

## Dichlorodistannoxane transesterification catalysts, pure Lewis acids

Bernard Jousseume,\* Christian Laporte, Marie-Claude Rascle and Thierry Toupance

Laboratoire de Chimie Organique et Organométallique, UMR CNRS 5802, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence, France

Received (in Cambridge, UK) 10th April 2003, Accepted 25th April 2003

First published as an Advance Article on the web 16th May 2003

Dialkoxy- or diacyloxy-distannoxanes were transformed into unsymmetrical acyloxyalkoxydistannoxanes during a transesterification reaction where they were used as catalysts, while more active dichlorodistannoxanes were recovered unchanged.

Esterifications and transesterifications are very important reactions in organic synthesis as well as in academic laboratories as in industry, for instance for the preparation of polyesters from alcohols and acids or esters. These reactions can be made spontaneous by using Dean–Stark apparatus or high temperature conditions. However, they are very often catalyzed for a better efficiency, higher reaction rates and milder conditions. Common catalysts include acids, Lewis acids such as titanium or aluminium alkoxides, or bases such as alkali-metal alkoxides, DMAP, DBL or other amines.<sup>1</sup> Among organometallic compounds, organotin derivatives as organotin oxides, alkoxides and carboxylates are the most popular compounds used in esterification and transesterification processes.<sup>1b,2,3</sup> Otera *et al.* recently developed this aspect of organotin chemistry by demonstrating that diversely substituted tetraorganodistannoxanes show very high catalytic activity allowing their use at very low concentration when the alcohol is used in large excess.<sup>4</sup> This work has been extended to various selective acylation reactions and novel dimeric organotin cations.<sup>5</sup> The mechanism commonly admitted to explain the very high efficiency of tetraorganodistannoxanes involves first the displacement of a substituent on the tin by a molecule of alcohol leading to an alkoxytetraorganodistannoxane. Then, this alkoxytetraorganodistannoxane would deliver the alkoxide group to a carbonyl, after the coordination of this carbonyl to a tin atom of the distannoxane.<sup>1b,c</sup> This scheme was logically supported by the ability of organotin alkoxides to displace the alkoxide moiety of esters<sup>3a</sup> and by the formation of small amounts of alkoxytetraorganodistannoxanes upon heating dichlorotetraorganodistannoxanes and alcohols.<sup>6</sup> We were recently interested in the search for new organotin catalysts for silicone curing and polyurethane preparation, especially with latent properties and enhanced activity.<sup>7</sup> To design more efficient catalysts for the preparation of polyesters through transesterification reactions, it appeared interesting to determine the nature of the active organotin species in the catalytic cycle. The results we obtained in this field are reported here.

The kinetic parameters of the transesterification of ethyl butyrate with 1-heptanol were first determined, in order to compare the activity of the tetraorganodistannoxanes used in this study.

The reaction order in methyl butyrate was determined by heating a solution of methyl butyrate, a 10-fold excess of 1-heptanol, dodecane as internal standard and 1,3-diacetoxy-1,1,3,3-tetrabutylidistannoxane in toluene at 100 °C. A 5% amount of catalyst was used to facilitate its analysis after the reaction as will be described later. A short path column allowed ethanol to escape. Aliquots of the reaction mixture were analyzed by GC to monitor the conversion of ethyl butyrate in heptyl butyrate. An order of 1 was obtained by comparing the variation of concentration in ester formed with calculated curves for different values of order. The global order was

determined by the same method from data obtained with identical concentrations of the reactants. It was found equal to 2 indicating a first order dependency on alcohol. Then, the reaction was conducted in the presence of various organotin catalysts with a stoichiometric amount of ethyl butyrate and 1-heptanol and the rate constants calculated in order to test their activity in our reaction conditions.

The data presented in Table 1 indicate that almost identical results were obtained with 1-acetoxy-3-methoxy-1,1,3,3-tetrabutylidistannoxane and 1,3-diacetoxy-1,1,3,3-tetrabutylidistannoxane. 1,3-Dimethoxy-1,1,3,3-tetrabutylidistannoxane led to a higher rate which was almost doubled with respect to other catalysts. However, 1,3-dichloro-1,1,3,3-tetrabutylidistannoxane gave the best results. In this case the rate of the transesterification reaction increased again by a factor of two. An almost identical ratio was found when the reaction was conducted at 90 °C. These results are in agreement with the reports where higher yields were obtained with 1,3-dichloro-1,1,3,3-tetrabutylidistannoxane, using a ten-fold excess of alcohol.<sup>4d</sup>

Then the same type of reaction was conducted with ethyl acetate and ethanol, for an easier recovery of the catalyst after the reaction, under reflux at 100 °C for 6 h in the presence of a 5% amount of tetrabutylidistannoxane. After evaporation of ethyl acetate and ethanol, the catalysts were analyzed by <sup>119</sup>Sn, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The spectra were compared either to authentic samples or to relevant data from the literature. The amount of recovered catalyst was higher than 95%. When 1,3-diacetoxy-1,1,3,3-tetrabutylidistannoxane was used as catalyst, NMR analysis revealed its transformation into 1-acetoxy-3-ethoxy-1,1,3,3-tetrabutylidistannoxane. Under the same conditions, 1-acetoxy-3-methoxy-1,1,3,3-tetrabutylidistannoxane gave 1-acetoxy-3-ethoxy-1,1,3,3-tetrabutylidistannoxane.<sup>9</sup> Analogous distannoxanes were already formed when dibutyltin oxide was used as catalyst in a transesterification reaction at high temperature.<sup>10</sup> Then, the more active 1,3-dichloro-1,1,3,3-tetrabutylidistannoxane was used. It was recovered unchanged after the reaction (Table 2).<sup>11</sup> When a ten-fold excess of alcohol was used, 2% of the complex ClBu<sub>2</sub>SnOSnBu<sub>2</sub>Cl; ClBu<sub>2</sub>SnOSnBu<sub>2</sub>OAc<sup>12</sup> were detected in the recovered catalyst. When the amount of catalyst was reduced to 0.5% and the reaction heated for 24 h, the same by-product was accompanied by 5% of the complex ClBu<sub>2</sub>SnOSnBu<sub>2</sub>Cl; ClBu<sub>2</sub>SnOSnBu<sub>2</sub>OR.<sup>13,14</sup>

Table 1 Rate constants of organotin catalysed transesterifications<sup>8</sup>

Catalyst	Rate constant/L mol <sup>-1</sup> min <sup>-1</sup>
(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OAc)	7.8 × 10 <sup>-3 a</sup>
(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OMe)	6.4 × 10 <sup>-3 a</sup>
(MeO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OMe)	13 × 10 <sup>-3 a</sup>
(MeO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OMe)	3 × 10 <sup>-3 b</sup>
(MeO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> Cl	20 × 10 <sup>-3 a</sup>
ClBu <sub>2</sub> SnOSnBu <sub>2</sub> Cl	27 × 10 <sup>-3 a</sup>
ClBu <sub>2</sub> SnOSnBu <sub>2</sub> Cl	7.5 × 10 <sup>-3 b</sup>

<sup>a</sup> Reaction conducted at 100 °C. <sup>b</sup> Reaction conducted at 90 °C.

**Table 2** Nature of the catalyst after transesterification

Catalyst	Recovered catalyst
(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OAc)	(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OEt)
(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OMe)	(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OEt)
(MeO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OMe)	(AcO)Bu <sub>2</sub> SnOSnBu <sub>2</sub> (OEt)
ClBu <sub>2</sub> SnOSnBu <sub>2</sub> Cl	ClBu <sub>2</sub> SnOSnBu <sub>2</sub> Cl

These results showed that tetraorganodistannoxanes substituted with two acetoxy or alkoxy groups were transformed during the reaction into unsymmetrically substituted 1-acyloxy-3-alkoxy-1,1,3,3-tetrabutylidistannoxanes which thus could be in this case the real catalysts of the transesterification reaction. Their presence was in favour of a transfer of alkoxy group from the tin to the carbonyl of the ester.<sup>15</sup> However, the results obtained with 1,3-dichloro-1,1,3,3-tetrabutylidistannoxane, which was recovered unchanged, gave the higher rate constants and where the transfer of an alkoxy group cannot take place, favours the occurrence of an alternate more efficient catalytic process where no transfer of alkoxy group linked to the metal occurs. Thus, the catalytic efficiency of 1,3-dihalodistannoxanes is better described in terms of Lewis acidity, the chlorine atoms inducing higher accepting properties than alkoxy or acyloxy groups.<sup>16</sup> The presence of two electropositive tin atoms could favour either the formation of a six-membered transition state involving catalyst, ester and alcohol, or the double activation of the ester through the coordination of each oxygen atom to a tin of the distannoxane.<sup>17</sup> This interpretation is fully consistent with the observation of very strong solvent effects in the distannoxane-catalysed transesterification reaction where polar solvents such as acetonitrile or diglyme decrease the reaction rate in a spectacular way.<sup>4c</sup> This strong inactivation of the catalyst would come from the coordination of vacant sites by the solvent acting as a ligand.

In summary, it is shown that 1,1,3,3-tetrabutylidichlorodistannoxane was recovered unchanged in a transesterification reaction where it was used as catalyst, while dialkoxy- and diacyloxy-distannoxanes were transformed into unsymmetrical acyloxyalkoxydistannoxane. Dichlorodistannoxanes showed a higher activity than other distannoxanes, and being recovered unchanged after reaction, their efficiency in the transesterification reaction comes more from their unique bidentate coordination properties as Lewis acids than from their ability to transfer alkoxy groups. This finding is in agreement with the discovery of very high activity for novel organotin cations<sup>5</sup> and could be helpful for the design of new catalysts.<sup>18</sup>

We are indebted to Dr J.-M. Bernard for fruitful discussions.

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