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Trimerization of Aliphatic Aldehydes to 1,3-Diol Monoesters Catalyzed by $Cp^*{}_2Sm(thf)_2$

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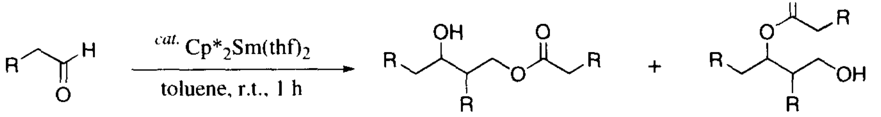
Abstract : Aliphatic aldehydes underwent trimerization in the presence of a catalytic amount of $Cp^*{}_2Sm(thf)_2$ under ambient conditions to form 1,3-diol monoesters in good yields. For example, the reaction of acetoaldehyde catalyzed by $Cp^*{}_2Sm(thf)_2$ gave 4-acetoxy-2-butanol (**2a**) and 3-acetoxy-1-butanol (**3a**) in 86% yield. © 1998 Elsevier Science Ltd. All rights reserved.

The trimerization of aldehydes, which produces 1,3-diol monoesters, is known to be facilitated by a weak base such as magnesium alkoxide[1] and by polynuclear carbonylferrates.[2] Recently, the aldol reaction of aldehydes is efficiently catalyzed by $Ln(O^iPr)_3$, in particular $La(O^iPr)_3$, under mild conditions,[3] while lanthanide compounds such as EtLnI (Ln = Pr, Nd, Sm) catalyze the Tishchenko reaction of aldehydes.[4] In addition, SmI_2 is reported to catalyze the Tishchenko reduction of β-hydroxy ketones with aldehydes[5] and the Reformatsky-type reaction of bromo acetates.[6] Similar Tishchenko reduction of β-hydroxy ketones with aldehydes has also been catalyzed by Cp_2ZrH_2.[7] In recent years, it has been reported that normal and asymmetrical aldol-Tishchenko reactions of aldehydes with ketones are respectively promoted by $BuTi(O^iPr)_4Li$[8] and by asymmetric heterobimetallic catalysts consisted of La and Li.[9] However, there has been little study on the trimerization of aldehydes catalyzed by lanthanide compounds. Previously, we showed that the 1:2 coupling reaction of vinyl acetate with aldehydes is catalyzed by samarium complexes such as $Cp^*{}_2Sm(thf)_2$.[10] In the course of this study, we found that $Cp^*{}_2Sm(thf)_2$ catalyzes the trimerization of aliphatic aldehydes at room temperature to give 1,3-diol monoesters in fair to good yields. In this paper, we wish to report the trimerization of aldehydes to 1,3-diol monoesters catalyzed by $Cp^*{}_2Sm(thf)_2$ (Eq. 1).



1a-h **2a-h** **3a-h** (1)

A typical reaction is carried out as follows. To a solution of $Cp^*{}_2Sm(thf)_2$ (0.1 mmol) in toluene (1 mL) was added acetaldehyde (**1a**) (3 mmol), and the mixture was stirred under ambient conditions for 1 h. After quenching with wet ether, the solvent was removed under reduced pressure. Column chromatography on silica gel, with hexane/ethyl acetate (4/1 v/v %) gave an 81:19 mixture of 4-acetoxy-2-butanol (**2a**) and 3-acetoxy-1-butanol (**3a**) in 86% yield. The ratio of **2a** and **3a** was ditermined by GC and ^{1}H-NMR.

Table 1 shows the representative results for the trimerization of **1a** by various lanthanide compounds. $Cp^*{}_2Yb(thf)_2$ also promoted the present reaction, but it was slightly less active than the corresponding samarium complex (Run 2). Although the amount of $Cp^*{}_2Sm(thf)_2$ was halved, the results were almost the same as those of Run 1 (Run 3). To improve the selectivity for the trimerization of **1a**, the reaction was carried out at 0 °C under these conditions. However, the ratio of **2a** to **3a** was not improved as expected (Run 4). SmI_2 did not catalyze the trimerization of **1a** at room temperature, but when the reaction was carried out at 50 °C, about a 1:1 mixture of **2a** and **3a** was obtained in 74% yield (Run 5).

The trimerization using a samarium (III) compound as catalyst was examined. The reaction of **1a** by $Sm(O^iPr)_3$[11] which is thought to act as a base rather than a Lewis acid afforded a 75:25 mixture of **2a** and **3a** in

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Table 1. Trimerization of Acetaldehyde (1a) to 4-Acetoxy-2-butanol (2a) and 3-Acetoxy-1-butanol (3a) Catalyzed by Various Lanthanoid Compounds[a]

Run	Catalyst	Solvent	Temp. / °C	Total Yield / %	Ratio of **2a** / **3a**
1	$Cp^*_2Sm(thf)_2$	toluene	r.t.	86	81 / 19
2	$Cp^*_2Yb(thf)_2$	toluene	r.t.	59	73 / 27
3[b]	$Cp^*_2Sm(thf)_2$	toluene	r.t.	84	77 / 23
4	$Cp^*_2Sm(thf)_2$	toluene	0	63	80 / 20
5	SmI_2	THF	50	74	51 / 49
6	$Sm(O^iPr)_3$	THF	r.t.	70	75 / 25
7	$Sm(OTf)_3$	THF	r.t.	no reaction	
8	SmI_3	THF	50	trace	

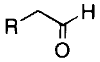
[a] **1a** (3 mmol) was allowed to react in the presence of catalyst (0.1 mmol) in toluene (1 mL) at room temperature for 1 h under Ar atmosphere. [b] $Cp^*_2Sm(thf)_2$ (0.05 mmol) was used.

70% yield, while $Sm(OTf)_3$ which serves as a Lewis acid did not catalyze the trimerization of **1a** (Runs 6 and 7). Unlike SmI_2, SmI_3 was inactive even at 50 °C (Run 8). Okano *et al.* have recently reported that $La(O^iPr)_3$ promotes efficiently the aldol reaction of aliphatic aldehydes at 0 °C to give the corresponding aldols in good yields,[3] but the formation of a trimerization product is not indicated.

On the basis of these results, a variety of aldehydes were allowed to react in the presence of $Cp^*_2Sm(thf)_2$ at room temperature for 1 h (Table 2).

Aldehydes, **1b**-**1f**, were trimerized in the same way as **1a** to give the corresponding 1,3-diol monoesters, **2b**-**2f** and **3b**-**3f**, in good yields. For instance, propanal (**1b**) was trimerized to form 1,3-diol monoesters, **2b** and **3b**, in about a 3:1 ratio in 82% yield. The resulting monoesters **2b** as well as **3b** were found to consist of a 1:1 diastereoisomeric mixture. The trimerization of butanal (**1c**) and pentanal (**1d**) took place in a similar manner as **1b** to give the corresponding 1,3-diol monoesters. Hexanal (**1f**) afforded monoesters, **2f** and **3f**, in a slightly lower yield (51%) (Run 5).

Table 2. Trimerization of Various Aldehydes to 1,3-Diol Monoesters Catalyzed by $Cp^*_2Sm(thf)_2$[a]

Run	Aldehyde			Product (Yield / %)[b]		Ratio of **2** / **3**
1		R = CH_3	**(1b)**	**2b** + **3b**	(82)	73 / 27
2		R = C_2H_5	**(1c)**	**2c** + **3c**	(87)	76 / 24
3		R = $^nC_3H_7$	**(1d)**	**2d** + **3d**	(95)	70 / 30
4		R = $^iC_3H_7$	**(1e)**	**2e** + **3e**	(71)	86 / 14
5		R = $^nC_4H_9$	**(1f)**	**2f** + **3f**	(51)	82 / 18

[a] Aldehyde (3 mmol) was allowed to react in the presence of $Cp^*_2Sm(thf)_2$ (0.1 mmol) in toluene (1 mL) at room temperature for 1 h under Ar atmosphere. [b] Aldehydes were almost consumed in every run.

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11. $Sm(O^iPr)_3$ was purchased from High Purity Chemicals Laboratory Co.Ltd..