verley Reduction of Ketones [a)]

Substrate	Yield of alcohol/% [b)]							
	Al(i-PrO)$_3$	Ln = Nd	Eu	Gd	Dy	Er	Tm	Yb
Cyclohexanone[c)]	0.5 (9)[e)]	73	84	99	91	98	89	55
$(CH_3)_3CCOCH_3$[d)]		25		51				4
Acetophenone[d)]	1 (10)[e)]	57		58		22		5

a) The reactions were carried out by refluxing a mixture of ketone(20 mmol), 2-propanol(130 mmol), and Ln(i-PrO)$_3$ or Al(i-PrO)$_3$(0.2 mmol). b) GC yields based on ketone. c) At 30 °C for 30 min. d) At 50 °C for 1 h. e) Al(i-PrO)$_3$ (2.0 mmol) was used.

and 2-propanol. These propoxides, as well as Al(i-PrO)$_3$, were moisture-sensitive, and needed handling under anhydrous conditions. The catalytic MPV reduction was carried out by stirring a mixture of carbonyl compound, 2-propanol, and Ln(i-PrO)$_3$. In this system, 2-propanol was used both as a hydrogen donor and as a solvent. Since the MPV reduction is reversible, the measurements of the catalytic activities of Ln(i-PrO)$_3$ were achieved in a closed system, and the yields at early stages were determined by GC. The results are summarized in Table 1. In the reduction of cyclohexanone, Gd(i-PrO)$_3$ was the most active catalyst, and was estimated to be 10^3 times as active as Al(i-PrO)$_3$ from the measurement of initial rates. In fact, although a ten-fold amount of Al(i-PrO)$_3$ was used, cyclohexanol was obtained only in a 9% yield. Eu(i-PrO)$_3$, Dy(i-PrO)$_3$, Er(i-PrO)$_3$, and Tm(i-PrO)$_3$ were also highly active, while Nd(i-PrO)$_3$ and Yb(i-PrO)$_3$ were less active than the propoxides of middle lanthanide elements. A similar result was also obtained in the reduction of 3,3-dimethyl-2-butanone. On the other hand, in the MPV reduction of acetophenone, Nd(i-PrO)$_3$ was as active as Gd(i-PrO)$_3$. These facts suggest that the activity depends on the combination of catalyst and substrate.

The applicability to some carbonyl compounds was examined by using Gd(i-PrO)$_3$ without distilling the acetone from the mixtures. If we suppose that the chemical potentials of all these components are equal, the yield of alcohol should reach 87% in the equilibrium state. In the MPV reduction of ketones, the yields were in the range from 70 to 100%, so that these reactions can be considered to reach the equilibrium under these conditions. In fact, the yields were scarcely increased with prolonged reaction times. The reductions of six-membered cyclic ketones were very rapid, and gave the corresponding alcohols in almost quantitative yields even at 30 °C. In this reduction, 4-t-butylcyclohexanone afforded a mixture of cis- and trans-alcohols of which composition (21:78) was nearly equal to that of the thermal equilibrium state,[7)] though the cis-alcohol content (25%) at an early stage of the reduction (conversion:31%) was slightly higher. Seven- and five-membered ring compounds had reactivities different from the six-membered cyclic ketones. The reactivity of cycloheptanone was similar to that of acyclic ketones, whereas cyclopentanone was rapidly consumed but gave cyclopentanol in only 21% yield. The latter result is analogous to that of the MPV reduction by $Al(i\text{-}PrO)_3$.[8)] β-Diketones such as acetylacetone and 1-phenyl-1,3-butadione were not reduced, but an acetylacetonate complex, $Gd(acac)_3$, which had no activity was isolated from the reaction mixture. Thus, the addition of β-diketones resulted in the deactivation of the catalysis. Similar deactivation with a β-diketone is also known for the MPV reduction mediated by $Al(i\text{-}PrO)_3$.[9)] The reduction of aldehydes

Table 2. Meerwein-Ponndorf-Verley Reduction Catalyzed by $Gd(i\text{-}PrO)_3$ [a)]

Substrate	Alcohol yield/% [b)]	Substrate	Alcohol yield/% [b)]
2-Methylcyclohexanone [c)]	98	$PhCH{=}CHCOCH_3$	73
4-t-Butylcyclohexanone [c)]	99	Acetophenone	82
1-Benzyl-4-piperidone	99	3-Nitroacetophenone	97
Cycloheptanone	73	Methyl 4-pyridyl ketone	70
Cyclopentanone	21	Benzophenone	85
2-Octanone	85	Heptanal [d)]	25
4-Methyl-2-pentanone	78	$(CH_3)_2CHCHO$ [e)]	74
3,3-Dimethyl-2-butanone	76	Cyclohexanecarboaldehyde [f)]	61
$PhCOCH_2COCH_3$	0	Benzaldehyde [g)]	52
$CH_3COCH_2COCH_3$	0	1-Naphthalenecarboaldehyde [g)]	62

a) Reductions were carried out by refluxing a mixture of a carbonyl compound (20 mmol), 2-propanol(130 mmol), and $Gd(i\text{-}PrO)_3$(0.4 mmol) with stirring at 80 °C for 2 h. b) GC yields based on the carbonyl compounds. c) At 30 °C for 1 h. d) Toluene(10 ml) was used as a solvent; at -10 °C for 1 h. e) At 30 °C for 2 h. f) At 30 °C for 5 min. g) Benzene(5 ml) was used as a solvent; at 0 °C for 2 h.

was extremely fast and completed within 15 min at a temperature below 30 °C. However, the yields of alcohols were lower than those in the reduction of ketones. The results under our best conditions are also shown in Table 2. This reduction was accompanied with side reactions which caused a deactivation of the catalyst to give an inorganic precipitate. From the reaction mixture of benzaldehyde, both 4-phenyl-3-buten-2-one and 1,5-diphenyl-1,4-pentadien-2-one (2.5 and 0.6% yields based on benzaldehyde, respectively) were detected. This fact indicates one of the side reactions is the condensation between aldehyde and acetone, suggesting that the deactivation is a hydrolysis of $Gd(i\text{-}PrO)_3$ to give Gd_2O_3.

It should be noted that $Yb(i\text{-}PrO)_3$ exhibits more efficient catalytic activity than $Gd(i\text{-}PrO)_3$ for the MPV reduction of aldehydes. The reduction with $Yb(i\text{-}PrO)_3$ was slow but the side reactions were not serious. The consequence was that 31%, 71%, and 70% yields of alcohols were obtained in the reductions of heptanal, benzaldehyde, and cyclohexanecarboaldehyde, respectively, under the same conditions as for the corresponding aldehyde in Table 2.

The corresponding reactions with other lanthanide alkoxides and other carbonyl compounds are now in progress.

References

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