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Direct Synthesis of Organotin Compounds. II. Diallyltin Dibromide and Its Derivatives

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Diallyltin dibromide was prepared by the reaction of allyl bromide with tin powder in boiling toluene. The catalytic effect of mercuric chloride and some organic bases on this reaction was examined and optimum conditions for preparation were determined. Allylic rearrangements in this reaction were investigated. The same reaction in boiling water or butanol yielded propylene.

In the previous paper¹ a direct preparation of di- or tribenzyltin chloride using toluene or water as a reaction medium, respectively, was reported. This reaction is considered to be of a radical nature.^{1,2} In view of their similar behavior as radical sources, allyl halides were expected to react with tin in somewhat the same way,³ if the high temperatures necessary for the initiation of the reaction could be reached.¹ When a solution of allyl bromide in toluene was refluxed for ten hours in the presence of tin powder diallyltin dibromide was obtained in a 14% yield. Addition of mercuric chloride accelerated this reaction to give the tin compound in a 44% yield. Search for a suitable catalyst led to the discovery that amines such as pyridine, triethylamine, dimethylaniline, or morpholine increased the yield of diallyltin dibromide to about 70%. Triphenylphosphine and -arsine also showed slight activities. Presumably mercuric chloride activated the tin powder by amalgamation, while the amines aided polarization of the carbon-bromine bond of allyl bromide so as to facilitate radical formation by the tin metal.

Triethanolamine did not act as a catalyst but inhibited the reaction. Sodium methoxide also inhibited the reaction.

Although the simultaneous addition of both mercuric chloride and an amine in toluene formed a curdy precipitate consisting of the addition complex,⁴ which showed no catalytic effect, preliminary treatment of tin powder with mercuric chloride in boiling toluene followed by addition of triethylamine led to the production of the allyltin compound in a yield of 81.7%.

Presence of water in the reaction medium influenced the results due to the ready hydrolyzability of allyltin compounds. Under absolutely anhydrous conditions, in the absence of catalyst, the reaction gave the product in a 2% yield, whereas

use of moistened tin powder¹ gave a yield of 14%. In a reaction catalyzed by mercuric chloride and triethylamine anhydrous toluene as a solvent furnished an 81.7% yield, while use of toluene saturated with water afforded only a 44% yield.

Recovered tin powder from these preparations could not be used again in another run, for it was always contaminated with a yellow gum which could not be removed by extraction with any solvent. This was probably formed by oxidation of an insoluble allyltin compound during filtration in air. In order to avoid a futile consumption of materials the use of tin and halide in a 1:2 molar ratio was examined, but it resulted in a lowering of the yield to 37%.

Results of these experiments are summarized in Table I.

For the identification of liquid diallyltin dibromide, its crystalline pyridine adduct,⁵ (CH₂=

TABLE I
PREPARATION OF DIALLYLTIN DIBROMIDE^a

Catalyst ^b	Reaction Time, Hr.	Diallyltin Dibromide ^c Yield	
		g.	%
None	10.0	0.6	2.2
None ^d	10.0	3.9	14.4
HgCl ₂	8.0	12.0	44.4
C ₆ H ₅ N	4.0	19.0	70.2
(C ₂ H ₅) ₃ N	4.0	19.1	70.3
C ₆ H ₅ N(CH ₃) ₂	4.0	18.9	69.4
Morpholine	4.0	19.0	69.8
(C ₆ H ₅) ₃ P	4.0	15.8	58.3
(C ₆ H ₅) ₃ As	4.0	10.7	39.9
N(CH ₂ CH ₂ OH) ₃	4.0	(Recovery of materials)	
CH ₃ ONa	4.0	(Recovery of materials)	
HgCl ₂ , ^e C ₆ H ₅ N	1.5	21.6	79.9
HgCl ₂ , ^e (C ₂ H ₅) ₃ N	1.5	22.3	81.7
HgCl ₂ , ^e (C ₂ H ₅) ₃ N ^f	4.0	11.1	40.8
HgCl ₂ , ^e (C ₂ H ₅) ₃ N ^g	4.0	10.1	37.4

^a All reactions except the last one were carried out with 0.15 mole of allyl bromide and 0.15 mole of tin in 150 ml. of refluxing toluene (stored over sodium, unless otherwise stated) under a nitrogen atmosphere. ^b 2-3 millimoles of catalyst was used. ^c Fraction boiling at 77-79°/2 mm. ^d Tin powder containing 2-3% of water was used. ^e See details in Experimental. ^f Toluene saturated with water was used. ^g 0.075 mole of tin powder was used.

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$\text{CHCH}_2)_2\text{SnBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}^-$, was utilized. This dipyridino adduct, when dissolved in such a solvent as an aromatic or paraffinic hydrocarbon, carbon tetrachloride, chloroform, or ethyl acetate dissociated into the monopyridino compound, $(\text{CH}_2=\text{CHCH}_2)_2\text{SnBr}_2 \cdot \text{C}_5\text{H}_5\text{N}$, which separated as a white precipitate. This precipitate dissolved again on addition of excess pyridine or such solvents as alcohols or dimethylformamide.

Reactions of tin with allylic *n*-butenyl bromides are of interest because of possible allylic rearrangements. In the case of Grignard reactions, studies on this rearrangement concerned only the final products⁶ and the constitution of the intermediary organometallic compounds has scarcely been discussed. Recently, Gaudemar⁷ has claimed, on the basis of absorptions at 1615–1645 cm^{-1} , that all of the organomagnesium, aluminum, and zinc compounds of crotyl bromide consist exclusively of the primary crotyl isomer. Lanpher,⁸ however, has not recognized any absorption in the normal double bond stretching region (1620–1680 cm^{-1}) with crotyllithium, -sodium, and -magnesium bromide, but found a strong absorption due to a double bond stretching frequency at 1500–1560 cm^{-1} .

The reactions of both primary crotyl bromide and secondary methylvinylcarbinyl bromide with tin were carried out to give dibutenyltin dibromides. The products were separated by fractional distillation. Two distinctly different fractions were obtained from each in yields of 5 and 6% as well as 67 and 70%, respectively. Each corresponding fraction was proved to be the same by comparing the infrared spectra and in some cases mixed melting point determinations. Because of their instability, identification of these compounds could not be carried out by chemical methods such as oxidative degradation. Two strong absorptions at 915 and 985 cm^{-1} were found in the spectra of the lower boiling fraction. Since strong absorptions at 905 and 985 cm^{-1} were also found in diallyltin dibromide, these absorptions could be assigned to a vinyl group.⁹ The higher boiling fraction showed a strong absorption at 955 cm^{-1} which was hardly recognized in the former and not in diallyltin dibromide. The absorptions could be assigned to a *trans*-disubstituted ethylene structure.⁹ These facts indicated that both of the reactions gave the same products in the same proportions suggesting existence of an equilibrium. The main fraction consisted of dicrotyltin dibromide and the minor of bis-

(methylvinylcarbinyl)tin dibromide. Contamination with crotyl(methylvinylcarbinyl)tin bromide, however, was not absolutely excluded. Absorption bands arising from the double bond stretching were observed in both butenyltin compounds as well as in diallyltin dibromide in the 1635–1660 cm^{-1} region.

Allyl chloride showed practically no sign of reaction on heating with tin under various conditions. Due to difficulty in stirring, which must be very vigorous¹ in these reactions in order to keep the tin powder as a suspension, an attempt to use an autoclave was abandoned. Also allylic dodecenylyl chloride¹⁰ gave no product, although its higher boiling point permitted better contact with the tin.

Diallyltin dibromide is a pale yellow oil having a pungent leek-like odor. It was comparatively unstable in air but more stable in a nitrogen atmosphere. On storing in air for a day or in nitrogen for six months it gave a pale yellow jelly, in which the characteristic absorptions of a double bond were not recognized.

Catalytic hydrogenation of diallyltin dibromide was investigated for the purpose of finding a new synthetic route to dialkyltin dibromides. All attempts made using Raney nickel were unsuccessful.

Diallyltin dibromide and its homologs were readily hydrolyzed on shaking with water, forming bromide anion and a white curdy precipitate, the aqueous part becoming acidic to litmus. Taking advantage of this phenomenon, halogen bound to tin could easily be determined by a back-titration method as described in the Experimental. Volumetric analyses have recently been applied to the determination of acyl groups¹¹ and halogen atoms¹² in organotin compounds.

Attempted preparation of triallyltin bromide by the reaction of allyl bromide with dispersed tin powder in boiling water or in butanol at 100° resulted in the formation of propylene in yields of 84 and 67%, respectively. This may be accounted for by the decomposition of the allyltin compounds by the acids produced by hydrolysis of allyl bromide or stannous bromide. The fact that diallyltin dibromide, when boiled with hydrochloric acid, cleaved with elimination of propylene supports this explanation. This may also be in line with the easy cleavage of the allyl group from allyltin derivatives by acetic acid as reported by Rosenberg *et al.*¹³

EXPERIMENTAL¹⁴

Analyses of tin in organic compounds. Detection¹⁵ and determination¹⁶ of tin were performed by a method similar

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(8) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Methuen & Co., London, 1958, p. 34.

to that previously¹ described. In the quantitative analysis the sample was wetted with a few drops of glacial acetic acid in a crucible before the addition of mixed acid.^{16,17}

Analyses of ionically bound halogen. About 0.2 g. of a sample was weighed accurately and added to 30 ml. of 0.1N ethanolic potassium hydroxide solution in an Erlenmeyer flask. This was warmed with shaking in a water bath at 40° for 20 min. and unconsumed alkali was titrated on cooling with 0.1N aqueous hydrochloric acid solution using phenolphthalein as an indicator.

Tin powder. Chemically pure tin powder¹⁸ or commercial tin powder was used after treatment as described in the previous paper.¹ There was no difference between the two.

Reaction of allyl bromide with tin in toluene; diallyltin dibromide. Results of reactions of allyl bromide with tin in the presence of various catalysts are summarized in Table I. All reactions and distillations were carried out in a nitrogen atmosphere. A representative procedure is as follows.

To 17.8 g. (0.15 mole) of tin powder in 150 ml. of toluene was added 0.5 g. (0.002 mole) of mercuric chloride and the resulting mixture was heated to reflux for 30 min. with stirring. After cooling 0.2 g. (0.002 mole) of triethylamine was added.

The mixture was again refluxed and to this was added dropwise 18.2 g. (0.15 mole) of allyl bromide with efficient stirring. After initial depression of the boiling point to 103°, the reaction temperature rose gradually, reaching a temperature of 111° in 1.5 hr. When the yield of the product was low, the final temperature was lower.

Unchanged tin together with an unidentified amorphous solid (10.4 g. in total) were filtered off and the filtrate was evaporated under reduced pressure. The residual oil (27.0 g.) was distilled *in vacuo* yielding 22.3 g. (81.7%) of diallyltin dibromide, b.p. 77–79°/2 mm., d_4^{20} 1.8640, (lit.⁵ b.p. 77–79°/2 mm.), infrared absorptions (neat): 3090 (m), 2920 (w), 1810 (w), 1635 (vs), 1427 (m), 1395 (m), 1304 (w), 1182 (s), 1100 (m), 1030 (m), 985 (s), 905 (vs), 760 (s), and 740 (w) cm^{-1} .

The product gave correct analyses for tin and bromine.

Diallyltin dibromide gave a pyridine adduct, m.p. 101–103° (see below).

Removal of insoluble by-product from the recovered tin using various solvents was unsuccessful. Dimethylformamide dissolved the mass only incompletely; the extracted material consisted of an infusible organic matter containing tin and halogen.

Reaction of crotyl bromide with tin. Pure crotyl bromide,¹⁹ b.p. 44–47°/90 mm., n_D^{25} 1.4788 (lit.¹⁹ b.p. 49°/93 mm., n_D^{25} 1.4795), was prepared by the method of Young *et al.*¹⁹ from the corresponding alcohol. To a suspension of 17.8 g. (0.15 mole) of tin powder treated with 0.5 g. (0.002 mole) of mercuric chloride in 150 ml. of toluene was added, in the presence of 0.2 g. (0.002 mole) of triethylamine, 20.1 g. (0.15 mole) of crotyl bromide following the same procedure as the preparation of diallyltin dibromide. After 1.5 hr. refluxing 24.3 g. of yellow oil was obtained on removal of the solvent. Distillation of this oil *in vacuo* gave two fractions: 1.5 g. (5.0%) of bis(methylvinylcarbinyl)tin dibro-

mid, b.p. 60–63°/0.20 mm., infrared absorptions (neat): 3090 (m), 3010 (m), 2970 (vs), 2930 (s), 2660–80 (sh), 1660 (w), 1640 (m), 1520 (m), 1495 (w), 1453 (s), 1425 (sh), 1380 (vs), 1310 (m), 1260 (s), 1075 (s), 1035 (s), 985 (vs), 915 (vs), 807 (m), and 745 (s) cm^{-1} .

Anal. Calcd. for $\text{C}_5\text{H}_{14}\text{Br}_2\text{Sn}$: Sn, 30.54; Br, 41.12. Found: Sn, 29.86; Br, 40.79.

and 20.4 g. (70.2%) of dicrotyltin dibromide, b.p. 104–106°/0.20 mm., m.p. 30–31°, infrared absorptions (neat): 3020 (s), 2970 (s), 2930 (s), 2680 (m), 1660 (m), 1640 (w), 1450 (m), 1403 (m), 1380 (w), 1370 (w), 1303 (w), 1150 (m), 1100 (m), 1065 (m), 1035 (m), 955 (vs), 790 (m), 765 (m), and 730 (m) cm^{-1} .

Anal. Calcd. for $\text{C}_5\text{H}_{14}\text{Br}_2\text{Sn}$: Sn, 30.54; Br, 41.12. Found: Sn, 30.01; Br, 40.94.

Reaction of methylvinylcarbinyl bromide with tin. Pure methylvinylcarbinyl bromide¹⁹ b.p. 31–34°/93 mm., n_D^{25} 1.4610 (lit.¹⁹ b.p. 31°/93 mm., n_D^{25} 1.4602) was prepared by the method of Young, *et al.*,¹⁹ from the corresponding alcohol, and the same procedure was repeated as above using 20.1 g. (0.15 mole) of methylvinylcarbinyl bromide instead of crotyl bromide. The products were separated into 1.7 g. (6.0%) of bis(methylvinylcarbinyl)tin dibromide and 19.5 g. (67.2%) of dicrotyltin dibromide and were identified by the infrared absorptions, respectively, as well as the mixed melting point when the product was crystalline.

Reaction of allyl chloride with tin in toluene. In 150 ml. of toluene 17.8 g. (0.15 mole) of tin powder activated with 0.5 g. (0.002 mole) of mercuric chloride was caused to react with 11.5 g. (0.15 mole) of allyl chloride in the presence of 0.2 g. (0.002 mole) of triethylamine. After 40 hr. refluxing, unchanged tin (17.4 g.) was filtered off and the filtrate was fractionated to recover 10.7 g. of allyl chloride. Upon distillation of 1.1 g. of yellow oil which remained in the still no product containing tin was obtained.

Reaction of dodecenylyl chloride with tin in toluene. To a suspension of 17.8 g. (0.15 mole) of tin powder activated with mercuric chloride in 150 ml. of toluene was added 26.1 g. (0.15 mole) of "dodecenylyl chloride"¹⁰ containing 92.5% of 1-chloro-5,5,7,7-tetramethyl-2-octene. After 40 hr. boiling 17.5 g. of tin powder and 25.8 g. of the starting halide were recovered.

Reaction of allyl bromide with tin in water. To a suspension of 17.8 g. (0.15 mole) of tin powder in 150 ml. of water was added dropwise 18.2 g. (0.15 mole) of allyl bromide under vigorous stirring over a period of 20 min. with such caution that loss of organic halide by steam distillation was avoided. Toward the end of addition the mixture became grayish and there was observed a vigorous evolution of gas which lasted for 15 min. The reaction apparatus had been fitted with a reflux condenser from whose upper end was connected a tube to two ice-cooled traps each containing 5 ml. of bromine in order to catch the gas. Resultant oil in the traps was freed from bromine, washed with sodium carbonate and water. Distillation gave 27.7 g. (84%) of 1,2-dibromopropane, b.p. 141–142°, n_D^{20} 1.5191 (lit.²⁰ b.p. 139–142°, n_D^{20} 1.5193), which gave the correct analytical values for carbon and hydrogen.

Another run with 17.8 g. (0.15 mole) of tin powder and 18.2 g. (0.15 mole) of allyl bromide using 1-butanol as a solvent also gave 22.1 g. (67.4%) of 1,2-dibromopropane.

Reaction of diallyltin dibromide with aqueous hydrochloric acid. To a stirred suspension of 10.3 g. (0.03 mole) of diallyltin dibromide in 30 ml. of water was added dropwise 30 ml. of 6N aqueous hydrochloric acid and the mixture was boiled for 30 min. Gaseous substances evolved was caught by bromine and treated as above to afford 8.7 g. (72.5%) of 1,2-dibromopropane.

Pyridine-adduct of diallyltin dibromide. Upon mixing of 5 g. (0.014 mole) of diallyltin dibromide and 5 g. (0.064 mole)

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