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Preliminary communication

CHEMISTRY OF ORGANOLANTHANOIDS: LANTHANOID-CATALYZED TISHCHENKO CONDENSATION OF ALDEHYDES TO ESTERS

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Summary

Ethyllanthanoid iodide complexes, 'EtLnI'*, prepared from Ln (Ln = Pr, Nd, Sm) and EtI, have been found to serve as catalyst precursors for the Tishchenko condensation of aldehydes such as benzaldehyde, *p*-chlorobenzaldehyde, *p*-tolualdehyde, *p*-anisaldehyde, and pivalaldehyde, to the corresponding esters.

We have recently reported that organolanthanoid σ-complexes, RLnI, which are prepared in situ from lanthanoid metals (Ln) and organic iodides (RI) [1], react with a variety of substrates to show unique reactivities [2]. In a continuing study of organolanthanoids, we have found that alkyllanthanoids, especially ethyllanthanoid complexes, 'EtLnI'*, prepared from Ln (Ln = Pr, Nd, Sm) and EtI, serve as catalyst precursors for the Tishchenko condensation of aldehydes. We report herein the lanthanoid-catalyzed Tishchenko condensation of aldehydes such as benzaldehyde, *p*-chlorobenzaldehyde, *p*-tolualdehyde, *p*-anisaldehyde, and pivalaldehyde, to give the corresponding esters.

$$2\ \mathrm{RCHO} \xrightarrow[\mathrm{THF}]{\mathrm{EtLnI}} \mathrm{RCO_2CH_2R}$$

(R = C_6H_5, *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, t-Bu)

First, reactions were carried out using stoichiometric amounts of lanthanoid metals as follows. Freshly cut Ln (1.0 mg-atom) and a magnetic stirring bar were placed in a 50-ml centrifuge tube and the tube was sealed with a cerum

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*The designation 'EtLnI' is used since the initially formed divalent species, EtLnI, would be transformed to a more stable trivalent species which further undergoes β-H elimination to give a Ln—H species, an actual catalyst, under reaction conditions [1,2d,3].

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cap. After the tube was dried by heating under a stream of nitrogen, 4 ml of THF, which had been freshly distilled under nitrogen from sodium benzophenone ketyl, was added by a syringe. After iodoethane (2.0 mmol) was added dropwise to the tube with stirring at 65° C, the mixture was stirred for an additional 2 h. Then the aldehyde (1 mmol) was added slowly to the resulting grey THF solution of the 'EtLnI' at 65° C. The reaction mixture was stirred overnight (15—20 h) at 65° C and then hydrolyzed with aqueous NH_4Cl and 2 *N* HCl, and the products were extracted with ether. The products were identified by comparison with authentic samples. The results are summarized in Table 1.

TABLE 1

REACTIONS OF ALDEHYDES WITH A STOICHIOMETRIC AMOUNT OF 'EtLnI' [a]

Aldehyde (1 mmol)	Ln	Ester	Yield (%) [b]
Benzaldehyde	Nd	$PhCO_2CH_2Ph$	40 [c,d]
Benzaldehyde	Pr	$PhCO_2CH_2Ph$	32 [c,d]
Benzaldehyde	Sm	$PhCO_2CH_2Ph$	30 [c,e]
p-Chlorobenzaldehyde	Nd	$(p\text{-Cl})C_6H_4CO_2CH_2C_6H_4(p\text{-Cl})$	40 [f,g]
p-Tolualdehyde	Nd	$(p\text{-CH}_3)C_6H_4CO_2CH_2C_6H_4(p\text{-CH}_3)$	40 [f,h]
p-Anisaldehyde	Nd	$(p\text{-CH}_3\text{O})C_6H_4CO_2CH_2C_6H_4(p\text{-CH}_3\text{O})$	11 [i,j]
Pivalaldehyde	Nd	$(t\text{-Bu})CO_2CH_2(t\text{-Bu})$	37 [i]

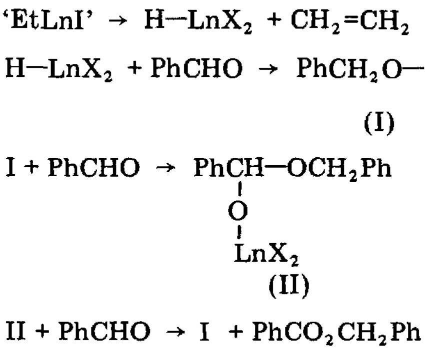
[a] 'EtLnI' was prepared by treating Ln (1 mg-atom) with EtI (2 mmol) in THF (4 ml) at 65° C. [b] Yields are based on starting amounts of the aldehyde. [c] Determined by GC. [d] Benzyl alcohol and benzoin were also formed in 5 and 6% yields, respectively. [e] Benzyl alcohol was also formed in 19% yield. [f] Isolated yield. [g] $(p\text{-Cl})C_6H_4CH_2OH$ and $(p\text{-Cl})C_6H_4C(O)CHOHC_6H_4(p\text{-Cl})$ were also formed in 12 and 7% yields, respectively. [h] Small amounts of $(p\text{-CH}_3)C_6H_4CH_2OH$ and $(p\text{-CH}_3)C_6H_4C(O)CHOHC_6H_4(p\text{-CH}_3)$ were also formed. [i] Determined by NMR. [j] $(p\text{-CH}_3\text{O})C_6H_4CH_2OH$ and $(p\text{-CH}_3\text{O})C_6H_4C(O)CHOHC_6H_4(p\text{-CH}_3\text{O})$ were also formed in 13 and 7% yields, respectively.

As is apparent from Table 1, both arylic and aliphatic aldehydes undergo the reaction, and the reactivity of Pr, Nd, and Sm is almost the same. It is of interest to note that Pr, Nd, and Sm cause the reaction whereas Yb and Eu the divalent states of which are more stable than those of Pr, Nd, and Sm, bring about the Grignard-type addition predominantly [2].

We also investigated whether the reaction would proceed catalytically with respect to lanthanoid metals. The results are listed in Table 2. The data in Table 2 clearly show that the reaction proceeds catalytically in lanthanoid metals. Substitution of other lanthanoid metals such as Yb and Eu resulted in lower yields.

Although aluminum trialkoxides ($Al(OR)_3$) are usually used as catalysts for the Tishchenko condensation, it is of great interest from the lanthanoid chemical points of view that 'RLnI' (Ln = Pr, Nd, Sm) can serve as catalyst precursors for this reaction.

The mechanism of this reaction appears to be closely related to that of the reaction with $Al(OR)_3$. Probably a Ln-alkoxide complex, $PhCH_2O{-}LnX_2$ (I), is formed from the reaction of 'EtLnI' and PhCHO via β-H elimination, followed by the addition of a further 2 mol of PhCHO, to give $PhCO_2CH_2Ph$ plus $PhCH_2O{-}LnX_2$ (I) (Scheme 1).



$$\text{'EtLnI'} \rightarrow \text{H—LnX}_2 + \text{CH}_2\text{=CH}_2$$

$$\text{H—LnX}_2 + \text{PhCHO} \rightarrow \underset{\text{(I)}}{\text{PhCH}_2\text{O—LnX}_2}$$

$$\text{I} + \text{PhCHO} \rightarrow \underset{\text{(II)}}{\text{PhCH}(\text{O—LnX}_2)\text{—OCH}_2\text{Ph}}$$

$$\text{II} + \text{PhCHO} \rightarrow \text{I} + \text{PhCO}_2\text{CH}_2\text{Ph}$$

SCHEME 1

TABLE 2

REACTIONS OF BENZALDEHYDE WITH A CATALYTIC AMOUNT OF 'EtLnI' [a]

Lanthanoid (0.5 mg-atom)	Reaction temp. (°C)	Yield of benzyl benzoate (%) [b]
Pr	65	199 (40) [c]
Nd	65	116 (23) [d]
Sm	r.t.	290 (58) [e]

[a] The reactions were carried out by using PhCHO (5 mmol) and 'EtLnI' prepared from the lanthanoid metal (0.5 mg-atom) and EtI (1 mmol). in THF (3—4 ml) with stirring overnight. [b] Yields are based on starting amounts of the lanthanoid metal and numbers in parentheses indicate yields based on starting amounts of PhCHO. [c] Benzyl alcohol and benzoin were also formed in 56 and 6% yields, respectively. [d] Benzyl alcohol and benzoin were also formed in 23 and 8% yields, respectively. [e] Benzyl alcohol and benzoin were also formed in 6 and 3% yields, respectively.

Although the tungsten-promoted Tishchenko condensation has recently been reported [4], this is the first example of a lanthanoid-catalyzed Tishchenko-type reaction.

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