

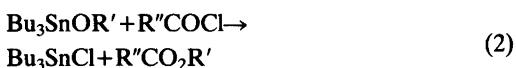
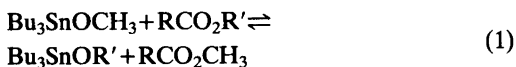
Reactions of Tributyltin Methoxide with Chloromethyl Esters

JOUKO VIHANTO

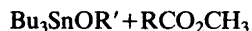
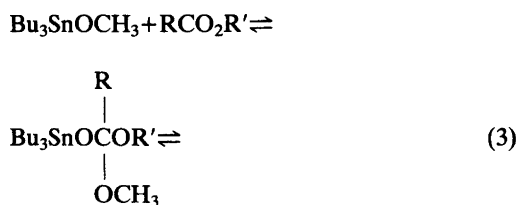
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Reactions of tributyltin methoxide with esters $\text{RCO}_2\text{R}'$ ($\text{R}' = \text{CH}_2\text{Cl}$, CHCl_2 or CCl_3) have been performed to study the influence of the halogens in the alkyl component of an ester on the course of the reaction. In all reactions tributyltin chloride and methyl ester were formed whereas the subsequent reaction depended on the number of halogens in the methyl group.

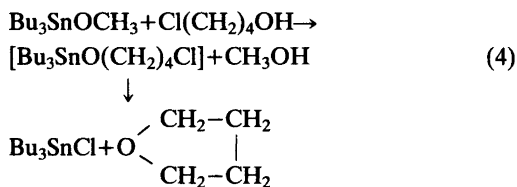
The versatility of organotin alkoxides in transesterification and related reactions is well known.¹ Exchange of the acyl group in an ester can be accomplished, *e.g.*, by reactions (1) and (2).



An explanation for the ability of organotin alkoxides to promote ester exchange is the fact that an alkoxy group attached to tin is in rapid exchange between different tin sites. The rate of the exchange depends largely on the size of the alkoxy group. Thus it has been found that the rate for tributyltin methoxide at -20°C is of the same order as that for tributyltin 2-propoxide at a temperature above 160°C .² It has also been proposed that the transesterification would be an addition–elimination process³ which leaves the most slowly exchanging group attached to tin, reaction (3).



Most of the known organotin alkoxides have no halogens attached to the alkoxy group. Delmond *et al.* have shown that also stable alkoxides containing 2-halogens in the alkoxy group can be prepared from tributyltin ethoxide and 2-haloalcohols.⁴ These alkoxides react intramolecularly at $70\text{--}210^\circ\text{C}$ giving principally epoxides. Tributyltin 3-bromoalkoxides undergo a similar reaction at 170°C giving oxetanes in an 80–90 % yield.⁵ On the contrary, tributyltin methoxide gives with 4-chlorobutanol no isolable tributyltin alkoxide, but directly tributyltin chloride and tetrahydrofuran.⁶ Yet, the reaction intermediate is found to be tributyltin 4-chlorobutoxide, reaction (4).



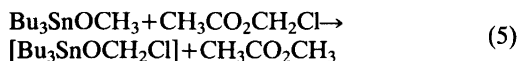
In general, however, quite little is known about reactions of organotin alkoxides with halogenated esters. We have found when attempt-

ing to prepare chloromethyl esters *via* reactions (1) and (2) that no transesterification took place. This led us to study the effect of halogens in methyl esters on the reaction with tributyltin methoxide.

RESULTS AND DISCUSSION

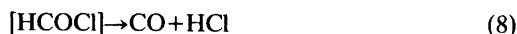
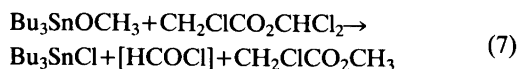
Three chloromethyl esters ($\text{CH}_3\text{CO}_2\text{CH}_2\text{Cl}$, $\text{CH}_2\text{ClCO}_2\text{CHCl}_2$ and $\text{CCl}_3\text{CO}_2\text{CCl}_3$) were allowed to react with tributyltin methoxide. These esters have different acyl groups but, according to our results, the acyl group is unreactive towards tributyltin methoxide, the reaction instead taking place on the alkoxy group. This was confirmed by studying the reaction between tributyltin methoxide and ethyl chloroformate or ethyl trichloroacetate. In both cases the only reaction was transesterification to an extent of 45–50 %. No formation of tributyltin chloride, and thus no reaction of tributyltin methoxide with the halogens in the acyl group, could be detected.

The reaction of tributyltin methoxide with chloromethyl acetate gave tributyltin chloride, methyl acetate and paraformaldehyde. The formation of methyl acetate suggests that transesterification is the first stage in this reaction. Another product would then be tributyltin chloromethoxide, which decomposes rapidly to tributyltin chloride and formaldehyde, reactions (5) and (6).



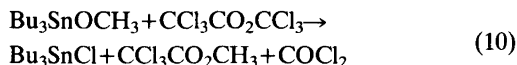
We were not able to detect the presence of tributyltin chloromethoxide by the ^1H NMR spectrum obtained immediately after mixing the reagents, and it could not be trapped with trimethylchlorosilane either. Further, reactions (1) and (2) gave no positive results in attempts to synthesize other chloromethyl esters. This suggests that tributyltin chloromethoxide is a very short-lived species if it exists at all. This instability compared with corresponding 2- and 3-haloalkoxides is, however, in accord with the observed dependence of exchange rates on the size of the alkoxy group.

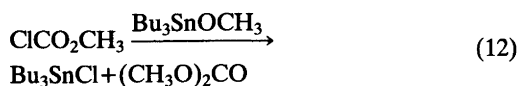
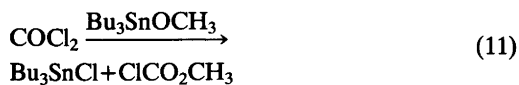
The reaction of tributyltin methoxide with dichloromethyl chloroacetate (molar ratio 2:1, see experimental part) produced methanol and carbon monoxide in addition to tributyltin chloride and methyl chloroacetate. Now the first products from the reaction of equimolar amounts of starting materials appear to be, disregarding the possible existence of tributyltin dichloromethoxide, tributyltin chloride, methyl chloroacetate, and formyl chloride which further decomposes to hydrogen chloride and carbon monoxide, reactions (7) and (8). The reaction of hydrogen chloride with another mol of tributyltin methoxide finally yields tributyltin chloride and methanol, reaction (9).



Traces of water found in some experiments may then come from reaction of methanol with hydrogen chloride. Formyl chloride could, in principle, react with tributyltin methoxide too. However, no methyl formate from such a reaction was detected. This is probably due to the fact that formyl chloride decomposes much faster than it reacts with alkoxide.

Tributyltin methoxide reacted with trichloromethyl trichloroacetate (molar ratio 3:1, see experimental part) forming methyl trichloroacetate, tributyltin chloride, and dimethyl carbonate. Equimolar amounts of reagents produced some methyl chloroformate in addition to dimethyl carbonate. This indicates that the first reaction product is carbonyl chloride, which can react further with tributyltin methoxide forming tributyltin chloride and methyl chloroformate, reactions (10) and (11). According to Röse,⁷ methyl chloroformate forms dimethyl carbonate and hydrogen chloride with methanol. In this case tributyltin methoxide can serve as a source of the alkoxy group, thus the final products are tributyltin chloride and dimethyl carbonate, reaction (12).





In the light of the reactions studied it seems obvious that organotin alkoxides containing 1-halogens are not sufficiently stable to be used as a source of chloromethoxy groups. Possible explanations for this instability may be, in addition to steric reasons, the greater exchange ratio of the chloromethoxy group compared to 2- and 3-haloalkoxy groups. These considerations do not, however, explain the instability of tributyltin 4-chlorobutoxide, which indicates that also other factors have to be present.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 180 IR spectrometer, and ^1H NMR spectra were obtained on a Jeol JNM-PMX 60 spectrometer in CCl_4 .

Chloromethyl acetate,⁸ dichloromethyl chloroacetate,⁹ trichloromethyl trichloroacetate⁸ and tributyltin methoxide² were prepared according to procedures described in the literature. The purity of reagents was checked by ^1H NMR and IR spectroscopy or by GLC using a 25 m silica capillary column coated with OV 101 or OV 17 liquid phase. The products formed in the reactions studied were characterized by physical constants and by comparing their IR and NMR spectra with those of authentic samples.

Reaction of tributyltin methoxide with chloromethyl acetate. Tributyltin methoxide (3.47 g, 10.8 mmol) and chloromethyl acetate (1.18 g, 10.9 mmol) were mixed. After mixing, there was no apparent change but the NMR spectrum showed that the signals of initial reagents had disappeared. Heating at 90 °C for an hour yielded a white stiff substance. Part of this was soluble in carbon tetrachloride, and the NMR spectrum revealed that it consisted of tributyltin chloride (δ 0.7–2.0) and methyl acetate (δ 1.98 and 3.65). The insoluble solid component proved to be paraformaldehyde. Distillation of the mixture at 10 Pa gave tributyltin chloride, b.p. 83–85 °C, and methyl acetate and paraformaldehyde, which were collected in the cold trap. The reaction took place in a similar way when

chloromethyl acetate was replaced by chloromethyl propanoate or 2-methylpropanoate.

Reaction of tributyltin methoxide with dichloromethyl chloroacetate. A preliminary experiment with equimolar amounts of starting materials showed that dichloromethyl chloroacetate reacted only partially. It was consumed totally when the amount of tributyltin methoxide was doubled.

The ester (1.50 g, 8.46 mmol) was placed in a flask equipped with a stirrer, a pressure-equalizing dropping funnel and a gas-collecting device. Tributyltin methoxide (5.42 g, 16.9 mmol) was added slowly from the dropping funnel. The subsequent reaction was exothermic and the mixture frothed vigorously. The IR spectrum of the collected gas showed absorption at 2140 cm^{-1} which was assigned to carbon monoxide. Collected volume (NTP) was 184 cm^3 (97 %). The NMR spectrum of the remaining liquid showed a broad absorption at δ 0.7–2.0 assigned to tributyltin chloride, and singlets δ 2.05, 2.35 (methanol), 3.77 and 3.97 (methyl chloroacetate). The samples obtained by fractional distillation were further characterized by methods described above. A trace of water was occasionally present in duplicate experiments.

Reaction of tributyltin methoxide with trichloromethyl trichloroacetate. When equimolar amounts of tributyltin methoxide and trichloromethyl trichloroacetate were mixed, the analysis of the resulted mixture revealed that it consisted of tributyltin chloride, methyl trichloroacetate, methyl chloroformate and unreacted trichloromethyl trichloroacetate. Hence, the amount of tributyltin methoxide was increased until all starting ester was consumed. In a second experiment, tributyltin methoxide (7.52 g, 23.4 mmol) was added during 15 min to the melted ester (2.20 g, 7.82 mmol). After the exothermic reaction had ceased, NMR analysis of the mixture showed that it consisted of tributyltin chloride (δ 0.7–2.0), dimethyl carbonate (δ 3.73), and methyl trichloroacetate (δ 3.99). Examination of the samples obtained by fractional distillation confirmed the analysis.

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