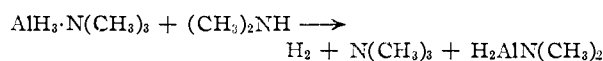


constants of the symmetrical bis-amine alanes shows that the order of stability with the various amines is the same and that the mixed bis-amine alane complexes are more stable. This is to be expected from the steric arguments presented earlier.

Displacement Reactions.—Unlike the analogous boron compound, dimethylamino alane did not react with trimethylamine. Brown has reported a similar example⁵ in that no interaction was observed between trimethylamine and dimethylaminodimethylaluminum. Evidently the formation of nitrogen bridges stabilizes the aluminum toward nucleophilic attack. The greatly reduced acidity of the aluminum was again demonstrated in the reaction between dimethylamine and trimethylamine alane.

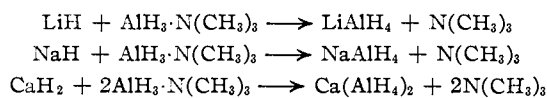


Quantitative yields of hydrogen and trimethylamine were obtained.

The facile displacement of trimethylamine from trimethylamine alane by the dimethylamino group suggested that other strong nucleophiles should behave similarly. Treatment of trimethylamine alane with hydride ion in the form of lithium,

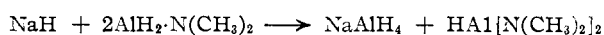
(8) N. Davidson and H. C. Brown, *THIS JOURNAL*, **64**, 316 (1942).

sodium or calcium hydride resulted in the formation of the metal aluminum hydrides. This method



appears to be a convenient laboratory preparation for sodium or calcium aluminum hydride. The unreacted trimethylamine alane, if any, may be extracted with ether, leaving a product of high purity. Commercial grade magnesium hydride did not react with trimethylamine alane under similar conditions.

Although dimethylamino alane failed to react with trimethylamine, it did react with sodium hydride in a manner analogous to that reported for dimethylamino borane. Disproportionation of the alane occurred with the formation of bisdimethylamino alane and sodium aluminum hydride



Acknowledgment.—The authors wish to thank Mr. R. Donald Strahm for the aluminum analyses. The work was performed for the Army Rocket and Guided Missile Agency, an element of the Army Ordnance Missile Command, under U. S. Contract No. DA-01-021 ORD-5135.

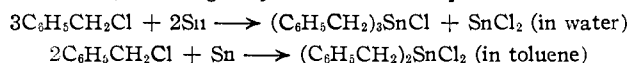
[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, KYÔTO UNIVERSITY, KYÔTO, JAPAN]

Direct Synthesis of Organotin Compounds. I. Di- and Tribenzyltin Chlorides

BY KEIITI SISIDO, YOSIYUKI TAKEDA AND ZIRÔ KINUGAWA

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Benzyl chloride and tin powder suspended in water at 100° gave tribenzyltin chloride, while the same suspension in toluene at 111° afforded dibenzyltin chloride, both in good yields. Over-all equations of the reactions are



Although the direct syntheses of organotin compounds from the metal and organic halides originated with the second paper of the discovery of this group of substances by E. Frankland¹ and were followed by A. Cahours² as well as by T. Karantassis and C. Vassiliadès,³ the indirect syntheses using a Grignard or other reagent were later found more suitable and were regarded as customary methods.⁴ Recent development of the applications of organotin compounds, however, necessitated the revision, and the reactions of halides on

metallic tin are being studied⁵ from other point of view.

During the research to extend the Wurtz-Fittig type reaction by iron^{6,7} it was found that the action of benzyl chloride on tin powder suspended in water at the boiling point of the medium gave tribenzyltin chloride in a 94% yield calculated on the basis of the halide. The yield of this synthesis far surpassed the known ones.⁸⁻¹⁰ Since stannous chloride was obtained from the aqueous layer in a

(1) E. Frankland, *Ann.*, **85**, 329 (1853).

(2) A. Cahours, *ibid.*, **114**, 373 (1860); A. Cahours and E. Demarcay, *Bull. soc. chim. France*, **34**, 475 (1880); *Compt. rend.*, **88**, 1112 (1879).

(3) T. Karantassis and C. Vassiliadès, *ibid.*, **205**, 460 (1937).

(4) For review of literatures not cited here, see E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 182-190, as well as G. E. Coates, "Organometallic Compounds," Methuen & Co., Ltd., London, England, 1956, pp. 118-133. Also an article by R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Revs.*, **60**, 459 (1960).

(5) B. Emmert and W. Eller, *Ber.*, **44**, 2328 (1911); R. W. Leeper, *Iowa State Coll. J. Sci.*, **18**, 57 (1943); H. Gilman and R. W. Leeper, *J. Org. Chem.*, **16**, 466 (1951); A. C. Smith and E. G. Rochow, *THIS JOURNAL*, **75**, 4103, 4105 (1953); E. G. Rochow, U.S. 2,679,506; *C.A.*, **49**, 4705 (1955); S. Matuda and H. Matuda, *J. Chem. Soc. Japan, Ind. Chem. Section*, **63**, 114 (1960).

(6) K. Sisido, Y. Udô and H. Nozaki, *THIS JOURNAL*, **82**, 434 (1960).

(7) See also: K. Sisido and H. Nozaki, *ibid.*, **70**, 778 (1948); K. Sisido, H. Nozaki and H. Kuyama, *J. Org. Chem.*, **14**, 1124 (1949).

(8) P. Pfeiffer and K. Schnurmann, *Ber.*, **37**, 319 (1904).

(9) T. A. Smith and F. S. Kipping, *J. Chem. Soc.*, **101**, 2556 (1912).

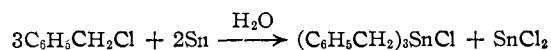
(10) M. M. Nad and K. A. Kocheshkov, *J. Gen. Chem. U.S.S.R.*, **8**, 42 (1938); *Chem. Zentr.*, **100**, I, 2175 (1939).

TABLE I
 REACTION OF BENZYL HALIDE DERIVATIVES WITH TIN IN WATER^a

Halide	React. time (hr.)	Product	Solvent for recrystalliz.	M.p. (°C.)	Yield (%)	Analyses, Sn (%) Calcd.	Found
C ₆ H ₅ CH ₂ Cl	1.5	(C ₆ H ₅ CH ₂) ₃ SnCl	Ethyl acetate	142-144	85.2	27.76	27.46
<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ Cl	1.5	(<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂) ₃ SnCl ^b	CCl ₄	100 (decomp.)	40.3	22.93	22.95
<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	1.5	(<i>o</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ^c	Hexane	88-91	60.7	25.28	24.96
<i>m</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	1.5	(<i>m</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ^d	Petroleum ether	35-40	70.0	25.28	25.01
<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	1.5	(<i>p</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ^e	MIBK	208 (decomp.)	55.5	25.28	25.40
<i>o</i> -FC ₆ H ₄ CH ₂ Cl	2.5	(<i>o</i> -FC ₆ H ₄ CH ₂) ₃ SnCl	Hexane	40-41	75.6	24.65	24.38
<i>p</i> -FC ₆ H ₄ CH ₂ Cl	2.5	(<i>p</i> -FC ₆ H ₄ CH ₂) ₃ SnCl	MEK	124-126	77.4	24.65	24.69
<i>o</i> -ClC ₆ H ₄ CH ₂ Cl	2.5	(<i>o</i> -ClC ₆ H ₄ CH ₂) ₃ SnCl	Cyclohexane	38-40	68.3	22.36	22.00
<i>p</i> -ClC ₆ H ₄ CH ₂ Cl	2.5	(<i>p</i> -ClC ₆ H ₄ CH ₂) ₃ SnCl	Cyclohexane	114-116	74.8	22.36	22.30
<i>p</i> -BrC ₆ H ₄ CH ₂ Br	1.5	(<i>p</i> -BrC ₆ H ₄ CH ₂) ₃ SnBr ^f	MEK	92-94	48.2	16.72	16.41
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ Br	0.5	Resinous materials

^a All reactions were carried out with 0.15 mole of the halide and 0.15 mole of tin in 150 ml. of water at 100°. ^b The corresponding benzyl alcohol was obtained as a by-product in a 38.5% yield. ^c Same, in an 18.6% yield. ^d Same, 14.4%. ^e Same, 31.1%. ^f Same, 19.7%.

yield of 85%, the over-all reaction may be written



The direct reaction of the ingredients in the absence of water or any other dispersing media yielded a resinous, untreatable product containing tin. The two components did not react until the system reached a temperature of 110-120°, but when this temperature had been reached, they reacted all at once to give non-crystallizable and non-distillable material. Water and vigorous stirring seemed to be necessary in order to keep mild the otherwise too violent exothermic reaction. Even in water, insufficient stirring caused such a local heating as to melt the tin powder into a solid mass, and this was a reason for a lower yield of the reaction. Tribenzyltin chloride was obtained in an 80% yield, when 1-butanol was used at the boiling point as a reaction medium instead of water, but when boiling ethyl alcohol was used, almost all of the starting materials were recovered. A yield of 15% was noticed by the reaction with 50% aqueous ethanol. The failure of the reaction in ethanol may be ascribed, at least to some extent, to the lower boiling temperature at which the reaction cannot be realized.

Similar reaction with cadmium in water yielded toluene, while the reaction with magnesium, nickel (including Raney nickel), cobalt or lead afforded bibenzyl. Arsenic or silicon showed no reaction.

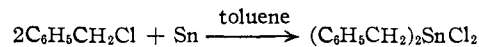
The reactions of tin metal with ring-substituted benzyl chloride derivatives are summarized in Table I.

With the benzyl chloride derivatives having an electron-donating group such as methyl or methoxy, a concurrent hydrolysis reaction yielded the corresponding benzyl alcohol at the expense of the tin compounds. This lowering of the yield, however, cannot be accounted for solely by the alcohol formation in view of the mechanism^{11,12} of the hydrolysis. Heat evolved by the more reactive benzyl chloride seemed to cause the tin powder to form a molten mass resulting in the decrease of the reacting metal surface. Also the benzyl alcohol, which is oily at

the reaction temperature, may hinder the contact of the reacting components.

In the case of halobenzyl chlorides with an electron-withdrawing atom the reaction was somewhat slow, but practically no hydrolysis was remarked. *p*-Nitrobenzyl bromide gave an insoluble resinous matter.

The reaction of benzyl chloride on tin powder suspended in toluene at the boiling point gave dibenzyltin chloride in a yield of 88%. Since this reaction left no inorganic tin salt, the over-all reaction may be written as

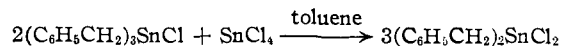


The use of benzene or ligroin instead of toluene gave the same product but in a lower yield. The results of these reactions including the ring-substituted derivatives are summarized in Table II. An electron-donating substituent on the nucleus raised the yield, while a withdrawing one lowered.

The fact that *o*-halobenzyl chlorides did not react with tin in toluene cannot be attributed to a steric hindrance, since the *o*-fluoro compound which should exhibit a minute effect also did not react, while the *o*-methyl derivative with a fairly bulky group gave a good yield.

It is very interesting to know that the reactions in toluene did not occur when the system was absolutely anhydrous. As is well known, the solubility of water in toluene is very small and the commercial toluene contains ordinarily a negligible quantity of water. This trace of water, however, was sufficient to set up the reaction. Toluene stored over sodium, however, when used with carefully dried tin powder, gave no reaction, while addition of a drop of water for each 50 ml. portion of this toluene can initiate the reaction. In this case, the addition of water in the tin powder gave a better result than that in toluene. The addition of 1-butanol or ethanol instead of water was not valid for this purpose. The surface of the tin powder presumably needs to be wetted with a minute quantity of water for the performance of the reaction.

Dibenzyltin chloride also was obtained, when tribenzyltin chloride was treated with stannic chloride in toluene or benzene.



(11) T. Chitani, *Bull. Chem. Soc. Japan*, **6**, 152 (1931).

(12) Y. Yamasita and T. Simamura, *J. Chem. Soc. Japan, Ind. Chem. Section*, **61**, 1185 (1958).

TABLE II
 REACTION OF BENZYL HALIDE DERIVATIVES WITH TIN IN TOLUENE^a

Halide	React. time (hr.)	Product	Solvent for recrystalliz.	M.p. (°C.)	Yield (%)	—Sn Analyses%—	
						Calcd.	Found
C ₆ H ₅ CH ₂ Cl	3.0	(C ₆ H ₅ CH ₂) ₃ SnCl ₂	Ethyl acetate	163–164	80.4	31.92	31.41
<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ Cl	2.0	(<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂) ₃ SnCl ₂	CCl ₄	117 (decomp.)	87.2	27.48	26.81
<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	2.0	(<i>o</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ₂	Hexane	128–130	84.5	29.68	29.43
<i>m</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	2.0	(<i>m</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ₂	CCl ₄	133–135	80.0	29.68	29.55
<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ Cl	2.0	(<i>p</i> -CH ₃ C ₆ H ₄ CH ₂) ₃ SnCl ₂	MIBK	214 (decomp.)	87.1	29.68	29.60
<i>o</i> -FC ₆ H ₄ CH ₂ Cl	4.0	Recovery of materials
<i>p</i> -FC ₆ H ₄ CH ₂ Cl	4.0	(<i>p</i> -FC ₆ H ₄ CH ₂) ₃ SnCl ₂	2-Propanol	179–180	72.8	29.10	29.41
<i>o</i> -ClC ₆ H ₄ CH ₂ Cl	4.0	Recovery of materials
<i>m</i> -ClC ₆ H ₄ CH ₂ Cl	4.0	(<i>m</i> -ClC ₆ H ₄ CH ₂) ₃ SnCl ₂	Hexane	116–118	69.7	26.93	26.84
<i>p</i> -ClC ₆ H ₄ CH ₂ Cl	4.0	(<i>p</i> -ClC ₆ H ₄ CH ₂) ₃ SnCl ₂	Ethyl acetate	205 (decomp.)	74.1	26.93	26.77
<i>p</i> -BrC ₆ H ₄ CH ₂ Br	4.0	(<i>p</i> -BrC ₆ H ₄ CH ₂) ₃ SnBr ₂	Acetone	175–177	82.3	19.15	19.32
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ Br	4.0	Recovery of materials

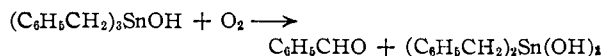
^a All reactions were carried out with 0.15 mole of the halide and 0.15 mole of wetted tin in 150 ml. of toluene at 111°.

Only by the choice of the dispersing medium a preferential formation can be carried out between the two tin compounds from the same starting materials under practically the same reaction conditions. Although a study on the mechanisms of the reactions is now under way, it is tentatively assumed, in view of the analogy of the previous research on the case of benzyl chloride and iron,⁶ that the reaction proceeds *via* a radical formation.

The radical nature of the reaction can be assumed, since the reaction did not occur when benzyl chloride was mixed with nitrobenzene, a known inhibitor of a radical reaction. Radical inhibitors of phenolic series, however, did not show the effect, due probably to the reaction with the ingredients.

In order to keep the reproducibility of the reactions, tin powder must be cleaned by the method described in Experimental.

The treatment of tri- and dibenzyltin chloride with sodium hydroxide gave tribenzyltin hydroxide and dibenzyltin oxide,^{13,14} respectively. These compounds are known to be unstable and among the decomposition products of dibenzyltin oxide benzaldehyde and bibenzyl are described.¹⁴ Since now, along with benzaldehyde, dibenzyltin hydroxide (or dibenzyltin oxide) was identified as dibenzyltin chloride in the degradation products of tribenzyltin hydroxide, the decomposition may be written



Also it was found that tris- and bis-(*p*-methoxybenzyl)-tin chlorides were unstable; they decomposed in air into a reddish brown mass.

Experimental¹⁵

Analyses of Tin.—The qualitative detection of tin in a sample was performed by the method of Gilman and Goreau,¹⁶ while the quantitative determination of tin by total oxidation was carried out according to Gilman and Rosenberg¹⁷ with a slight modification as to the use of a mixed acid consisting of 95% of concd. sulfuric acid and 5% of concd. nitric acid. About 0.2 g. of a sample was weighed in a porcelain crucible and after adding 1.0 ml. of the mixed

acid the procedure of the analysis was followed in essentially the same way.

Purification of Tin Powder.—An analytically pure (assay: more than 99% Sn) or a commercial reagent grade tin powder of 150–200 mesh grain size was added to about twice its weight of 10% aqueous sodium hydroxide solution and shaken vigorously for 10 minutes. This treatment removed the oxide film on the surface of the powder and stearic acid or a similar substance which sometimes was added for the pulverization. The powder then was washed with water until the washings had shown no alkalinity to litmus and rinsed with methanol. Since the air-dried powder formed lumps, these were pulverized in a mortar. There was no difference noticed between the uses of pure and ordinary tin powder.

Substituted Benzyl Halides.—*o*-,¹⁸ *m*-¹⁹ and *p*-²⁰ methylbenzyl chlorides, *o*-²¹ and *p*-²² fluorobenzyl chlorides as well as *o*-,²¹ *m*-²³ and *p*-¹⁹ chlorobenzyl chlorides were obtained by the chlorination of the corresponding toluene derivatives according to the preparation of *m*-methyl- and *p*-chlorobenzyl chlorides by Kharasch and Brown.¹⁹ *p*-Bromo-²⁴ and *p*-nitro²⁴ benzyl bromides were obtained by the bromination of the toluenes and *p*-methoxybenzyl chloride²⁵ was prepared by the chloromethylation of anisole.

Reaction of Benzyl Chloride with Tin in Water; Tribenzyltin Chloride.—To 17.8 g. (0.15 mole) of tin powder suspended in 150 ml. of boiling water kept in an oil-bath at 100° with efficient stirring was added 19.2 g. (0.15 mole) of benzyl chloride in 2 minutes. In a little while the tin powder began to show a sandy appearance. Refluxing and vigorous stirring were continued for 1.5 hr. and, after cooling, solid mass containing the product and unreacted tin powder was filtered and dried in air. When this was extracted with acetone for 4 hr. in a Soxhlet apparatus, 6.2 g. (0.05 mole) of metallic tin was recovered. Evaporation of the acetone solution under diminished pressure gave 20.2 g. (94%, calculated on the basis of benzyl chloride) of pale yellow crystals, which on recrystallization from ethyl acetate gave 18.0 g. (84%) of colorless needles, m.p. 142–144°. This product showed no depression when admixed with an authentic specimen of tribenzyltin chloride prepared by the method of Smith and Kipping.⁹

When the aqueous filtrate was evaporated in vacuum to almost dryness and stored in a refrigerator for 2 days, 9.6 g. (85% of the calculated amount) of colorless needles, m.p. 36.5°, were obtained. These were proved to be stannous chloride dihydrate (SnCl₂·2H₂O) from the positive reactions of stannous cation and chloride anion as well as the m.p. and the solubility in water.

(18) M. S. Newman, *ibid.*, **62**, 2295 (1940).

(19) M. S. Kharasch and H. C. Brown, *ibid.*, **61**, 2124 (1939).

(20) C. K. Ingold and E. Rothstein, *J. Chem. Soc.*, 1278 (1928).

(21) G. M. Bennett and B. Jones, *ibid.*, 1818 (1935).

(22) J. Kenner and E. Witham, *ibid.*, **119**, 1460 (1921).

(23) J. B. Shoosmith and R. H. Slater, *ibid.*, 219 (1926).

(24) G. H. Coleman and G. E. Honeywell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 443.

(25) R. Quelet, *Compt. rend.*, **202**, 956 (1936).

(13) P. Pfeiffer, *Z. anorg. u. allgem. Chem.*, **68**, 102 (1910).
 (14) T. A. Smith and F. S. Kipping, *J. Chem. Soc.*, **103**, 2034 (1913).
 (15) All m.p. reported here are uncorrected.
 (16) H. Gilman and T. N. Goreau, *J. Org. Chem.*, **17**, 1470 (1952).
 (17) H. Gilman and S. D. Rosenberg, *THIS JOURNAL*, **75**, 3592 (1953).

Ring-substituted Tribenzyltin Chlorides.—All preparations listed in Table I were carried out in essentially the same way as above. When a low-melting tribenzyltin derivative was produced or the corresponding benzyl alcohol was formed as a by-product, however, as in the case with *p*-methoxy-, *o*- and *m*-methyl-, *o*-chloro and *o*-fluorobenzyl chlorides as well as *p*-bromobenzyl bromide, since the reaction mixture turned into a pasty mass, a modified procedure must be adopted in order to separate the product. Thus, after the end of the reaction, the mass was shaken with 150 ml. of carbon disulfide in order to separate water as the upper layer, and the carbon disulfide layer containing unreacted tin powder and insoluble matters was filtered. The filtrate solution was washed with aqueous hydrochloric acid to remove stannous chloride and the solvent was evaporated. The residual solid was extracted with either petroleum ether (b.p. 30–50°) or 50% aqueous ethanol to remove the benzyl alcohol and the remaining organotin compound was recrystallized from the proper solvent as indicated in the table. Insoluble organic matter in carbon disulfide was extracted from unreacted tin with methyl ethyl ketone (MEK) and recrystallized to give a further quantity of organotin compound. The evaporation residue of the petroleum ether or 50% ethanol solution consisted of a ring-substituted benzyl alcohol, which was identified as such, as phenylurethan or as 3,5-dinitrobenzoate and by the mixed m.p.

In the case of tardily reacting *p*-fluoro- or *p*-chlorobenzyl chloride, on the other hand, the addition of the halide onto the tin suspension must be done slowly, namely, during 20 minutes or more instead of 2 minutes. Rapid addition of these halides caused a break of the dispersing system and the oil layer of the halide contained the tin powder, so that "the reaction without dispersing medium" (see below) occurred. This resulted in the production of insoluble matters and lowering of the yield.

Reaction of Benzyl Chloride in 1-Butanol.—A suspension of 17.8 g. (0.15 mole) of tin powder in 150 ml. of 1-butanol was treated at 110° with 19.2 g. (0.15 mole) of benzyl chloride for 3 hr. and the reaction mixture was evaporated *in vacuo* to almost dryness. The residue was extracted with acetone and the acetone solution was poured with stirring into 700 ml. of aqueous 3 *N* hydrochloric acid. The white precipitate thus formed was separated and washed with water and after drying, recrystallized with ethyl acetate to give 16.9 g. (80%) of tribenzyltin chloride, m.p. 141–143°.

The reactions in ethyl alcohol and 50% aqueous ethanol were carried out in essentially the same manner giving a trace and a 15% yield of tribenzyltin chloride, respectively, recovering unreacted benzyl chloride.

Reaction of Benzyl Chloride without Dispersing Medium.—17.8 g. (0.15 mole) of tin powder and 19.2 g. (0.15 mole) of benzyl chloride were mixed and under efficient stirring the temperature was raised gradually. The mixture showed no evidence of a reaction until the temperature had reached about 110°, when, however, a violent reaction took place together with a sudden evolution of heat. Resinous matter of brown color thus formed was insoluble in an ordinary solvent and cannot be treated in the usual manner.

Reaction of Benzyl Chloride with Magnesium in Water.—To a suspension of 3.65 g. (0.15 mole) of magnesium powder in 150 ml. of water was added at 100° 19.2 g. (0.15 mole) of benzyl chloride and after 3 hr. refluxing under an upright condenser, the content was distilled through a downward condenser to remove unreacted benzyl chloride as far as possible. After cooling the content was filtered and the filtrate was extracted with ether. The solid containing magnesium powder was also extracted with ether and the

combined ether solution was evaporated. When the residue was distilled *in vacuo*, there were obtained 3 g. of crystals, m.p. 52°, which was identified as bibenzyl by the mixed m.p. The reactions with other metal powders were carried out in a similar procedure.

Reaction of Benzyl Chloride with Tin in Toluene: Dibenzyltin Chloride.—To 17.8 g. (0.15 mole) of tin powder was added 3 drops (or 1–2% of the weight of tin) of water and kneaded together. The tin powder was suspended in 150 ml. of toluene under efficient stirring and heated to the boiling point of the dispersing agent. To this suspension was added dropwise 19.2 g. (0.15 mole) of benzyl chloride during 3 minutes and refluxing was continued for an additional 3 hr. The use of a simple type of a reflux condenser, e.g., Liebig condenser, is recommended in this reaction in order not to hold water drops on the cooling surface. After 2 hr. refluxing there appeared fine crystals in the mixture and the content of the reaction vessel became grayish. The slurry was filtered after cooling and the residue was extracted with acetone and the acetone solution was evaporated under diminished pressure, leaving 21.6 g. of yellow solid. When the toluene solution was evaporated, 3.0 g. of solid was obtained. Both of these solids were combined (24.6 g. or 88%) and recrystallized from ethyl acetate to give 22.4 g. (80%) of white crystals with silky appearance, m.p. 161–163°. This product showed no depression on admixture with authentic dibenzyltin chloride prepared according to the literature.⁹

Extraction of the recovered tin powder (9.1 g. or 0.076 mole) with water gave no inorganic tin salt.

Reaction of Benzyl Chloride and Tin under Absolutely Anhydrous Condition.—To 150 ml. of toluene stored over metallic sodium was added 17.8 g. (0.15 mole) of tin powder dried in a desiccator and worked up as above with 19.2 g. (0.15 mole) of benzyl chloride. After 3 hr. refluxing the tin powder remained intact and the solution was colorless. Solid was filtered, washed twice with a small quantity of acetone and dried in air; 17.2 g. (97%) of tin was recovered. The toluene solution was evaporated and the residual oil was distilled *in vacuo* giving 17.4 g. (92%) of benzyl chloride.

Addition of several drops of 1-butanol or ethanol instead of water in the tin powder in this reaction showed no effect and the recoveries of tin and benzyl chloride amounted to 96 and 92%, respectively, in the case of 1-butanol.

Ring-substituted Dibenzyltin Chlorides.—All preparations listed in Table II were carried out in essentially the same way as above. Since the products from *p*-substituted benzyl halides were in general sparingly soluble in acetone, extractions of the organotin compounds should be performed with methyl ethyl ketone or methyl isobutyl ketone (MIBK).

Dibenzyltin Chloride from Tribenzyltin Chloride.—To a solution of 10 g. of tribenzyltin chloride in 25 g. of benzene 3 g. of stannic chloride was added dropwise at 70–75°, and after heating for 3 hr. at the same temperature, the hot mixture was filtered. The crystal product separated on cooling from the filtrate was dibenzyltin chloride, m.p. and mixed m.p. 162–164°, yield 5 g. (38.4%).

Tribenzyltin Hydroxide.—Tribenzyltin hydroxide prepared according to the literature¹⁸ showed a gradual lowering of the m.p. on exposure to air and the fine, crisp crystals then changed to a sticky mass, to a colorless liquid after about a month. When 10 g. of this liquid was dissolved in 50 ml. of benzene and 5 ml. of concd. hydrochloric acid was added, there separated white crystals, which were identified as dibenzyltin chloride by a mixed m.p.

Treatment of a drop of the colorless liquid with a drop of phenylhydrazine in 12 ml. of boiling ethanol afforded benzaldehyde phenylhydrazone, m.p. and mixed m.p. 153–154°.