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ORGANIC DERIVATIVES OF TIN

I. REACTIONS OF TRIBUTYLTIN ALKOXIDES WITH AMIDES

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Summary

Reactions of tributyltin isopropoxide and ethoxide with amides ($RCONH_2$) in different molar ratios yield products of the type $RCONH_{2-x}(SnBu_3)_x$ ($R = CH_3$; CH_2; CH; C_6H_5 and $x = 1, 2$). These derivatives are volatile with the exception of the benzamide derivatives, which decompose on being heated to ~210°C under vacuum. The structures of the compounds are discussed in the light of their physical and chemical properties.

Introduction

Some alkyltin alkoxides have been synthesized in our laboratories in recent years [1]. In view of the interesting results obtained in the reactions of alkyltin alkoxides with alkanol amines and related derivatives [1], it was thought worthwhile to study the reactions of these alkoxides with amides. Except for the reaction of triethyltin methoxide with (thio)acylamides and (thio)carbamates [2], no previous work appears to have been carried out in this field.

Results and discussion

Tributyltin isopropoxide reacts with a variety of amides ($RCONH_2$) in different molar ratios to give products of the type $RCONH_{2-x}(SnBu_3)_x$:

$$x\mathrm{Bu_3Sn(OPr\text{-}i)} + \mathrm{H_2NCOR} \xrightleftharpoons{C_6H_6} \mathrm{RCONH_{2-x}(SnBu_3)_x} + x\mathrm{Pr\text{-}i\text{-}OH}$$

($R = CH_3$; $CH_2{=}CH$; C_6H_5 and $x = 1, 2$)

As the reactions are slow, they have to be pushed to completion by distilling off the liberated isopropanol azeotropically with benzene. The progress of the reactions was followed by determining the isopropanol liberated. Even under these conditions, the reactions require a long time for completion.

Since steric hindrance might be responsible for the slownes of the reaction tributyltin ethoxide was similarly treated with acetamide in 1/1 or 2/1 molar ratio, but the reactions were almost equally slow.

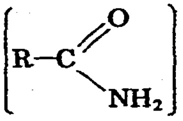
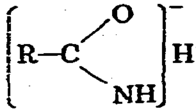
All products are colourless liquids except for the benzamide derivative (A), which is a low melting solid. They are hygroscopic and soluble in common organic solvents. Except for the benzamide derivatives, they were purified by distillation in vacuum. The mono-substituted benzamide derivative A was purified by crystallisation from benzene. All the products were monomeric.

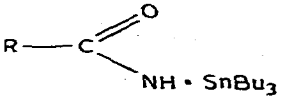
The reverse reaction of the benzamide derivative A with isopropanol is very fast:

$$\underset{(A)}{C_6H_5CONH \cdot SnBu_3} + \underset{(excess)}{i\text{-}PrOH} \xrightarrow{C_6H_6} Bu_3Sn(OPr\text{-}i) + C_6H_5CONH_2$$

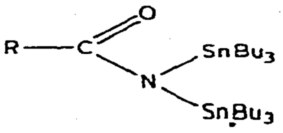
The derivative A also reacts with butanethiol:

$$\underset{(A)}{C_6H_5CONH \cdot SnBu_3} + BuSH \xrightarrow{C_6H_6} Bu_3Sn(SBu) + C_6H_5CONH_2$$

The free amides can in principle exist in ketonic  or enolic  H⁺ forms. All the amides show a strong absorption band near 1650 cm^{-1}. From the presence of this band in N,N-disubstituted amides and the shifts shown in its position on substitution by electrophilic groups on the nitrogen atom, this absorption has been ascribed to the C=O rather than to the C=N group [3] in the amides. Comparisons of IR spectra of the free amides and our mono- as well as the di-tributyltin substituted derivatives show that the position and nature of this band are very similar to those in the parent amides. This suggests that in both the mono and di derivatives, the substitution is at the NH_2 group:



(I)



(II)

Pump and Rochow [4], concluded from PMR studies that a number of bis-(trimethylsilyl)amides had *N*-silylsilylimidate structure. Klebe and coworkers [5], on the other hand, concluded from their PMR studies that in both mono- and bis-(trimethylsilyl)-substituted ureas the substitution is at the NH_2 group. Similarly, in their study of the products of the reactions of trimethyltin methoxide with acylamides and the thiocylamides. Noltes [2] concluded that the bonding of tin is through nitrogen in the acylamides but through sulphur in the thio analogues.

In corroboration of our conclusion, the mono-substituted derivatives I show a weak absorption due to ν(NH) near 3350 cm^{-1} but this disappears in the di-substituted derivatives II, confirming complete replacement of both the hydrogen atoms of the amido group.

The high reactivity of both types of products I and II with isopropanol and butanethiol is consistent with the conclusion that the bonding in these derivatives is through nitrogen rather than oxygen.

Experimental

Stringent precautions were taken to exclude moisture. Benzene was dried over sodium and finally azeotropically with ethanol. Amides were distilled before use.

Molecular weights were determined ebulliometrically using thermistor sensing in boiling benzene. Infrared spectra were recorded with neat samples on a Perkin—Elmer 621 grating spectrophotometer. Tin was estimated as oxide after ignition. Nitrogen was estimated by the Kjeldahl method.

(1) Reaction between $Bu_3Sn(OPr\text{-}i)$ and CH_3CONH_2 in 2/1 molar ratio

A mixture of $Bu_3Sn(OPr\text{-}i)$ (2.89 g, 8.29 mmol) and CH_3CONH_2 (0.245 g, 4.15 mmol) in benzene (ca. 70 ml) was refluxed (bath temperature 100°C) for about 8 h and the isopropanol was collected azeotropically. The alcohol estimation showed that the reaction was not complete. Hence, ca. 50 ml more benzene was added and the mixture was refluxed for about 6 h more with collection of the azeotrope. The process was repeated till the distillate showed no alcohol content. The excess of solvent was then removed in vacuum. The colourless liquid obtained was then distilled under vacuum at 165°C/0.8 mmHg. (Yield 88%, 2.33 g).

Analyses: Azeotrope-found: 0.45 g; calcd. (for 2 mol): 0.50 g; found: N, 2.18; Sn, 36.90. $CH_3CON(SnBu_3)_2$ calcd.: N, 2.20; Sn, 37.26%.

The products obtained from analogous reactions of $Bu_3Sn(OPr\text{-}i)$ with CH_3CONH_2, $CH_2{=}CH \cdot CONH_2$, $C_6H_5CONH_2$ and $CH_3CONH \cdot CH_3$, in different molar ratios, are listed in Table 1.

(2) Reaction of $C_6H_5CONH \cdot SnBu_3$ with i-PrOH

To a solution of $C_6H_5CONH \cdot SnBu_3$ (0.603 g) in benzene (~7 ml), isopropanol (~5 ml) was added. The mixture was shaken, refluxed for about 1 h at 100°C bath temperature, then allowed to cool. The solid was separated by decantation and a liquid was obtained by evaporation of the solution. The two products were dried in vacuum. The analyses of the soluble portion and the solid corresponded to $Bu_3Sn(OPr\text{-}i)$ and $C_6H_5CONH_2$, respectively.

$Bu_3Sn(OPr\text{-}i)$: yield 0.509 g; calcd. 0.513 g; found: Sn, 33.92; calcd. 34.01%. $C_6H_5CONH_2$: found: N, 11.31; calcd. 11.58%.

(3) Reaction of $C_6H_5CONH \cdot SnBu_3$ with BuSH

To a solution of $C_6H_5CONH \cdot SnBu_3$ (0.610 g) in benzene (ca. 10 ml) was added BuSH (0.135 g). After heating and refluxing for about 1 h at a bath

TABLE 1

REACTIONS OF TRIBUTYLTIN ALKOXIDES WITH AMIDES

$Bu_3Sn(OR)$ (g)	Amide (g)	Molar ratio (Refluxing (h))	Alcohol liberated (g, found (calcd.))	Product formed [a]	B.p. (°C/mmHg) (% yield)	Analyses (found (calcd.) (%))		Mol. wt. (found (calcd.))
						Sn	N	
$Bu_3Sn(OPr\text{-}i)$ (2,069)	CH_3CONH_2 (0.347)	1/1 (68)	0,34 (0,35)	$CH_3CONHSnBu_3$	157/0,8 (98)	33,90 (34,10)	3,99 (4,02)	358 (348)
$Bu_3Sn(OEt)$ (2,051)	CH_3CONH_2 (0,360)	1/1 (68)	0,22 (0,28)	$CH_3CONHSnBu_3$	151/0,5 (96)	33,96 (34,10)	3,96 (4,02)	— (348)
$Bu_3Sn(OPr\text{-}i)$ (2,895)	CH_3CONH_2 (0,245)	2/1 (68)	0,45 (0,50)	$CH_3CON(SnBu_3)_2$	165/0,8 (88)	36,90 (37,20)	2,18 (2,20)	632 (637)
$Bu_3Sn(OEt)$ (2,184)	CH_3CONH_2 (0,191)	2/1 (66)	0,26 (0,30)	$CH_3CON(SnBu_3)_2$	160/0,5 (87)	36,94 (37,26)	2,18 (2,20)	— (637)
$Bu_3Sn(OPr\text{-}i)$ (2,186)	$CH_2{=}CHCONH_2$ (0,445)	1/1 (74)	0,32 (0,38)	$CH_2{=}CHCONHSnBu_3$	162/0,6 (67)	32,46 (32,96)	3,80 (3,89)	364 (360)
$Bu_3Sn(OPr\text{-}i)$ (2,442)	$CH_2{=}CHCONH_2$ (0,248)	2/1 (62)	0,38 (0,42)	$CH_2{=}CHCON(SnBu_3)_2$	163/0,6 (89)	36,40 (36,57)	2,17 (2,16)	662 (649)
$Bu_3Sn(OPr\text{-}i)$ (3,425)	$C_6H_5CONH_2$ (1.161)	1/1 (78)	0,47 (0,58)	$C_6H_5CONHSnBu_3$ [b]	decomp. ~210/0,5 (94)	28,56 (28,94)	3,44 (3,41)	370 (410)
$Bu_3Sn(OPr\text{-}i)$ (3,592)	$C_6H_5CONH_2$ (0.623)	2/1 (90)	0,60 (0,62)	$C_6H_5CON(SnBu_3)_2$	decomp. ~210/0,5 (94)	33,74 (33,95)	2,01 (2,00)	683 (699)
$Bu_3Sn(OPr\text{-}i)$ (3,790)	$CH_3CONHCH_3$ (0.791)	1/1 (86)	0,63 (0,65)	$CH_3CON(CH_3)SnBu_3$	158/0,8 (92)	32,67 (32,78)	3,81 (3,87)	358 (362)

[a] All the products are colourless liquids. [b] Colourless solid.

temperature of 100°C, the mixture was allowed to cool. The solid amide and the supernatant solution were separated by decantation and the two products obtained by drying in vacuum were analysed.

The analyses of the two portions are: From solution, $Bu_3Sn(SBu)$: Found: Sn, 30.89; calcd. 31.29%. Solid. $C_6H_5CONH_2$: Found: N, 11.42; calcd. 11.58%.

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