Preliminary communication

SOME REACTIONS OF DIALKYLTIN OXIDES WITH ACETYL CHLORIDE AND TRIMETHYLCHLOROSILANE

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Summary

Dialkyltin oxides react with acetyl chloride to give $R_2 SnClOAc$ or $R_2 SnCl_2$, depending on the stoichiometry, and with $Me_3 SiCl$ to give $(ClR_2 Sn)_2 O$.

It has been shown that dimethyltin dichloride reacts with acetic anhydride or glacial acetic acid to give dimethyltin chloride acetate [1] and that the reactions of various *sym*-(dichlorotetraalkyl)distannoxanes with acetic acid also give the corresponding chloride acetates [2].

Such chloride acetates now have been prepared by the reaction of dialkyltin oxide with an equimolar amount of acetyl chloride. Upon further addition of acetyl chloride, the dialkyltin chloride acetates were converted into the corresponding dichlorides. These also were easily formed from the oxides and a large excess of acetyl chloride.

$R_2 SnO + AcCl \longrightarrow R_2 SnClOAc$

excess AcCl

$\downarrow$ AcCl

$\longrightarrow R_2 SnCl_2$
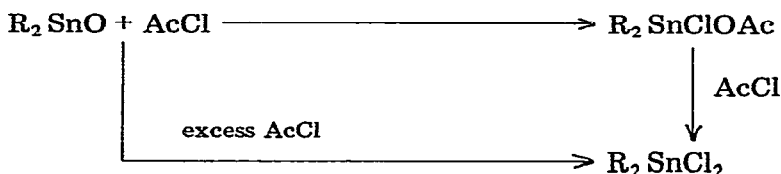
$(R = CH_3, C_2 H_5, n\text{-}C_3 H_7, n\text{-}C_4 H_9, n\text{-}C_8 H_{17})$

It was found that the rate of digestion of dialkyltin oxides in acetyl chloride followed the sequence $CH_3 < C_2 H_5 < n\text{-}C_3 H_7 < n\text{-}C_4 H_9 < n\text{-}C_8 H_{17}$ for alkyl groups.

Similar treatment of dialkyltin oxides with organic halides such as ethyl bromide, t-butyl chloride, allyl chloride and benzyl chloride resulted in recovery of the starting materials.

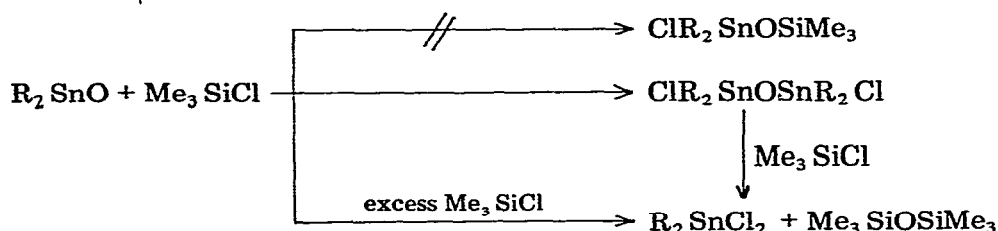Unlike the case with acetyl chloride, the reaction of dialkyltin oxides

TABLE 1

REACTIONS BETWEEN DIALKYLTIN OXIDES AND HALIDES

| Reactants R₂SnO (g)	Halide (g)	Product	M.p. (°C) Found (Lit.)	Yield (g(%))	Analysis (%) Found (calcd.)				Mol.wt. Found (calcd.)
					Sn	C	H	Cl	
R = Me (4)	AcCl 1.9	Me₂SnCl(OAc)	189-190 (189) [1]	4.6 (78)	48.81 (48.79)				
R = Me (4)	Me₃SiCl 2.6	(ClMe₂Sn)₂O	200 (—) [3]	3.3 (71)	61.74 (61.75)				
R = Et (2)	AcCl 0.8	Et₂SnCl(OAc)	93-94 (94) [2]	2.2 (80)	43.74 (43.75)				
R = Et (2)	Me₃SiCl 1.1	(ClEt₂Sn)₂O	174 (175.5) [4]	1.8 (79)	53.88 (53.88)				
R = n-Pr (2)	AcCl 0.7	Pr₂SnCl(OAc)	74-75 (73) [2]	2.2 (82)	39.72 (39.65)	31.92 (32.09)	5.75 (5.72)		316 (299)
R = n-Pr (2)	Me₃SiCl 1.0	(ClPr₂Sn)₂O	121-122 (122) [4]	2.0 (89)	47.82 (47.79)				
R = n-Bu (2)	AcCl 1.0	Bu₂SnCl(OAc)	65-66 (61) [2]	3.3 (84)	36.48 (36.25)	36.39 (36.65)	6.54 (6.49)	10.84 (10.83)	351 (327)
R = n-Bu (3)	Me₃SiCl 1.3	(ClBu₂Sn)₂O	112-113 (111-112) [5]	2.8 (85)	42.90 (42.95)				
R = n-Oct (3)	AcCl 0.7	Oct₂SnCl(OAc)	76	3.2 (87)	26.97 (26.99)	48.96 (48.18)	8.60 (8.48)	8.03 (8.06)	443 (439)
R = n-Oct (3)	Me₃SiCl 0.9	(ClOct₂Sn)₂O	88-89	2.7 (84)	30.51 (30.54)	49.27 (49.45)	9.90 (8.82)	8.65 (9.12)	1500 [a] (777)

[a] As dimer.

with an equimolar quantity of trimethylchlorosilane did not give the expected trimethylsilyldialkylstannoxanes. Instead, *sym*-(dichlorotetraalkyl)distannoxanes were formed. The resulting distannoxanes were converted to dialkyltin dichlorides by further addition of trimethylchlorosilane. A large excess of trimethylchlorosilane, of course, converted the dialkyltin oxides directly to the dialkyltin dichlorides.

$$R_2SnO + Me_3SiCl \nrightarrow ClR_2SnOSiMe_3$$
$$R_2SnO + Me_3SiCl \rightarrow ClR_2SnOSnR_2Cl \xrightarrow{Me_3SiCl} R_2SnCl_2 + Me_3SiOSiMe_3$$
$$R_2SnO + Me_3SiCl \xrightarrow{\text{excess } Me_3SiCl} R_2SnCl_2 + Me_3SiOSiMe_3$$

$(R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, n\text{-}C_8H_{17})$

It was confirmed that in the early stages of this reaction the dialkyltin dichlorides existed in a liquid layer of the reaction mixture. A possible explanation of the formation of the distannoxane is the reaction between initially produced dichloride and the unreacted oxide. Evidence for this was provided by our finding that equimolar quantities of dialkyltin dichloride and dialkyltin oxide react quantitatively to yield the distannoxane. Thus the reaction steps for the formation of *sym*-(dichlorotetraalkyl)distannoxane are:

$$R_2SnO + 2 Me_3SiCl \longrightarrow R_2SnCl_2 + Me_3SiOSiMe_3$$

$$R_2SnCl_2 + R_2SnO \longrightarrow ClR_2SnOSnR_2Cl$$
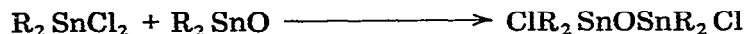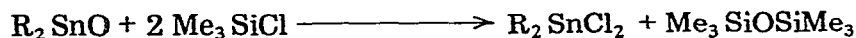
Typical examples are shown in Table 1 (the octyl derivatives are new compounds)

Acetyl chloride and dialkyltin oxides reacted exothermally when they were mixed in chloroform. On the other hand, since trimethylchlorosilane and the oxides did not react smoothly under the same conditions, they were heated at reflux until the oxide dissolved. The solvent then was removed under reduced pressure and the dialkyltin chloride acetates or *sym*-(dichlorotetraalkyl)distannoxanes were recrystallized from petroleum ether. They were characterized by m.p., analysis and, in some cases, by molecular weight determination.

References

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