

A CONVENIENT SYNTHESIS OF (C₁-C₁₈) ALKYL TIN TRIHALIDES

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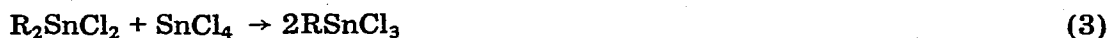
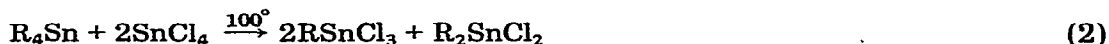
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Summary

Alkyltin trihalides with chain lengths up to eighteen carbon atoms can be readily prepared in high yields by the direct reaction of stannous halides with alkyl halides in the presence of trialkylantimony catalysts.

Introduction

Although known for over half a century, alkyltin trihalides are still difficult to make. In the commonly used redistribution reactions (eqns. 1 and 2), tri- or di-organotin halides, respectively, are formed as by-products. Reaction 3 only proceeds under special conditions, e.g. in the presence of a mixture of POCl₃ and P₂O₅ [1].



A more direct approach involves the reaction of stannous halides with alkyl halides (eqn. 4). However, except for the reaction of methyl iodide with stannous iodide, which was reported to give about 25% of methyltin triiodide at 160 °C [2], reactions of stannous bromide or chloride with alkyl bromides or chlorides do not proceed in the absence of catalysts [3]. A variety of catalysts have been reported in the patent literature, e.g. organic disulphides [4], primary amines [5], quaternary ammonium halides [6], phosphonium halides [7]. The rate of reaction 4 decreases rapidly in the order SnI₂ > SnBr₂ > SnCl₂, RI > RBr

> RCl and with increasing chain length of the alkyl group. The catalysts mentioned are insufficiently active for the synthesis of long-chain alkyltin trihalides (cf. ref. 7).



(R = alkyl; X, X' = halogen)

In the present paper we report our studies of the organoantimony-catalyzed synthesis of short- and long-chain alkyltin trihalides according to eqn. 4*.

Results

The results in Table 1 show that trialkylantimony compounds are very effective catalysts for the reaction of stannous halides with alkyl halides. The reactions were carried out without solvent, a 200% excess of alkyl halide being used to provide the reaction medium. The progress of the reaction can be monitored

TABLE 1
REACTION OF SnX_2 WITH RX' CATALYZED BY $\text{R}'_3\text{Sb}$
Molar ratio $\text{SnX}_2/\text{RX}' = 1/3$; catalyst concentration: 5 mole %

Expt. No.	SnX_2 X	RX'		$\text{R}'_3\text{Sb}$ R'	Reaction conditions		SnX_2 conversion (%)	$\text{RSnX}'\text{X}_2$ (%) ^a
		R	X'		t (h)	T (°C)		
1	Br	$\text{C}_{18}\text{H}_{37}$	Br	—	48	160	19	
2	Br	$\text{C}_{18}\text{H}_{37}$	Br	Oct	24	150	68 ^b	
					48	150	82.5 ^b	
					72	150	92.5	~100 ^c
3	Br	$\text{C}_{18}\text{H}_{37}$	Br	Bu	17	150	90	
4	Br	$\text{C}_{18}\text{H}_{37}$	Br	Et	10	150	97	100 ^c
5	Br	$\text{C}_{18}\text{H}_{37}$	Br	Bu	4	150	43	
6	Br	$\text{C}_{18}\text{H}_{37}$	Br	Et	4	150	69	
7	Br	$\text{C}_{18}\text{H}_{37}$	Br	Me	4	150	80	
8	Br	$\text{C}_{18}\text{H}_{37}$	Br	(Et_2SbBr)	48	150	53	
9	Br	$\text{C}_{18}\text{H}_{37}$	Br	Ph	48	150	23	
10	Br	$\text{C}_{12}\text{H}_{25}$	Br	Et	48	150	91	62 ^d
11	Br	Oct	Br	Oct	48	150	93	90 ^e
12	Br	C_5H_9	Br	Et	4	130 ^f	56	62 ^d
13	Br	Bu	Br	Bu	48	101 ^f	91	94 ^g
14	Br	Me	Br	Et	8	130	63	100 ^g
15	Br	Ph	Br	Et	15	160	0	
16	Br	Oct	Br	Et	18	150	97	93 ^c
17	Br	Oct	Cl	Et	48	150	78	
18	Cl	Oct	Br	Et	20	150	94	
19	Cl	Oct	Cl	Et	96	150	31	
20	Br	Bu	Br	Et	24	100 ^h	92.5	
21	Br	iso-Bu	Br	Et	24	100 ^h	4	

^a Isolated product yields based on the amount of SnX_2 converted. ^b Titrimetric determination of the ionic bromide present in solution. ^c RSnOOH . ^d RSnCl_3 (after treatment with NaOH and with HCl). ^e Determined by GLC analysis. ^f Reflux. ^g RSnBr_3 ^h Experiments in sealed tubes.

* For a preliminary account see ref. 8.

either by filtration of the residual stannous halide or by titrimetric determination of the ionic bromine present*.

Without a catalyst, reaction of 1-bromooctadecane with SnBr_2 gave <20% conversion after 48 h at 160°C (Expt. 1). In contrast, reaction catalyzed by 5 mole % of trioctylantimony (based on the amount of SnBr_2) gave after 24, 48 and 72 h at 150° , a SnBr_2 conversion of 68.5%, 82.5% and 92%, respectively (Expt. 2). Attempts to purify the very high boiling octadecyltin tribromide (b.p. $> 180^\circ\text{C}/5 \times 10^{-4}$ mmHg) resulted in extensive decomposition with the formation of SnBr_2 (the reverse of reaction 4). Treatment of the reaction mixture with aqueous sodium hydroxide gave a quantitative yield of the new octadecylstannonic acid (see Experimental).

Comparative experiments (Expts. 3-7) demonstrated that the catalytic activity of the trialkylantimony catalyst, R_3Sb , increases markedly with decreasing chain length of the alkyl groups: $\text{R} = \text{Oct} < \text{Bu} < \text{Et} < \text{Me}$. Dialkylantimony halides or triphenylantimony are much less effective catalysts than trialkylantimony compounds (cf. Expts. 4, 6, 8 and 9).

As regards the influence of the alkyl halide, RX , the reaction was found to be generally suitable for the synthesis of methyl- to octadecyl-tin trihalides (Expts. 9-14). The rate of the reaction again increases with decreasing chain length of the alkyl group. The high catalytic activity of the trialkylantimony compounds is demonstrated by the fact that with alkyl halides boiling around 100°C , satisfactory results are obtained under reflux conditions (Expts. 12, 13; atmospheric pressure). Even the reaction of methyl bromide gas with solid SnBr_2 catalyzed by triethylantimony at 130°C proceeds readily at atmospheric pressure (Expt. 14; cf. Experimental).

Alkyl bromides are more reactive than alkyl chlorides (cf. Expts. 16 and 17, 18 and 19). Furthermore, stannous bromide is more reactive than stannous chloride (cf. Expts. 17 and 19). However, the reaction rate seems to be determined largely by the type of halogen bound to carbon, rather than by the type of halogen bound to tin (cf. Expts. 16 and 18, 17 and 19).

Bromobenzene failed to react with SnBr_2 after 15 h at 160°C in the presence of triethylantimony (Expt. 15).

Discussion

In the absence of more extensive experimental data a discussion of the mechanism of this heterogeneous reaction is necessarily speculative. Comparison of our results with the scanty information in the patent literature indicates that the most pronounced catalytic activity is found for the Group V Lewis bases R_3Z ($\text{Z} = \text{N}, \text{P}, \text{Sb}$). The activity seems to increase in the order $\text{N} < \text{P} < \text{Sb}$, that is with decreasing base strength of R_3Z .

Reaction of alkyl halides with organo-nitrogen and -phosphorus compounds gives the highly stable quaternary ammonium and phosphonium halides, which show very little tendency towards dissociation [9]. Oxidative addition of alkyl halides to trialkylantimony compounds to give stable tetraalkylstibonium

* Under the moderate conditions employed, monoalkyltin trihalides are the sole tin halides formed.

halides is only known to occur for the reaction of trimethylantimony with methyl halides. However, it is quite probable that other trialkylantimony compounds will reversibly form weak complexes with other alkyl halides, resulting in activation of the carbon-halogen bond, thereby facilitating a carbenoid-like insertion of the stannous halide into the carbon-halogen bond.



Decreasing the basicity of the organoantimony catalyst by introducing electron-attracting substituents (e.g. Et_2SbBr , Ph_3Sb) decreases the catalytic activity. The decrease in catalytic activity with increasing chain length of the alkyl bound to antimony may be accounted for by steric effects. The importance of steric effects in this reaction is demonstrated by the considerable difference in reactivity between butyl bromide and isobutyl bromide (Table 1, Expts. 20, 21).

Whether a polar or a free radical type mechanism operates in this reaction remains to be investigated. Our studies of the non-catalyzed oxidative addition reactions of dicyclopentadienylnitrogen(II) and of tin(II) bis(1,3-diketonates) with alkyl halides suggest the occurrence of a free-radical pathway [10].

It is clear that the reaction of stannous halides with alkyl halides catalyzed by trialkylantimony compounds offers a convenient synthesis for methyl- to octadecyl-tin trihalides. The applicability of this method to the preparation of functionally substituted alkyltin trihalides will be considered in a separate paper.

Experimental

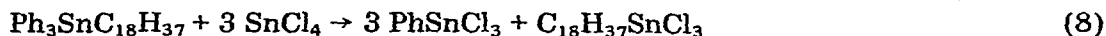
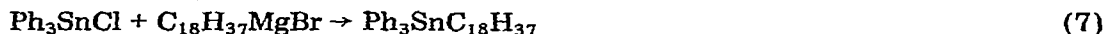
The reactions were performed under dry, oxygen-free nitrogen. Unless otherwise indicated the starting materials were prepared by published procedures or purchased. All materials were purified under nitrogen before use. Typical experiments are described below.

3. Reaction of SnBr_2 with $\text{C}_{18}\text{H}_{37}\text{Br}$ catalyzed by Oct_3Sb (Table 1, Expt. 2)

The synthesis of octadecylstannonic acid and of octadecyltin trichloride. A mixture of 7 g (25 mmol) of anhydrous SnBr_2 , 25 g (75 mmol) of $\text{C}_{18}\text{H}_{37}\text{Br}$ and 0.6 g (1.3 mmol) of Oct_3Sb was stirred for 72 h at 150°C (under nitrogen). After 24 h, 48 h and 72 h, respectively, a sample was taken, filtered and analyzed for ionic bromine (see Table 1). The reaction mixture was diluted with 150 ml of benzene and filtered to give 0.52 g (7.5%) of recovered SnBr_2 . The filtrate was refluxed for 2.5 h with 80 ml of 1 N aqueous sodium hydroxide. The white solid was filtered off, washed with benzene and with acetone and dried to give 7.95 g of octadecylstannonic acid. Treatment of the mother liquor with acetone gave another 1.75 g, bringing the total yield of octadecylstannonic acid to 9.7 g (100% based on the converted amount of SnBr_2). $\text{C}_{18}\text{H}_{37}\text{SnOOH}$: m.p. $65\text{--}66^\circ\text{C}$. (Anal.: Found: C, 53.3; H, 9.6; Sn, 29.8. Calcd.: C, 53.36; H, 9.45; Sn, 29.29%.)

Treatment of octadecylstannonic acid for 3 h with boiling 6 N HCl and subsequent distillation of the organic phase in high vacuum resulted in extensive thermolysis to give SnCl_2 .

A sample of pure octadecyltin trichloride was obtained by the reactions of eqns. 7 and 8.



$\text{Ph}_3\text{SnC}_{18}\text{H}_{37}$: m.p. 67-70°C. (Anal.: Found: Sn, 19.2. Calcd.: Sn, 19.67%.)

$\text{C}_{18}\text{H}_{37}\text{SnCl}_3$: b.p. ~110°C/5 × 10⁻⁴ mmHg; n_D^{20} 1.498. (Anal.: Found: Cl, 22.0. Calcd.: Cl, 22.23%.)

Reaction of SnBr₂ with C₁₂H₂₅Br catalyzed by Et₃Sb (Table 1, Expt. 10)

The synthesis of dodecylstannonic acid and of docecyltin trichloride. A mixture of 83.7 g (0.3 mol) of anhydrous SnBr₂, 205 g (0.82 mol) of C₁₂H₂₅Br and 2.5 g (0.015 mol) of Et₃Sb was stirred for 48 h at 150°C (under nitrogen). Filtration gave 7.5 g (9%) of unchanged SnBr₂. The excess of C₁₂H₂₅Br was recovered by distillation in vacuum (121 g) and the brown oily residue was refluxed with 1 litre of 1 N aqueous NaOH. Treatment of the resulting crude dodecylstannonic acid with 200 ml of concentrated hydrochloric acid and subsequent distillation of the organic phase in vacuum gave 73.2 g (62%) of pure dodecyltin trichloride. C₁₂H₂₅SnCl₃: b.p. 93-95°C/5 × 10⁻⁴ mmHg; n_D^{20} 1.4987. (Anal.: Found: C, 36.7; H, 6.4; Cl, 27.1. Calcd.: C, 36.55; H, 6.39; Cl, 26.9%.)

Reaction of dodecyltin trichloride with 1 N aqueous NaOH gave pure dodecylstannonic acid. C₁₂H₂₅SnOOH: m.p. >200°C. (Anal.: Found: Sn, 36.9. Calcd.: Sn, 36.97%.)

Reaction of SnBr₂ with BuBr catalyzed by Bu₃Sb (Table 1, Expt. 13)

A mixture of 3.5 g (12.5 mmol) of anhydrous SnBr₂, 5.5 g (37.5 mmol) of BuBr and 0.11 g (0.6 mmol) of Bu₃Sb was refluxed for 48 h. The mixture was diluted with 75 ml of benzene and filtered to give 0.3 g (9%) of recovered SnBr₂. GLC analysis of a methylated sample of the filtrate showed that only BuSnMe₃ was formed and no trace of Bu₂SnMe₂ or Bu₃SnMe was detected.

Evaporation of the filtrate gave 4.4 g (94%) of crude BuSnBr₃, n_D^{20} 1.5945 (lit. n_D^{20} 1.5952). (Anal.: Found: Sn, 29.27. Calcd.: Sn, 28.5%.)

Reaction of SnBr₂ with MeBr catalyzed by Et₃Sb (Table 1, Expt. 14)

In a reaction flask filled with nitrogen was placed 1.75 g (6.25 mmol) of anhydrous SnBr₂. The flask was evacuated and an atmosphere of methyl bromide gas was applied. After addition of 0.05 g (0.25 mmol) of Et₃Sb the mixture was stirred for 8 h at 130°C, a constant pressure (77 cm Hg) of methyl bromide being maintained. Extraction of the semi-solid mixture gave 0.65 g (37%) of unchanged SnBr₂. Evaporation of the benzene filtrate gave 1.5 g of crude MeSnBr₃, m.p. 47-50°C (lit. m.p. 53°C), a yield of 100% based on the amount of SnBr₂ consumed.

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