Journal of Organometallic Chemistry, 99 (1975) C44—C46

Preliminary communication

SOME REACTIONS OF DIALKYLTIN OXIDES WITH ACETYL CHLORIDE AND TRIMETHYLCHLOROSILANE

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(Received August 8th, 1975)

Summary

Dialkyltin oxides react with acetyl chloride to give $R_2SnClOAc$ or R_2SnCl_2, depending on the stoichiometry, and with Me_3SiCl to give $(ClR_2Sn)_2O$.

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.

$$\begin{tikzcd}
R_2SnO + AcCl \arrow[r] \arrow[dr, "\text{excess AcCl}"'] & R_2SnClOAc \arrow[d, "AcCl"] \\
& R_2SnCl_2
\end{tikzcd}$$

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

It was found that the rate of digestion of dialkyltin oxides in acetyl chloride followed the sequence $CH_3 < C_2H_5 < n\text{-}C_3H_7 < n\text{-}C_4H_9 < n\text{-}C_8H_{17}$ 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

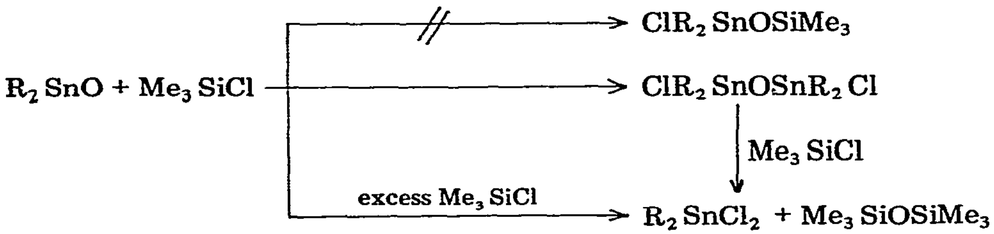
TABLE 1

REACTIONS BETWEEN DIALKYLTIN OXIDES AND HALIDES

Reactants		Product	M.p. (°C) Found (Lit.)	Yield (g(%))	Analysis (%) Found (calcd.)				Mol.wt. Found (calcd.)
R_2SnO (g)	Halide (g)				Sn	C	H	Cl	
R = Me	AcCl	$Me_2SnCl(OAc)$	189-190	4.6	48.81				
(4)	1.9		(189) [1]	(78)	(48.79)				
R = Me	Me_3SiCl	$(ClMe_2Sn)_2O$	200	3.3	61.74				
(4)	2.6		(—) [3]	(71)	(61.75)				
R = Et	AcCl	$Et_2SnCl(OAc)$	93-94	2.2	43.74				
(2)	0.8		(94) [2]	(80)	(43.75)				
R = Et	Me_3SiCl	$(ClEt_2Sn)_2O$	174	1.8	53.88				
(2)	1.1		(175.5) [4]	(79)	(53.88)				
R = n-Pr	AcCl	$Pr_2SnCl(OAc)$	74-75	2.2	39.72	31.92	5.75		316
(2)	0.7		(73) [2]	(82)	(39.65)	(32.09)	(5.72)		(299)
R = n-Pr	Me_3SiCl	$(ClPr_2Sn)_2O$	121-122	2.0	47.82				
(2)	1.0		(122) [4]	(89)	(47.79)				
R = n-Bu	AcCl	$Bu_2SnCl(OAc)$	65-66	3.3	36.48	36.39	6.54	10.84	351
(3)	1.0		(61) [2]	(84)	(36.25)	(36.65)	(6.49)	(10.83)	(327)
R = n-Bu	Me_3SiCl	$(ClBu_2Sn)_2O$	112-113	2.8	42.90				
(3)	1.3		(111-112) [5]	(85)	(42.95)				
R = n-Oct	AcCl	$Oct_2SnCl(OAc)$	76	3.2	26.97	48.96	8.60	8.03	443
(3)	0.7			(87)	(26.99)	(48.18)	(8.48)	(8.06)	(439)
R = n-Oct	Me_3SiCl	$(ClOct_2Sn)_2O$	88-89	2.7	30.51	49.27	8.90	8.65	1500 [a]
(3)	0.9			(84)	(30.54)	(49.45)	(8.82)	(9.12)	(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.



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

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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