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DIORGANOTIN OXIDE/CARBOXYLIC ESTER REACTIONS*

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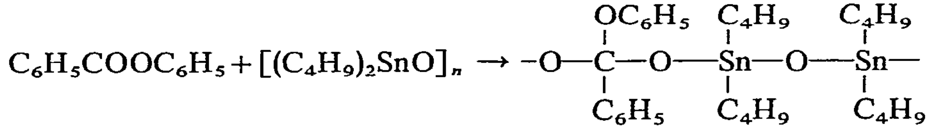
SUMMARY

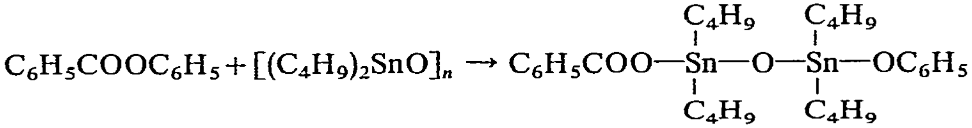
Di-n-butylin oxide dimer and phenyl benzoate react to give 1/1 as well as the reported 2/1 adducts. The reaction of equimolar amounts of each reactant yields phenoxydi-n-butyltin benzoate and is believed to proceed by cleavage followed by insertion of the organotin oxide into the carboxylic group of the ester. Butyl thiobenzoate and di-n-butyltin oxide react similarly to form (butylthio)di-n-butyltin benzoate.

Only the 2/1 addition products of organotin oxides with carboxylic esters were reported in the past[1]. The structure of an ortho acid derivative of eqn. (1) was assigned to them and molecular weight measurements indicated that they were predominantly polymeric[2].



$$C_6H_5COOC_6H_5 + [(C_4H_9)_2SnO]_n \rightarrow -O-\underset{C_6H_5}{\overset{OC_6H_5}{C}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}- \qquad (1)$$

Since bis(trialkyltin) oxides cleave carboxylic esters and lead to transesterifications[3], it was reasonable to believe that the reaction with a poly(dialkyltin oxide) could possibly proceed by cleavage followed by the insertion of the oxide into the carboxyl group (eqn. 2).



$$C_6H_5COOC_6H_5 + [(C_4H_9)_2SnO]_n \rightarrow C_6H_5COO-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-OC_6H_5 \qquad (2)$$

Such a hypothesis was difficult to substantiate experimentally because the products of both eqns. (1) and (2) would be titratable with potassium hydroxide, thus making a differentiation impossible. Also, both structures would imply the reaction of more than two moles of oxide per mole of ester but the infrared spectra of these compounds lack the strong 560–580 cm^{-1} absorptions, characteristic of repetitive Sn–O–Sn–O groups[4].

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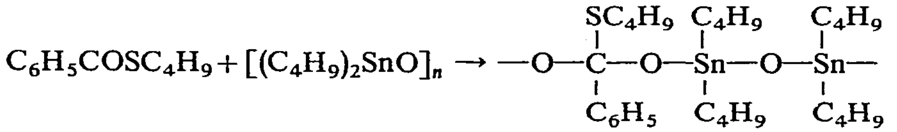
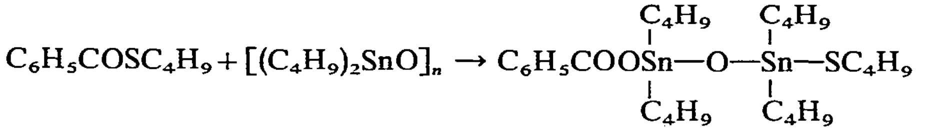
We have found that up to two moles of poly(dibutyltin oxide) easily dissolve and react with one mole of butyl thiobenzoate. If the general action for the carboxylic ester and the thioester is similar, then it becomes easier to differentiate experimentally between the two possible structures of eqns. (3) and (4).



$$C_6H_5COSC_4H_9 + [(C_4H_9)_2SnO]_n \rightarrow -O-\underset{C_6H_5}{\overset{SC_4H_9}{C}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}- \quad (3)$$



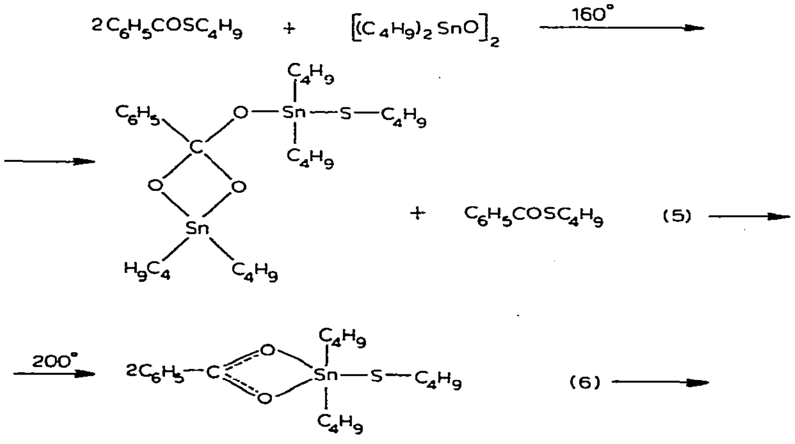
$$C_6H_5COSC_4H_9 + [(C_4H_9)_2SnO]_n \rightarrow C_6H_5COO\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-SC_4H_9 \quad (4)$$

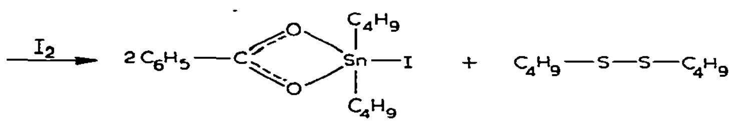
The product of eqn. (4) contains a tin–sulfur bond titratable with iodine or potassium iodate[5], whereas the product of eqn. (3) would not be expected to oxidize easily (butyl thiobenzoate cannot be titrated with iodine at room temperature).

In an attempt to prepare a 1/1 organotin oxide/ester adduct we allowed equimolar amounts of butyl thiobenzoate and dimeric di-n-butyltin oxide to react. The progress of the reactions was monitored by infrared spectroscopy.

At 160°, the clear solution contained a substantial amount of the 2/1 adduct, as evidenced by strong absorptions at 1540 and 1600 cm^{-1} characteristic of organotin carboxylates[6], but free unreacted thio ester (1200, 1660 and 1720 cm^{-1}) also was present. The new, strong absorption at 625 cm^{-1} is characteristic of the 2/1 reaction product and can reasonably be associated with O–Sn–O groups in which two different oxygens are linked to the same tin atom[7]. At a reaction temperature of 200°, the absorption at 625 cm^{-1} as well as the absorptions characteristic of the thio ester disappeared and an iodometric titration indicated the formation of quantitative amounts of the 1/1 adduct (eqn. 7).

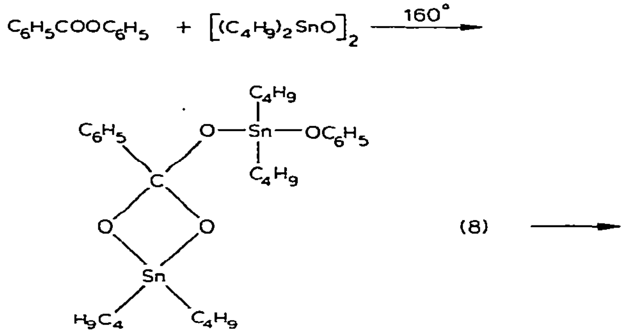
These results seem to show that in a first step only one di-n-butyltin oxide inserts while the other remains covalently bound to the carboxyl carbon, thus leaving half of the thio ester unreacted and recoverable (eqn. 5). Further heating leads to the pentacoordinated organotin thio ester of eqn. (6).





(7)

Phenyl benzoate reacts similarly with di-n-butyltin oxide dimer. The 1/1 adduct can be obtained easily by decomposition of the 2/1 adduct at 230° (eqns. 8 and 9).



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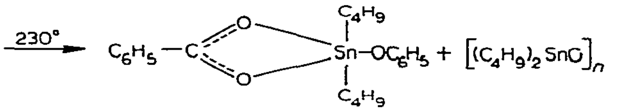

(9)

The strong absorption at 635 cm^{-1} characteristic of the 2/1 adduct is replaced by one at 610 cm^{-1} for the 1/1 insertion compound. Such an absorption is to be expected of a compound containing an $Sn-OC_6H_5$ group[8,9]. The two strong absorptions at 1560 and 1600 cm^{-1} are in accordance with the reported vibrations characteristic of covalent organotin esters with a pentacoordinated tin atom[10]. All reaction products were isolated by molecular distillation and found to be monomeric in benzene solution.

EXPERIMENTAL

Di-n-butyltin oxide dimer

A 30% aq. soln. of ammonia (130 g) was added to 500 ml of water. Under agitation and at 50°, 304 g of recrystallized di-n-butyltin dichloride was added slowly over a period of 30 min. The reaction mixture was maintained at 100° under agitation for 1 h. After filtration, the di-n-butyltin oxide obtained was dissolved in 2000 ml of toluene and dehydrated by azeotropic distillation. It was recrystallized from the same solvent and the molecular weight was determined in freezing benzene (found 449, calcd. 498).

Di-n-butyltin oxide/butyl thiobenzoate reaction

The 1/1 adduct was obtained by adding slowly 19.4 g of freshly distilled butyl thiobenzoate to a solution of 25 g of di-n-butyltin oxide dimer in 200 ml of toluene refluxing under nitrogen. The temperature was increased slowly to 190° and the reaction progress was monitored either by infrared analysis until elimination of the absorptions characteristic of the thiocarboxylic ester (1725, 1670 and 1205 cm^{-1}) or by iodine titration of the organotin mercaptide group[5]. Molecular distillation of the resulting product yielded 40 g of the pure 1/1 insertion compound, b.p. 215° decomp., n_D^{20} 1.5294. (Found: C, 51.49; H, 7.16; O, 7.20; S, 7.18; Sn, 26.76; mol. wt., 461. $C_{19}H_{32}O_2SSn$ calcd.: C, 51.51; H, 7.26; O, 7.22; S, 7.22; Sn, 26.79%; mol. wt., 443.)

Di-n-butyltin oxide/phenyl benzoate reaction

Following the general procedure above, 20 g of phenyl benzoate was treated with 25 g of di-n-butyltin oxide dimer in 200 ml of toluene. The reaction mixture was kept at 200° until complete disappearance of the carbonyl vibration at 1740 cm^{-1}. Pure, colorless 1/1 adduct (37 g) was obtained by molecular distillation, b.p. 250° decomp., n_D^{20} 1.5542. (Found: C, 56.30; H, 6.27; O, 10.81; Sn, 26.62; mol. wt., 471. $C_{21}H_{28}O_3Sn$ calcd.: C, 56.42; H, 6.30; O, 10.73; Sn, 26.55%; mol. wt., 447.)

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