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Lanthanoid-Catalyzed Aldehyde Dimerization and Its Application to Polyester Synthesis

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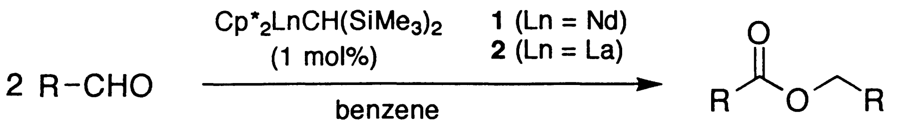
A wide variety of aldehydes are efficiently dimerized to esters by a catalytic amount of $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Nd, La). The reaction is applicable to the synthesis of polyesters from dialdehydes. A stoichiometric reaction of the lanthanum complex with benzaldehyde indicates the intermediacy of alkoxo complexes in the catalysis.

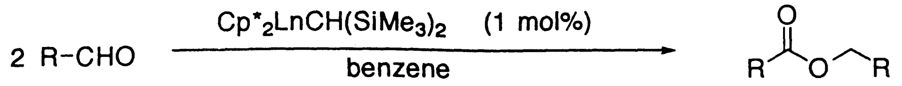
In the last several years, increasing number of papers have dealt with catalysis by group III complexes with cyclopentadienyl ligands,1) revealing their unique reactivities as compared with group VIII catalysts. However, most of the works so far have been devoted to transformation of carbon-carbon double or triple bonds; catalysis involving hetero unsaturated bonds is rather limited. During the reactivity study of pentamethylcyclopentadienyl (Cp*) lanthanoids,2) we have found that these complexes are quite reactive toward carbon-oxygen double bonds. Here, we wish to report the catalytic dimerization of aldehydes by lanthanoid complexes.3)

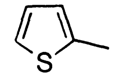
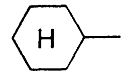
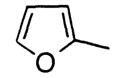
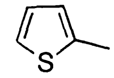
Previously, we have reported the hydrosilylation of olefins catalyzed by $Cp^*{}_2NdR$ (R = $CH(SiMe_3)_2$ or H).2a) An attempted hydrosilylation of benzaldehyde with $PhMe_2SiH$ by the same catalyst unexpectedly resulted in the formation of benzyl benzoate without yielding hydrosilylated products.4) Further investigation revealed that the dimerization took place smoothly even without hydrosilanes (Eq.1). The results with various aldehydes are summarized in Table 1. An aromatic aldehyde (benzaldehyde) was converted to the corresponding ester by neodymium complex **1** in a high yield at room temperature (entry 1). This contrasts with the recently reported group IV-catalyzed aldehyde dimerization, in which benzaldehyde was difficult to convert into benzyl benzoate.3b) Although the neodymium catalyst was not very effective for dimerization of a bulky aliphatic or a sulfur-containing aldehyde (entries 2 and 3), the drawbacks were easily circumvented by the use of lanthanum complex **2** (entries 4 and 7). An enolizable aliphatic aldehyde with an α-hydrogen (entry 5) and an oxygen-containing heteroaromatic aldehyde (entry 6) were also converted to the esters by **2** in



(1)

Table 1. Lanthanoid-catalyzed dimerization of aldehydes[a)]

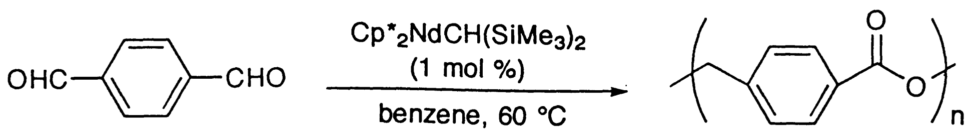


Entry	R-	Ln	Yield / %[b)]	
1	Ph-	Nd	88	(76)
2	^{t}Bu-	Nd	46	
3		Nd	31	
4	^{t}Bu-	La	quant.	
5		La	95	(88)
6		La	77	(77)
7		La	quant.	(84)

a) Conditions: Lanthanoid complex 0.01 mmol, aldehyde 1.0 mmol, benzene 1.0 cm^3, room temperature (entries 1 and 5) or 60 °C (entries 2,3,4,6, and 7), 3 d.
b) GLC yields. Figures in parentheses are isolated yields.

high yields. It is noteworthy that furfural was reported to be hard to dimerize in iron- and aluminum-catalyzed aldehyde reactions.[3d, 5)] Thus, dimerization of diverse aldehydes including aromatic, heteroaromatic, and aliphatic ones proceeded in an excellent manner.

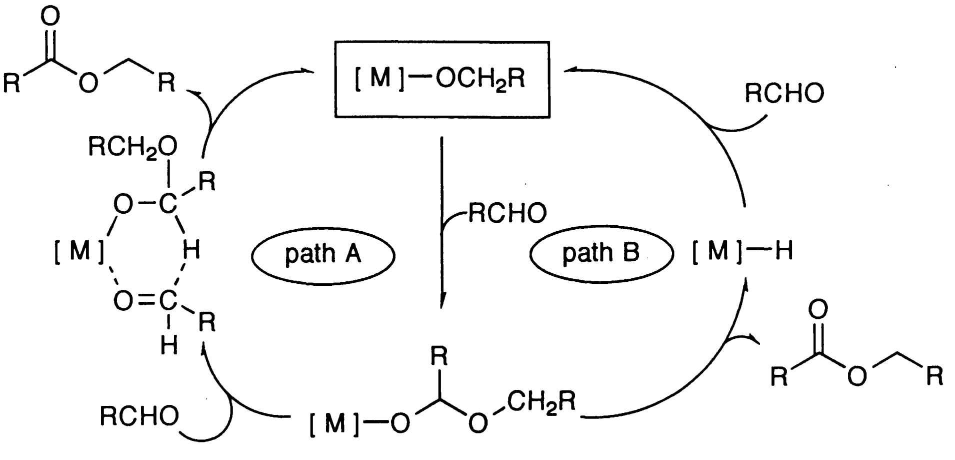
As aldehyde dimerization progressed readily in the presence of lanthanoid complexes, the procedure was applied to polyester synthesis starting with dialdehydes. The reaction of terephthalaldehyde with a catalytic amount of **1** at 60 °C in benzene resulted in the formation of a white precipitate in a few minutes. After continued heating at that temperature for 7 days, the resulting solid was filtered off and washed with hexane to give an almost quantitative amount of the polymer, which was soluble in chloroform but not in benzene, toluene, and tetrahydrofuran (Eq. 2).[6)] The number-average molecular weight of the polymer was calculated to be 4000 based on the integral ratio of methylene and terminal aldehyde group in ^{1}H NMR; this agrees well with the GPC-based molecular weight. Since two (1 : 1) and three (1 : 1 : 1) methylene signals were observed in ^{1}H and ^{13}C NMR, respectively, microstructure of the polymer is irregular.



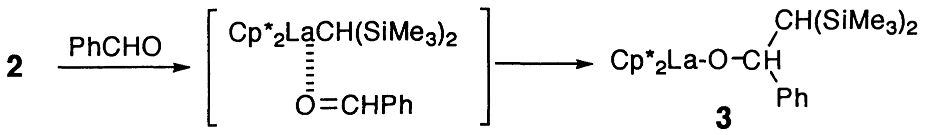
(2)

After 2d, 97%, Mw = 5000, Mn = 2900
After 7d, 97%, Mw = 7000, Mn = 3800

Aldehyde dimerization to esters is generally catalyzed by metal alkoxides (Scheme 1).3,5) Preliminary mechanistic studies shown below also indicate the intermediacy of alkoxo lanthanoids in the present catalysis. Upon addition of a stoichiometric amount of benzaldehyde to a benzene solution of **2**, the reaction mixture immediately became deep red and the aldehyde proton in ^1H NMR diminished, possibly because of the coordination of benzaldehyde to **2**. Then, the color of the solution turned pale red in several minutes and alkoxo complex **3** was detected by ^1H NMR: the two characteristic methines, the one connected to the two silicon atoms and the benzylic one, were observed as two mutually coupled doublets (70% NMR yield after 5 minutes) (Eq. 3).7) Carbon-13 NMR data also correspond with this structure. Unequivalence of the two trimethylsilyl groups in ^1H and ^{13}C NMR is also consistent with diastereotopic nature of **3**.

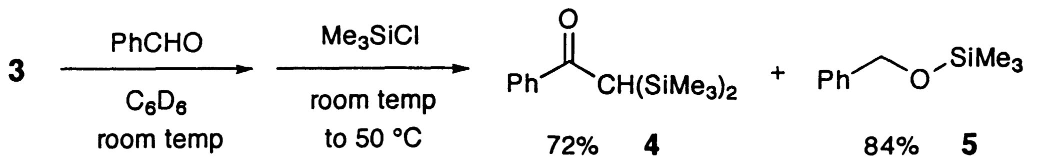


Scheme 1.



$$\mathbf{2} \xrightarrow{PhCHO} \left[\begin{array}{c} Cp^*_2LaCH(SiMe_3)_2 \\ \vdots \\ O{=}CHPh \end{array} \right] \longrightarrow \underset{\mathbf{3}}{Cp^*_2La\text{-}O\text{-}CH(Ph)CH(SiMe_3)_2} \qquad (3)$$

Addition of another equivalent of benzaldehyde to **3** afforded a complicated products mixture that contained, as judged by ^1H NMR, ketone **4** and, presumably, $PhC\underline{H_2}O$- species (several signals at δ 4.5–5.5). GCMS analysis of the mixture after treatment with trimethylsilyl chloride revealed the formation of benzyl ether **5** in a high yield (Eq. 4). This strongly suggests the intermediacy of (phenylmethoxo)lanthanums, possible active species in the benzaldehyde dimerization. The formation of **4** is also consistent with the conversion of **3** to phenylmethoxo complexes; benzaldehyde was presumably reduced by β-hydrogen transfer from **3** through a six-membered intermediate or a hydride complex (c.f. paths A and B, Scheme 1). Complex **3** being a precursor of active catalytic species is also supported by the fact that addition of an excess amount (11 equivalents) of benzaldehyde to a benzene solution of **3** resulted in the formation of benzyl benzoate (60% yield based on PhCHO, after 2 h at room temperature).



(4)

(GLC yields based on La.)

In summary, aldehydes of various structures can be dimerized to esters by lanthanoid complexes in high yields. Based on this observation, a new methodology to synthesize polyesters from dialdehydes has been developed. Modification of the monomer structure to obtain soluble and high molecular weight polymers and further mechanistic studies are now under way.

References

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5) Al-catalyzed reaction. W. C. Child and H. Adkins, *J. Am. Chem. Soc.*, **47**, 798 (1925); F. J. Villani and F. F. Nord, *ibid.*, **69**, 2605 (1947); I. Lin and A. R. Day, *ibid.*, **74**, 5133 (1952).

6) Molecular weights were determined by high-temperature GPC based on polystyrene standards. Physical and spectral data of the polymer: mp 130 - 140 °C; IR (KBr) 1718 (CO_2R); ^1H NMR ($CDCl_3$) $\delta = 5.38$ and 5.42 (2H, each s, CH_2O), 7.25-8.12 (4H, m, aromatic), 10.03 (0.07H, s, CHO); ^{13}C NMR ($CDCl_3$) $\delta = 66.0, 66.4, 66.8$ (CH_2O), 127.4 - 141.4 (20 signals, aromatic), 165.4, 165.5, 165.8, 166.0 (CO_2R); Found: C, 72.27; H, 4.63%. Calcd for $(C_8H_6O_2)_n$: C, 71.64; H, 4.51%.

7) Spectral data of **3**: ^1H NMR (C_6D_6) $\delta = -0.16, 0.23$ (18H, each s, $SiCH_3$), 0.94 (1H, d, J = 10.8 Hz, $CHSi_2$), 1.95 (30H, s, $C_5(CH_3)_5$), 5.33 (1H, d, J = 10.8 Hz, O-CH-Ph), 7.0 - 7.5 (5H, m, Ph); ^{13}C NMR (C_6D_6) $\delta = 1.6, 2.0$ ($SiCH_3$), 11.0 ($C_5(\underline{C}H_3)_5$), 29.5 ($CHSi_2$), 78.9 (O-CH-Ph), 119.3 ($\underline{C_5}(CH_3)_5$), 126.4, 127.5, 128.2, 150.7 (aromatic).

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