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DIRECT SYNTHESIS OF ORGANOTIN COMPOUNDS
IV*. REACTION OF BENZYL CHLORIDE WITH METALLIC TIN

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In a previous paper[1] it was reported that when benzyl chloride was treated with metallic tin powder suspended in toluene or water, di- or tribenzyltin chloride respectively, was produced. Depending only on the solvent used di- or tribenzyltin chloride was obtained preferentially under the similar reaction conditions.

Elucidation of the solvent effect of this direct synthesis of organotin compounds was undertaken, based on a newly developed method of analysis of benzyltin compounds.

The reactions of benzyl chloride with metallic tin were carried out in an autoclave with high speed rotatory stirrer using different kinds of solvents. Results of these experiments are summarized in Table 1.

TABLE 1

REACTION OF BENZYL CHLORIDE WITH TIN IN SOME SOLVENTS[a]

Solvent	*Reaction time (h)*	*Yield*[b]			
		Dibenzyltin dichloride		*Tribenzyltin chloride*	
Benzene	2	11.5 g	62%	1.4 g	10%
Benzene	4	11.0	59	2.8	20
Toluene	4	12.7	68	1.6	11
Diethyl ether	1	9.8	52	2.7	19
Diethyl ether	2	9.9	53	4.0	28
Diethyl ether	4	7.6	41	5.9	41
Diethyl ether	10	6.6	36	6.4	45
Tetrahydrofuran	4	7.0	38	7.0	49
Dioxane	4	6.1	33	7.3	51
Acetone	4	6.4	34	6.0	42
n-Butanol	4	0.6	3	8.7	61
Water	1	0.0	0	7.3	51[c]
Water	4	0.0	0	7.6	53[d]

[a] All reactions were carried out 0.10 mole of benzyl chloride and 0.10 g-atom of tin powder and 100 ml of solvent at 108–114° in an autoclave with high speed rotatory stirring (1000 rpm). [b] Yields are based on benzyl chloride. [c] Besides of tribenzyltin chloride, 1.8 g (11 %) of bis(dibenzylchlorotin) oxide was obtained. [d] Besides tribenzyltin chloride 2.8 g (21 %) of tribenzyltin hydroxide was obtained.

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* For previous papers see refs. 1–3.

In non-polar solvents such as benzene and toluene, the main product was dibenzyltin dichloride. The increase in the polarity of the solvent raised the yield of tribenzyltin monochloride. The product of the reaction carried out in water included no dibenzyltin dichloride. The comparison of the composition of the products with reaction time (Fig. 1–4) showed that tribenzyltin chloride was produced at the expense of dibenzyltin dichloride.

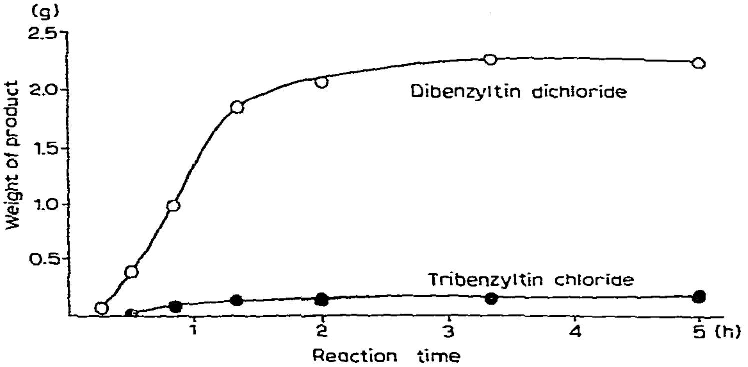

Fig. 1. Reaction of benzyl chloride with tin in toluene at the refluxing temperature. Starting materials were 38.0 g of benzyl chloride, 35.5 g of tin powder, 0.1 g of mercuric chloride and 300 ml of anhydrous toluene. All samples were obtained by taking up each 20 ml portions of the reacting mixture.

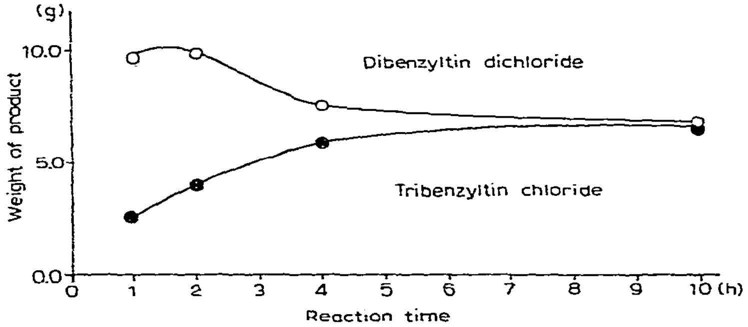

Fig. 2. Reaction of benzyl chloride with tin in diethyl ether. All reactions were carried out with 0.1 mole of benzyl chloride and 0.1 g-atom of tin powder in 100 ml of diethyl ether at 110°.

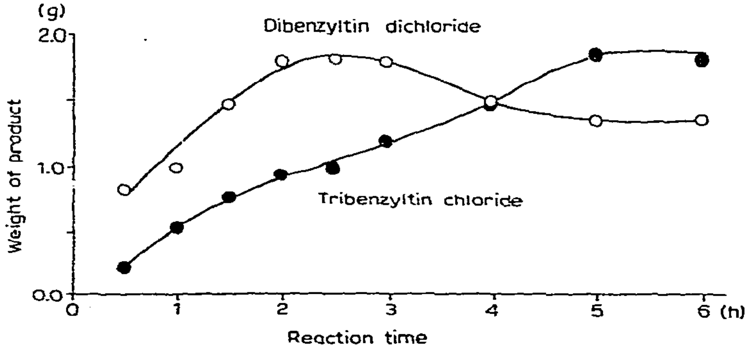

Fig. 3. Reaction of benzyl chloride with tin in boiling dioxane. Starting materials were 38.0 g of benzyl chloride, 35.5 g of tin powder, 0.1 g of mercuric chloride and 300 ml of anhydrous dioxane. All samples were obtained by taking up each 20 ml portions of the reacting mixture.

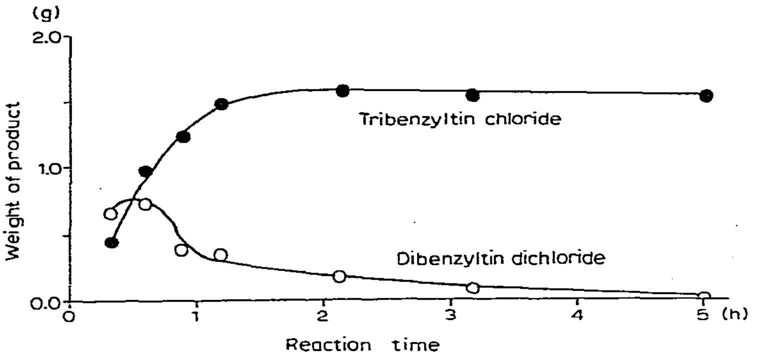

Fig. 4. Reaction of benzyl chloride with tin in boiling n-butanol. Starting materials were 38.0 g of benzyl chloride, 35.5 g of tin powder, 0.1 g of mercuric chloride and 300 ml of n-butanol. All samples were obtained by taking up each 20 ml portions of the reacting mixture.

In a reaction carried out with water for 1 hour, no dibenzyltin dichloride, but a small quantity of bis(dibenzylchlorotin) oxide was found. This suggested that in water also, dibenzyltin dichloride could be produced as an intermediate. Dibenzyltin dichloride, when added to boiling water, yielded quantitatively bis(dibenzylchlorotin) oxide* and hydrochloric acid when there was no tin metal.

It was demonstrated that reaction of dibenzyltin dichloride with metallic tin in polar solvents gave tribenzyltin chloride and stannous chloride. Water hydrolyzed dibenzyltin dichloride to form bis(dibenzylchlorotin) oxide. In the presence of tin powder, however, the bis-oxide was converted readily and quantitatively into tribenzyltin chloride.

These results have revealed that metallic tin and benzyl chloride give initially dibenzyltin dichloride, and conversion from dibenzyltin dichloride into tribenzyltin chloride occurs in a polar solvent, the conversion rate increasing with increasing of the solvent polarity.

It must be noted that even in the earlier part of the reaction, no monobenzyltin monochloride was detected. Although this compound is presumed to be an intermediate, it seems to be very unstable**.

The conversion of dibenzyltin dichloride into tribenzyltin chloride in water was carried out with cadmium, magnesium, zinc or aluminum in place of tin. The same conversion did not take place with titanium, copper, iron, ferrous chloride or stannous chloride. The results are tabulated in Tables 2 and 3. In the presence of iron, dibenzyltin oxide was obtained in an 89% yield due to the hydrolysis of bis-(dibenzylchlorotin) oxide. When cadmium, tin, magnesium, zinc or aluminum was used, further reaction of tribenzyltin chloride caused hydrolysis to give the hydroxide in considerable yield. The flow sheet for reactions could be as follows:

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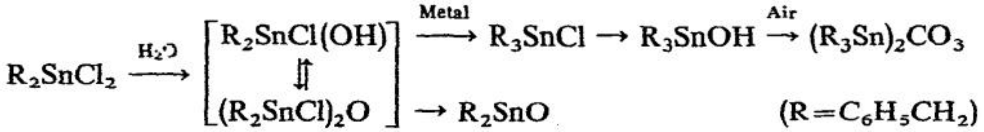
* In the infrared spectrum of the product, neither characteristic band of Sn–O–H deformation vibration at about 900 cm^{-1}, nor that of OH stretching vibration at 3700 cm^{-1}, but that of Sn–O–Sn stretching vibration at 600 cm^{-1} was present. In general, dialkylhydroxytin halide, $R_2SnX(OH)$, which might be produced at the first hydrolysis of dialkyltin dihalide, is so unstable that condensed dimeric form of bis-(dialkylchlorotin) oxide is isolated. See refs. 4 and 5.

** Attempted preparation of mono-n-butyltin monoiodide from di-n-butyltin and stannous iodide failed. This reaction gave di-n-butyltin diiodide and metallic tin.



$$R_2SnCl_2 \xrightarrow{H_2O} \begin{bmatrix} R_2SnCl(OH) \\ \Updownarrow \\ (R_2SnCl)_2O \end{bmatrix} \begin{matrix} \xrightarrow{\text{Metal}} R_3SnCl \rightarrow R_3SnOH \xrightarrow{\text{Air}} (R_3Sn)_2CO_3 \\ \\ \rightarrow R_2SnO \qquad\qquad (R{=}C_6H_5CH_2) \end{matrix}$$

From the above results, it might be concluded that the conversion of the bis-oxide into tribenzyltin chloride is carried out by tin or other metals which act as a reducing agent.

It was reported in a preceding paper[1] that nitrobenzene, nitromethane and *p*-benzoquinone inhibited the direct reaction of benzyl chloride with metallic tin,

TABLE 2

REACTION OF DIBENZYLTIN DICHLORIDE WITH SOME REAGENTS IN WATER[a]

Reagents added	*(mole)*	*Tin (g-atom)*	*Reaction time (h)*	*Yield*[b] *(%)*			
				Di[c]	*BDTO*[d]	*Tri*[e]	*TriOH*[f]
None		0.00	1.0	17	82	0	0
Stannous chloride	0.01	0.00	4.0	8	91	0	0
Benzyl chloride	0.01	0.00	4.0	10	88	0	0
None		0.01	4.0	2	24	73	0
None		0.02	0.5	0	22	75	0
None		0.02	1.0	0	4	92	4
None		0.02	4.0	0	0	59	34
Nitrobenzene	0.002	0.01	4.0	0	68	33	0
Nitrobenzene	0.02	0.01	4.0	0	97	3	0
Nitromethane	0.02	0.02	4.0	0	69	23	0
p-Benzoquinone	0.02	0.02	0.5	0	65	14	0
p-Benzoquinone	0.02	0.02	4.0	0	0	73	11
Hydroquinone	0.02	0.02	4.0	0	5	66	24
N,N-dimethylaniline	0.02	0.02	4.0	0	0	66	30

[a] All reactions were carried out with 0.01 mole of dibenzyltin dichloride and reagents in 100 ml of boiling water. [b] Yields are based on benzyl group. [c] Dibenzyltin dichloride recovered. [d] Bis(dibenzylchlorotin) oxide. [e] Tribenzyltin chloride. [f] Tribenzyltin hydroxide.

TABLE 3

REACTION OF DIBENZYLTIN DICHLORIDE WITH VARIOUS METALS IN WATER[a]

Metal	*(g-atom)*	*Yield*[b] *(%)*			
		DTO[c]	*BDTO*[d]	*Tri*[e]	*TriOH*[f]
Cadmium	0.04	4	2	1	90
Magnesium	0.04	14	2	63	22
Magnesium[g]	0.02	89	2	10	0
Zinc	0.02	39	9	17	26
Aluminum	0.04	7	17	50	26
Iron	0.04	89	3	5	0
Titanium	0.04	0	99	0	0
Copper	0.04	0	98	0	0
Ferrous chloride	(1.0 g)	0	98	0	0

[a] All reactions were carried out with 0.01 mole of dibenzyltin dichloride and metal in 100 ml of boiling water for 4 h. [b] Yields are based on benzyl group. [c] Dibenzyltin oxide. [d] Bis(dibenzylchlorotin) oxide. [e] Tribenzyltin chloride. [f] Tribenzyltin hydroxide. [g] 0.01 mole of nitrobenzene was added.

while hydroquinone did not retard the reaction. Analogous results were obtained in the reaction of dibenzyltin dichloride with metallic tin in boiling water: nitrobenzene and nitromethane inhibited the reaction of bis(dibenzylchlorotin) oxide with metallic tin, *p*-benzoquinone retarded the reaction at first, but after all *p*-benzoquinone was reduced into hydroquinone the reaction began to occur. Hydroquinone and N,N-dimethylaniline had little effect on the reaction.

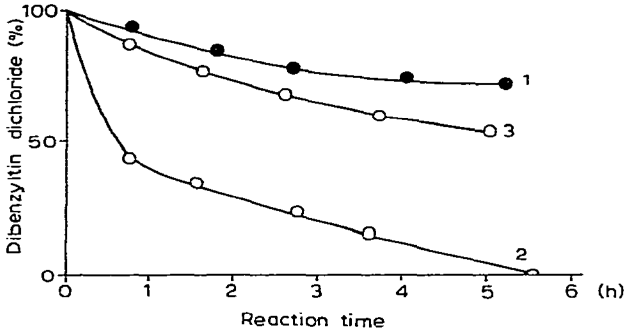


Fig. 5. Conversion of dibenzyltin dichloride into tribenzyltin chloride; 1: in dioxane, 2: in n-butanol, 3: in n-butanol containing 20% of stannous chloride.

Reaction of dibenzyltin dichloride with metallic tin was also carried out in dioxane and n-butanol at the respective boiling point (Fig. 5). Tribenzyltin chloride was formed at faster rate in n-butanol than in dioxane. In the presence of 20% of anhydrous stannous chloride in n-butanol, the conversion rate decreased remarkably as compared with the case of pure n-butanol. These results suggested that the conversion rate apparently depended upon the solubility of anhydrous stannous chloride in the solvents. This assumption might also be supported by the results that in the direct reaction of benzyl chloride with tin in diethyl ether or dioxane the composition of dibenzyltin dichloride and tribenzyltin chloride reached to a certain definite ratio and that the ratio scarcely changed in prolonged reaction (Fig. 2 and 3).

EXPERIMENTAL

Analysis of benzyltin compounds

About 0.2 g of the weighed sample of benzyltin compounds was dissolved in 50 ml of boiling isopropyl ether. Bis(dibenzylchlorotin) oxide* insoluble in isopropyl ether was filtered and dried to weigh. To the filtrate was added 2,2'-bipyridine which formed with dibenzyltin dichloride a 1:1 adduct insoluble in isopropyl ether and precipitated quantitatively. Dibenzyltin dichloride was determined by weighing the precipitates. Tribenzyltin chloride was determined by chlorine analysis of the filtrate. Evaporated residue of the filtrate was dissolved in 25 ml of acetone and the chlorine content was analyzed by potentiometric titration[6,**].

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* The bis-oxide was identified by the chlorine analysis[6] and the infrared absorption band at 745 cm^{-1} which is absent in the other benzyltin compounds.

** Presence of unchanged benzyl chloride in the filtrate did not disturb the analysis of tribenzyltin chloride. When a mixture of benzyl chloride and 2,2'-bipyridine in isopropyl ether was allowed to stand at room temperature for 2 h and the isopropyl ether was evaporated, the residual oil had no detectable chlorine by the potentiometric titration.

tained no bis(dibenzylchlorotin) oxide, but 4.77 g (82%, 0.0111 mole) of tribenzyltin chloride and 1.00 g (18%, 0.0024 mole) of tribenzyltin hydroxide.

The benzene-insoluble matter contained 4.78 g of unchanged tin powder and 0.61 g of stannic acid.

The aqueous filtrate gave positive test for stannous cation[9], and the evaporation of water gave 0.734 g (0.00386 mole) of anhydrous stannous chloride, which on exposure to air for 4 h gave 0.892 g of stannous chloride dihydrate, m.p. 36° (lit.[10] 37.7°).

Bis(dibenzylchlorotin) oxide in boiling water in the absence of metallic tin

A stirred suspension of 6.89 g (0.0100 mole) of bis(dibenzylchlorotin) oxide in 100 ml of water was heated to reflux for 3 h. The solids were filtered, washed with water and dried over sulfuric acid to give 6.62 g of pale yellow solids. Extraction of this with 100 ml of hot benzene gave 1.00 (18%) of insoluble dibenzyltin oxide and 5.60 g (81%) of bis(dibenzylchlorotin) oxide. The aqueous filtrate gave negative test for stannous cation[9] and contained 0.0031 mole (15%) of hydrochloric acid.

Reaction of dibenzyltin dichloride with some metals in water

All reactions were carried out with 3.72 g (0.01 mole) of dibenzyltin dichloride and metal powder in 100 ml of boiling water with stirring. Results of the experiments are tabulated in Table 3.

Reaction of dibenzyltin dichloride in water in the presence of some reagents

All reactions were carried out with 3.72 g (0.01 mole) of dibenzyltin dichloride, 2.38 g (0.02 g-atom) of metallic tin powder and reagents in 100 ml of boiling water. Results are shown in Table 2.

Conversion of dibenzyltin dichloride into tribenzyltin chloride in n-butanol or dioxane

A mixture of 3.72 g (0.01 mole) of dibenzyltin dichloride and 2.37 g (0.02 g-atom) of metallic tin powder and 0.01 g of mercuric chloride in 40 ml of solvent was heated to reflux with vigorous stirring. Reaction time was measured from the start of the refluxing. All samples were filtered, washed with 25 ml of acetone and evaporated to dryness *in vacuo* on a water bath. The solids were extracted with 50 ml of hot benzene to remove stannous chloride and tin powder. Evaporation of the benzene extract gave white crystals whose components were analyzed by an analogous way. Results of these experiments are shown in Fig. 5.

SUMMARY

By the investigation of the solvent effects in the reaction of benzyl chloride and tin powder, it was elucidated that dibenzyltin dichloride was formed at first, and the conversion into tribenzyltin chloride occurred in polar solvents. In water, bis(dibenzylchlorotin) oxide was an intermediate in the conversion. Catalytic effects in the reaction was also studied.

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