Transesterification Catalyzed by Lanthanoid Tri-2-propoxides

Tamon Okano,* Keiichi Miyamoto, and Jitsuo Kiji
Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680

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The transesterification of esters with alcohols was efficiently catalyzed by $Ln(OPr^i)_3$. The catalytic activity of $Ln(OPr^i)_3$ decreased in the following order; La > Nd > Gd > Yb, and was much higher than those of $Al(OPr^i)_3$ and $Ti(OPr^i)_4$.

Transesterification is in general use industrially as well as synthetically.[1] The most important class of catalysts for this reaction is the alkoxides of positive and hard elements such as Al,[2] Ti,[3,4] Zr,[3] Hf,[3] and Sn,[5] including alkali and alkaline earth metals.[1] Lanthanoids are typically hard and rather positive elements. Therefore, we investigated the transesterification of esters with alcohols using lanthanoid tri-2-propoxides as catalysts.

The transesterification of ethyl benzoate in refluxing methanol was efficiently catalyzed by $La(OPr^i)_3$[6] (2 mol%), and gave methyl benzoate in an excellent yield. This reaction was applicable to the transesterification of the ethyl and methyl esters with various primary and secondary alcohols. The reactivity of primary alcohols was higher than that of secondary alcohols. An important feature of this catalyst was good applicability to the reaction with alcohols having a long alkyl chain such as benzyl alcohol and 1-hexanol. The transesterification of 2-propyl benzoates was also achieved in the presence of $La(OPr^i)_3$ to give esters in considerable yields, though the 2-propyl ester was less reactive than the ethyl and methyl esters. Unfortunately, tertiary alcohols and their esters were inactive under these conditions. The transesterification of ethylene glycol diacetate with methanol gave the monoacetate (45%) and ethylene glycol (39%) at 30°C for 30 min. It is known that the diacetate is selectively converted into the monoacetate in the presence of 1,3-dichlorotetrabutyldistannoxane.[5c] Our reaction was nonselective, though the La catalyst was superior to the Sn complex in reactivity.

$$RCOOR' + R''OH \xrightarrow{Ln(OPr^i)_3\ (2\ mol\%)} RCOOR'' + R'OH$$

The catalytic activity of $Ln(OPr^i)_3$ was much higher than those of $Al(OPr^i)_3$ and $Ti(OPr^i)_4$ in the transesterification. The high efficiency may be due to easy exchange of the alkoxy ligands of lanthanoid with alcohols. Among the lanthanoid 2-propoxides, the catalytic activity decreased in the order La > Nd > Gd > Yb, which depends on metal ion size. A similar result is observed in the ester interchange reaction.[7] These facts suggest that the transesterification is substantially effected by the basic action of the alkoxides. In fact, $Yb(OTf)_3$ which is a typical Lewis acid was inactive for the transesterification under these conditions.

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Table 1. Catalytic Transesterification of Esters with Alcohols[a]

Ester	Alcohol	Catalyst	Temp/°C	Time/h	Yield/%
PhCOOEt	MeOH	$La(OPr^i)_3$	reflux	2	97
PhCOOEt	MeOH	$Yb(OPr^i)_3$	reflux	2	50
PhCOOEt	MeOH	$Al(OPr^i)_3$	reflux	2	1
PhCOOEt	MeOH	$Ti(OPr^i)_4$	reflux	2	1
PhCOOEt	1-Propanol	$La(OPr^i)_3$	60	3	92
PhCOOEt	Allyl alcohol	$La(OPr^i)_3$	60	3	84
PhCOOEt	1-Hexanol	$La(OPr^i)_3$	60	2	86
PhCOOEt	2-Butanol	$La(OPr^i)_3$	100	20	78
PhCOOEt	$PhCH_2OH$	$La(OPr^i)_3$	100	7	96
PrCOOEt	$PhCH_2OH$	$La(OPr^i)_3$	100	1	81
PhCOOMe	EtOH	$La(OPr^i)_3$	reflux	2	94
$PhCH_2COOMe$	$PhCH_2OH$	$La(OPr^i)_3$	100	2	89
PhCHCHCOOMe	$PhCH_2OH$	$La(OPr^i)_3$	100	2	90
$PhCOOPr^i$	MeOH	$La(OPr^i)_3$	reflux	5	64
$PhCOOPr^i$	1-Propanol	$La(OPr^i)_3$	60	20	86
$PhCOOPr^i$	1-Butanol	$La(OPr^i)_3$	60	5	84
$PhCOOPr^i$	1-Hexanol	$La(OPr^i)_3$	60	5	90
$PhCOOPr^i$	$PhCH_2OH$	$La(OPr^i)_3$	100	60	73
$PhCOOPr^i$	2-Butanol	$La(OPr^i)_3$	100	60	80
$PhCOOPr^i$	2-Butanol	$La(OPr^i)_3$	100	10	54
$PhCOOPr^i$	2-Butanol	$Nd(OPr^i)_3$	100	10	16
$PhCOOPr^i$	2-Butanol	$Gd(OPr^i)_3$	100	10	4
$PhCOOPr^i$	2-Butanol	$Yb(OPr^i)_3$	100	10	2
$PhCOOPr^i$	2-Butanol	$Yb(OTf)_3$	100	10	0.2
$PhCOOPr^i$	$(CH_3)_3COH$	$La(OPr^i)_3$	60	5	1
$PhCOOBu^t$	EtOH	$La(OPr^i)_3$	reflux	20	5

[a] The reaction was carried out using a mixture of $Ln(OPr^i)_3$ (0.1 mmol) and ester (5 mmol) in alcohol (5 cm^3), and the yield based on the starting ester was determined by GLC using internal calibration standards.

References and Notes

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