[Contribution from the Department of Chemistry, Drexel Institute of Technology]

ESTER EXCHANGE REACTIONS OF TRIALKYLTIN ESTERS AND MERCAPTIDES

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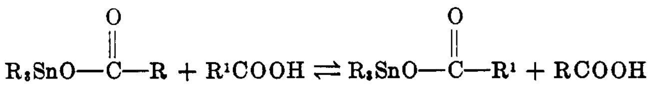
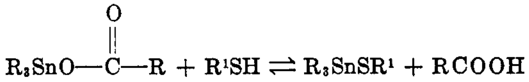
This paper presents ester exchange reactions of trialkyltin esters and mercaptides. Previous to this study there appeared in the literature several examples of ester exchange reactions of trialkyl germanium (1) and trialkyl silicon esters (2). Krause and Becker converted tri-cyclohexyltin fluoride into the acetate by treating the former compound with acetic acid (3).

This study of triethyltin and tri-*n*-propyltin esters and mercaptides shows that the following equilibria shift to the right when either RCOOH or RSH can be removed from the reaction mixture by fractional distillation.

1. 

$$R_3SnO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R + R^1COOH \rightleftharpoons R_3SnO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R^1 + RCOOH$$

2. $R_3SnSR + R^1SH \rightleftharpoons R_3SnSR^1 + RSH$

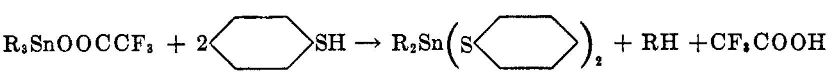
3. 

$$R_3SnO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R + R^1SH \rightleftharpoons R_3SnSR^1 + RCOOH$$

Eight tri-*n*-propyltin esters and mercaptides were prepared in essentially the same way as described in a previous paper (4). The tri-*n*-propyl derivatives are less thermally stable than the corresponding triethyltin derivatives. Reliable boiling points at atmospheric pressure could not be obtained, because these compounds decomposed badly upon being heated. The properties of tri-*n*-propyltin esters and mercaptides are summarized in Table I.

Eleven ester exchange reactions were successful. Triethyltin isopropyl mercaptide reacted partially with phenol, while triethyltin trifluoroacetate did not react at all with phenol. The results are summarized in Table II.

The reaction between tri-*n*-propyltin trifluoroacetate and benzenethiol surprisingly yielded di-*n*-propyltin diphenyl mercaptide:



EXPERIMENTAL

All melting points are corrected, and were determined by stirring a bulb thermometer immersed in the cooling molten compounds, and recording that temperature for melting points at which the compound partially solidified. All boiling points at 760 mm. pressure are corrected and were measured by the dynamic method.

Bis-(tri-n-propyltin) oxide. Three liters of 1.5 *molar* *n*-propylmagnesium chloride (4.5 moles) were added over a three hour period, with occasional shaking, to 390 g. of stannic chloride (1.5 moles) dissolved in 500 ml. of dry benzene immersed in an ice-water bath. The reaction mixture was allowed to stand overnight. After gradual decomposition of the unchanged *n*-propylmagnesium chloride with a 10% aqueous hydrochloric acid solution,

TABLE I
n-PROPYLTIN ESTERS

Compound	B.p., (1 mm.), °C.	M.P., °C.	d_4^{20}	n^{20}	Analyses					
					Mol. Wt.		Sulfur		Tin	
					Calc'd	Found	Calc'd	Found	Calc'd	Found
$(n\text{-}C_3H_7)_3Sn(CH_3COO)$	81–83	82			307	316			38.6	38.5
$(n\text{-}C_3H_7)_3Sn(C_6H_5COO)$	158–160	45–46			369	349			32.2	31.7
$(n\text{-}C_3H_7)_3Sn(p\text{-}CH_3C_6H_5S)$	157–159		1.2125	1.5516	372	367	8.65	8.7 8.8		
$(n\text{-}C_3H_7)_3Sn(CH_3CH_2COO)$	88–89	70			321	309			37.0	37.2
$(n\text{-}C_3H_7)_3Sn(CH_3CH_2CH_2COO)$	102–104	66			335	318			35.6	36.0
$(n\text{-}C_3H_7)_3Sn(C_6H_5O)$	145–147		1.2167	1.5284	341	316			34.8	34.5
$(n\text{-}C_3H_7)_3Sn(C_6H_5S)$	157–159		1.2373	1.5626	357	374	9.0	8.9 8.9		
$(n\text{-}C_3H_7)_2Sn(C_6H_5S)_2$	226–230			1.6298	423	405	15.12	14.9 15.1		
$(n\text{-}C_3H_7)_3Sn(CF_3COO)$	88–90	80			361	346			34.3	33.9

TABLE II
ESTER EXCHANGE REACTIONS

Reactants		Products	
$(C_2H_5)_3Sn(C_2H_5S)$	$i\text{-}C_3H_7SH$	$(C_2H_5)_3Sn(i\text{-}C_3H_7S)$	C_2H_5SH
$(C_2H_5)_3Sn(i\text{-}C_3H_7S)$	$(CH_3)_2\text{—}CHCH_2CH_2SH$	$(C_2H_5)_3Sn[(CH_3)_2CHCH_2CH_2S]$	$i\text{-}C_3H_7SH$
$(C_2H_5)_3Sn[(CH_3)_2CHCH_2CH_2S]$	$p\text{-}CH_3C_6H_4SH$	$(C_2H_5)_3Sn(p\text{-}CH_3C_6H_4S)$	$(CH_3)_2CHCH_2CH_2SH$
$(C_2H_5)_3Sn(C_2H_5S)$	$(CH_3)_2CHCH_2SH$	$(C_2H_5)_3Sn[(CH_3)_2CHCH_2S]$	C_2H_5SH
$(C_2H_5)_3Sn[(CH_3)_2CHCH_2S]$	C_6H_5OH	$(C_2H_5)_3Sn(C_6H_5O)$	$(CH_3)_2CHCH_2SH$
$(C_2H_5)_3Sn[(CH_3)_2CHCH_2S]$	H_2SO_4	$[(C_2H_5)_3Sn]_2SO_4$	$(CH_3)_2CHCH_2SH$
$(C_2H_5)_3Sn(p\text{-}CH_3C_6H_4S)$	H_2SO_4	$[(C_2H_5)_3Sn]_2SO_4$	$p\text{-}CH_3C_6H_4SH$
$(C_2H_5)_3Sn(i\text{-}C_3H_7S)$	CH_3COOH	$(C_2H_5)_3Sn(CH_3COO)$	$i\text{-}C_3H_7SH$
$(n\text{-}C_3H_7)_3Sn(CH_3COO)$	C_6H_5COOH	$(n\text{-}C_3H_7)_3Sn(C_6H_5COO)$	CH_3COOH
$(n\text{-}C_3H_7)_3Sn(CH_3CH_2COO)$	$p\text{-}CH_3C_6H_4SH$	$(n\text{-}C_3H_7)_3Sn(p\text{-}CH_3C_6H_4S)$	CH_3CH_2COOH
$n\text{-}(C_3H_7)_3Sn(CF_3COO)$	C_6H_5SH	$(n\text{-}C_3H_7)_2Sn(SC_6H_5)_2$	$CF_3COOH + C_3H_8$

the organotin layer was separated and shaken with 400 ml. of 3*M*. sodium hydroxide solution for 30 minutes to convert tri-*n*-propyltin chloride to bis-(tri-*n*-propyltin) oxide. The ether-benzene layer was separated from the aqueous layer, and the aqueous layer was extracted with 400 ml. of hexane. The organotin solution was then dried over sodium sulfate and the solvent was removed by distillation at atmospheric pressure. Distillation under 1 mm. pressure yielded 89 g. of crude tetra-*n*-propyltin at 80–135°. Further distillation under 1 mm. pressure yielded 69 g. of bis-(tri-*n*-propyltin) oxide boiling at 142–144°. Boiling point reported 195–198° at 21 mm. (5).

I. PREPARATION OF TRI-*n*-PROPYL ESTERS AND MERCAPTIDES

Tri-*n*-propyltin acetate, benzoate, propionate, butyrate, and trifluoroacetate. When 5.1 g. (0.001 mole) of bis-(tri-*n*-propyltin) oxide was mixed with 0.02 mole of the appropriate acid heat was evolved, and the esters precipitated almost immediately. After gentle heating under reflux for 15 minutes, water and the excess acid were removed by distillation. The esters then were distilled under dimmished pressure. The yields were essentially quantitative.

Tri-*n*-propyltin phenoxide and phenyl and *p*-tolyl mercaptides. When 5.1 g. (0.01 mole) of bis-(tri-*n*-propyltin) oxide was mixed with 0.011 mole of phenol or the appropriate mercaptan, heat was evolved and an emulsion formed. After heating under gentle reflux for 15 minutes, water and the excess reactants were removed by distillation. The products were then distilled at 1 mm.; the yields were essentially quantitative.

Analyses and properties of the compounds. Tri-*n*-propyltin acetate, benzoate, propionate, butyrate, and trifluoroacetate are white solids; the phenoxide and mercaptides are colorless liquids. Sulfur was determined by titration with standard iodine solution of an alcoholic solution of the mercaptide which was acidified with hydrochloric acid solution. Tin was determined as SnO_2 by the method of Kulmiz (6).

II. ESTER EXCHANGE REACTIONS

Triethyltin sulfate. When 1.24 g. (0.0042 mole) of triethyltin isobutyl mercaptide was mixed with 0.4 g. of 100% sulfuric acid, the sulfate was precipitated and isobutyl mercaptan distilled out of the reaction mixture.

Similarly, 1.34 g. (0.0041 mole) of triethyltin *p*-tolylmercaptide and 0.4 g. of 100% sulfuric acid also yielded triethyltin sulfate. The *p*-tolyl mercaptan was removed by distillation.

Triethyltin phenoxide. To 2.73 g. (0.0092 mole) of triethyltin isobutyl mercaptide was added a total of 0.952 g. (0.01 mole) of phenol in two approximately equal portions. The mixture was boiled under gentle reflux for ten minutes before and after the final addition of phenol. The isobutyl mercaptan was removed by distillation at 100 mm. after the first addition of phenol. Additional isobutyl mercaptan and excess phenol were removed by distillation after the second addition of phenol. Distillation at 1 mm. pressure yielded 2.4 g. of triethyltin phenoxide, boiling point 112–115°. The normal boiling point was found to be 259°. Reported boiling point is 260° (4).

Triethyltin acetate. Similarly when 1 g. (0.0167 mole) of glacial acetic acid was added to 3.678 g. (0.0131 mole) of triethyltin isopropyl mercaptide, isopropyl mercaptan was removed by distillation and the acetate was precipitated. Distillation yielded 2.1 g. of triethyltin acetate; the boiling range was 223–226°. The melting point was found to be 119°. The reported melting point is 119°, and the reported normal boiling point is 223° (4).

Tri-n-propyltin benzoate. In like manner, a mixture of 2.2 g. (0.0072 mole) of tri-*n*-propyltin acetate and 1.0 g. (0.0082 mole) of benzoic acid yielded acetic acid by distillation under 70 mm. pressure. Distillation under 1 mm. pressure yielded 1.4 g. of tri-*n*-propyltin benzoate at 158–162°; melting point 44–45°.

Triethyltin isopropyl mercaptide. Similarly 2.4 g. (0.0316 mole) of isopropyl mercaptan and 5.75 g. (0.0214 mole) of triethyltin ethyl mercaptide yielded ethyl mercaptan which was removed by distillation. Further distillation under 1 mm. pressure yielded 5.1 g. of product boiling at 78–80° (4).

Anal. Calc'd for $C_9H_{22}SSn$: S, 11.4. Found: S, 11.2.

Triethyltin isopentyl mercaptide. In like manner, a mixture of 2.3 g. (0.0221 mole) of isopentyl mercaptide and 4.7 g. (0.0167 mole) of triethyltin isopropyl mercaptide gave isopropyl mercaptan which was removed by distillation. Further distillation under 1 mm. pressure at 95–97° yielded 4.6 g. of triethyltin isopentyl mercaptide. The reported boiling point for this compound is 96° at 1 mm. (4). The product was further identified by titration with standard iodine solution.

Anal. Calc'd for $C_{11}H_{26}SSn$: S, 10.3. Found: S, 10.1.

Triethyltin isobutyl mercaptide. When 1.95 g. (0.0217 mole) of isobutyl mercaptan was added to 4.34 g. (0.0157 mole) of triethyltin ethyl mercaptide and the mixture was treated in the usual manner, ethyl mercaptan was removed by distillation. Further distillation under 1 mm. pressure at 84–86° yielded 4.0 g. of triethyltin isobutyl mercaptide. The normal boiling point of this compound was found to be 244°; the reported boiling point is 248° (4).

Triethyltin p-tolyl mercaptide. When a mixture of 1.38 g. (0.0103 mole) of *p*-tolyl mercaptan and 3.32 g. (0.0107 mole) of triethyltin isopentyl mercaptide was heated, isopentyl mercaptan was removed by distillation. Continued distillation under 1 mm. pressure yielded 2.65 g. of triethyltin *p*-tolyl mercaptide at 125–126°. The reported boiling point for this compound at 1 mm. pressure is 123–125°. The product was further identified by titration with standard iodine solution (4).

Anal. Calc'd for $C_{13}H_{22}SSn$: S, 9.7. Found: S, 9.6.

Tri-n-propyltin p-tolyl mercaptide. Similarly a mixture of 0.9 g. (0.0072 mole) of *p*-tolyl mercaptan and 2 g. (0.00624 mole) of tri-*n*-propyltin propionate yielded propionic acid which was removed by distillation. Continued distillation resulted in the isolation of tri-*n*-propyltin *p*-tolyl mercaptide. The yield of product boiling at 157–159° at 1 mm. was 1.2 g.

Anal. Calc'd for $C_{16}H_{28}SSn$: S, 8.6. Found: S, 8.8.

Di-n-propyltin diphenyl mercaptide. When a mixture of 1.23 g. (0.011 mole) of phenyl mercaptan and 3.7 g. (0.01 mole) of tri-*n*-propyltin trifluoroacetate was heated, trifluoroacetic acid was removed by distillation. Further distillation under 1 mm. pressure resulted in 1.8 g. of unchanged trifluoroacetate. Continued distillation yielded 1.1 g. of di-*n*-propyltin diphenyl mercaptide at 226–230° at 1 mm. See Table I for analysis and physical constants.

SUMMARY

1. Tri-*n*-propyltin mercaptides and esters were prepared.

2. Ester exchange reactions of triethyltin and tri-*n*-propyltin esters and mercaptides were studied.

PHILADELPHIA 4, PENNSYLVANIA

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