Pergamon

Tetrahedron Letters 39 (1998) 6901–6902

TETRAHEDRON
LETTERS

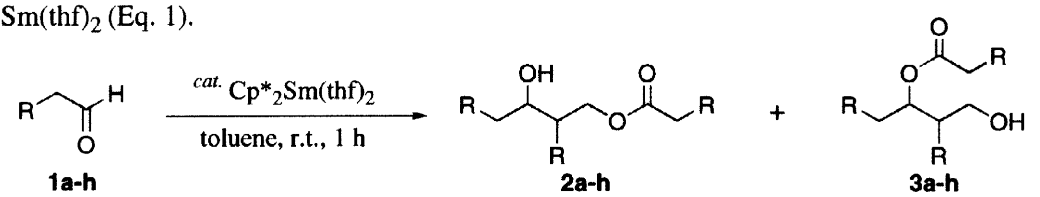
Trimerization of Aliphatic Aldehydes to 1,3-Diol Monoesters Catalyzed by $Cp^*_2Sm(thf)_2$

Akira Miyano, Daisuke Tashiro, Yumi Kawasaki, Satoshi Sakaguchi and Yasutaka Ishii*
Department of Applied Chemistry, Faculty of Engineering & High Technology
Research Center, Kansai University, Suita, Osaka 564-8680, Japan

Received 27 April 1998; revised 2 July 1998; accepted 10 July 1998

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.

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).



(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 ^1H-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

0040-4039/98/$ - see front matter
PII: S0040-4039(98)01447-6

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	

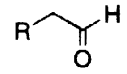
[a] **1a** (3 mmol) was allowed to react in the presence of catalyst (0.1 mmol) in toluene (1 mL) at room temperature for 1 h under Ar atmosphere. [b] $Cp*_2Sm(thf)_2$ (0.05 mmol) was used.

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.

Acknowledgment This work is supported by a Grant-in-Aid for Scientific Research (No. 10132262) on Priority Areas (No. 283, "Innovative Synthetic Reactions" from Monbusho.

References and Footnotes

1. Kulpinski, M. S.; Nord, F. F. *J. Org. Chem.* **1943**, *8*, 256-270.
2. Ito, K.; Kamiyama, N.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1983**, 657-660.
3. Okano, T.; Satou, Y.; Tamura, M., Kiji, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1879-1885.
4. Yokoo, K.; Mine, N.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1985**, *279*, C19.
5. Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 6447-6449.
6. Molander, G. A.; Etter, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 6556-6558.
7. Umekawa, Y.; Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1997**, *62*, 3409-3412.
8. Mahrwald, R.; Costisella, B. *Synthesis*, **1996**, 1087-1089.
9. Yamada, Yoichi M. A.; Yoshikawa, N.; Sasai, H.; Shibasaki, M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1871-1872.
10. Takeno, M.; Kikuchi, S.; Morita, K.; Nishiyama, Y.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1995**, *60*, 4974-4975.
11. $Sm(O^iPr)_3$ was purchased from High Purity Chemicals Laboratory Co.Ltd..