ORGANOTIN COMPOUNDS

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I. INTRODUCTION

Organotin compounds are substances in which at least one tin–carbon bond is present. The first such compound was described in 1852 by Löwig (527). Many significant contributions were made in this field during the next few decades. The assignment of the first accurate atomic weights of the Group IVA metals was facilitated by the study of their alkyl compounds. A comparison of the organometallic derivatives of silicon, tin, and lead formed part of the basis of Mendeléeff's famous prediction of a new element, eka-silicon (germanium). In the years that followed, largely because of important applications, principal interests in organometallic chemistry shifted to other areas, first to organoarsenic and organomagnesium compounds and later to organolead and organosilicon compounds. Not until the late 1940's was there a noticeable renaissance in the field of organotin chemistry; a quick glance at the dates of the references at the end of this review will give an estimate of the accelerated interest in this field during the past few years.

Tin, the element of atomic number 50, is a member of Group IVA of the Periodic Table. In the atom of any element of this group there are four electrons in the valence level. All orbitals in lower levels are completely occupied, so that differing valences will not be due to employment of more or fewer lower-lying orbitals in bond formation. The four valence electrons are not all equivalent. The ground state for these atoms is (in the Russell–Saunders notation) a ^3P state, derived from an s^2p^2 configuration (593). There are two electrons in the s subshell, necessarily with spins coupled, and in this state only the two unpaired electrons in the p subshell should be available for bonding. A covalence of two would be expected, arising from this ground state of the atom. In order to form the usual four-covalent state, it is necessary to uncouple the s electrons; the Pauli principle requires that one of the s electrons be promoted to a higher energy level. The next level is the p level of the same shell, and promotion of an s electron to this level gives an sp^3 configuration, for which the lowest term is a ^5S state with four uncoupled electrons. To prepare the atom for bond formation, the linear combinations of these sp^3 orbitals which give the best bonds are sought, and the familiar tetrahedral orbitals result. The common four-covalent state is derived from the sp^3 ^5S state of the atom, which is not the ground state but the first excited state.

Covalences of two and four would then be expected for these elements in neutral molecules. The two-covalent state may be represented as in structure I (where A is any covalently bound atom or group) and the four-covalent state as in II. These two states

$$\overset{\ldots}{\text{Sn}}\text{—A} \qquad \overset{\text{A}}{\underset{\text{A}}{\text{A—Sn—A}}}$$

I   II

are not at all analogous chemically. In structure I the central tin atom has only six electrons in the valence shell and should be able readily to accommodate another pair to form the stable octet. Structure II, in contrast, is a structure with two more covalent bonds and with a complete octet around the central atom. The latter state occurs far more frequently than the former and the great majority of organotin compounds possess a four-covalent tin atom. Because of the sp^3 hybridization, the organometallic compounds of Group IVA are relatively stable and possess relatively low chemical reactivity; thus, tetramethyltin is unreactive toward air and water, in strong contrast to trimethylindium and trimethylstibine. The marked increase in stability of R_4Sn compounds over R_2Sn types also demonstrates the effect of increased hybridization.

The discussion above emphasizes some similarities in compound formation by all of the elements of this group. Among these elements there are also differences, which lead in some cases to rather widely different chemical behavior of their compounds. There is considerable difference in electronegativity, especially in the transition from carbon to silicon. The polarity of the metal–carbon bond increases as the group is descended, and the bond becomes more sensitive to attack by polar reagents; also, the increase in polar character of the halogens in compounds such as R_3MX is evident. In the R_3MOH series, the basicity increases from silicon to lead. The metal–carbon bond strengths decrease and the bond distances increase going down the group, resulting in progressively decreasing thermal stability.

The carbon atom is in a special situation within the group. Since it is a second-period element, it cannot expand its valence shell beyond eight electrons. For silicon and other elements in higher periods, such an expansion is theoretically not forbidden and may account for some of the differences between the chemistry of these elements and that of carbon. Although the elements of this group, with the exception of carbon, show no tendency to form double bonds $(p_\pi—p_\pi)$ of the ethylene type, there is good evidence that the d orbitals of the elements other than carbon are used for bonding $(d_\pi—p_\pi)$. For example, with the four acids of the type $p\text{-}R_3MC_6H_4COOH$, where M represents carbon, silicon, germanium, or tin, carbon is the most electronegative of the four elements and should enhance the acid strength to the greatest extent. Actually, the carbon compound shows the lowest acid strength, indicating that $d_\pi—p_\pi$ bonding is operative in the other three compounds (128). Several other examples of multiple bonding involving d orbitals are listed in a survey in which the behavior of silicon is examined in detail (820).

The tendency to maintain the divalent state apparently increases, in this group, as the atomic number or atomic weight increases. Except for multiple-bonded compounds such as carbon monoxide, the only divalent compounds of carbon are the carbenes and the methylenes, which have been shown to exist as unstable reaction intermediates (170, 403, 783a, 898). Several divalent organotin compounds are stable and isolable substances (see Section III). A larger number of divalent organolead derivatives might be expected but have not been reported, probably because of the generally poorer stability of organolead compounds.

The latest complete review (467) of organotin chemistry covers the literature up to about 1935. More recently several brief expositions concerning this subject have been published (144, 233, 530, 560, 720, 779). Since organotin chemistry appears to be on the threshold of large-scale commercial development, this seems to be an appropriate time to review and summarize the present state of knowledge in the field. In this paper the original literature is covered, as thoroughly as circumstances allow, through 1959. Tables are included which present an essentially complete listing of published organotin compounds, with literature references. In almost every case, all references known to the authors are given.

There has been considerable inconsistency in the nomenclature of organometallic compounds, and the organotin literature is not exceptional in this respect. Throughout this review, including the tables, the authors have endeavored to follow the nomenclature system presently used by *Chemical Abstracts* (17). Although the naming of organosilicon and organogermanium compounds is based on organic nomenclature and requires the endings "silane" and "germane," for organotin and organolead compounds inorganic nomenclature is now employed and the endings "stannane" and "plumbane" have been replaced by "tin" and "lead." When two or more groups are to be named prior to the ending "tin," the groups are arranged in alphabetical order. Alkyl groups not otherwise designated are normal or straight chain. With a few compounds, the inorganic nomenclature becomes unwieldy or impossible; therefore the prefix "stannyl" is used for the group $R_3Sn—$. The nomenclature employed is best elucidated by exemplifying both the present (inorganic) and the older (organic) systems; table 1 lists a few examples of both systems.

TABLE 1

Some examples of old and new nomenclature of organotin compounds

Formula	Present Name	Older Name
$(C_2H_5)_4Sn$	Tetraethyltin	Tetraethylstannane
$(C_2H_5O)(C_6H_5)_3Sn$	Ethoxytriphenyltin	Ethoxytriphenylstannane
		Triphenyltin ethoxide
$(C_6H_5)_3SnSn(C_6H_5)_3$	Hexaphenylditin	Hexaphenyldistannane
$(CH_3)_2SnH_2$	Dimethyltin dihydride	Dimethylstannane
$(C_6H_5)_3SnCl$	Triphenyltin chloride	Chlorotriphenylstannane
$(C_2H_5)_3SnOH$	Triethyltin hydroxide	Triethylstannanol
$(C_6H_5)_2SnO$	Diphenyltin oxide	Diphenylstannone
CH_3SnOOH	Methanestannonic acid	Methylstannoic acid
$(C_6H_5CH_2)(C_6H_5)(C_7H_7)_2Sn$	Benzylphenyldi-p-tolyltin (groups in alphabetical order)	

II. ORGANOTIN COMPOUNDS OF FOUR-COVALENT TIN

A. SYMMETRICAL ORGANOTIN COMPOUNDS

1. General

Symmetrical organotin compounds are substances of the type R_4Sn (table 2) in which the R groups are all the same; R may be alkyl or aryl. The tetra-alkyltins are colorless, and the compounds of lower molecular weight are liquids at room temperature; tetratetradecyltin and analogs of higher molecular weight are low-melting solids. The tetraaryltins are solids with melting points above 170°C. The lower tetraalkyltins can be distilled at atmospheric pressure without decomposition.

The lower-molecular-weight compounds are soluble in the common organic solvents. The higher-molecular-weight substances are only difficultly soluble in many of the more common solvents and solution can be effected only by such solvents as benzene, pyridine, or chloroform.

These compounds are regarded, as stated previously, as possessing typical covalent bonds. They are quite stable in the presence of air or water and are unreactive in such organometallic reactions as addition to a carbonyl group. They are not highly sensitive toward strong aqueous bases, but cleavage of the carbon–tin bond occurs readily with halogens, hydrogen halides, or strong aqueous acids.

2. Preparation

Symmetrical organotin compounds have been prepared in numerous ways but two procedures have been employed most frequently. These are preparations involving the action of a moderately reactive organometallic compound (such as a Grignard reagent or an organolithium compound) on tin(IV) chloride, and preparations employing a tin–sodium alloy and an alkyl halide. The former method is superior either for laboratory syntheses or for commercial processes.

Pope and Peachey (672) were the first to prepare organotin compounds by means of the Grignard reagent. In general the yield of the organotin compound

$$4RMgX + SnX_4 \rightarrow R_4Sn + 4MgX_2$$
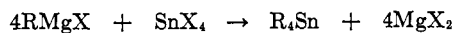
is between 50 and 95 per cent except in cases which are influenced by steric factors. An excess of the Grignard reagent usually is required for a more complete conversion; even so, the product may contain some of the R_3SnX compound which, especially with the aliphatic derivatives, is difficult to remove. A pure product can be obtained by repeated fractional distillation (167), or by shaking an ethereal solution of the reaction product with an alcoholic solution of

potassium fluoride (464). In the former method, alkaline hydrolysis of the R_3SnX compound to the $(R_3Sn)_2O$ derivative prior to distillation is helpful; in the latter method, the R_3SnX compound is converted to the insoluble R_3SnF derivative, which can easily be removed by filtration. Another purification procedure involves passing dry ammonia through the ethereal solution of the reaction product; the R_3SnX impurity is converted to an insoluble complex, $R_3SnX \cdot 2NH_3$ (886). Where the organic group is large, it is sometimes necessary first to prepare the R_3SnX compound, which is subsequently allowed to react with the corresponding Grignard reagent (468). Ethyl ether or an ethyl ether–hydrocarbon mixture usually is employed as a solvent. Recently, the use of tetrahydrofuran (761, 769) or of butyl ether (189) as a solvent has been reported to give improved yields. Anhydrous tin(IV) chloride is most commonly used, although the bromide and iodide give equally good results. (The following references indicate the extent to which this method has been used: 51, 52, 57, 79, 167, 189, 225, 228, 239, 240, 283, 286, 315, 365, 380, 383, 384, 391, 409, 413, 427, 464, 466, 469, 473, 474, 512, 514, 524, 562, 564, 565, 566, 570, 608, 660, 661, 672, 683, 685, 687, 728, 739, 745, 747, 761, 769, 811, 812, 855.)

With aliphatic secondary or tertiary Grignard reagents yields are often poor; in the preparation of tetracyclohexyltin a considerable amount of hexacyclohexylditin is formed by reduction of the intermediate tricyclohexyltin halide by the Grignard reagent (468). With tert-butylmagnesium chloride and tin(IV) chloride, the intermediate di-tert-butyltin dichloride is reduced by the excess Grignard reagent to di-tert-butyltin (475).

An interesting modification of this method has been reported by Kipping (402) and Smith and Kipping (794), who prepared R_4Sn compounds without the previous preparation of the Grignard reagent. The organic halide is added to magnesium and tin(IV) chloride in ether. This method has received attention recently (595, 683, 698, 699); the ether is frequently replaced by a hydrocarbon solvent.

Tetrabutyltin is formed as an intermediate in a cyclic process for the preparation of dibutyltin dichloride. In this procedure, dibutyltin dichloride is treated with butylmagnesium chloride to form tetrabutyltin. This symmetrical organotin compound then is cleaved to dibutyltin dichloride with tin(IV) chloride; a portion of the product is then used to repeat the cycle (518).

Reactions of various other organometallic reagents also have been employed for the preparation of symmetrical organotin derivatives. These reagents

TABLE 2

R₄Sn compounds

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Tetraallyltin		87–88/4 mm.	1.5324 (at 32°)	(435, 855)
		69–70/1.5 mm.		
Tetraamyltin		182/10 mm.	1.4720	(121, 122, 324, 357, 365, 366, 530,
		138–144/0.8–0.9 mm.		856, 888, 914)
Tetraamyltin[113]				(119)
Tetra-*dl*-amyltin		174/10 mm.		(365, 888)
Tetrabenzyltin	42–43			(310, 337, 514, 794)
Tetra-2-biphenylyltin	300–301			(46)
Tetra-3-biphenylyltin	145.5–145.8			(46)
Tetra-4-biphenylyltin	260			(46, 260)
	268.5			
Tetrabutyltin		145/10 mm.	1.4727	(70, 121, 122, 137, 151, 167, 186,
		127/1.7 mm.	1.4736	251, 269, 324, 332, 335, 355, 356,
		109–112/0.3 mm.		357, 360, 363, 365, 366, 376, 512,
				518, 526, 530, 567, 579, 646, 667,
				668, 685, 687, 698, 699, 812, 850,
				856, 888, 905, 914)
Tetracyclohexyltin	263–264			(283, 432, 468)
Tetra-1-cyclopentadienyltin	71–73			(239)
Tetradodecyltin	15–16		1.4736	(265, 569, 570)
Tetraethyltin	137–147°K.	178.5/760 mm.	1.4719	(38, 54, 89, 100, 117, 120, 167, 206,
		180.5–181/760 mm.	1.4691	216, 219, 220, 225, 228, 229, 234,
		78/13 mm.	1.4693 (at 25°)	251, 260, 269, 286, 289, 293, 324,
				343, 357, 363, 365, 366, 377, 378,
				383, 409, 427, 484, 491, 512, 516,
				517, 528, 530, 555a, 557, 567,
				579, 611, 661, 672, 747, 785, 806,
				810, 811, 812, 826, 850, 856, 886,
				888, 911, 917)
Tetraethyltin[113]				(118)
Tetra-9-fluorenyltin	210			(920, 921)
Tetraheptyltin		219–221/2 mm.	1.4702	(121, 324, 335, 365, 366, 564, 856,
		239/10 mm.		888)
Tetrahexadecyltin	41.5–42.5			(569, 570)
Tetrahexyltin		209/10 mm.		(117, 121, 167, 365, 366, 384, 530,
		187–190/1.5 mm.		856, 888)
Tetra-1-indenyltin	215			(920, 921)
Tetraisoamyltin		188/24 mm.	1.4791	(122, 282, 464, 656, 667, 856, 888)
		170/11 mm.	1.47242 (at 16°)	
Tetraisobutyltin		128–129/8 mm.	1.4760	(122, 228, 286, 289, 357, 627, 809,
		155–155.5/24 mm.	1.4772 (at 20.5°)	907)
		130/10 mm.	1.4751 (at 19.5°)	
		143/16.5 mm.		
Tetraisopropenyltin		66–67/8 mm.	1.5110	(615, 617)
Tetraisopropyltin		89/4 mm.	1.4851 (at 20.2°)	(122, 123, 269, 363, 380, 530, 555a,
		103–104/10 mm,		579, 745, 757)
Tetrakis(bromomethyl)tin	57			(901, 903)
Tetrakis(*o*-chlorobenzyl)tin	96.5			(51)
Tetrakis(1-chloroethyl)tin		142/2 mm.		(901, 903)
Tetrakis(chloromethyl)tin	49–49.5	148.5/8 mm.		(901, 903)
Tetrakis(*p*-chlorophenyl)tin	199			(248, 421, 474, 530, 599, 862)
	194.5–195			
Tetrakis(*p*-dimethylaminophenyl)tin	198–199			(41, 256, 900)
Tetrakis(*p*-dimethylaminophenyl)tin, tetramethiodide	Decomposes at 190			(256)
Tetrakis(*p*-dimethylaminophenyl)tin, tetramethosulfate	Decomposes at 195			(256)
Tetrakis(*p*-ethoxyphenyl)tin	104			(831, 913)
Tetrakis(2-ethylhexyl)tin				(384)
Tetrakis(*p*-fluorophenyl)tin	144–145			(222)
Tetrakis(*m*-hydroxyphenyl)tin	Decomposes at 178–179			(240)
Tetrakis(*p*-methoxyphenyl)tin	253–254			(346, 683, 831, 912, 913)
	134.8			
Tetrakis(*p*-nitrophenyl)tin	Deflagrates at 350			(858)
Tetrakis(phenylethynyl)tin	Decomposes at 174			(315)
Tetrakis(*p*-phenoxyphenyl)tin	171			(474)
Tetrakis(2-phenylethyl)tin		288/12 mm.		(365)
Tetrakis(*m*-trifluoromethylphenyl)tin	143–144			(222)
Tetrakis(3,5,5-trimethylhexyl)tin				(384)
Tetrakis(trimethylsilylmethyl)tin		94/0.2 mm.	1.4839 (at 25°)	(761)
Tetrakis(*p*-trimethylsilylphenyl)tin	343–345			(571)

TABLE 2—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Tetramesityltin...............................	Decomposes at 320			(47, 514)
Tetramethyltin................................	−54 (218.8°K.)	78/760 mm. 76.8/760 mm.	1.4386 (at 25°) 1.4405 (at 25°)	(54, 56, 57, 93, 101, 117, 120, 161, 162, 165, 167, 189, 190, 229, 278, 291, 324, 331, 335, 341, 363, 366, 427, 447, 480, 484, 489, 512, 514, 524, 529, 530, 555a, 608, 641, 642, 647, 748, 773, 780, 781, 782, 811, 812, 837, 849, 856, 865, 888, 911)
Tetra-1-naphthyltin...........................	Decomposes at 310–320			(47, 341, 514, 683)
Tetraoctadecyltin.............................	47			(569, 570)
Tetraoctyltin.................................		250–255/5 mm. 268/10 mm.	1.4681	(117, 121, 269, 363, 365, 366, 384, 530, 564, 579, 856, 888)
Tetra-9-phenanthryltin........................	Decomposes at 360			(47)
Tetraphenyltin...............................	224–225 229			(39, 43, 58, 65, 126, 137, 145, 146, 158, 172, 223, 224, 228, 236, 237, 243, 247, 249, 252, 253, 254, 255, 271, 307, 338, 339, 341, 345, 347, 355, 356, 357, 397, 401, 402, 429, 431, 432, 437, 530, 599, 610, 633, 638, 639, 641, 646, 661, 666, 667, 668, 672, 683, 684, 705, 706, 730, 743, 785, 807, 827, 829, 830, 831, 832, 833, 895, 896, 904, 912, 913)
Tetra-1-propenyltin...........................				(694)
Tetrapropyltin...............................	−109 (163.9°K.)	222–225/760 mm. 110–111/10 mm. 116/13 mm.	1.4748	(103, 117, 121, 122, 186, 286, 305, 335, 365, 366, 512, 528, 530, 555a, 660, 745, 809, 812, 855, 856, 888, 914)
Tetratetradecyltin............................	33–34			(569, 570)
Tetra-2-thienyltin............................	156			(191, 209, 469)
Tetra-o-tolyltin..............................	216–217			(254, 466, 473, 514, 595, 723)
Tetra-m-tolyltin..............................	122–123 128.5			(254, 413, 466, 514, 559, 723, 846)
Tetra-p-tolyltin..............................	234–235 238			(41, 52, 146, 254, 466, 514, 515, 599, 660, 831, 913)
Tetravinyltin.................................		55–57/17 mm. 67–70/28 mm. 160–163/766 mm.	1.4993 (at 25°) 1.4914 (at 25°)	(62, 694, 727, 728, 769, 772)
Tetra-2,4-xylyltin............................	224			(466)
Tetra-2,5-xylyltin............................	278			(466)

include organolithium, organozinc, organosodium, and organoaluminum compounds.

As a supplement to the use of Grignard reagents, Austin (41) introduced the reaction of organolithium compounds with tin(IV) halides. This contribution permits the synthesis of symmetrical organotin compounds which are otherwise rather inaccessible because of difficulties encountered in the preparation of the necessary Grignard reagents or because of steric factors. The method is especially useful for the preparation of tetraaryltins (256, 571, 831, 920, 921).

The use of organozinc reagents was introduced by Buckton (90), who prepared tetraethyltin from diethylzinc and tin(IV) chloride. Chambers and Scherer (126) have prepared tetraphenyltin by this method. Similarly, tetrakis(p-chlorophenyl)tin has been prepared from bis(p-chlorophenyl)zinc and tin(IV) chloride (421). The reaction of an organozinc compound with an organotin halide was employed by some of the earlier workers (89, 219, 669) for the preparation

of R_4Sn compounds. In the early work of Frankland and Lawrence (220), tetraethyltin was prepared from diethylzinc and tin(II) chloride; presumably diethyltin was first formed and then decomposed to give tetraethyltin and metallic tin. These procedures offer no advantages, especially since the organozinc reagents are usually prepared via other organometallic intermediates.

Recent reports have appeared concerning the preparation of symmetrical organotin compounds by the reaction of organoaluminum reagents with tin(IV) chloride (363, 907) or with an R_3SnX compound (819). Again, the use of these reagents appears to offer no advantages.

Tetrakis(phenylethynyl)tin has been prepared by the reaction of the sodium derivative of phenylacetylene with tin(IV) chloride in tetrahydrofuran (315). Several tetraaryltin compounds have been obtained from the reaction of aryl halides and tin(IV) halides with sodium in refluxing ether or benzene (307,

339, 515, 829). Probably organosodium intermediates are involved in these reactions.

The first organotin compounds were prepared by the reaction of tin alloys with alkyl halides; through the years this method has received considerable attention. A similar reaction using a lead–sodium alloy is of economical importance for the production of tetraethyllead. The early workers—Cahours (100, 103), Grimm (282), Ladenburg (484), and Werner and Pfeiffer (886)—heated an alkyl iodide with a tin-sodium alloy and obtained a mixture of products containing the tetraalkyltin compound. Other alkyl halides, usually under pressure, have been used instead of the iodide (70, 181, 304, 446, 447, 611, 667); a few reports of the use of aryl halides have appeared (666, 667). Letts and Collie (516, 517) obtained a 50 per cent yield of tetraethyltin by heating ethyl iodide with a tin–zinc–copper alloy; ethyl iodide did not react with an alloy of tin and copper under these conditions.

Harada (290, 291, 293, 305) has investigated the effect of zinc as a third component in the sodium–tin alloy. Excellent yields of tetraethyltin were obtained by refluxing an alloy containing 14 per cent sodium and 12–22 per cent zinc with ethyl bromide. A 60 per cent excess of ethyl bromide and the use of an inert solvent such as cyclohexane have been reported to be desirable for a smooth reaction and a good yield (38, 234, 530). With butyl chloride and a sodium–tin alloy containing 2 per cent zinc, tributyltin chloride is the major product obtained (914).

According to Krause and von Grosse (467, 530), the following reactions may explain the products obtained in this method:

$$Sn + 2RX \rightarrow R_2SnX_2$$
$$R_2SnX_2 + RX + 2Na \rightarrow R_3SnX + 2NaX$$
$$R_3SnX + RX + 2Na \rightarrow R_4Sn + 2NaX$$
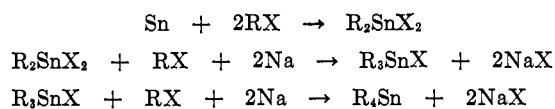
A mixture of trialkyltin halide and tetraalkyltin results. By-products are dialkyltin and hexaalkylditin, formed by the following reactions:

$$R_2SnX_2 + 2Na \rightarrow R_2Sn + 2NaX$$
$$2R_3SnX + 2Na \rightarrow R_3SnSnR_3 + 2NaX$$
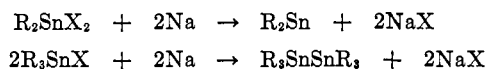
More recently (914), the following reactions have been proposed to explain the products obtained:

$$2NaSn + 2RCl \rightarrow R_2Sn + 2NaCl + Sn$$
$$R_2Sn + RCl \rightarrow R_3SnCl$$
$$2R_2Sn \rightarrow R_4Sn + Sn$$
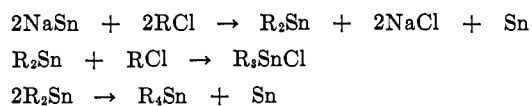
Luijten and van der Kerk (377, 530) have made an extensive investigation of the use of a magnesium-tin alloy to replace the sodium–tin alloy in the prep-

$$Mg_2Sn + 4C_2H_5X \rightarrow (C_2H_5)_4Sn + 2MgX_2$$
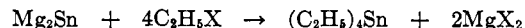
aration of tetraethyltin. The magnesium–tin alloy is easily obtained by melting together the calculated amounts of tin and magnesium; in contrast to sodium-tin alloys, Mg_2Sn can be handled quite safely. For smooth reaction and good yields, a mercury or mercury(II) chloride catalyst, a temperature of about 160°C., autogenous pressure, and an inert solvent such as cyclohexane are required. A slight excess of the alkyl halide is desirable; however, a large excess of alkyl halide or long reaction times favor the formation of alkyltin halides. Either ethyl bromide or ethyl chloride may be employed, but better yields of tetraethyltin are obtained with the former. Other alkyl halides as well as bromobenzene have been used in this reaction with some success and several patents have appeared on this subject (206, 343, 530, 668).

As mentioned previously, tetraphenyltin can be prepared by the reaction of chlorobenzene and tin(IV) chloride with sodium. More recently, this Wurtz-type reaction has been extended to the preparation of tetraalkyltins by Luijten and van der Kerk (380, 384, 530). Usually, a mixture of tin(IV) chloride and the alkyl halide is added to refluxing solvent containing

$$SnCl_4 + 4RX + 8Na \rightarrow R_4Sn + 4NaCl + 4NaX$$
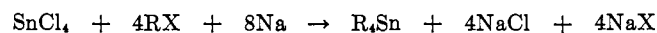
the sodium. For the preparation of tetrabutyltin from butyl chloride, a solvent of low-boiling petroleum ether and a sodium sand of about 1 mm. diameter gave optimum results (530); however, in a recent patent, a higher-boiling hydrocarbon and molten sodium are suggested for the synthesis of tetradodecyltin (265). The method may prove quite useful for the preparation of symmetrical tetraalkyltin compounds, especially derivatives of higher molecular weight (384).

A modification of the above method has been suggested for the preparation of dibutyltin dichloride (376, 530). In this cyclic process dibutyltin dichloride reacts with butyl chloride and sodium to form tetrabutyltin. The tetrabutyltin is then treated with

$$(C_4H_9)_2SnCl_2 + 2C_4H_9Cl + 4Na \rightarrow$$
$$(C_4H_9)_4Sn + 4NaCl$$
$$\downarrow SnCl_4$$
$$2(C_4H_9)_2SnCl_2$$
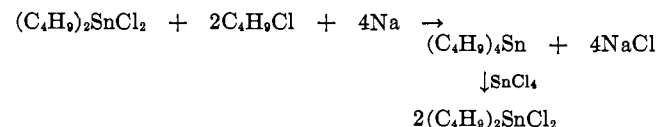
tin(IV) chloride to form dibutyltin dichloride; with sufficiently high yields in these reactions, a portion of this dichloride may be used to repeat the cycle. A small amount of hexabutylditin accompanies the tetrabutyltin; the ditin compound also can be converted to dibutyltin dichloride by cleavage with chlorine to tributyltin chloride and subsequent reaction with the calculated amount of tin(IV) chloride.

A number of other less important methods have been used for the preparation of symmetrical organo-

tin compounds. Letts and Collie (516, 517) obtained tetraethyltin by heating ethylzinc iodide with powdered tin at 150°C. for several hours. Nad and Kocheshkov (599) treated phenylmercury chloride with an alloy of tin and sodium in xylene and obtained a 50 per cent yield of tetraphenyltin; when diphenylmercury was employed the yield of tetraphenyltin was very small. Other tetraaryltin compounds were prepared in this manner.

When aryllithium compounds and finely divided tin or a tin amalgam are refluxed in ether, a low yield of the corresponding tetraaryltin can be obtained (830, 831). Triaryltinlithium compounds, prepared from the aryllithium derivatives and tin(II) chloride, react with the corresponding aryl halide to give the tetraaryltin derivative (254); this reaction also has been successful in the aliphatic series (251).

Nad and Kocheshkov (599) obtained a 37 per cent yield of tetraphenyltin from the reaction of triphenyltin chloride with an alloy of sodium and tin. Gilman and Barnett (236) converted triphenyltin halides into tetraphenyltin in poor yield by the action of hydrazine hydrate.

Diazomethane reacts with tin(IV) chloride in benzene to form chloromethyltin trichloride; the product, in turn, reacts with an excess of diazomethane to give tetrakis(chloromethyl)tin (901, 903). When diethyltin is heated above 150°C., tin and tetraethyltin are formed (73, 90, 100, 218, 293).

$$2(C_2H_5)_2Sn \rightarrow Sn + (C_2H_5)_4Sn$$
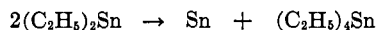
Diallyldiphenyltin, when heated above 160°C., undergoes disproportionation to give tetraphenyltin (435),

3. Physical properties

The absorption spectra of the tetraphenyl derivatives of silicon, tin, and lead from 2100 to 3000 A. (in chloroform and in ethanol) have been given by Milazzo (588). Riccoboni (715) has discussed critically the ultraviolet absorption spectra of tetraethyllead, tetraethyltin, triethyllead chloride, triethyltin chloride, and diethyltin dichloride in hexane and in methanol. Both of these authors concluded that the nature of the curves for the tin derivatives, in contrast to those for the lead compounds, indicates no dissociation. The ultraviolet absorption spectrum of triethylphenyltin from 2000 to 2800 A. has been presented and discussed by Bowder and Braude (79),

The relative fluorescence efficiencies of a number of organic compounds, including tetraphenyltin, have been reported (224). The scintillation counting behavior of a group of pure crystalline organic compounds, including tetraphenyltin, has been studied (743).

The Raman and infrared spectra of tetramethyltin have been studied by several workers (54, 190, 397a,

524, 640a, 780, 781, 906a); considerable disagreement appears to exist as to the actual observed spectrum and to its interpretation. The infrared spectra of the tetraphenyl derivatives of carbon, silicon, germanium, tin, and lead have been studied (633). There is one sharp strong band which shifts in a characteristic way between 9 and 9.5 μ in this series: R_4Si (9.05 μ), R_4Ge (9.18 μ), R_4Sn (9.34 μ), and R_4Pb (9.45 μ); this band is clearly absent in the spectra of tetraphenylmethane and of tetraethyltin. Infrared spectra of tetraethyltin (386b), tetravinyltin (62, 386b), (2-cyanoethyl)triphenyltin (385), ethyltriphenyltin (631, 634), ethylenebis(triphenyltin) (631, 634), and compounds of the type $R_3SnC_nF_{2n+1}$ (368) have been reported.

Force constants for tetramethyltin have been calculated (773, 781, 782).

The C^{13} nuclear magnetic resonance spectrum of tetramethyltin has been obtained (489). The nuclear magnetic resonance spectrum of dibutylbis(1,1,2,2-tetrafluoroethyl)tin also has been reported (476).

With microwave magnetic resonance of the unpaired electrons, the effect of ionizing x-rays on tetramethyltin in the solid state has been studied (278); the radicals produced could not be definitely identified, but one type appears to be $(C_2H_4)^+$.

The atomic coefficients of magnetization for several tetraalkyltin compounds were determined by Pascal (642). The diamagnetic susceptibility has been measured for several symmetrical alkyl derivatives of tin (366). The molar magnetic rotations of several tetraalkyltin compounds have been determined (857).

X-ray studies of crystals of a number of tetraaryltin compounds have been made (227, 230, 345, 346, 347, 846, 912, 913). Tetraphenyltin, tetra-m-tolyltin, tetra-p-tolyltin, and tetrakis(p-methoxyphenyl)tin form tetragonal crystals; there are two molecules per unit cell. Tetrakis(p-ethoxyphenyl)tin, however, forms monoclinic crystals with four molecules per unit cell. The crystal symmetry decreases with increasing size of the aryl groups. Additional work on the crystal structure of tetraaryltin derivatives has been reported by Buttgenbach (99).

Brockway and Jenkins investigated the structure of tetramethyltin by electron diffraction (85); the tin–carbon bond distance was found to be 2.18 ± 0.03 A.

Numerous determinations of the atomic refractivity of tin when attached to primary alkyl groups have been made, ·but the agreement between the values found by the different investigators is only fair (229, 260, 365, 836). Krause and Schmitz (473) found that values of the atomic refraction and dispersion of tin calculated from ethyltriphenyltin are appreciably higher than those calculated from methyltriphenyltin.

More recently, by analysis of the refraction data in the literature for liquid organotin compounds, a system of bond refractions for tin has been established (157, 856, 888, 889).

Smith and Andrews (793) have determined the molal heat capacities of tetraphenyltin between 100° and 320°K. From the molal heats of vaporization of tetramethyltin, ethyltrimethyltin, and triethylpropyltin, Bullard and Haussman (93) concluded that these compounds are "normal" liquids. More recently, the heats of combustion, heats of formation, and related thermodynamic functions of several tetraalkyltin compounds have been determined (54, 167, 365, 524, 646); heats of bromination of several R_4Sn compounds also have been reported (646, 647). Mean dissociation energies for various tetraalkyltin compounds have been calculated (524, 528, 597).

Waring and Horton (865) investigated the thermal decomposition of tetramethyltin between 440° and 493°C. over a range between 5 and 185 mm. initial pressure. Above 80 mm. initial pressure the reaction was found to be predominantly first order; at lower initial pressures the order increased, approaching that of second. The reaction was found to be homogeneous once the reaction vessel was thoroughly coated with a deposit of tin and carbon. Nitric oxide produced no inhibition but instead caused a slight catalytic acceleration of the primary process. The predominant gaseous product was methane, together with some hydrogen and ethylene. A possible reaction mechanism was proposed. Later, Sathyamurthy, Swaminathan, and Yeddanapalli (748) recalculated the results of Waring and Horton and found a better fit with a 1.5-order reaction and a free-radical mechanism. Long (529) has attributed methane formation to the reaction of methyl radicals among themselves, not on a first collision, but in a series of subsequent steps, all of which are to be associated with more favorable activation energies and steric factors.

Incidental to the investigation of the antiknock properties of the low-molecular-weight alkyl R_4Sn compounds, the limits of flammability of various explosive gaseous mixtures containing organotin compounds have been studied (587, 600, 601, 602, 603, 604, 605, 606, 607, 835, 836, 837, 838, 839, 840, 841, 842).

Volume effects of tetraisopropyltin in benzene, carbon tetrachloride, and cyclohexane have been studied (757); these solutions belong to the class in which the structure of the solvent is not altered, and the total volume change is due to distortion of the structure of the solute.

The distribution of $(C_6H_5)_4Pb^*$ between solid and liquid phases in the systems tetraphenylsilane–benzene and tetraphenyltin–benzene was determined by meas-urement of the radioactivity of both phases after agitation in a sealed ampoule (610).

Molecular-weight determinations show that the compounds of these types are not associated (for example, see references 427 and 826). In connection with the melting points of the aryl R_4Sn compounds it is interesting to note that the melting point of tetraphenyltin is depressed only a few degrees when the compound is mixed with several different tetraphenyl organometallic compounds (65, 172, 641a).

The vapor pressure of tetramethyltin between 18° and 78.9°C. has been determined (93, 837, 849). An equation has been given for the calculation of the boiling points of tetraalkyltins (365).

Experiments indicate that tetraethyltin can crystallize in at least ten forms (810, 811, 812, 850); the melting points of all of these lie between 137° and 148°C. A less complete investigation of tetraethyllead has revealed at least six crystalline modifications (811); two forms of tetraethylgermane have been obtained, while tetraethylsilane and the tetramethyl derivatives of the Group IVA elements appear to crystallize in only one form (812). With tetraethyltin, the crystalline form obtained appears to depend on factors such as the degree of purity, the nature of the surface of the confining vessel, and the thermal history of the sample before crystallization. It is suggested that this unusual polymorphism of tetraethyltin and tetraethyllead arises because the molecules of these two substances exhibit in the solid state a form of rotational isomerism (811, 812). In connection with these studies, the various melting points, heats of fusion and transition, and heat capacities from about 95°K. to about 20° above the melting point have been measured (812).

As expected, the dipole moment for tetraethyltin was found to be zero; the dipole values for triethylphenyltin and ethyltriphenyltin are 0.5 and 0.73 Debye unit, respectively (557).

The parachor value for tetraethyltin was found by Garner and Sugden (225) to be 441.1. The supercooling and glass-formation properties of tetramethyltin have been investigated (161, 162). The behavior of counter tubes with tetramethyltin filling has been studied (56).

The dissociation constants of (p-carboxyphenyl)-trimethyltin and (p-carboxyphenyl)triethyltin have been found to be 1.05×10^{-6} and 1.17×10^{-6}, respectively (128).

4. Chemical properties

Most of the reactions of R_4Sn compounds involve the replacement of one or more of the organic groups. Of these, the most important reactions are cleavages of R_4Sn compounds to organotin halides with halogens, halogen acids, or tin(IV) halides.
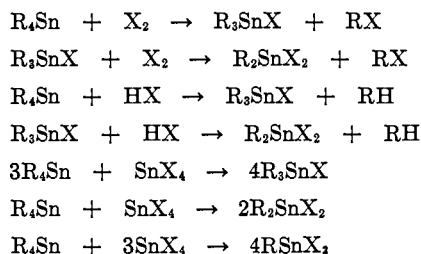
$$R_4Sn + X_2 \rightarrow R_3SnX + RX$$

$$R_3SnX + X_2 \rightarrow R_2SnX_2 + RX$$

$$R_4Sn + HX \rightarrow R_3SnX + RH$$

$$R_3SnX + HX \rightarrow R_2SnX_2 + RH$$

$$3R_4Sn + SnX_4 \rightarrow 4R_3SnX$$

$$R_4Sn + SnX_4 \rightarrow 2R_2SnX_2$$

$$R_4Sn + 3SnX_4 \rightarrow 4RSnX_3$$

Other inorganic halides cleave R_4Sn compounds to give organotin halides; these include mercury(II) halides, bismuth chloride, thallium(III) chloride, arsenic(III) halides, and phosphorus(III) bromide. All of the above reactions are discussed in a later section (Section II,C). Alkyldihaloboranes are conveniently prepared by treating boron trihalides with tetraalkyltin compounds (82b); better yields are obtained by warming the reactants.

Tetraalkyltin compounds are cleaved by mercaptans to R_3SnSR' derivatives (747, 760); vinyl groups are especially easily cleaved (760, 765).

$$R_4Sn + R'SH \rightarrow R_3SnSR' + RH$$
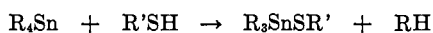
Tetraethyltin is cleaved by phenol to give triethylphenoxytin (512, 747). Similarly, tetraorganotin compounds may be cleaved by organic acids (222, 435, 511, 512, 724, 739, 745, 747, 760, 761, 765);
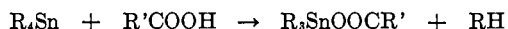
$$R_4Sn + R'COOH \rightarrow R_3SnOOCR' + RH$$

vinyl groups are cleaved more readily than normal alkyl groups but less readily than phenyl groups (739, 760). In liquid ammonia, R_4Sn compounds react with sodium to form R_3SnNa derivatives (52, 126, 293,

$$R_4Sn + 2Na + NH_3 \rightarrow R_3SnNa + RH + NaNH_2$$

462); with tetraphenyltin, some diphenyltindisodium is formed. In tetrahydrofuran, tetraphenyltin is cleaved by lithium metal to give a low yield of triphenyltinlithium (246).

It has been shown that symmetrical organotin compounds are cleaved by organolithium reagents (248, 897). This cleavage may occur as a side reaction in

$$R_4Sn + R'Li \rightarrow R_3SnR' + RLi$$

the preparation of R_4Sn compounds; it is not a suitable method for preparing R_3SnR' derivatives. Recently, however, advantage was taken of the ease of cleavage of the vinyl grouping to develop a very satisfactory method of preparing vinyllithium (770, 772). Phenyllithium reacts with tetravinyltin in ether or hydrocarbon solutions to give a 50–75 per cent yield
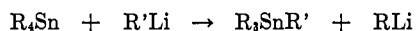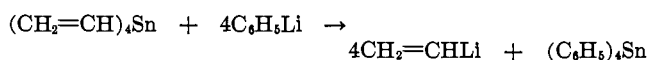
$$(CH_2{=}CH)_4Sn + 4C_6H_5Li \rightarrow$$
$$4CH_2{=}CHLi + (C_6H_5)_4Sn$$

of vinyllithium. Tetraphenyltin precipitates almost quantitatively, but the insolubility of this product

does not seem to be the determining factor in the reaction; a suitable yield of vinyllithium can be obtained by the reaction of phenyllithium with tributylvinyltin even though the tributylphenyltin formed is soluble (770). Tetraphenyltin is cleaved by diethylstrontium or diethylbarium to give, subsequent to carbonation, 10–32 per cent yields of benzoic acid (243).

Symmetrical organotin compounds may be cleaved by hydrogen (228, 342, 428, 429, 430). Tetraphenyltin undergoes hydrogenolysis at 60 atm. and 200°C. to yield metallic tin and benzene;

$$(C_6H_5)_4Sn + 2H_2 \rightarrow 4C_6H_6 + Sn$$
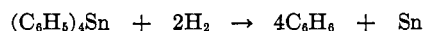
only a trace of biphenyl is obtained. Similarly, with tetraethyltin and tetraisobutyltin, reaction with hydrogen yields principally ethane and isobutane, respectively (228).

Alkyl halides may cleave tetraaryltin compounds (78, 514); from the reaction of tetraphenyltin and *tert*-butyl bromide an 8 per cent yield of *tert*-butylbenzene was obtained, accompanied by an unsaturated hydrocarbon, hydrobromic acid, and triphenyltin bromide (78). Acid halides react slightly or not at all with tetraorganotin compounds; however, if aluminum chloride is added, cleavage takes place readily to give the expected ketone and either organotin halides or inorganic tin compounds (77, 514, 785).

Cleavage of R_4Sn compounds is effected also by a variety of compounds in addition to those mentioned above: by sulfuric acid (77, 794); by chlorosulfonic acid (794); by sulfur (77, 78, 711); by sulfur dioxide in the presence of air (220); by aluminum borohydride (331); and by benzenesulfonyl chloride and sulfuryl chloride (77, 78, 785).

Vorländer (858) reported that nitration of tetraaryltins could be effected without cleavage; other authors (77, 78) reported only cleavage of organotin compounds by nitric acid. Tetrakis(*p*-nitrophenyl)tin is reported by Vorländer to have been prepared by the action of a mixture of fuming nitric acid and concentrated sulfuric acid on tetraphenyltin. Benzenediazonium nitrate is obtained by the action of N_2O_3 and NO on tetraphenyltin (556).

B. UNSYMMETRICAL ORGANOTIN COMPOUNDS

1. General

Unsymmetrical organotin compounds are substances of the type R_4Sn in which the R groups are not all the same. Many compounds having two or three different R groups attached to the same tin atom have been reported (see tables 3, 4, 5, and 6); the R groups may be all alkyl, all aryl, or mixed aryl and alkyl. These substances are usually lower melting, more soluble in organic solvents, and somewhat more reactive chemically than related symmetrical compounds.

TABLE 3

R₃R'Sn compounds
$R_3R'Sn$ *compounds*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
[2-(p-Acetamidophenyl)ethyl]triphenyltin	154–155			(387, 631, 634)
(3-Acetamidopropyl)triphenyltin	95–98			(387)
(2-Acetoxyethyl)triphenyltin	44.5–46.5			(391, 631, 634)
(3-Acetoxypropyl)triphenyltin	65–66			(387, 631, 634)
Allyltributyltin		155/17 mm.		(364, 771)
Allyltriethyltin		76–77/10 mm.		(364)
Allyltrimethyltin		125.5/642 mm.	1.4734 1.4741 (at 25°)	(649, 769)
Allyltriphenyltin	73.5–74.5			(237, 387, 435)
(3-Aminopropyl)tripropyltin		143–144/12 mm.		(389, 631, 634)
Amyltributyltin				(357)
Amyltriethyltin		102/10 mm.		(287, 365, 856, 888)
Amyltrimethyltin		171–172/721 mm.	1.4559	(562)
(2-Benzoylethyl)tripropyltin	79–80			(389, 631, 634)
(2-Benzoylethyl)tripropyltin		158–165/0.05–0.03 mm.		(389, 631, 634)
Benzyltrimethyltin		90/9 mm. Decomposes at 215/760 mm.		(442, 646)
Benzyltriphenyltin	90–91			(249)
Benzyltri-o-tolyltin	108–109			(254, 723)
(5-Bromoamyl)triethyltin		155.5/15 mm.		(287)
(5-Bromoamyl)trimethyltin		124/18 mm.		(287)
(Bromomethyl)trimethyltin		46–50/11 mm.	1.5070 (at 25°)	(767)
[2-(4-Bromophenylazo)-5-dimethylaminophenyl]triphenyltin	199–200			(250)
[3-(4-Bromophenylazo)-4-dimethylaminophenyl]triphenyltin	170–172			(250)
(p-Bromophenyl)triethyltin		150–151/6 mm.		(128, 862, 908)
(p-Bromophenyl)trimethyltin		124/15 mm.		(128, 908)
(p-Bromophenyl)triphenyltin	133–135			(242, 256, 474, 900, 908, 909)
(p-Bromophenyl)tripropyltin		168/4 mm.		(908)
(1-Bromo-3,3,3-trichloropropyl)triethyltin		115–119/0.65–0.9 mm.	1.5425 (at 25°)	(784)
(2-Butyl-4-pyridylmethyl)triethyltin		144–145/3–4 mm.	1.5364	(917)
Butyltriethyltin		73–75/4 mm.	1.4736	(381, 530, 562)
Butyltrimethyltin		149–150/726 mm.	1.4560 (at 21.5°)	(381, 530, 570, 856, 888)
Butyltriphenyltin	61–62	222/3 mm.		(355, 356, 357, 402, 573)
Butyltripropyltin		137–138/37 mm.	1.4741	(365, 563, 567, 856, 888)
Butyltrivinyltin		77–78/8.6–8.5 mm.	1.4851 (at 25°)	(769)
(2-Carbamylethyl)triphenyltin	123–124			(391, 631, 634)
(2-Carbamylethyl)tripropyltin	44–47	155–161/4 mm.		(391, 631, 634)
(2-Carbethoxybutyl)triphenyltin	58–59			(388, 631, 634)
(2-Carbethoxy-1-methylethyl)tripropyltin		111–112/0.6 mm.		(387, 631, 634)
(3-Carbethoxypropyl)tripropyltin		117–119/0.7 mm.		(387, 631, 634)
(2-Carbomethoxyethyl)triphenyltin	46.5–47			(385, 391, 631, 634)
(2-Carbomethoxyethyl)tripropyltin		145–150/2 mm.		(391, 631, 634)
(2-Carbomethoxypropyl)triphenyltin		173–176/0.0002 mm.		(387, 631, 634)
(3-Carbomethoxypropyl)triphenyltin				(388, 631, 634)
(4-Carboxybutyl)triphenyltin	100–102			(388, 631, 634)
(2-Carboxyethyl)triphenyltin (sodium salt)				(388, 631)
(2-Carboxyethyl)tripropyltin (sodium salt)				(388, 631, 634)
(Carboxymethyl)triphenyltin	122–122.5			(126)
[2-(4-Carboxyphenylazo)-5-dimethylaminophenyl]triphenyltin	Decomposes at 358			(250, 864)
(p-Carboxyphenyl)triethyltin	44.5–46.5 86			(128, 910)
(p-Carboxyphenyl)trimethyltin	131–132			(128)
(p-Carboxyphenyl)triphenyltin	166–168 (d.)			(37, 38, 126, 234)
(3-Carboxypropyl)triphenyltin	130–131			(388, 631, 634)
(Chloromethyl)trimethyltin		44–48/15 mm.	1.4860 (at 25°)	(767)
[3-(4-Chlorophenylazo)-4-dimethylaminophenyl]triphenyltin	162–165			(250)
(p-Chlorophenyl)triphenyltin	139–140			(158, 474, 723, 908, 909)
[3-(2-Cyanoethoxy)propyl]triphenyltin	59–61			(387, 631, 634)
(1-Cyanoethyl)triphenyltin	115–116			(631, 632, 634)
(2-Cyanoethyl)triphenyltin	93–94			(385, 391, 631, 632, 634)
(2-Cyanoethyl)tripropyltin		157–160/12 mm.		(391, 631, 632, 634)
(2-Cyano-1-methylethyl)triphenyltin	103–104			(385, 391, 631, 634)
(Cyanomethyl)tributyltin		140–144/1.3 mm.		(382, 530)
(Cyanomethyl)triphenyltin	106–109			(382, 530)
(1-Cyano-2-phenylethyl)tripropyltin		130–141/0.0002 mm.		(387, 631, 634)
(3-Cyanopropyl)triphenyltin	80–81			(385, 391, 631, 634)
(3-Cyanopropyl)tripropyltin		78–79/0.001 mm.		(387, 631, 634)
Cyclohexyltriphenyltin	131–132			(468)
1-Cyclopentadienyltriphenyltin	130–131			(239)
Decyltrimethyltin		67/0.5 mm.	1.4602 (at 25°)	(724)
Decyltrivinyltin		90–94/0.05 mm.	1.4820 (at 25°)	(724)
1,1-Diethoxy-3-(triphenylstannyl)-2-propyne				(362)

TABLE 3—*Continued*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
[3-(Diethylamino)propyl]triphenyltin				(256, 900)
[3-(Diethylamino)propyl]triphenyltin, methiodide	173–175			(256, 900)
[3-(Diethylamino)propyl]triphenyltin, methosulfate	118–132			(256)
[4-Dimethylamino-3-(4-bromophenylazo)phenyl]triphenyltin	170–172			(723)
[5-Dimethylamino-2-(4-bromophenylazo)phenyl]triphenyltin	199–200			(723)
[5-Dimethylamino-2-(4-carboxyphenylazo)phenyl]triphenyltin	Decomposes at 358			(723)
[4-Dimethylamino-3-(4-chlorophenylazo)phenyl]triphenyltin	162–165			(723)
[9-(2-Dimethylaminofluoroenyl)]triphenyltin	150–151			(916, 920)
[4-Dimethylamino-3-(4-nitrophenylazo)phenyl]triphenyltin	190–192			(37, 250, 723)
[5-Dimethylamino-2-(4-nitrophenylazo)phenyl]triphenyltin	205			(250, 723)
(p-Dimethylaminophenyl)triethyltin		172–173/3 mm.		(422, 625)
(o-Dimethylaminophenyl)triphenyltin	110–112			(37, 38, 234)
(m-Dimethylaminophenyl)triphenyltin	90–91			(250, 723)
(p-Dimethylaminophenyl)triphenyltin	132–134			(37, 38, 234)
(p-Dimethylaminophenyl)triphenyltin, methiodide	164			(256, 900)
(p-Dimethylaminophenyl)triphenyltin, methosulfate	244–246			(256, 900)
Dodecyltriethyltin		158–164/1.1 mm.		(381, 530)
Dodecyltrimethyltin		158–160/14 mm. 93–98/0.15 mm.	1.4610 (at 25°)	(381, 530, 724)
Ethyltriisobutyltin		115/10 mm.		(286, 357, 365, 888)
Ethyltrimethyltin		106/746 mm. 108.2/760 mm.	1.4527	(93, 96, 101, 102, 110, 111, 167, 563, 608, 669, 762)
Ethyltriphenyltin	56–58			(243, 246, 249, 253, 473, 510, 530, 557)
Ethyltripropyltin		101/10 mm.		(286, 365, 856, 888)
Ethynyltriphenyltin	34			(313)
(9-Fluorenyl)triphenyltin	129			(920)
(p-Fluorophenyl)triphenyltin	171			(908, 909)
2-Furyltriphenyltin	160–161			(159, 239, 242)
Heptyltriisoamyltin		158–160/3 mm.	1.4696	(564, 856, 888)
1-Hexenyltripropyltin		75–80/0.1 mm.		(387, 631, 632, 634)
Hexyltriphenyltin	54			(724)
Hexyltrivinyltin		57–61/0.03 mm.	1.4851 (at 25°)	(724)
(5-Hydroxyamyl)triphenyltin	64–66			(389, 631, 634)
(4-Hydroxybutyl)triphenyltin	75–76			(389, 631, 634)
(2-Hydroxy-3-chloropropyl)triphenyltin	97–99			(254, 723)
(2-Hydroxyethyl)triphenyltin	66–67			(37, 234, 254, 388, 631, 634)
(o-Hydroxymethylphenyl)triphenyltin	158–159			(37, 38, 234)
(p-Hydroxymethylphenyl)triphenyltin	98–100			(37, 38, 234)
(3-Hydroxy-2-methylpropyl)triphenyltin	100–102			(387, 631, 634)
(Hydroxymethyl)trimethyltin		58–59/6.5 mm.		(766)
(o-Hydroxyphenyl)triphenyltin	Decomposes at 176–177			(38, 234)
(m-Hydroxyphenyl)triphenyltin	207–208			(240)
(p-Hydroxyphenyl)triphenyltin	201–203			(37, 38, 234)
(3-Hydroxy-1-propenyl)triphenyltin	115–125			(387, 631, 634)
(3-Hydroxy-1-propenyl)tripropyltin		120–122/0.006 mm.		(387, 631, 632, 634)
(3-Hydroxypropyl)triphenyltin	105			(391, 631, 634)
1-Indenyltriphenyltin	129–130			(239, 907, 920)
(Iodomethyl)trimethyltin		53–54/6.5 mm.	1.5510 (at 25°)	(767)
(p-Iodophenyl)triphenyltin	143			(908, 909)
Isoamyltriisobutyltin		152.9/16.5 mm.		(286, 856, 888)
Isoamyltrimethyltin		162–164/725 mm.	1.4470 (at 21°)	(562, 856, 888)
Isobutyltrimethyltin		140–141/726 mm.	1.4544 (at 21.5°)	(562, 856, 888)
Isobutyltripropyltin		128/18 mm.		(286, 888)
(3-Ketobutyl)tripropyltin		84–89/0.2 mm.		(389, 631, 634)
(5-Ketohexyl)triphenyltin	70–71			(387, 888)
(2-Ketopropyl)tripropyltin		98–100/1 mm.	1.4865	(626)
1-(2-Ketopyrrolidino)ethyltriphenyltin	74–76			(391)
Mesityltriphenyltin	157–158			(253, 723)
Methallyltriphenyltin				(771)
(o-Methoxymethylphenyl)triphenyltin	94.5–95.5			(37, 38, 235)
(o-Methoxyphenyl)triphenyltin	130–131			(253, 723)
(p-Methoxyphenyl)triphenyltin	151–152			(253, 723)
(Methyldichlorosilylmethyl)trimethyltin		58–59/4 mm.	1.4824 (at 25°)	(768)
(Methyldimethoxysilylmethyl)trimethyltin		77.5–81/18 mm.	1.4523 (at 25°)	(768)
(Methylethynyl)triphenyltin	43			(313)
(4-Methyl-1-naphthyl)trivinyltin				(694)
Methyltriphenyltin	60–61			(95, 252, 473, 645)
Methyltripropyltin		94–96/11 mm. 49–53/1.1 mm.		(365, 389, 509, 631, 634)
1-Naphthyltriphenyltin	125			(473, 665)
Octyltriphenyltin	54–55			(223, 391, 631, 632, 634)
Octyltrivinyltin		90–93/0.2 mm.	1.4819 (at 25°)	(694, 724)
(Pentafluoroethyl)triphenyltin				(368)
4-Pentenyltriphenyltin				(237)

TABLE 3—*Continued*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
(2-Phenoxyethyl)triphenyltin	82.5–83			(391, 631, 634)
(p-Phenoxyphenyl)triphenyltin	161–162			(474)
(2-Phenylethyl)tripropyltin		118–121/0.007 mm.		(387, 631, 634)
(Phenylethynyl)tri-p-tolyltin	106			(312)
Phenyltripropyltin		150/15 mm.		(510)
Phenyltri-2-thienyltin				(191)
Phenyltrivinyltin		73–75/0.45 mm.	1.5478 (at 25°)	(694, 769)
Sodium p-(2-triphenylstannyl-4-dimethylaminophenylazo)-benzoate				(723)
(Thiocyanomethyl)trimethyltin		104–105/4 mm.	1.5247 (at 25°)	(767)
Triallylbutyltin		116–119/10.0 mm.	1.5162 (at 25°)	(724)
Triamylbutyltin				(357)
Triamylpropyltin		163/10 mm.		(365, 856, 888)
Tribenzylbutyltin				(577, 882)
Tribenzylethyltin	31–32			(308, 794)
Tribenzylphenyltin		290/5 mm.		(402)
Tribenzyl-p-tolyltin				(402)
Tributyl-sec-butyltin		143–144/3 mm.	1.4796 (at 15°)	(888)
Tributyl(2-carbomethoxyethyl)tin		140–141/0.4 mm.		(385, 391, 631, 634)
Tributyl(2-carboxyethyl)tin				(388, 631, 634)
Tributyl(2-cyanoethyl)tin		132–138/0.2 mm.		(385, 391, 631, 634)
Tributyl(cyanomethyl)tin		145–148/1.4 mm.	1.4814 (at 18°)	(509)
Tributyl{dimethyl[2-(dimethylchlorosilyl)ethyl]silylmethyl}-tin		180/30 mm.	1.4836 (at 25°)	(572)
Tributyl(dimethylhydrogensilylmethyl)tin		133/5 mm.	1.4764 (at 25°)	(572)
Tributyl(ethoxydimethylsilylmethyl)tin		147/5 mm.	1.4682 (at 25°)	(572)
Tributylethyltin		129/10 mm.		(365, 856, 888)
Tributylhexyltin		165/7 mm.	1.4762 (at 17°)	(564, 888)
Tributyl(3-hydroxy-3-methylbutyl)tin		133–138/0.7 mm.		(389, 631, 634)
Tributyl(3-hydroxypropyl)tin		117–119/12 mm.		(389, 631, 634)
Tributyl-1-indenyltin				(541, 550)
Tributyl-3-indenyltin				(547)
Tributyl(iodomethyl)tin		108–112/0.5 mm.	1.4801	(757)
Tributylisoamyltin		177–178/20 mm.	1.4715	(563, 856, 888)
Tributyl(2-ketocyclohexyl)tin		155–156/1 mm.	1.4805	(626)
Tributylmethyltin		121/10 mm.		(365, 509, 856, 888)
		122–124/12 mm.		
Tributyl(phenylethynyl)tin		174/4 mm.		(314)
Tributylphenyltin		142/2.5 mm.	1.5155	(131, 251, 355, 357, 723, 770, 771)
		139/0.6 mm.		
Tributylstannylacetic acid, ethyl ester		159–163/10 mm. Decomposes at 210/760 mm.		(509)
2-(Tributylstannyl)acetoacetic acid, 1,3-dimethylbutyl ester				(547)
Tributylstannylacetone		130–134/14 mm.	1.4842	(509, 626)
		130–132/2 mm.		
α-(Tributylstannyl)acetophenone		200–205/3 mm.		(509)
α-(Tributylstannyl)acetophenone, semicarbazone	80			(509)
(Tributylstannyl)ethylmalonic acid, diethyl ester			1.4576	(547)
(Tributylstannyl)malonic acid, dibutyl ester			1.4634	(541, 547)
(Tributylstannyl)malonic acid, diethyl ester				(541)
(Tributylstannyl)malonic acid, dimethyl ester				(541)
3-(Tributylstannyl)-2,4-pentanedione				(114, 547, 548)
Tributylvinyltin		114/3 mm.	1.4761 (at 25°)	(581, 694, 728, 769, 770, 772)
		95/1.5 mm.	1.4751 (at 25°)	
Tricyclohexylethyltin		227–228/15 mm.		(468)
Tricyclohexylmethyltin		221/15 mm.		(468)
Tricyclohexylphenyltin	191–192			(468)
Tricyclohexyl-p-tolyltin	111			(468)
Tri-1-cyclopentadienylphenyltin	64–65			(239)
Tri-1-cyclopentadienylvinyltin				(694)
Triethylhexyltin		102–104/0.75 mm.		(381, 530)
Triethyl(o-hydroxyphenyl)tin		155–156/15 mm.	1.5379 (at 25°)	(38, 234, 422, 625, 856, 888)
		197–200/3 mm.		
Triethyl(p-iodophenyl)tin		174–175/760 mm.		(908)
Triethylisoamyltin		111/18.5 mm.		(286, 365, 856, 888)
Triethylisobutyltin		86/10 mm.		(286, 357, 365, 856, 888)
Triethyl(p-isopropenylphenyl)tin		129–130/2 mm.	1.5441 (at 25°)	(42, 427a)
			1.5448 (at 25°)	
Triethylisopropyltin		192–194/719 mm.	1.4772 (at 19°)	(564, 856, 888)
Triethyl(2-ketocyclohexyl)tin		116–117/4 mm.	1.5057	(626)
Triethylmethyltin		162–163/760 mm.	1.4656	(102, 110, 111, 167, 563, 856, 888)
		159/745 mm.		
Triethyloctyltin		135–138/3–4 mm.		(381, 530)
Triethyl(phenylethynyl)tin		162/15 mm.		(312)

TABLE 3—*Concluded*

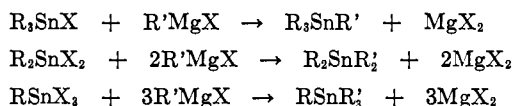| Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Triethylphenyltin..		254/760 mm.	1.5653	(79, 422, 481, 482, 510, 530, 557, 625)
		159/745 mm.		
		113–114/6 mm.		
Triethylpropyltin..		112/50 mm.	1.4726	(286, 364, 365, 464, 563, 672, 856, 888)
		77/10 mm.	1.47410 (at 16.6°)	
Triethyl(2-pyridylmethyl)tin.............................		120–121/3–4 mm.	1.531	(917)
Triethylstannylacetone......................................		100.5–101/6 mm.	1.4991	(626)
Triethyl(1,3,3,3-tetrachloropropyl)tin....................		100/0.3 mm.	1.5230 (at 25°)	(763)
Triethyl(3,3,3-trichloropropyl)tin........................		74/0.25 mm.	1.5086 (at 25°)	(763)
Triethyl(2-trichlorosilylethyl)tin.........................		85/0.6 mm.		(763)
Triethyl(2-trimethoxysilylethyl)tin.......................		78/0.4 mm.	1.4638 (at 25°)	(763)
Triethylvinyltin...		174–175/760 mm.	1.4780	(648, 694, 763, 769)
		60–62/12–13 mm.	1.4738 (at 25°)	
Triisoamylmethyltin..		138–140/4 mm.	1.4700 (at 15°)	(563, 856, 888)
Trimethyloctyltin...		102–118/12 mm.	1.4587 (at 25°)	(381, 530, 724)
		56–58/0.03 mm.		
Trimethylphenyltin...		203–208/760 mm.		(95, 646)
Trimethylpropyltin..		130.8/760 mm.	1.47410	(93, 672)
(Trimethylsilylmethyl)triphenyltin........................		162–163/2 mm.	1.5943 (at 25°)	(641)
Trimethyl(trifluoromethyl)tin..............................	−50.5	100.0/760 mm.		(368, 484a)
Trimethyl(trimethylsilylmethyl)tin........................		165–166/760 mm.	1.4569 (at 25°)	(641, 761)
		64–65/24 mm.	1.4594 (at 25°)	
Trimethylvinyltin...		99–100/760 mm.	1.4544 (at 25°)	(460, 646, 766, 769)
1-Triphenylgermyl-2-triphenylstannylethane...............				(632)
Triphenyl(phenylethyl)tin..................................	127–127.5			(385, 391, 631, 632, 634)
Triphenyl(phenylethynyl)tin...............................	62			(312)
Triphenylpropyltin..	74–74.5			(510)
Triphenyl[2-(4-pyridyl)ethyl]tin...........................	112–113			(387, 631, 634)
Triphenyl(2-pyridyl)tin.....................................	178–179			(242)
Triphenyl(3-pyridyl)tin.....................................	220			(242)
Triphenyl(3-pyridyl)tin, methiodide........................	183–184			(242)
1-Triphenylsilyl-2-triphenylstannylethane..................				(632)
7-(Triphenylstannyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid, diethyl ester.............................	107–108			(239)
7-(Triphenylstannyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diethyl ester................................	109.5–111			(239)
7-(Triphenylstannyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride...	144–145			(239)
9-[2-(Triphenylstannyl)ethyl]carbazole....................	207			(387, 631, 634)
1-[2-(Triphenylstannyl)ethyl]2-pyrrolidone................	74–76			(631, 634)
m-Triphenylstannylphenoxyacetic acid, ethyl ester.........	97–98			(639)
3-(Triphenylstannyl)propanal, diethyl acetal...............	35.5–37.5			(385, 391, 631, 634)
Triphenyl-β-styryltin.......................................	119–120			(387, 631, 632, 634)
Triphenyl-2-thienyltin......................................	206			(191, 470)
Triphenyl-o-tolyltin...	165			(253, 402, 723)
Triphenyl-p-tolyltin...	124			(473, 723)
Triphenyl(p-trimethylsilylphenyl)tin.......................	132.5–133.5			(641)
Triphenyl(triphenylmethyl)tin..............................	Decomposes at 272–273			(52)
Triphenylvinyltin...	45.2–45.4			(694, 728, 730, 769)
Triphenyl-2,4-xylyltin......................................	113–115			(253, 723)
Triphenyl-2,5-xylyltin......................................	100.5			(253, 473, 723)
	97–99			
Triphenyl-2,6-xylyltin......................................	118–119			(253, 723)
Tripropyl[2-(4-pyridyl)ethyl]tin...........................		121–125/0.009 mm.		(387, 631, 634)
Tripropylstannylacetic acid, ethyl ester...................		217–219/760 mm.		(509)
		136–140/11 mm.		
α-(Tripropylstannyl)acetophenone.........................		155–160/3 mm.		(509)
Tripropyl-β-styryltin.......................................		119–120/0.0001 mm.		(387, 631, 634)
Tripropylvinyltin...		90/8.2 mm.	1.4776 (at 25°)	(739)
Tris(2-carbomethoxyethyl)butyltin.........................		139–141/0.0004 mm.		(387, 631, 634)
Tris(2-carbomethoxyethyl)propyltin........................		136–140/0.0008 mm.		(387, 631, 634)
Tris(2-carboxyethyl)propyltin, trisodium salt..............				(388, 631, 634)
Tris(p-chlorophenyl)phenylethynyltin......................	132			(312)
Tris(m-hydroxyphenyl)phenyltin...........................	203–205			(240)
Tri-m-tolyl-p-tolyltin.......................................	103			(402)
Tri-p-tolyl-o-tolyltin..	168			(402)

2. Preparation

Unsymmetrical organotin compounds of the types R_3SnR', R_2SnR_2', and $R_2SnR'R''$ usually are prepared from an organotin halide and a Grignard reagent.

In some cases they may be prepared conveniently from an organotin–metal compound and an organic halide or by addition of an organotin hydride to an unsaturated linkage. The preparation of organotin

halides and organotin hydrides is discussed in later sections.

The reaction of Grignard reagents with organotin halides as a method of preparation of unsymmetrical organotin compounds was introduced by Pope and Peachey (672) and is the method most commonly used at present. Any organotin halide, even the fluoride,

$$R_3SnX + R'MgX \rightarrow R_3SnR' + MgX_2$$
$$R_2SnX_2 + 2R'MgX \rightarrow R_2SnR_2' + 2MgX_2$$
$$RSnX_3 + 3R'MgX \rightarrow RSnR_3' + 3MgX_2$$

may be used; the R groups of both the organotin halide and the Grignard reagent may be either aliphatic or aromatic. In general, the yield of organotin compound by this method is very satisfactory. The usual solvent has been ethyl ether or, in some cases where the R group is bulky, benzene or toluene has been added. More recently, the use of tetrahydrofuran as a solvent has been recommended (648, 694, 724, 728, 739, 760, 761, 769). (The following references illustrate the wide application of this method: 52, 72, 79, 94, 95, 167, 223, 235, 237, 239, 240, 284, 364, 365, 380, 381, 391, 402, 464, 468, 470, 473, 474, 477, 490, 510, 562, 563, 564, 565, 572, 608, 632, 641, 646, 648, 649, 665, 672, 694, 724, 728, 739, 760, 761, 764, 766, 767, 769, 794, 889, 901, 903, 908.) The stepwise addition of two different groups via the Grignard

$$R_2SnX_2 \xrightarrow{R'MgX} R_2R'SnX \xrightarrow{R''MgX} R_2R'R''Sn$$
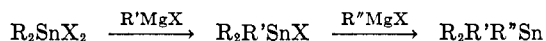
reagent is difficult and in most cases impossible (724); compounds of this type are best prepared by the following reaction sequence:

$$R_2SnX_2 \xrightarrow{2R'MgX} R_2SnR_2' \xrightarrow{X_2}$$
$$R_2R'SnX \xrightarrow{R''MgX} R_2R'R''Sn$$
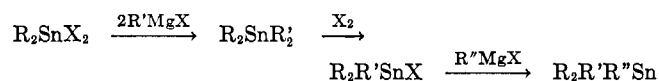
Tin heterocycles—(cyclopentamethylene)diethyltin and (cyclopentamethylene)dimethyltin—have been prepared from the di-Grignard derivative of 1,5-dichloropentane and the corresponding dialkyltin dibromide (287). Di-Grignard reagents react with R_3SnX compounds to form compounds containing two tin atoms per molecule (64, 312, 770); this is especially useful for preparing tin-substituted acetylene derivatives.

$$2R_3SnX + XMgC{\equiv}CMgX \rightarrow R_3SnC{\equiv}CSnR_3 + 2MgX_2$$
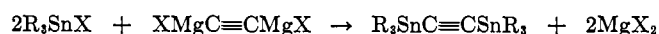
It has recently been reported that unsymmetrical organotin compounds also may be produced by the reaction of Grignard reagents with organotin oxides (728).

$$2CH_2{=}CHMgCl + (C_4H_9)_3SnOSn(C_4H_9)_3 \rightarrow$$
$$2(C_4H_9)_3SnCH{=}CH_2 + (MgCl)_2O$$
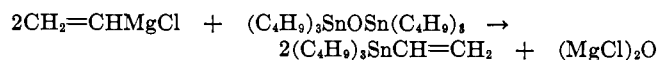
Other organometallic reagents react with organotin halides to form unsymmetrical organotin derivatives.

A number of reports of the use of organolithium reagents have appeared (42, 72, 242, 256, 314, 497, 770, 917, 919, 920, 921); the organolithium reagent has been employed principally for the introduction of vinyl or aryl groups. However, use of the organolithium reagent may result in cleavage and redistribution products (234, 248, 897, 909); in some cases increased yields are obtained if the organolithium compound is converted to the Grignard reagent prior to reaction with the organotin halide (234, 235, 240, 242).

The first organotin compound containing an aromatic group was prepared by Ladenburg (481, 482), who prepared triethylphenyltin by adding metallic sodium to an ether solution of triethyltin iodide and bromobenzene. Probably phenylsodium was an intermediate in this reaction. More recently, a patent lists the preparation of butyltriphenyltin from phenylsodium and butyltin trichloride in toluene (355). Sodium acetylide in liquid ammonia reacts with R_3SnX compounds to form $R_3SnC{\equiv}CSnR_3$ derivatives (64 312); silver acetylide derivatives in acetone similarly have been employed (362). Sodium salts of compounds containing an active methylene group also react with organotin halides in toluene (541).

Early workers—Cahours (101, 102), Frankland (219), Morgunoff (594), and Pope and Peachey (669)—prepared unsymmetrical organotin compounds by the reaction of dialkylzinc compounds and organotin

$$2(CH_3)_3SnI + (C_2H_5)_2Zn \rightarrow 2(CH_3)_3(C_2H_5)Sn + ZnI_2$$
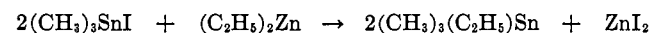
halides. Organozinc compounds are rather difficult to manipulate and offer no advantages over the Grignard reagent.

A number of unsymmetrical organotin compounds have been prepared by the reaction of an organotin-sodium compound, in liquid ammonia, with an organic halide. The preparation of organotin–alkali metal

$$R_xSnNa_y + yR'X \rightarrow R_xSnR_y' + yNaX$$
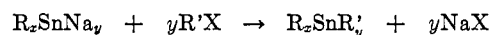
compounds is discussed in a later section. (The following references illustrate the general application of this reaction: 64, 94, 95, 96, 126, 199, 234, 387, 442.) Although functionally substituted compounds are difficult to prepare using this reaction, the method has been employed for the preparation of (carboxymethyl)-

$$(C_6H_5)_3SnNa + CH_2ClCOONa \rightarrow$$
$$(C_6H_5)_3SnCH_2COONa + NaCl$$
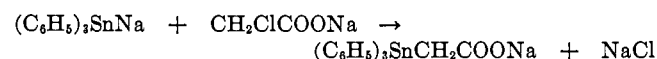
triphenyltin (126). (2-Hydroxyethyl)triphenyltin has been obtained from triphenyltinsodium and ethylene oxide in liquid ammonia (234). Bullard and Robinson (95) were unable to prepare dimethyldiphenyltin from dimethyltindisodium and bromobenzene in liquid ammonia; however, when diphenyltindisodium and methyl

TABLE 4

$R_2R_2'Sn$ compounds

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Bis(2-carbomethoxyethyl)diphenyltin		191–194/0.003 mm.		(387, 631, 632, 634)
Bis(2-carbomethoxyethyl)dipropyltin		119–121/0.001 mm.		(387, 631, 634)
Bis(2-carboxyethyl)dipropyltin, disodium salt				(388, 631, 634)
Bis(1-chloroethyl)bis(chloromethyl)tin		141–142/5 mm.	1.578	(901, 903)
Bis(1-chloroethyl)diethyltin		114–115/5 mm.	1.5083	(901, 903)
Bis(2-cyanoethyl)dipropyltin		113–117/0.0004 mm.		(387, 631, 634)
Bis(p-dimethylaminophenyl)diphenyltin				(256, 900)
Bis(p-dimethylaminophenyl)diphenyltin, dimethiodide	164–168			(256, 900)
Bis(p-dimethylaminophenyl)diphenyltin, dimethosulfate	Decomposes at 125			(256)
Bis(dimethylhydrogensilylmethyl)dimethyltin		101/20 mm.	1.4743 (at 25°)	(572)
Bis[3-(dimethylhydrogensilyl)propyl]dimethyltin		146/15 mm.	1.4730 (at 25°)	(572)
Bis(2-ethylhexyl)dimethyltin		101–102/0.2 mm.	1.4715 (at 25°)	(724)
Bis(o-hydroxyphenyl)diphenyltin	136–138			(37, 38, 234)
Bis(m-hydroxyphenyl)diphenyltin	189–190			(240)
	201–203			
Bis(p-methoxyphenyl)di-1-naphthyltin		98/0.4 mm.	1.5184 (at 25°)	(764)
Bis(p-methoxyphenyl)diphenyltin	125–126			(72)
Bis(p-methoxyphenyl)di-2-thienyltin	89–93			(72)
Bis(2-methyl-3-butenyl)divinyltin				(694)
Bis(2-phenylethyl)dipropyltin		172/0.015 mm.		(387, 631, 632, 634)
Bis(trimethylsilyl)divinyltin	106–109			(382)
Cyclooxy[bis(dimethylsilylmethyl)]dibutyltin		170/25 mm.	1.4800 (at 25°)	(572)
			1.4805 (at 25°)	
Cyclooxy[bis(dimethylsilylmethyl)]dimethyltin		95/21 mm.	1.4743 (at 25°)	(572)
Cyclooxy {bis[3-(dimethylsilyl)propyl]} dimethyltin		148/16 mm.	1.4840 (at 25°)	(572)
(Cyclopentamethylene)diethyltin		95/14 mm.		(287, 856, 888)
(Cyclopentamethylene)dimethyltin		63/15 mm.		(287, 856, 888)
Diallyldibutyltin		145–146/5 mm.	1.4986 (at 25°)	(364, 724)
		93/0.1 mm.		
Diallyldiethyltin		99–100/17 mm.		(364)
Diallyldiphenyltin		173–174/5 mm.	1.6025	(237, 435, 724)
		120–124/0.005 mm.	1.6013 (at 25°)	
Diamyldibutyltin				(357)
Di-tert-amyldibutyltin				(889)
Diamyldiethyltin		139–141/14 mm.		(381, 530)
Di-tert-amyldimethyltin		119.5–120/29 mm.	1.4870 (at 25°)	(856, 889)
Dibenzyldiethyltin		223–224/20 mm.		(794)
Dibenzyldiphenyltin				(108, 708, 709)
Dibutylbis(dimethylhydrogensilylmethyl)tin		130/5 mm.	1.4810 (at 25°)	(572)
Dibutylbis(ethoxydimethylsilylmethyl)tin		186/15 mm.	1.4655 (at 25°)	(572)
Dibutylbis(1,1,2,2-tetrafluoroethyl)tin		46–47/0.2 mm.		(476)
Dibutylbis(trimethylsilylmethyl)tin		98/0.45 mm.	1.4777 (at 25°)	(761)
Dibutyldi-tert-butyltin		123–125/40 mm.		(889)
Dibutyldicyclohexyltin		143/0.45 mm.	1.5126 (at 25°)	(764)
Dibutyldicyclopentyltin		128/0.3 mm.	1.5067 (at 25°)	(764)
Dibutyldiethyltin		112/10 mm.	1.4734	(167)
Dibutyldi-3-indenyltin				(114, 548)
Dibutyldiisopropyltin		102/2.9 mm.	1.4756 (at 25°)	(764)
Dibutyldimethyltin		70/4.4 mm.	1.4640 (at 25°)	(764)
Di-sec-butyldimethyltin		68/5.5 mm.	1.4738 (at 25°)	(764)
Di-tert-butyldimethyltin		84–85/40 mm.	1.4662 (at 25°)	(856, 889)
Dibutyldiphenyltin				(109, 357, 494, 889)
Dibutyldivinyltin		78–80/2 mm.	1.4824 (at 25°)	(555, 581, 694, 728, 766a, 769)
		54–55/0.35 mm.	1.4797 (at 25°)	
2,2'-(Dibutylstannylene)bis[acetoacetic acid], dibutyl ester				(547, 550)
2,2'-(Dibutylstannylene)bis[acetoacetic acid], diethyl ester				(547)
2,2'-(Dibutylstannylene)bis[2-acetylacetoacetic acid], diethyl ester				(547)
1,1'-(Dibutylstannylene)bis[1-benzenesulfonylacetone]	85–87			(547, 550)
(Dibutylstannylene)bis[benzoylacetic acid], diethyl ester				(547)
3,3'-(Dibutylstannylene)bis[3-benzoyl-2,4-pentanedione]				(114, 548)
(Dibutylstannylene)bis[benzylmalonic acid], tetraethyl ester				(541, 547)
(Dibutylstannylene)bis[cyanoacetic acid], dimethyl ester				(114, 547, 548)
3,3'-(Dibutylstannylene)bis[3-(2-ethylhexyl)-2,4-pentanedione]		130–132/1.6 mm.		(547)
2,2'-(Dibutylstannylene)bis[2-propylacetoacetic acid], diethyl ester				(547)
(Dibutylstannylene)dimalonic acid, dibutyldiphenyl ester				(114, 548)
(Dibutylstannylene)dimalonic acid, tetrabutyl ester			1.4544	(114, 541, 547, 548)
(Dibutylstannylene)dimalonic acid, tetraethyl ester			1.4665	(541, 547)
(Dibutylstannylene)dimalonic acid, tetrakis(2-ethylhexyl) ester				(547)
3,3'-(Dibutylstannylene)-2,4-pentanedione				(114, 547, 548, 550)
Dicyclohexyldimethyltin		98/0.4 mm.	1.5184 (at 25°)	(764)

TABLE 4—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Dicyclohexyldiphenyltin...............................	119–120			(72, 764)
Di-1-cyclopentadienyldiphenyltin.......................	105–106			(239)
Dicyclopentyldimethyltin..............................		76–77/0.3 mm.	1.5109 (at 25°)	(764)
Dicyclopentyldiphenyltin..............................	49–50.2			(764)
Diethyldiisoamyltin..................................		131/13.5 mm.		(286, 856, 888)
Diethyldiisobutyltin.................................		108.2/13 mm.		(286, 856, 888)
Diethyldimethyltin..................................		131–132/760 mm.	1.4650 (at 19°)	(94, 110, 111, 167, 219, 509, 565,
		144–146/760 mm.		594, 672)
Diethyldiphenyltin..................................		155–157/4 mm.		(94, 422, 510, 530, 625, 708, 709)
		135.5–137/ <1 mm.		
Diethyldipropyltin..................................		84.5/10–11 mm.		(94)
		205–207/760 mm.		
Di-1-indenyldiphenyltin..............................	108–110			(239)
Diisobutyldimethyltin................................		85/16.5 mm.		(286, 856, 888)
Diisopropyldimethyltin...............................		68/29.0 mm.	1.4621 (at 25°)	(764)
Dimethylbis(perfluorovinyl)tin........................		58/38 mm.		(368a)
Dimethylbis(trimethylsilylmethyl)tin...................		146.5–147.5/65 mm.	1.4644 (at 25°)	(641, 761)
		62/1.3 mm.	1.4702 (at 25°)	
		55/0.7 mm.		
5,5-Dimethyl-10,11-dihydrodibenzo[b,f]stanniepin.........		130–135/0.2 mm.	1.6130 (at 25°)	(477)
Dimethyldioctyltin..................................		121–122/0.2 mm.	1.4659 (at 25°)	(724)
Dimethyldiphenyltin.................................		127–140/3 mm.		(95)
Dimethyldivinyltin..................................		120–121/760 mm.	1.4720 (at 25°)	(728, 769)
Di-1-naphthyldiphenyltin.............................	209–210			(72)
Di-1-naphthyldi-2-thienyltin..........................	145–146			(72)
Di-4-pentenyldiphenyltin.............................		174–175/1.5 mm.	1.5598	(237)
Diphenylbis[p-(diphenylhydroxymethyl)phenyl]tin.........	265–266			(196)
Diphenylbis(trimethylsilylmethyl)tin...................		137/0.35 mm.	1.5499 (at 25°)	(641, 761)
Diphenylbis(p-trimethylsilylphenyl)tin.................	95–96			(641)
5,5-Diphenyl-10,11-dihydrodibenzo[b,f]stanniepin.........	146–147			(477)
Diphenyldipropyltin.................................		160–161/3 mm.		(510)
Diphenyldi-2-thienyltin..............................	207–210			(72, 191)
Diphenyldivinyltin..................................		153–154/5 mm.	1.5949 (at 25°)	(694, 728, 760)
		121.5/0.4 mm.	1.5929 (at 25°)	
Hexaphenylstannole..................................	>160			(490a)
1,1,4,4-Tetraphenyl-1-stanna-4-germacyclohexane.........				(632)
1,1,4,4-Tetraphenyl-1-stanna-4-silacyclohexane...........				(632)

iodide were used, they obtained dimethyldiphenyltin in satisfactory yields. These authors also were unable to prepare trimethylphenyltin from trimethyltinsodium and bromobenzene; similarly, Chambers and Scherer (126) were unable to obtain R₃SnR′ compounds from triphenyltinsodium and various aryl halides. The reaction of dialkyltindisodium compounds in liquid ammonia with dichloromethane yields polymeric products, $(R_2SnCH_2)_n$ (199, 545).

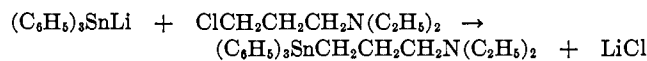In the above reactions an organotinlithium reagent may replace the organotinsodium compound, Ether is the usual solvent for the preparation and reactions of organotinlithium reagents.
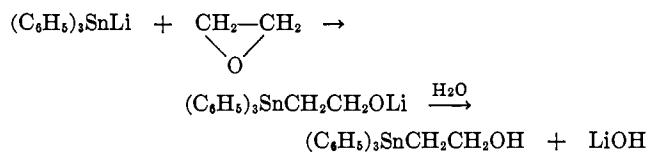
$$R_3SnLi + R'X \rightarrow R_3SnR' + LiX$$
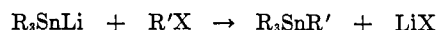
A number of R₃SnR′ compounds, where R and R′ may be either alkyl or aryl groups, have been prepared in this manner (249, 251, 253, 256). [3-(Diethylamino)propyl]triphenyltin has been prepared from triphenyltinlithium and 3-(diethylamino)propyl chloride (256).

TABLE 5

R₂R′R″Sn *compounds*

Compound	Boiling Point	$n_D^{25°}$	References
	°C.		
Benzylbutyldiphenyltin...	215/13 mm.		(402)
Benzyldibutylethyltin..	175–180/9 mm.		(490)
Benzylphenyldi-p-tolyltin..	265–270/23 mm.		(402)
Butyldiphenylvinyltin..			(694)
Dibenzylbutylethyltin..	207–209/9 mm.		(402, 490)
Dibenzylethylpropyltin...	220–225/15 mm.		(794)
Diethylmethylvinyltin..	56–59/26 mm.	1.4697	(769)
Ethyldiisoamylpropyltin..	141–142/17 mm.		(286, 856, 888)
Ethyldimethylpropyltin..	153/762 mm.		(608, 669, 672)
Ethylmethyldipropyltin..	183–184/758 mm.		(762)

$(C_6H_5)_3SnLi + ClCH_2CH_2CH_2N(C_2H_5)_2 \rightarrow$
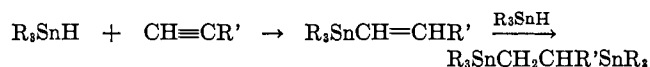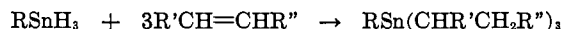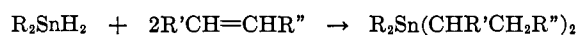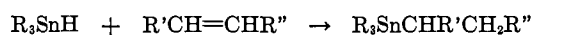$$(C_6H_5)_3SnCH_2CH_2CH_2N(C_2H_5)_2 + LiCl$$

Triphenyltinlithium reacts with ethylene oxide to form, subsequent to hydrolysis, (2-hydroxyethyl)-triphenyltin (254).

$$(C_6H_5)_3SnLi + \underset{\underset{O}{\diagdown \diagup}}{CH_2-CH_2} \rightarrow$$

$$(C_6H_5)_3SnCH_2CH_2OLi \xrightarrow{H_2O}$$
$$(C_6H_5)_3SnCH_2CH_2OH + LiOH$$

Epichlorohydrin similarly yields (2-hydroxy-3-chloropropyl)triphenyltin, indicating the epoxy linkage to be more reactive than the carbon–chlorine bond (254).

Organotin hydrides undergo addition reactions with many olefinic and acetylenic compounds. The reaction product usually is not contaminated with undesirable

$$R_3SnH + R'CH=CHR'' \rightarrow R_3SnCHR'CH_2R''$$
$$R_2SnH_2 + 2R'CH=CHR'' \rightarrow R_2Sn(CHR'CH_2R'')_2$$
$$RSnH_3 + 3R'CH=CHR'' \rightarrow RSn(CHR'CH_2R'')_3$$

$$R_3SnH + CH\equiv CR' \rightarrow R_3SnCH=CHR' \xrightarrow{R_3SnH}$$
$$R_3SnCH_2CHR'SnR_3$$

by-products, as is often the case with other methods of synthesis of unsymmetrical organotin compounds. The method is especially suited to the preparation of organotin compounds containing functional groups. These reactions are discussed in some detail in a later section (Section II,E).

"Redistribution" reactions of two symmetrical R_4Sn compounds have been used to prepare unsymmetrical organotin derivatives. A mixture of triethylmethyltin, diethyldimethyltin, ethyltrimethyltin, and starting materials was obtained on refluxing a pentane solution of tetraethyltin and tetramethyltin for 5 hr. in the presence of 2.5 mole per cent of aluminum chloride (110, 111). Fractionation of this reaction mixture showed that the yields of the various compounds corresponded to the calculated values on the basis of random distribution. Similarly, redistribution reactions have been run using tetraethyltin and tetraisobutyltin, tetrabutyltin and tetraamyltin, and tetraphenyltin and tetrabutyltin (356, 357). This method of preparation is limited, since the separation of the products requires very efficient fractional distillation. In a modification of this procedure (357), tetraphenyltin and tetrabutyltin in equimolar quantities were heated in the presence of a small amount of aluminum chloride; at 190–200°C. and 2.5 mm. pressure, tributylphenyltin and dibutyldiphenyltin were distilled from the reactor as they were formed and separated by fractional distillation. The tributylphenyltin was returned to the reactor to form more dibutyldiphenyltin by reaction with butyltriphenyltin; by this process, yields above 90 per cent of dibutyldiphenyltin were obtained.

Other less-used methods include cleavage reactions of hexaalkylditin compounds and the use of diazoalkanes. By heating hexaethylditin with phenylmercury chloride for 3 hr. at 150–160°C., a 30 per cent yield of triethylphenyltin was obtained (422, 625).

$(C_2H_5)_3SnSn(C_2H_5)_3 + C_6H_5HgCl \rightarrow$
$$(C_2H_5)_3SnC_6H_5 + Hg + (C_2H_5)_3SnCl$$
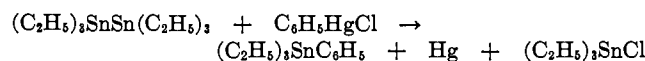
When diphenylmercury was used in place of phenylmercury chloride, the yield of triethylphenyltin was 40 per cent. This procedure was employed for the preparation of (p-dimethylaminophenyl)triethyltin and triethyl(o-hydroxyphenyl)tin (422, 625). A 60 per cent yield of diethyldiphenyltin was obtained when diethyltin and diphenylmercury were heated at 150°C. for 30 min. (422, 625). Perfluoroalkyl iodides cleave

$$(C_2H_5)_2Sn + (C_6H_5)_2Hg \rightarrow (C_2H_5)_2Sn(C_6H_5)_2 + Hg$$
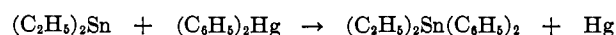
the tin–tin linkage of hexaalkylditin compounds, as illustrated by the following equation (368):

$$R_3SnSnR_3 + C_nF_{2n+1}I \rightarrow R_3SnC_nF_{2n+1} + R_3SnI$$
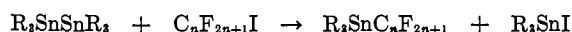
The $R_3SnC_nF_{2n+1}$ compounds also are formed, but in very small amounts, by the cleavage of symmetrical R_4Sn derivatives with perfluoroalkyl iodides.

Halomethyl derivatives of tin of the type R_3SnCH_2X may be prepared in good yield by the reaction of diazomethane with organotin halides (767).

$$R_3SnCl + CH_2N_2 \rightarrow R_3SnCH_2Cl + N_2$$
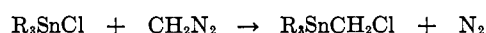
Organotin hydrides react with aliphatic diazo compounds to form unsymmetrical organotin compounds of the type R_3SnR' or $R_2SnR'_2$ (509).

$$R_3SnH + N_2CHR' \rightarrow R_3SnCH_2R' + N_2$$
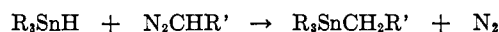
This method has been utilized to prepare organotin compounds containing keto, ester, or nitrile groups.

Triethylmethoxytin reacts with isopropenyl acetate to form triethylstannylacetone and methyl acetate (626). A number of other organotin ketones have been

$(C_2H_5)_3SnOCH_3 + CH_2=C(CH_3)OCOCH_3 \rightarrow$
$$(C_2H_5)_3SnCH_2COCH_3 + CH_3COOCH_3$$
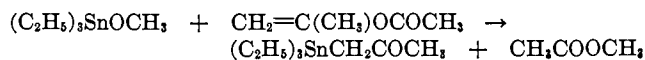
similarly prepared.

Triphenyltin cyanoacetate undergoes decarboxylation on heating in vacuo just above its melting point to give a 50 per cent yield of (cyanomethyl)triphenyltin (382).

$$(C_6H_5)_3SnOOCCH_2CN \rightarrow (C_6H_5)_3SnCH_2CN + CO_2$$
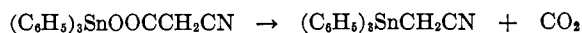
Triethyltin cyanoacetate does not decompose similarly, but gives tetraethyltin rather than the expected product; however, a 20 per cent yield of (cyanomethyl)-tripropyltin can be obtained by heating tripropyltin cyanoacetate (382).
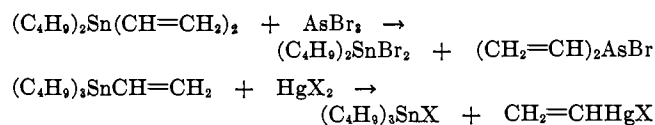
3. Physical properties

Physical investigations with organotin compounds have usually employed symmetrical substances, and there are few data which pertain in particular to unsymmetrical compounds. For this reason all references to physical properties were discussed in the analogous section under symmetrical organotin compounds.

4. Chemical properties

The chemical properties of unsymmetrical organotin compounds are basically the same as those of the symmetrical compounds; the discussion which follows will be confined for the most part to divergencies in the reactions of the two types. The conversion of tetraorganotin compounds to organotin halides by cleavage with halogens, halogen acids, or tin(IV) halides as well as the ease of cleavage of various groups are discussed in a later section (Section II,C).

It has already been mentioned that the reaction of tetravinyltin with phenyllithium is a useful method for preparing vinyllithium. Similarly, the reactions of alkylvinyltin compounds with arsenic(III) bromide (555) or mercury(II) halides (762) are useful routes to vinylarsenic halide or vinylmercury halide derivatives.

$$(C_4H_9)_2Sn(CH{=}CH_2)_2 + AsBr_3 \rightarrow$$
$$(C_4H_9)_2SnBr_2 + (CH_2{=}CH)_2AsBr$$
$$(C_4H_9)_3SnCH{=}CH_2 + HgX_2 \rightarrow$$
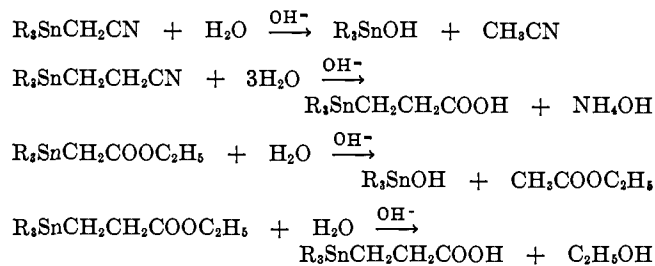$$(C_4H_9)_3SnX + CH_2{=}CHHgX$$

The reaction of phenyllithium with compounds of the type $(C_6H_5)_3SnC_6H_4X$, where X is a halogen atom or a methyl group, yields principally tetraphenyltin (909). Tetraphenyltin also is obtained from the reaction of butyllithium with 1-cyclopentadienyltriphenyltin (237). It appears that the unsymmetrical organotin compounds are cleaved by organolithium reagents and that the cleavage products undergo symmetrization. The reaction of (p-bromophenyl)triphenyltin with ethylmagnesium bromide similarly may give tetraphenyltin (910).

While most tetraorganotin compounds are stable in the presence of water and are not sensitive toward dilute aqueous solutions of alkalies, a few of the unsymmetrical types are quite easily hydrolyzed. Bis-(triphenylstannyl)acetylene is stable in cold water but hydrolysis takes place in the presence of a slight amount of base (64).

$$(C_6H_5)_3SnC{\equiv}CSn(C_6H_5)_3 + 2H_2O \rightarrow$$
$$2(C_6H_5)_3SnOH + CH{\equiv}CH$$
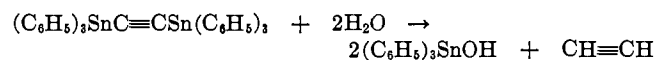
1-Cyclopentadienyltriphenyltin is readily hydrolyzed by water to bis(triphenyltin) oxide (239).

Cyanomethyl- and carbethoxymethyltin compounds react with aqueous alkali to give cleavage of the tin-carbon bond; however, when the ester or cyano group
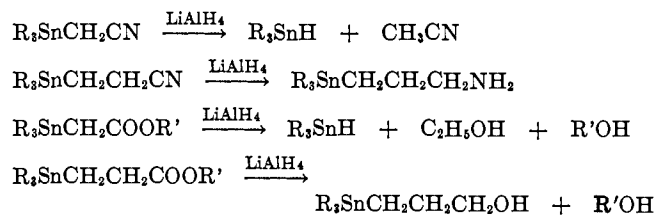
$$R_3SnCH_2CN + H_2O \xrightarrow{OH^-} R_3SnOH + CH_3CN$$
$$R_3SnCH_2CH_2CN + 3H_2O \xrightarrow{OH^-}$$
$$R_3SnCH_2CH_2COOH + NH_4OH$$
$$R_3SnCH_2COOC_2H_5 + H_2O \xrightarrow{OH^-}$$
$$R_3SnOH + CH_3COOC_2H_5$$
$$R_3SnCH_2CH_2COOC_2H_5 + H_2O \xrightarrow{OH^-}$$
$$R_3SnCH_2CH_2COOH + C_2H_5OH$$

is in the β-position or beyond with respect to the tin atom, they are readily hydrolyzed to the carboxylic acid derivatives (382, 388, 509). (2-Carboxyethyl)-triphenyltin is unstable at room temperature; other
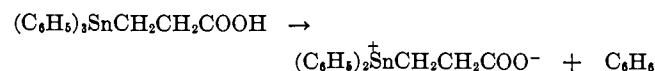
$$(C_6H_5)_3SnCH_2CH_2COOH \rightarrow$$
$$(C_6H_5)_2\overset{+}{S}nCH_2CH_2COO^- + C_6H_6$$

$R_3SnCH_2CH_2COOH$ compounds can be thermally decomposed to the corresponding inner salts (385, 388).

Similarly, reduction with lithium aluminum hydride of cyanomethyl- or carboalkoxymethyltin compounds results in cleavage of the carbon–tin bond; if the ester

$$R_3SnCH_2CN \xrightarrow{LiAlH_4} R_3SnH + CH_3CN$$
$$R_3SnCH_2CH_2CN \xrightarrow{LiAlH_4} R_3SnCH_2CH_2CH_2NH_2$$
$$R_3SnCH_2COOR' \xrightarrow{LiAlH_4} R_3SnH + C_2H_5OH + R'OH$$
$$R_3SnCH_2CH_2COOR' \xrightarrow{LiAlH_4}$$
$$R_3SnCH_2CH_2CH_2OH + R'OH$$

or cyano group is in the β-position or beyond, normal reduction products are obtained (389).

Methylmagnesium iodide reacts with (2-cyanomethyl)tripropyltin to give principally the addition product, (3-ketobutyl)tripropyltin, and a small amount of cleavage product, methyltripropyltin (389). With methylmagnesium iodide and tributyl(2-carbomethoxyethyl)tin, only the addition product, tributyl(3-hydroxy-3-methylbutyl)tin, is obtained (389).

Photochemical reactions of diethyldiphenyltin with carbon tetrachloride, chloroform, or methanol proceed through cleavage of the phenyl radical, which then reacts with the solvent (709). With carbon tetrachloride as a solvent, chlorobenzene, hexachloroethane, diethyltin dichloride, and a small amount of triphenyltin chloride were obtained. With chloroform, the products were benzene, tetraethyltin, and diethyltin dichloride. In methanolic solution, benzene, formaldehyde, metallic tin, tetraethyltin, and possibly diethyltin oxide were the reported products.

Unsymmetrical organotin compounds containing both alkyl and aryl groups react readily with silver nitrate solution, while the symmetrical alkyl compounds undergo no similar reaction at room temperature (64, 471, 473, 481, 510); tetraphenyltin is readily cleaved by silver nitrate (255). With trialkylphenyl-

tins and dialkyldiphenyltins, a yellow precipitate of a phenylsilver—silver nitrate complex is obtained; with alkyltriphenyltins, finely divided metallic silver is immediately deposited (510). A study of the mechanism of these reactions is in progress (510).

In attempting to prepare organometallic compounds via the Diels–Alder reaction, the reaction of tetracyclone with triphenylvinyltin in refluxing bromobenzene was examined (730). Among the products isolated were tetraphenyltin, 1,2,3,4-tetraphenylbenzene, 2,3,4,5-tetraphenylcyclopent-2-enone, and triphenyltin bromide; a reducing gas was evolved throughout the course of the reaction. To explain the products obtained, the following reactions were proposed:

$$(C_6H_5)_3SnH + C_6H_5Br \rightarrow (C_6H_5)_3SnBr + C_6H_6$$
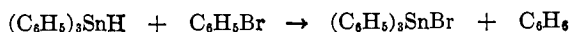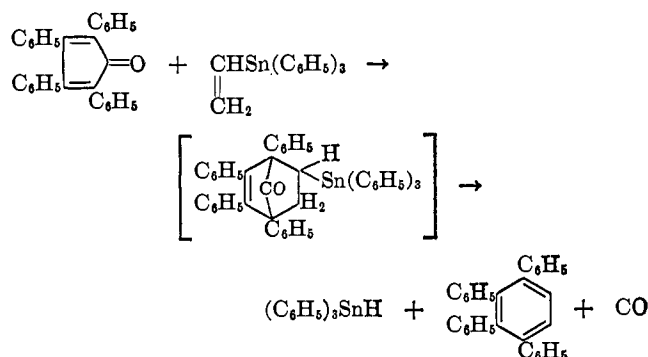
The expected addition products were obtained from the Diels–Alder reaction of (1-cyclopentadienyl)triphenyltin with maleic anhydride, with diethyl maleate, and with diethyl acetylenedicarboxylate (239).

Various other reactions that involve no cleavage of carbon–tin bonds have been reported for the unsymmetrical organotin compounds. (p-Bromophenyl)trialkyltin compounds may be converted to the corresponding Grignard reagents, whose subsequent carbonation gives (p-carboxyphenyl)trialkyltin compounds (128).
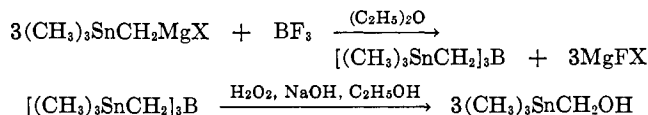
$$R_3SnC_6H_4Br \xrightarrow{Mg} R_3SnC_6H_4MgBr \xrightarrow[H^+]{CO_2}$$
$$R_3SnC_6H_4COOH$$
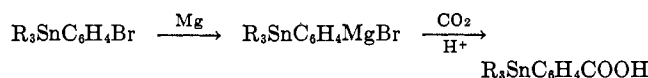
Polymerizable silanes containing tin have been prepared from organotin Grignard reagents (768) (Y may be a halogen atom or an alkoxy group):

$$R_3SnCH_2MgX + CH_3SiY_3 \rightarrow$$
$$R_3SnCH_2(CH_3)SiY_2 + MgXY$$
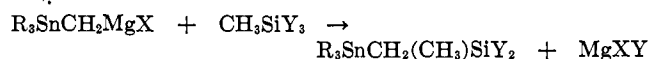
The reaction of organosilicon Grignard reagents with organotin halides also has been employed to prepare compounds of this type (572) ($m = 1$ or 3; $n = 1$ or 2; R = methyl or butyl):
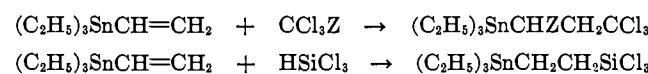
$$nH(CH_3)_2Si(CH_2)_mMgCl + R_{4-n}SnCl_n \rightarrow$$
$$[H(CH_3)_2Si(CH_2)_m]_nSnR_{4-n} + nMgCl_2$$
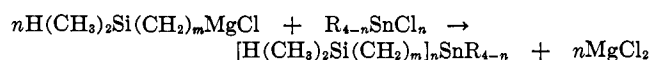
Tris(trimethylstannylmethyl)borane has been prepared by the Grignard method; oxidation of this compound gave the corresponding alcohol (766).

$$3(CH_3)_3SnCH_2MgX + BF_3 \xrightarrow{(C_2H_5)_2O}$$
$$[(CH_3)_3SnCH_2]_3B + 3MgFX$$
$$[(CH_3)_3SnCH_2]_3B \xrightarrow{H_2O_2, NaOH, C_2H_5OH} 3(CH_3)_3SnCH_2OH$$

Organotin compounds containing tertiary amino groups readily form the corresponding methiodide and methosulfate salts (256). Organotin compounds containing an azo linkage have been prepared by treating (m- or p-dimethylaminophenyl)triphenyltin with appropriate diazonium salts (234, 240, 250). Oxidation of (p-hydroxymethylphenyl)triphenyltin with potassium permanganate yields (p-carboxyphenyl)triphenyltin (234).

Polyhalomethanes and trichlorosilane add to triethylvinyltin in the presence of benzoyl peroxide at 90–95°C. (763) (Z = H, Cl, or Br):

$$(C_2H_5)_3SnCH=CH_2 + CCl_3Z \rightarrow (C_2H_5)_3SnCHZCH_2CCl_3$$
$$(C_2H_5)_3SnCH=CH_2 + HSiCl_3 \rightarrow (C_2H_5)_3SnCH_2CH_2SiCl_3$$

C. ORGANOTIN HALIDES

1. General

Although the organotin halides (see tables 7 to 13) have few direct applications, a large amount of research and a considerable number of patents have appeared in this field. The value of organotin halides lies in their utility as intermediates in the preparation of a great many other organotin compounds.

In general, the aliphatic tin halides, with the exception of the fluorides, are either liquids or low-melting solids; the corresponding aromatic compounds are solids, except for the $RSnX_3$ types which frequently are liquids at room temperature. All of the organotin fluorides are solids which usually melt or decompose above 200°C.

2. Preparation

The organotin halides are best prepared by halogenation of the fully substituted R_4Sn compounds or by various methods starting from metallic tin or its inorganic compounds. The lower-molecular-weight, and therefore more volatile, R_3SnX compounds have a strong penetrating odor and are potent vesicants and lachrymators; considerable care should be exercised in their manipulation.
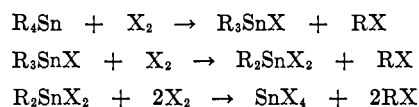
The halogens readily cleave R_4Sn compounds to R_3SnX, R_2SnX_2, or SnX_4, depending on the conditions and the relative amounts of materials employed (77, 78, 92, 94, 95, 96, 102, 126, 216, 219, 222, 234, 239, 287, 291, 293, 305, 380, 381, 382, 390, 402, 422, 442, 462, 463, 466, 468, 470, 474, 481, 482, 483, 561, 562, 563,

TABLE 6

*Compounds containing two or more tin atoms per molecule**

Compound	Melting Point	Boiling Point	$n_D^{25°}$	References
	°C.	°C.		
4,4'-Biphenylenebis(triphenyltin)	303			(908, 910, 919)
	235–236			
	298			
1,6-Bis(triphenylstannyl)-2,5-dimethylhexane	93–94			(387, 631, 634)
1,4-Bis[2-(triphenylstannyl)ethyl]benzene	136–142			(387, 631, 632, 634)
3,3'-Bis(triphenylstannyl)propionic anhydride	182–186			(387, 631, 632, 634)
Bis(3-triphenylstannylpropyl) ether	105–108			(387, 631, 632, 634)
1-Carbomethoxy-1,2-bis(triphenylstannyl)ethane	111–112			(387, 631, 634)
1-Carbomethoxy-1,2-bis(tripropylstannyl)ethane		120–123/0.0002 mm.		(387, 631, 634)
Decamethylenebis(triethyltin)		248/15 mm.		(287, 856, 888)
Dibutylmethylenetin (a polymer)				(199)
Dimethylmethylenetin (a polymer)				(199, 454)
Diphenylbis[2-(triphenylstannyl)ethyl]germane				(632)
Diphenylbis[2-(triphenylstannyl)ethyl]silane				(632)
Diphenyl(diphenylmethylene)tin (a polymer)				(199)
Ethylenebis(triphenyltin)	206–207			(387, 631, 634)
Ethyleneglycol bis(3-triphenylstannylpropionate)	93–96			(387, 631, 632, 634)
Ethynylenebis(tribenzyltin)	94			(312)
Ethynylenebis(triethyltin)	−52	294/760 mm.	1.5089 (at 20°)	(64)
		123/0.05 mm.		
Ethynylenebis(triphenyltin)	153	230–240/10⁻⁴ mm.		(64)
Ethynylenebis[tris(p-chlorophenyl)tin]	191			(312)
Ethynylenebis(tri-o-tolyltin)	143			(312)
Ethynylenebis(tri-p-tolyltin)	149			(312)
cis-(dl)-1,1,2,4,4,5-Hexaphenyl-1,4-distannacyclohexane				(632)
trans-1,1,2,4,4,5-Hexaphenyl-1,4-distannacyclohexane				(632)
Methylenebis(trimethyltin)		199–201/760 mm.		(459)
Methylenebis(triphenyltin)	104.5			(449)
(Methylene)diphenyltin (a polymer)				(199)
Methylidynetris(triphenyltin)	128			(449)
Pentamethylenebis(triethyltin)		205.5/14.5 mm.		(287, 856, 888)
Pentamethylene(trimethyllead)(trimethyltin)		162/17.5 mm.		(287)
1-Phenyl-1,2-bis(triphenylstannyl)ethane	139–140			(387, 631, 632, 634)
p-Phenylenebis(trimethyltin)	123–124			(462)
p-Phenylenebis(triphenyltin)	289–292			(916, 919)
sym-Tetramethylbis{2-[dimethyl(tributylstannylmethyl)silyl]ethyl}-disiloxane			1.4850	(572)
sym-Tetramethylbis(tributylstannylmethyl)disiloxane		240/<0.1 mm.	1.4852	(572, 632)
Tetramethylenebis(triphenyltin)	149–150.5			(916, 919)
Trimethylenebis(triphenyltin)	182–185			(387, 631, 634)
Tris(trimethylstannylmethyl)borane		90–91/0.15 mm.		(766)
Vinylenebis(trimethyltin)		194–195/760 mm.		(460)

* Compounds containing a tin–tin bond are discussed in Section II,G.

564, 565, 566, 594, 595, 608, 625, 665, 666, 669, 670, 683, 724, 725, 760, 761, 764, 765, 767, 794, 795, 855, 910).

$$R_4Sn + X_2 \rightarrow R_3SnX + RX$$
$$R_3SnX + X_2 \rightarrow R_2SnX_2 + RX$$
$$R_2SnX_2 + 2X_2 \rightarrow SnX_4 + 2RX$$

In this reaction the first two groups are cleaved stepwise but the remaining two groups are then cleaved simultaneously (561); thus, R_3SnX and R_2SnX_2 compounds may be prepared in this manner, but not the $RSnX_3$ compounds. A number of studies have been made to determine the relative ease of cleavage of various organic groups from tin (94, 561, 562, 563, 564, 565, 724, 725, 760, 765). The groups, arranged in order of decreasing ease of cleavage, are: o-tolyl > p-tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > isobutyl > butyl > isoamyl > amyl > hexyl > heptyl > octyl. With some un-

symmetrical R_4Sn compounds, cleavage of two different groups may occur. Thus, triethylisopropyltin on reaction with iodine gives both triethyltin iodide and diethylisopropyltin iodide (564). With a number of $R_2R_2'Sn$ compounds, either of the groups may be cleaved by iodine in benzene (764).

$$R_2R_2'Sn + I_2 \rightarrow RR_2'SnI + R_2R'SnI$$

With α-substituted organotin nitriles and esters, the functionally substituted group is easily cleaved, but when the substituent occupies the β-position or beyond with respect to the tin atom, the other groups are cleaved preferentially (390).

$$(C_3H_7)_3SnCH_2COOC_2H_5 + Br_2 \rightarrow$$
$$(C_3H_7)_3SnBr + BrCH_2COOC_2H_5$$

$$(C_4H_9)_3SnCH_2CH_2COOCH_3 + Br_2 \rightarrow$$
$$(C_4H_9)_2Sn(Br)CH_2CH_2COOCH_3 + C_4H_9Br$$
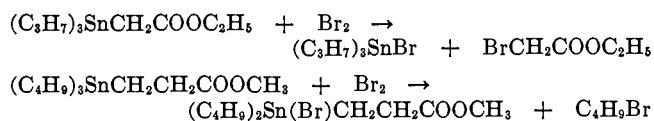
Chlorine is not often used in these reactions, since its manipulation presents many problems. When

TABLE 7

R_3SnX compounds (X = halogen)

Compound	Melting Point	Boiling Point	$n_D^{25°}$	References
	°C.	°C.		
Triamyltin bromide...................................		189/13 mm. 140/0.85 mm.		(365, 530, 856, 888)
Triamyltin chloride..................................				(914)
Triamyltin iodide....................................		198/15 mm. 168/4 mm.		(365, 561)
Tribenzyltin bromide................................	125–128			(660)
Tribenzyltin chloride...............................	148 143–145			(340, 522, 599, 631, 634, 660, 661, 738, 774, 775, 776, 794)
Tribenzyltin fluoride................................	242			(51, 472)
Tribenzyltin iodide..................................	102–103			(402)
Tri-2-biphenylyltin bromide.........................	167.5–168			(46)
Tributyltin bromide.................................		163/12 mm. 120–122/1.6–1.8 mm.	1.5022	(365, 760, 856, 888)
Tributyltin chloride.................................		145–147/5 mm. 98/0.45 mm.	1.4903	(70, 135, 149, 186, 262, 269, 356, 363, 364, 376, 382, 530, 541, 545, 566, 568, 574, 579, 630, 685, 687, 698, 699, 700, 760, 772, 856, 859, 888, 914)
Tri-tert-butyltin chloride............................		132/12 mm.		(475, 678)
Tri-tert-butyltin fluoride............................	Decomposes at 257			(475)
Tributyltin iodide...................................		168/8 mm. 172/10 mm.	1.5345 (at 20°)	(365, 561, 564)
Tri-tert-butyltin iodide..............................		147.5/12 mm.		(475)
Tricyclohexyltin bromide............................	77			(468)
Tricyclohexyltin chloride............................	129–130			(283, 468)
Tricyclohexyltin fluoride............................	Decomposes at 305			(468)
Tricyclohexyltin iodide..............................	65			(468)
Tridodecyltin chloride...............................	33			(569, 570)
Triethyltin bromide.................................	−13.5	97/13 mm. 224/760 mm.	1.5240 (at 20°) 1.5281	(10, 12, 101, 149, 216, 234, 286, 343, 377, 408, 409, 417, 479, 527, 530, 621, 736, 856, 888)
Triethyltin chloride.................................	15.5	94/13 mm. 210/760 mm.	1.5055 (at 20°)	(10, 12, 25, 42, 58, 90, 101, 149, 150, 167, 206, 216, 269, 286, 363, 364, 367, 369, 377, 380, 408, 409, 439, 479, 481, 482, 527, 530, 565, 567, 579, 630, 694, 738, 744, 797, 856, 888)
Triethyltin fluoride.................................	294.5 302			(10, 55, 149, 216, 310, 464)
Triethyltin iodide...................................	−34.5	105.5–106/16 mm. 117.5/13 mm. 234/760 mm.	1.5653 (at 18°)	(10, 100, 101, 149, 171, 286, 293, 479, 480, 484, 527, 530, 561, 563, 736, 852, 856, 886, 888)
Triheptyltin iodide..................................		235–240/12 mm.	1.4732 (at 30°)	(564)
Trihexyltin chloride.................................	55.5–56.5	178–180/1.5 mm.		(569, 570, 631, 634)
Trihexyltin fluoride.................................				(55)
Triisoamyltin bromide...............................		177/13 mm.		(286, 856, 888)
Triisoamyltin chloride...............................	30.2	174/13 mm.		(282, 286, 856, 888)
Triisoamyltin fluoride...............................	288			(55, 464)
Triisoamyltin iodide.................................		152/13 mm. 178–179/11 mm.	1.5209 (at 18°)	(107, 286, 563, 856, 888)
Triisobutyltin bromide..............................		148/13 mm.		(286, 856, 888)
Triisobutyltin chloride..............................		142/13 mm.		(286, 856, 888)
Triisobutyltin fluoride..............................	244			(55, 464)
Triisobutyltin iodide................................		151/13 mm.		(104, 107, 286, 856, 888)
Triisopropyltin chloride.............................				(269, 363, 579, 678)
Triisopropyltin iodide...............................		256–258/760 mm.		(106)
Trimethyltin bromide...............................	27	165/760 mm.		(367, 411, 458, 462, 647, 784)
Trimethyltin chloride...............................	37–38 42	152–154/760 mm.		(25, 296, 363, 406, 439, 445, 452, 530, 565, 641, 678, 784, 787, 788, 847, 848)
Trimethyltin fluoride................................	Decomposes at 375			(55, 367, 464)
Trimethyltin iodide.................................	3.4	67–68/15 mm. 170/760 mm.	1.5724 (at 20°)	(101, 286, 291, 480, 484, 523, 561, 608, 657, 738, 784, 787, 856, 888)
Tri-1-naphthyltin chloride...........................	204–205			(474)
Trioctadecyltin chloride.............................	61–62			(569, 570)
Trioctyltin chloride.................................		163–166/0.008 mm.		(143, 168, 169, 207, 269, 363, 579, 631, 634)
Trioctyltin iodide...................................		215–220/5 mm.		(564, 856, 888)
Triphenyltin bromide................................	121–122			(126, 159, 463, 504, 617, 631, 634, 646, 730)

TABLE 7—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{25°}$	References
	°C.	°C.		
Triphenyltin chloride..................................	105.5–107	249/13.5 mm.		(39, 40, 45, 55, 58, 145, 146, 158, 183, 234, 239, 242, 247, 356, 382, 402, 415, 463, 530, 598, 599, 617, 637, 641, 677. 678, 694, 708, 709, 738, 797, 847, 848, 896, 900, 918, 921)
Triphenyltin fluoride..................................	Decomposes at 357			(55, 183, 466, 847)
Triphenyltin iodide..................................	121			(74, 95, 126, 146, 234, 254, 390, 435, 463, 535, 562, 598, 631, 634, 809)
Tripropyltin bromide..................................		133/13 mm. 252–255/760 mm. (with slight decomposition)		(286, 303, 305, 390, 613, 634, 856, 888)
Tripropyltin chloride..................................		123/13 mm.		(149, 286, 439, 530, 568, 631, 634, 856, 888, 914)
Tripropyltin fluoride..................................	275 266–268			(55, 464, 631, 634)
Tripropyltin iodide..................................		140–141/15 mm. 259–264/760 mm. (with slight decomposition)		(103, 105, 106, 286, 303, 305, 561, 856, 888)
Tris(bromomethyl)tin bromide...........................		165/5 mm.		(901)
Tris(p-carbethoxyphenyl)tin chloride......................				(599)
Tris(2-carbomethoxyethyl)tin bromide.....................		154–158/0.005 mm.		(390, 631, 634)
Tris(o-chlorobenzyl)tin fluoride...........................	186–187			(51)
Tris(1-chloroethyl)tin chloride............................		130/3 mm.	1.5450 (at 20°)	(901, 903)
Tris(chloromethyl)tin chloride............................		138–140/5 mm.	1.593 (at 20°)	(901, 903)
Tris(p-chlorophenyl)tin bromide.........................	96–97			(474, 530)
Tris(p-chlorophenyl)tin chloride.........................	110–111			(474)
Tris(p-chlorophenyl)tin fluoride..........................				(474)
Tris(p-chlorophenyl)tin iodide...........................	93–95			(474, 599)
cis-Tris(2-chlorovinyl)tin chloride........................		119.5/1 mm.	1.5821 (at 20°)	(613, 619, 856, 888)
trans-Tris(2-chlorovinyl)tin chloride......................	120–121			(613, 619)
Tris(cyclopentadienyl)tin chloride........................				(694)
Tris(p-fluorophenyl)tin bromide..........................	109–110			(222)
Tris(p-methoxyphenyl)tin fluoride........................	Decomposes at 239			(474)
Tris(p-methylbenzyl)tin chloride..........................	190 (d.)			(775)
Tris(trimethylsilylmethyl)tin iodide.......................		105/0.3 mm.	1.5237	(761)
Tritetradecyltin chloride................................	46–47			(565, 569)
Tri-o-tolyltin bromide..................................	99.5 94–96			(466, 595)
Tri-p-tolyltin bromide..................................	98.5			(466)
Tri-o-tolyltin chloride..................................	105–106			(254, 415, 466)
Tri-m-tolyltin chloride..................................	108–109			(402, 415)
Tri-p-tolyltin chloride..................................	97.5–98			(415, 466, 599)
Tri-p-tolyltin fluoride..................................	Decomposes at 305			(466)
Tri-o-tolyltin iodide..................................	119.5			(466)
Tri-p-tolyltin iodide..................................	120.5			(466)
Trivinyltin bromide..................................		53–54/0.3–0.4 mm.		(760)
Trivinyltin chloride..................................		59–60/6.0 mm.	1.5235	(694, 725, 726, 727)
Trivinyltin fluoride..................................	Above 300			(760, 769)
Trivinyltin iodide..................................		60/1.8–1.9 mm.	1.5828	(760)
Tri-2,5-xylyltin bromide..............................	151			(466)
Tri-2,5-xylyltin chloride..............................	141.5			(466)
Tri-2,4-xylyltin fluoride..............................	209			(466)
Tri-2,5-xylyltin fluoride..............................	Decomposes at 247			(466)
Tri-2,5-xylyltin iodide..............................	159.5			(466)

bromine is employed, the reaction is often carried out below 0°C. and the bromine is added slowly to avoid excess cleavage; bromine is commonly used if the dihalide is desired. Iodine is the most convenient halogen for use in this reaction, especially for the preparation of monohalides. The reaction often is carried out in chloroform, carbon tetrachloride, or ether at room temperature or with some warming.

Halogens readily cleave the Sn—Sn linkage of ditin

compounds to the corresponding R_3SnX compounds (74, 100, 238, 360, 361, 376, 448, 450, 462, 466, 468, 474, 480, 490, 599).

$$R_3SnSnR_3 + X_2 \rightarrow 2R_3SnX$$
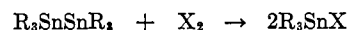
This method serves as a means of preparing very pure R_3SnX compounds; aside from this it is of little importance, since R_6Sn_2 compounds usually are prepared from R_3SnX derivatives. Calcium chloride and

TABLE 8

$R_2R'SnX$ *compounds* (X = *halogen*)

Compound	Melting Point	Boiling Point	$n_D^{25°}$	References
	°C.	°C.		
Allyldibutyltin bromide....................................		85–89/0.03 mm.		(724)
Allyldiphenyltin bromide...................................				(724)
Amyldiethyltin bromide....................................		135/15 mm.		(287, 856, 888)
Amyldiethyltin iodide.....................................		160–164/16 mm.		(381)
Amyldimethyltin iodide....................................		132–133/23 mm.	1.5440 (at 18°)	(562, 856, 888)
Bis(2-carbomethoxyethyl)propyltin bromide..................		120–122/0.002 mm.		(390, 631, 634)
Bis(1-chloroethyl)chloromethyltin chloride....................		128/3 mm.	1.555 (at 20°)	(901, 903)
(5-Bromoamyl)diethyltin bromide...........................		190.5/16 mm.		(287, 856, 888)
(5-Bromoamyl)dimethyltin bromide..........................		168/14.5 mm.		(287)
(Bromomethyl)dimethyltin bromide..........................		75–79/4 mm.	1.5683	(767)
(Bromomethyl)diphenyltin fluoride...........................	Above 290			(767)
(p-Bromophenyl)diethyltin bromide..........................				(380, 530)
(p-Bromophenyl)diethyltin chloride..........................				(380)
Butylbis(chloromethyl)tin chloride...........................		82–87/0.3 mm.	1.5394	(767)
Butylbis(trimethylsilylmethyl)tin iodide......................		105/0.4 mm.	1.5257	(761)
Butyldicyclohexyltin iodide.................................		160/0.7 mm.	1.5630	(764)
Butyldiethyltin iodide......................................		134–135/13 mm.	1.5460 (at 20°)	(381, 530, 562, 856, 888)
		124–128/12 mm.		
Butyldimethyltin iodide....................................		118–120/25 mm.	1.5467	(381, 530, 562, 764, 856, 888)
		88–89/5.4 mm.		
sec-Butyldimethyltin iodide.................................		84/5.5 mm.	1.5510	(764)
Butyldiphenyltin bromide...................................		155–159/0.2 mm.		(724)
Butyldipropyltin iodide....................................		159–160/24 mm.	1.5320 (at 20°)	(563, 856, 888)
Butyldivinyltin bromide....................................		70–72/0.6–0.75 mm.	1.5221	(762)
Butyldivinyltin chloride....................................		82–84/3 mm.	1.4970	(694, 728)
(2-Carbethoxy-1-methylethyl)dipropyltin bromide..............		119–120/0.02 mm.		(390, 631, 634)
(2-Carbomethoxyethyl)diphenyltin iodide....................	76			(390, 631, 634)
(o-Carbomethoxyphenyl)diphenyltin chloride..................	168–169			(234)
(Chloromethyl)dimethyltin chloride..........................		76–77/11 mm.	1.5263	(767)
(2-Cyanoethyl)diphenyltin iodide............................	121–122.5			(390, 631, 634)
(Cyanomethyl)diphenyltin iodide............................	99–100			(382, 530)
(3-Cyanopropyl)diphenyltin fluoride.........................	Shrinks and turns brown at about 280			(390, 631, 634)
Cyclohexyldimethyltin iodide................................		86/0.65 mm.	1.5717	(764)
(Cyclopentamethylene)vinyltin chloride......................				(694)
Cyclopentyldimethyltin iodide...............................		77/0.5 mm.	1.5758	(764)
Decyldimethyltin bromide..................................		110–114/0.2 mm.		(724)
Decyldivinyltin bromide....................................		96–100/0.01 mm.		(724)
Diallylbutyltin bromide....................................				(724)
Diamylethyltin iodide......................................		160–164/16 mm.		(530)
Dibutyl(2-carbomethoxyethyl)tin bromide....................		125–128/0.002 mm.		(390, 631, 634)
Dibutyl(chloromethyl)tin chloride...........................		106–110/3 mm.	1.5095	(767)
Dibutyl(2-cyanoethyl)tin bromide...........................		152–156/0.6 mm.		(631, 634)
Dibutylcyclohexyltin iodide.................................		136/0.6 mm.	1.5494	(764)
Dibutylcyclopentyltin iodide................................		125/0.4 mm.	1.5497	(764)
Dibutylhexyltin iodide.....................................		180/8 mm.	1.5246 (at 15°)	(564, 856, 888)
Dibutylisoamyltin iodide...................................		195/12 mm.	1.5254 (at 20°)	(563, 856, 888)
Dibutylmethyltin iodide....................................		82/0.35 mm.	1.5375	(764)
Di-sec-butylmethyltin iodide................................		71/0.25 mm.	1.5498	(764)
Dibutylphenyltin bromide..................................		120–124/0.001 mm.		(724)
Dibutyl(trimethylsilylmethyl)tin bromide.....................		91/0.2 mm.	1.5037	(761)
Dibutylvinyltin bromide...................................		72–73/0.03 mm.	1.4970	(725, 760, 765)
		96/0.55 mm.	1.5102	
Dibutylvinyltin chloride...................................		112–114/4 mm.	1.4973	(694, 728, 760, 765)
		82–83/0.6 mm.	1.4987 (at 20°)	
Dibutylvinyltin iodide.....................................		108.5–109.8/1.75 mm.	1.5384	(760, 765)
Dicyclohexylmethyltin iodide...............................		134/0.4 mm.	1.5786	(764)
Dicyclopentylmethyltin iodide..............................		115/0.7 mm.	1.5836	(764)
Diethylhexyltin iodide.....................................		98–100/0.25 mm.		(381, 530)
Diethylisoamyltin bromide.................................		137.5/17 mm.		(286, 856, 888)
Diethylisoamyltin chloride.................................		125.5–126/13 mm.		(286, 856, 888)
Diethylisobutyltin bromide.................................		122/17 mm.		(286, 365, 856, 888)
Diethylmethyltin bromide..................................		95–98/11 mm.		(769)
Diethyloctyltin iodide.....................................		132–133/0.9 mm.		(381, 530)
Diethylphenyltin bromide..................................				(380)
Diethylpropyltin bromide..................................		112.2/16 mm.		(286, 888)
Diethylpropyltin chloride..................................		108/17 mm.		(286, 856, 888)
Diethylpropyltin fluoride...................................	271			(464)
Diethylpropyltin iodide....................................		132–134/16 mm.	1.5582 (at 20°)	(563, 856, 888)
Diisopropylmethyltin iodide................................		96/7.6 mm.	1.5518	(764)
Dimethyloctyltin bromide..................................		77–81/0.01 mm.		(724)
Dimethyloctyltin iodide....................................		102–118/12 mm.		(381, 530)
Dimethyl(trimethylsilylmethyl)tin bromide...................		50/0.35 mm.	1.5101	(380)
Dimethylvinyltin bromide..................................		59–61/9.5 mm.	1.5350	(760, 765)

TABLE 8—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{25°}$	References
	°C.	°C.		
Dimethylvinyltin chloride		73–75/27 mm.	1.5105	(760, 765)
Dimethylvinyltin iodide		57.5–59/5.2 mm.	1.5762	(760, 765)
Diphenyloctyltin iodide				(530)
Diphenyl(2-phenylethyl)tin iodide	59–60			(390, 631, 634)
Diphenyl(triphenylmethyl)tin chloride	210			(52)
Diphenylvinyltin bromide				(724)
Diphenylvinyltin chloride				(694)
Diphenylvinyltin fluoride	Above 300; turns brown and shrinks above 285			(760)
Dodecyldiethyltin iodide		182–184/>1.5 mm.		(530)
Dodecyldimethyltin bromide		124–128/0.05 mm.		(724)
Dodecyldimethyltin iodide		156–158/1 mm.		(381, 530)
Ethyldiisoamyltin bromide		154–155/16 mm.		(286, 856, 888)
Ethyldiisobutyltin bromide		130.6/13 mm.		(286, 856, 888)
Ethyldimethyltin bromide		175–180/760 mm.		(96)
Ethyldimethyltin chloride		166–168/760 mm.	1.5082 (at 20°)	(565)
Ethyldimethyltin iodide		77–78/11 mm.	1.5705 (at 20°)	(563, 608, 669, 670)
		185–187/718 mm.		
Hexyldiphenyltin bromide				(724)
Hexyldivinyltin bromide		70–74/0.05 mm.		(724)
(3-Hydroxypropyl)diphenyltin bromide	127–128.5			(390, 631, 634)
(Iodomethyl)dimethyltin fluoride	Decomposes above 250			(767)
(Iodomethyl)dimethyltin iodide		111/5 mm.	1.6690	(767)
Isoamyldimethyltin iodide		115/15 mm.	1.5410 (at 21°)	(562, 855, 856, 888)
Isobutyldimethyltin iodide		95/15 mm.	1.5082 (at 20°)	(562, 855, 856, 888)
Isopropyldimethyltin iodide		77–78/9.2 mm.	1.5553	(764)
Methylbis(trimethylsilylmethyl)tin bromide		73/0.18 mm.	1.5018	(761)
Methylbis(trimethylsilylmethyl)tin iodide		85–86/0.35 mm.	1.5268	(761)
Octyldivinyltin bromide		82–86/0.01 mm.		(724)
Phenyldivinyltin chloride				(694)
Phenyldivinyltin fluoride	Above 300; turns tan and shrinks above 210			(760)

mercury(II) chloride also have been used to cleave R_6Sn_2 compounds to the corresponding R_3SnCl derivatives (462).

The halogen acids, in solution or in the gaseous state, also cleave R_4Sn compounds (45, 46, 47, 52, 90, 94, 402, 481, 509, 565, 570, 708, 709, 760, 765, 921). Usually, the monohalide is obtained, but in some cases

$$R_4Sn + HX \rightarrow R_3SnX + RH$$
$$R_3SnX + HX \rightarrow R_2SnX_2 + RH$$
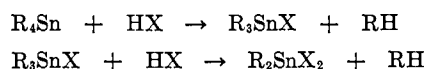
the dihalide may be prepared in this manner; care must be taken to avoid excess cleavage. The organotin compound is refluxed with the halogen acid or, more usually, the hydrogen halide is bubbled into a chloroform, ether, or benzene solution of the organotin compound.

The ease of cleavage of various groups is the same as that listed above for cleavage by the halogens. Again, predictions based on this cleavage series are not infallible; for example, both the methyl and the ethyl groups of diethyldimethyltin are cleaved by hydrogen chloride to give ethylmethyltin dichloride (94, 509). With $R_2Sn[CH_2Si(CH_3)_3]_2$ compounds, where R is methyl or butyl, the methyl or butyl groups are more easily cleaved by halogen; however, the (trimethylsilyl)methyl group is more easily cleaved by hydrogen halides (761). With tribenzylethyltin, the benzyl group is cleaved by halogen, but hydrochloric acid removes the ethyl group (402).

One of the most valuable methods for the preparation of organotin halides, especially in commercial quantities, involves the cleavage of organotin com-

TABLE 9

RR′R″SnX *compounds* (X = *halogen*)

Compound	Melting Point	Boiling Point	References
	°C.	°C.	
Benzylbutylphenyltin fluoride	218		(402)
Ethylmethylpropyltin iodide		108–111/11 mm.	(608, 609, 669, 670)

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TABLE 10

R_2SnX_2 compounds (X = halogen)

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Bis(bromomethyl)tin dibromide	87	155–160/5 mm.		(901, 903)
Bis(p-bromophenyl)tin dibromide	82			(418, 622, 908)
Bis(p-bromophenyl)tin dichloride	103			(418, 420, 622, 624)
Bis(p-bromophenyl)tin diiodide	79–80			(418, 622)
Bis(1-carbethoxyethyl)tin dibromide		82–85/1.5 mm.		(245)
Bis(carbethoxymethyl)tin dibromide	139			(245, 492)
Bis(carbethoxymethyl)tin diiodide	101.5			(194)
Bis(p-carbethoxyphenyl)tin dibromide	69–69.5			(196)
Bis(m-carbethoxyphenyl)tin dichloride	95–96			(679)
Bis(p-carbethoxyphenyl)tin dichloride	102–103			(196, 424)
Bis(o-carbethoxyphenyl)tin diiodide				(194)
Bis(p-carbethoxyphenyl)tin diiodide				(196)
Bis(2-carbomethoxyethyl)tin dibromide	138–140			(390, 631, 634)
Bis(1-chlorobutyl)tin dichloride	53	134/5 mm.		(901, 903)
Bis(1-chloroethyl)tin dichloride	12	112/4 mm.	1.5535	(901, 903)
Bis(chloromethyl)tin dichloride	89.5–90			(901, 903)
Bis(p-chlorophenyl)tin dibromide	73			(418, 474, 622)
Bis(p-chlorophenyl)tin dichloride	86.5			(418, 420, 424, 622, 624)
Bis(p-chlorophenyl)tin diiodide	46–47			(418, 622)
cis-Bis(2-chlorovinyl)tin dichloride		100–102/3 mm.	1.5675	(612, 613, 619, 856, 888)
trans-Bis(2-chlorovinyl)tin dichloride	77.5–78.5			(424, 612, 613, 619)
Bis[p-(dichloroiodo)phenyl]tin dichloride	82–82.5			(418, 622)
Bis(p-ethoxyphenyl)tin dichloride	46			(834)
Bis(2-ethylhexyl)tin dichloride		154–162/0.3 mm.		(384)
Bis(p-iodophenyl)tin dibromide	102			(418, 622)
Bis(p-iodophenyl)tin dichloride	147			(418, 420, 622)
Bis(p-iodophenyl)tin diiodide	88.5			(418, 622)
Bis(p-methoxyphenyl)tin dibromide	102			(834)
Bis(o-methoxyphenyl)tin dichloride	113			(420, 624)
Bis(p-methoxyphenyl)tin dichloride	76			(72, 834)
Bis(2-methyl-3-butenyl)tin dichloride				(694)
Bis(trimethylsilylmethyl)tin dibromide	38.6–39.8			(761)
Bis(trimethylsilylmethyl)tin diiodide	34.6–35.4			(761)
(Cyclopentamethylene)tin dichloride				(694)
Diallyltin dibromide		77–79/2.0 mm.		(855)
Di-tert-amyltin dibromide		166/13 mm.		(475)
Diamyltin dichloride	34.5–35.5			(543, 631, 634)
Di-tert-amyltin dichloride		153/12 mm.		(475)
Di-tert-amyltin difluoride	Decomposes at 264			(475)
Di-tert-amyltin diiodide		186/12 mm.		(475)
Dibenzyltin dibromide	130			(417, 621, 794)
Dibenzyltin dichloride	163–164			(402, 417, 621, 708, 709, 794)
Dibenzyltin diiodide	86–87			(794)
Di-p-biphenylyltin dibromide	144–145			(834)
Di-p-biphenylyltin dichloride	140			(46, 834)
Dibutyltin bromide chloride	34–34.5	104–106/0.55 mm.		(355, 361)
Dibutyltin dibromide	20			(2, 660)
Di-tert-butyltin dibromide		128/14 mm.		(475)
Dibutyltin dichloride	43	153–156/5 mm. 135/10 mm.		(70, 108, 130, 184, 186, 188, 262, 269, 356, 357, 358, 359, 360, 364, 376, 395, 518, 530, 541, 543. 545, 566, 567, 568, 579, 583, 643, 644, 660, 667, 685, 687, 694, 698, 699, 700, 741, 851, 852, 867, 868, 914)
Di-tert-butyltin dichloride	42	117/14 mm.		(475, 678)
Di-tert-butyltin difluoride	Decomposes at 254			(475)
Dicyclohexyltin dibromide	58			(283, 468)
Dicyclohexyltin dichloride	88–89			(72, 468)
Dicyclohexyltin difluoride	278			(468)
Dicyclohexyltin diiodide	42			(283, 468)
Didodecyltin dichloride	19.4	218/760 mm.		(535, 802)
Diethyltin dibromide	63	233/760 mm.		(101, 218, 287, 293, 343, 367, 377, 408, 411, 417, 527, 530, 611, 621, 651, 738, 886)
Diethyltin dichloride	89 84	277/760 mm.		25, 58, 94, 101, 112, 160, 167, 206, 216, 361, 364, 369, 378, 408, 409, 411, 417, 422, 423, 481, 527, 530, 565, 566, 567, 583, 617, 650, 651, 713, 716, 738, 749, 785, 797, 852, 867, 868, 886)
Diethyltin dichloride·xH₂O	74			(650, 886)
Diethyltin difluoride	Decomposes at 287–290			(101, 464, 902)

TABLE 10—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Diethyltin diiodide...........................	44–45 30–31	245–246/760 mm.		(100, 171, 218, 293, 370, 399, 480, 483, 491, 527, 558, 561, 651, 660, 738, 825, 886)
Dihexyltin dichloride.........................	45–47	134–138/1.5 mm.		(384)
Diisoamyltin dibromide.......................	−4 to −2			(660)
Diisoamyltin dichloride.......................	28			(282, 660)
Diisoamyltin diiodide.........................		202–205/8 mm.		(660)
Diisobutyltin dibromide.......................		144/15 mm.		(467)
Diisobutyltin dichloride.......................	9	135.5/15 mm.		(107, 467)
Diisobutyltin diiodide.........................		290–295/760 mm.		(107, 370)
Diisopropenyltin dibromide....................		102.5/9 mm.	1.5665	(615, 616, 617)
Diisopropyltin dibromide......................	54			(175)
Diisopropyltin dichloride......................	56.5–57.5 80–84			(106, 175, 678)
Diisopropyltin diiodide........................		256–258/760 mm.		(106)
Dimethyltin dibromide........................	74	209/760 mm.		(101, 408, 411, 454, 658, 659, 660, 784, 787)
Dimethyltin dichloride........................	107.5–108	185–190/760 mm.		(25, 101, 151, 258, 325, 423, 424, 454, 543, 565, 583, 641, 658, 660, 676, 718, 719, 721, 784, 786, 787, 788, 847, 848, 852, 867, 868)
Dimethyltin difluoride........................	Decomposes at 360			(464)
Dimethyltin diiodide..........................	30 44	228/760 mm.		(101, 370, 523, 561, 658, 660, 784, 856, 888)
Di-1-naphthyltin dibromide....................	142			(417, 616, 621, 665)
Di-2-naphthyltin dibromide....................	114–115			(417, 621)
Di-1-naphthyltin dichloride....................	137–137.5			(72, 417, 617, 621, 665, 683)
Di-2-naphthyltin dichloride....................	110–111			(417, 621)
Di-1-naphthyltin diiodide......................	160			(665)
Dioctyltin dichloride..........................	47.5–48.5	164–165/0.16 mm.		(116, 384)
Di-9-phenanthryltin dichloride.................				(47)
Diphenyltin bromide chloride..................	39			(39)
Diphenyltin chloride iodide....................	69			(39)
Diphenyltin dibromide........................	38			(39, 43, 126, 159, 417, 466, 530, 621, 666, 795)
Diphenyltin dichloride........................	42–44	333–337/760 mm.		(39, 58, 72, 125, 135, 196, 234, 240, 271, 356, 395, 402, 406, 407, 417, 423, 424, 541, 543, 616, 621, 624, 628, 641, 667, 694, 705, 785, 851, 900)
Diphenyltin difluoride........................	Above 360			(460)
Diphenyltin diiodide..........................	71–72	176–182/2 mm.		(95, 146)
Di-1-propenyltin dibromide....................		121–122/10 mm.	1.5663	(614, 615, 616, 694)
Di-1-propenyltin dichloride....................				(614)
Dipropyltin dibromide........................	49	263–265/760 mm.		(2, 303, 305, 365, 408, 411, 660)
Dipropyltin dichloride........................	80–81			(106, 327, 408, 411, 568, 583, 631, 634, 660, 738, 852, 867, 868)
Dipropyltin difluoride.........................	204–205			(464)
Dipropyltin diiodide...........................		166–167/10 mm.		(106, 305, 327, 370, 660)
Di-2-thienyltin dichloride.....................				(72)
Di-*p*-tolyltin dibromide.......................	74			(99, 417, 621, 654)
Di-*o*-tolyltin dichloride.......................	49–50			(412, 414, 420, 617, 624, 679)
Di-*m*-tolyltin dichloride.......................	39–40			(413)
Di-*p*-tolyltin dichloride.......................	49–50			(410, 412, 414, 417, 424, 616, 617, 795)
Divinyltin dibromide..........................		47/2 mm.	1.5920	(618)
Divinyltin dichloride..........................	13.2 74.5–75.5	54–56/3.0 mm.	1.5500 1.5490 (at 25°)	(618, 694, 725, 726, 727, 769)
Divinyltin difluoride..........................				(694)
Divinyltin diiodide...........................				(694)
Di-2,5-xylyltin dibromide......................				(99)

pounds with tin(IV) halides (70, 90, 102, 116, 158, 167, 234, 240, 247, 250, 262, 356, 358, 360, 361, 364, 376, 380, 382, 384, 406, 407, 408, 409, 411, 412, 413, 414, 415, 418, 477, 481, 482, 518, 574, 622, 630, 645, 647, 665, 667, 673, 705, 725, 726, 769, 834, 855, 859,

$$3R_4Sn + SnX_4 \rightarrow 4R_3SnX$$

$$R_4Sn + SnX_4 \rightarrow 2R_2SnX_2$$

$$R_4Sn + 3SnX_4 \rightarrow 4RSnX_3$$
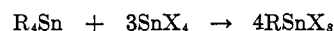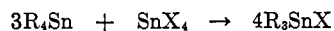
900, 908, 914, 921). The reactants usually are heated to 100–200°C.; both alkyl and aryl R₄Sn compounds undergo this reaction and either tin(IV) chloride or tin(IV) bromide may be used. Usually a mixture of products is obtained, but the desired halide can be produced in excellent yields by the use of an appropriate ratio of starting materials and a proper temperature range. Halides produced as side products can be returned to the reaction container and allowed to

TABLE 11

RR'SnX$_2$ compounds (X = halogen)

Compound	Melting Point*	References
	°C.	
Benzylphenyltin dibromide..........	74–75	(92)
Benzylphenyltin dichloride..........	83–84	(402)
Butylphenyltin dichloride..........	50	(402)
Butylpropyltin dichloride..........	67–68	(567)
Butylvinyltin dibromide...........		(694)
Butylvinyltin dichloride...........	27–28	(694, 728)
	99–101/3 mm. (b.p.)	
	$n_D^{25°}$ = 1.5254	
(2-Carbomethoxyethyl)phenyltin		
dibromide......................	111–114	(390, 631, 634)
(3-Cyanopropyl)phenyltin dibromide.	101–102	(390, 631, 634)
(Cyclopentadienyl)vinyltin		
dichloride.....................		(694)
Ethylmethyltin dichloride...........	52	(94, 509)
Ethylphenyltin dichloride..........	45	(481)
Ethylpropyltin dichloride...........	57–58	(94, 794)
(5-Methylthienyl)vinyltin dichloride..		(694)
Phenylvinyltin dichloride..........		(694)
Thienylvinyltin dichloride..........		(694)

* The values given are melting points except as otherwise noted.

react with additional amounts of R$_4$Sn or SnX$_4$ to form the desired product.

$$2R_3SnX + SnX_4 \rightarrow 3R_2SnX_2$$

$$2RSnX_3 + R_4Sn \rightarrow 3R_2SnX_2$$

$$R_2SnX_2 + R_4Sn \rightarrow 2R_3SnX$$

$$R_2SnX_2 + SnX_4 \rightarrow 2RSnX_3$$

The preparation of organotin halides by this method offers an advantage over other cleavage methods in that none of the substituents attached to the tin atom is lost; the method is undesirable, however, for the preparation of organotin halides in which all of the organic groups are not identical.

In the above methods for the preparation of organotin halides, heating is sometimes required and the products are usually purified by distillation; in a few cases, care must be taken since thermal redistribution may occur and the desired product may not be obtained (725, 760, 765, 781).
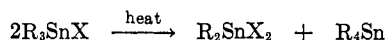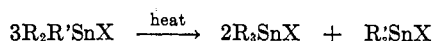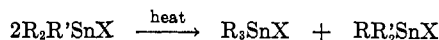
$$2R_2R'SnX \xrightarrow{\text{heat}} R_3SnX + RR'_2SnX$$

$$3R_2R'SnX \xrightarrow{\text{heat}} 2R_3SnX + R'_3SnX$$

$$2R_3SnX \xrightarrow{\text{heat}} R_2SnX_2 + R_4Sn$$

Other inorganic halides cleave R$_4$Sn compounds to give organotin halides; these include mercury(II) chloride (419, 422, 471, 473, 565, 623, 625, 641), mercury(II) bromide (761), aluminum chloride (111, 566), bismuth chloride (567, 765), thallium(III) chloride (272), arsenic (III) halides (765), phosphorus (III) bromide (736, 765), and phosphorus and iodine (736). These reagents offer no advantages for preparative methods.

The reaction of an alkyl halide with a sodium–tin alloy was employed by Löwig (527) in the synthesis of the first organotin compounds and was the method used by most of the early investigators for the preparation of organotin halides. Usually, the alkyl halide and a sodium–tin alloy, containing 10 to 20 per cent sodium, are heated for several hours at 100–200°C. Many of the low-molecular-weight R$_3$SnX compounds have been prepared by this method. R$_4$Sn, R$_2$SnX$_2$, and R$_6$Sn$_2$ compounds are also formed in the reaction; if the sodium content of the alloy is low, the principal product is the dihalide. The method is not in general use at present, but the following references illustrate how widely this method was used formerly (70, 100, 101, 103, 106, 107, 116, 291, 480, 484, 527, 611, 914). Variations of this reaction include the use of a tin–magnesium alloy (206, 343, 377) or a tin–copper alloy (786, 867) rather than an alloy of tin and sodium.

Molten tin reacts with an alkyl halide at elevated temperatures to form, primarily, a dialkyltin dihalide. This reaction was used by many of the early investigators for the preparation of R$_2$SnI$_2$ compounds (100,

$$Sn + 2RX \xrightarrow{\text{heat}} R_2SnX_2$$
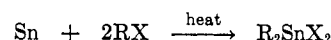
106, 107, 194, 218, 282, 328, 370, 527, 886). The reaction is also successful with alkyl bromides and chlorides and has received increasing attention in recent years (2, 245, 287, 370, 718, 748, 775, 788). Catalytic amounts of copper or zinc are sometimes added (718, 786). Methylene bromide and granulated tin, when heated at 180–220°C. in a sealed tube, react to give a nearly quantitative yield of methyltin tribromide (404, 407). Methyl iodide reacts with molten tin at elevated temperatures to produce methyltin triiodide (787).

Alkyl halides react, at elevated temperatures, with tin(II) oxide in the presence of metallic copper to form, primarily, alkyltin trihalides; if tin(IV) oxide is used, the dialkyltin dihalides may be obtained (787).

The reaction of a Grignard reagent with a tin(IV) halide has been used for the preparation of organotin

$$RMgX + SnX_4 \rightarrow RSnX_3 + MgX_2$$

$$2RMgX + SnX_4 \rightarrow R_2SnX_2 + 2MgX_2$$

$$3RMgX + SnX_4 \rightarrow R_3SnX + 3MgX_2$$
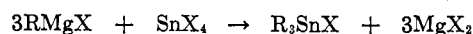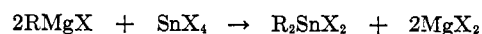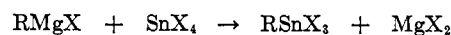
halides; this method is somewhat limited in application, since in most cases mixtures of R$_4$Sn, R$_3$SnX, R$_2$SnX$_2$, and RSnX$_3$ are obtained, even though the correct molecular quantities of reactants are employed (46, 116, 186, 392, 402, 447, 657, 661, 685, 694, 744, 794, 802). It has been reported (794) that increased yields are obtained by adding the organic halide to a mixture of magnesium and tin(IV) chloride, rather than using the preformed Grignard reagent. The

TABLE 12

RSnX$_3$ *compounds* (X = *halogen*)

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Allyltin tribromide (trimer)	109			(803)
Bromomethyltin tribromide		109/5 mm.		(901, 903)
(p-Bromophenyl)tin tribromide	49–50			(908)
(p-Bromophenyl)tin trichloride	64.5–65			(418, 622)
Butyltin trichloride		93/10 mm.		(186, 262, 355, 356, 358, 359, 392,
		102–103/12 mm.		530, 574, 631, 634, 699, 700)
(o-Carbomethoxyphenyl)tin trichloride	164			(420, 624)
(1-Chloroethyl)tin trichloride		69–71/4 mm.		(901)
(Chloromethyl)tin trichloride		72.5–73/5 mm.	1.5689	(901, 903)
(p-Chlorophenyl)tin trichloride	39			(418, 622)
trans-(2-Chlorovinyl)tin trichloride		63–65/4 mm.	1.5602 (at 29°)	(613, 856, 888)
(Cyclopentadienyl)tin trichloride				(694)
p-(Dichloroiodo)phenyltin trichloride	50–70 (d.)			(418, 622)
(1,2-Diphenylvinyl)tin trichloride	108–110			(620)
Ethyltin tribromide	Decomposes at 310	103–106/14 mm.		(174, 408, 530)
Ethyltin trichloride	−10	196–198/760 mm.	1.5408	(167, 364, 378, 530)
Ethyltin triiodide		181–184.5/19 mm.		(845)
(1-Fluorovinyl)tin trichloride				(694)
(p-Iodophenyl)tin tribromide	80–80.5			(418, 622)
(p-Iodophenyl)tin trichloride	55–56			(418, 622)
Isopropyltin tribromide	112			(175)
Isopropyltin trichloride		75/16 mm.		(845)
(4-Methyl-1-naphthyl)tin trichloride				(694)
Methyltin tribromide	53	211/760 mm.		(173, 202, 404, 405, 658, 671, 673, 778, 784, 787)
Methyltin trichloride	45–46			(173, 325, 404, 405, 585, 645, 656,
	42–43			658, 659, 671, 673, 713, 784, 787, 788)
Methyltin triiodide	85			(173, 404, 405, 657, 658, 671, 673,
	86.5			738, 784, 787, 845)
1-Naphthyltin trichloride	77–78			(665)
Octyltin trichloride				(694)
Phenyltin tribromide		182–183/29 mm.		(406, 407, 856, 888)
Phenyltin trichloride		142–143/25 mm.	1.5844	(80, 158, 240, 356, 406, 407, 530,
		96/1.4 mm.		856, 888, 900)
		245/760 mm.		
Phenyltin triiodide		Decomposes above 220/760 mm.		(406, 407, 845)
Propyltin tribromide				(176)
Propyltin trichloride		98–99/12 mm.		(176, 631, 634)
Propyltin triiodide		200/16 mm. (partial decomposition)		(845)
o-Tolyltin trichloride		157–158/20 mm.		(412, 414)
m-Tolyltin trichloride		150–151/23 mm.		(413)
p-Tolyltin trichloride		156–157/23 mm.		(412, 414)
Vinyltin tribromide (trimer)	119			(803)
Vinyltin trichloride		64–65/15 mm.	1.5361 (at 25°)	(694, 725, 726, 727, 769, 803)
		48–50/5.2–5.3 mm.		

method is more successful when the organic group is large, e.g., 1-naphthyl (474) or 2-biphenylyl (46). The reaction of one equivalent of a Grignard reagent with an organotin dihalide or trihalide is very difficult (724) but has been successful in a few cases (380, 699, 728).

$$RSnX_3 + R'MgX \rightarrow RR'SnX_2 + MgX_2$$
$$R_2SnX_2 + R'MgX \rightarrow R_2R'SnX + MgX_2$$
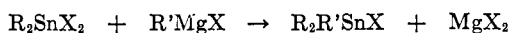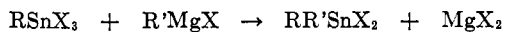
By using an excess of Grignard reagent, the fully substituted organotin compounds are more easily obtained; an interesting cyclic process for the preparation of R$_2$SnX$_2$ compounds has been reported (518):

$$R_2SnX_2 + 2RMgX \rightarrow R_4Sn$$
$$R_4Sn + SnX_4 \rightarrow 2R_2SnX_2$$

The Wurtz reaction of an alkyl halide and a tin(IV) halide with sodium usually is employed only for the preparation of R$_4$Sn compounds; however, it has been reported that dibutyltin dichloride can be prepared in this manner (643). Organoaluminum compounds can be treated with tin(IV) halides to form organotin halides (363, 369).

Organotin dihalides may be prepared by the reaction of a tin(II) halide with an organomercury compound. Aronheim (39) first used a method of this type, preparing diphenyltin dichloride from diphenylmercury and tin(IV) chloride. Later, Kocheshkov and Nesmeyanov (196, 417, 418, 612, 615, 617, 620, 621 622) investigated the reaction, using a tin(II) halide. The following equations serve to illustrate the usefulness and limitations of this method:

TABLE 13

Other organotin halides

Compound	Melting Point	References
	°C.	
Allylpentabromostannic acid...................		(364)
5,5-Dichloro-10,11-dihydrodibenzo[b,f]stanniepin.	106–107	(477)
Ethylpentachlorostannic acid....................		(174)
1,1,2,2-Tetraamylditin 1,2-dichloride............	96.5–97.5	(361)
1,1,2,2-Tetrabutylditin 1,2-dibromide...........	103–104	(361)
1,1,2,2-Tetrabutylditin 1,2-dichloride..........	110–112	(360, 361)
	115–116	
1,1,2,2-Tetraethylditin 1,2-dichloride...........	170–176 (d.)	(361)
1,1,2,2-Tetraphenylditin 1,2-dichloride.........	185–187 (d.)	(361)
1,1,2,2-Tetrapropylditin 1,2-dichloride.........	120.5–121.5	(361)
Tropylium stannichloride......................	252 (d.)	(88)

(A) $R_2Hg + SnX_2 \rightarrow R_2SnX_2 + Hg$

(B) $R_2SnX_2 + R_2Hg \rightarrow R_3SnX + RHgX$

(C) $R_2Hg + SnX_2 + 2C_2H_5OH \rightarrow$
$\qquad\qquad 2RH + Hg + (C_2H_5O)_2SnX_2$

(D) $2RHgX + 2SnX_2 \rightarrow R_2SnX_2 + 2Hg + SnX_4$

(E) $2RHgBr + SnBr_2 \rightarrow R_2SnBr_2 + 2HgBr$
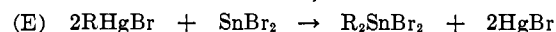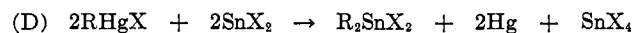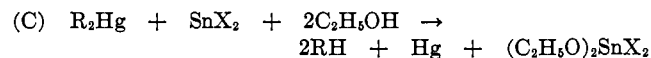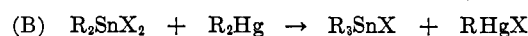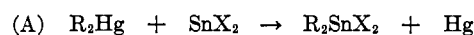
Usually reaction A occurs; however, with slowly reacting substances reaction B may also take place, giving a mixture of products. Aryl compounds all react readily in acetone according to equation A, while in ethyl alcohol the reaction depends on the organic group; with large groups or substituted phenyl groups reaction C may take place. When aryl RHgCl compounds are used, the reaction proceeds according to equation D. Aryl RHgBr compounds react simultaneously according to equations D and E. Aliphatic RHgX compounds undergo little reaction with tin(II) halides. The above reactions sometimes are useful for the preparation of organotin compounds which cannot be obtained with a Grignard reagent. At least in some cases, the organomercury compound may be replaced by R_2PbX_2 or R_2TlX compounds in this method (423, 616, 618). Heating an RHgX compound with powdered tin or with sodium–tin alloy in benzene produces the corresponding R_3SnX compound (599, 613).

Löwig (527) prepared diethyltin diiodide by treating diethyltin with iodine. Later, Krause and Becker (466) obtained diphenyltin dibromide from the reaction of diphenyltin with bromide. This method generally is not used for the preparation of R_2SnX_2 compounds.

Treatment of an R_3SnX compound with a dilute basic solution produces the corresponding hydroxide; the hydroxide derivatives may be reconverted to the organotin halide by treatment with the appropriate halogen acid. This method is often employed for the

$$R_3SnX + MOH \rightarrow R_3SnOH + MX$$
$$R_3SnOH + HX' \rightarrow R_3SnX' + H_2O$$
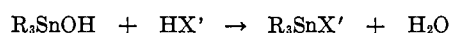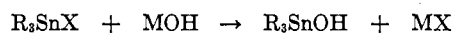
interchange of halogens in an organotin halide. The reaction usually is carried out by shaking an ethereal solution of the organotin hydroxide with an aqueous solution of a halogen acid, or by adding the halogen acid to an alcoholic solution of the organotin hydroxide. Any halogen acid may be used, although the fluorides are more conveniently prepared by other means. A few of the numerous references to articles containing a description of this method illustrate its general use (101, 106, 126, 402, 466, 468, 472, 474, 479, 527).

Similarly, an R_2SnX_2 compound may be taken to the corresponding organotin oxide and the oxide then converted to the desired organotin halide. (The extensive use of this method is indicated by the following

$$R_2SnX_2 + 2MOH \rightarrow R_2SnO + 2MX + H_2O$$
$$R_2SnO + 2HX' \rightarrow R_2SnX_2' + 2H_2O$$
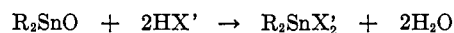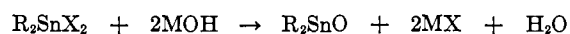
ing references: 39, 51, 101, 106, 126, 175, 218, 293, 413, 468, 482, 527, 667, 767, 794, 795, 802, 886.) Various other reagents, such as phosphorus(V) chloride, phosphorus(III) chloride, or tin(IV) bromide, have been used instead of the halogen acid in this reaction (10, 101). Direct displacement of chlorine by iodine can be accomplished in some cases by the use of sodium iodide in acetone (418, 622, 665, 767).

$$(CH_3)_2SnCl_2 + 2NaI \rightarrow (CH_3)_2SnI_2 + 2NaCl$$
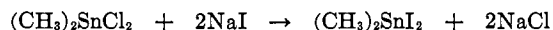
Organotin hydrides react with concentrated hydrochloric acid or with halogens to form the corresponding organotin halides (451, 631, 896).

$$R_3SnH + HCl \rightarrow R_3SnCl + H_2$$
$$R_3SnH + X_2 \rightarrow R_3SnX + HX$$
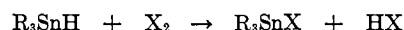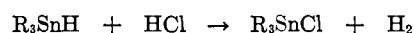
Alkyl halides and bromobenzene react with triphenyltin hydride to give the corresponding hydrocarbon and triphenyltin halide (386, 635, 730).
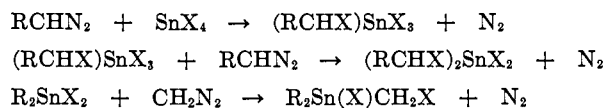
On mixing chilled solutions of an aryldiazonium chloride and tin(IV) chloride, a crystalline precipitate of $(ArN_2Cl)_2 \cdot SnCl_4$ is obtained. When this salt is added slowly to boiling ethyl acetate containing powdered tin, decomposition takes place according to the reaction (420, 624):

$$(ArN_2Cl)_2 \cdot SnCl_4 + 2Sn \rightarrow Ar_2SnCl_2 + 2N_2 + 2SnCl_2$$
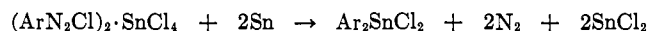
Powdered copper or zinc may replace the powdered tin in this reaction. Several aryltin dichlorides have been prepared in this manner, but the yields were low. Bis(p-nitrophenyl)tin dichloride could not be obtained, and with p-carbomethoxybenzenediazonium chloride the corresponding organotin trichloride was produced. Tin(II) chloride does not form double salts with diazonium compounds. However, if aryldiazonium fluoborates are decomposed by zinc powder in the presence of tin(II) chloride, organotin compounds are

obtained; after hydrolysis, the principal product is the diaryltin oxide (627).

When tin(IV) chloride reacts with a diazoalkane, one or more of the halogen atoms are replaced by α-halogenated alkyl groups (767, 901, 903). Alkyltin halides may be used rather than tin(IV) halides to give compounds containing both alkyl and α-haloalkyl groups.

$$RCHN_2 + SnX_4 \rightarrow (RCHX)SnX_3 + N_2$$
$$(RCHX)SnX_3 + RCHN_2 \rightarrow (RCHX)_2SnX_2 + N_2$$
$$R_2SnX_2 + CH_2N_2 \rightarrow R_2Sn(X)CH_2X + N_2$$

The organotin fluorides are commonly prepared by treating an aqueous or alcoholic solution of an R_3SnOH, R_3SnX, or R_2SnX_2 compound with potassium fluoride; the less soluble, solid organotin fluorides usually will precipitate from the solution (51, 402, 464, 466, 468, 472, 474, 475). The reaction of diethoxydiethyltin with acetyl fluoride produces diethyltin difluoride (902).

As mentioned above, organotin trihalides may be prepared by the reaction of an R_4Sn compound with a tin(IV) halide. Another common method involves the treatment of an organostannonic acid with a halogen acid; this reaction also is used for the interchange

$$RSnOOH + 3HX \rightarrow RSnX_3 + 2H_2O$$
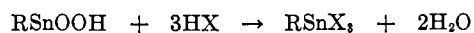
of halogens in an $RSnX_3$ compound through the intermediate formation of the stannonic acid (173, 175, 413, 658, 673, 803). Methyltin triiodide has been prepared by heating methyl iodide and tin(II) iodide in a sealed tube (657); methyltin trichloride has been prepared in a similar manner (787). Several $RSnI_3$ compounds have been obtained by heating $KSnCl_3$ with an organic iodide (245, 845). Kocheshkov (404, 407) heated methylene bromide with granulated tin in a sealed tube and obtained a good yield of methyltin tribromide; the reaction met with little success when methylene chloride or methylene iodide was substituted.

3. Physical properties

The crystal structure of several organotin halides has been studied, and it has been found that dimethyl-, diethyl-, and dipropyltin dichlorides form rhombic crystals (39, 99, 327). Molecular-weight determinations of diethyltin diiodide indicate that it is unassociated (886). The dipole moments of several organotin halides have been determined (367, 637, 797, 806); all evidence points toward a tetrahedral arrangement of the atoms in these compounds. The values of the dipole moment for various organotin chlorides have been used to calculate minimum values for the moment of the tin–chlorine bond; from these, the minimum ionic character in the tin–chlorine bond has been esti-

mated to be 27 per cent (637, 796, 797). This is in fair agreement with the 35 per cent value obtained from thermal data (796).

Infrared and Raman spectral data have been reported for several organotin halides (171, 523, 568, 749). The ultraviolet spectra of triethyltin chloride and diethyltin dichloride have been studied (715). The various methyltin halides have been investigated by electron diffraction (784); as the number of halogen atoms replacing hydrogen or methyl on the tin atom is increased, the tin–halogen bonds become progressively shorter.

A necessary condition for the dissociation of an organotin halide is the presence of an electron donor (678):

$$R_3SnX + {:}Y \rightleftarrows R_3SnY^+ + X^-$$
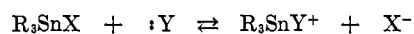
The R_3SnY^+ species may or may not undergo subsequent reaction; e.g., proton transfer if Y is H_2O:

$$R_3SnOH_2^+ + H_2O \rightleftarrows R_3SnOH + H_3O^+$$
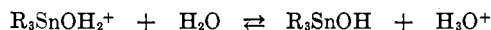
The extent of this reaction depends on the nature of both the R and the Y groups. Conductivity measurements of ethyltin and methyltin halides have shown that these compounds are not true electrolytes in the pure state but when dissolved in methyl or ethyl alcohol, water, pyridine, or acetone, they are relatively good conductors; in benzene, ethyl ether, nitrobenzene, or nitromethane these compounds are poor conductors (440, 445, 452, 778, 848, 923). The ionization constant for trimethyltin chloride in ethyl alcohol was found to be 3.5×10^{-5} at 25°C. (440). Dimethyltin dichloride dissociates almost completely in water (722):

$$(CH_3)_2SnCl_2 + nH_2O \rightarrow (CH_3)_2Sn(H_2O)_n^{++} + 2Cl^-$$
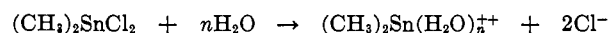
The resulting solutions are acidic; thus some hydrolysis must occur.

$$(CH_3)_2Sn(H_2O)_n^{++} + H_2O \rightleftarrows$$
$$(CH_3)_2Sn(H_2O)_{n-1}OH^+ + H_3O^+$$
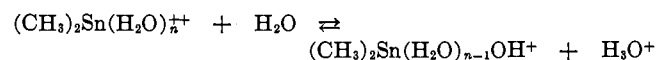
The degree of hydrolysis depends on the concentration, and for most dilute solutions is less than 10 per cent (721); dimethyltin dichloride is hydrolyzed in pure water to the extent of 10.5 per cent in 0.064 molal concentration at 25°C. (258). The solvolyses of various R_3SnCl compounds in ethyl alcohol, isopropyl alcohol, and water–dioxane have been studied (678). Solutions of various organotin chlorides in N,N-dimethylformamide have been investigated conductometrically and have been found not to undergo dissociation into organotin cations and chloride ions (847).

The partial resolution of ethylmethylpropyltin iodide has been accomplished by conversion to the (+)-camphorsulfonate or (+)-bromocamphorsulfonate salts and subsequent reconversion to the iodide (608, 609,

669, 670). An R_3Sn^+ ion would have the planar sp^2 configuration, leading to immediate racemization; presumably, tetrahedral configuration is preserved by solvent coördination (144).

The molecular volume at 20°C., the molecular refractivity, and the atomic refractivity for several alkyl R_3SnBr and R_2SnBr_2 compounds have been reported (365). More recently, data on bond refraction for several organotin halides have been listed (856, 888). Values have been derived for the heats of formation of trimethyltin bromide and trimethyltin iodide (461, 647).

The thermal decomposition of dimethyltin dichloride has been studied by the toluene carrier technique between 555° and 688°C. (676). Rate constants for the overall reaction

$$(CH_3)_2SnCl_2 \rightarrow SnCl_2 + 2CH_3\cdot$$
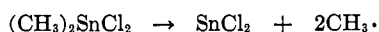
were calculated; the decomposition is homogeneous and the rate constant is independent of variations of the alkyl concentration between 1.01×10^{-9} and 4.36×10^{-9} mole/cm.^{3}

Several polarographic studies of organotin halides have been made (149, 714, 716, 738, 852). The reduction potential of the tin in the organotin halides differs from that of tin in a normal metal ion; it is a function of pH and the i_d in many cases is proportional to concentration (852). R_2Sn substances appear to be formed in the electrolysis of both R_3SnX and R_2SnX_2 compounds (149, 716), although other reactions also may occur.

4. Chemical properties

Organotin halides frequently are used in the preparation of other organotin compounds; those reactions discussed under other headings will be mentioned only briefly here.

The organotin halides react with organometallic compounds such as RMgX, R_2Sn, and RLi to form R_4Sn compounds.

$$R_2SnX_2 + 2R'M \rightarrow R_2SnR_2' + 2MX$$
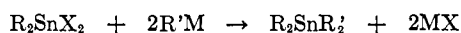
These reactions have been discussed in connection with the preparation of symmetrical and unsymmetrical R_4Sn compounds (Sections II,A and II,B).

When organotin halides are treated with alkaline solutions, the following conversions take place:

$$R_3SnX + MOH \rightarrow R_3SnOH + MX$$
$$R_2SnX_2 + 2MOH \rightarrow R_2SnO + 2MX + H_2O$$
$$RSnX_3 + 3MOH \rightarrow RSnOOH + 3MX + H_2O$$
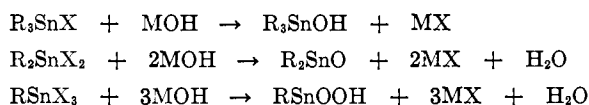
A more detailed discussion of these reactions is given later (Section II,D).

Sodium reacts with R_3SnX compounds in inert solvents with the formation of R_3SnSnR_3 compounds. These compounds are discussed in Section II,G. The
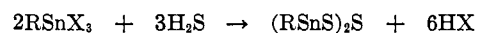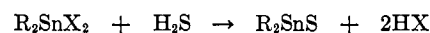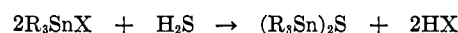
$$2R_3SnX + 2Na \rightarrow R_3SnSnR_3 + 2NaX$$
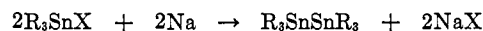
R_2SnX_2 compounds react with sodium in liquid ammonia to form R_2SnNa_2 derivatives. These reactions in liquid ammonia are discussed in connection with

$$R_2SnX_2 + 4Na \rightarrow R_2SnNa_2 + 2NaX$$
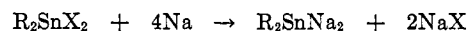
the preparation of R_3SnNa and R_2SnNa_2 compounds (Section II,F). R_2SnCl_2 compounds react with triethylamine or with sodium in alcoholic solution to form the corresponding $R_2Sn(Cl)Sn(Cl)R_2$ derivatives (361, 364).

When an alcoholic solution of an organotin halide is treated with hydrogen sulfide, either the sulfide or the trisulfide is formed.

$$2R_3SnX + H_2S \rightarrow (R_3Sn)_2S + 2HX$$
$$R_2SnX_2 + H_2S \rightarrow R_2SnS + 2HX$$
$$2RSnX_3 + 3H_2S \rightarrow (RSnS)_2S + 6HX$$

These reactions are discussed in Section II,D.

Metalloörganic oxides (ROM) react with R_3SnX and R_2SnX_2 compounds to form the corresponding R_3SnOR' and $R_2Sn(OR')_2$ derivatives (discussed in Section II,D).

$$R_2SnX_2 + 2MOR' \rightarrow R_2Sn(OR')_2 + 2MX$$
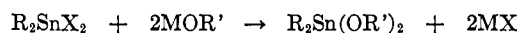
The formation of salts from the organotin halides by reaction with inorganic salts such as silver nitrate or with organic acids also is discussed in Section II,D.

Lithium aluminum hydride readily reduces organotin halides to the corresponding organotin hydrides (see Section II,E).
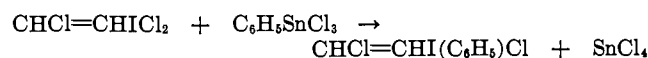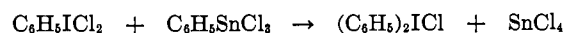
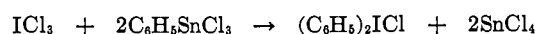$$2R_2SnX_2 + LiAlH_4 \rightarrow 2R_2SnH_2 + LiX + AlX_3$$
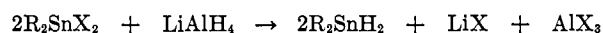
Mercury(II) chloride reacts with aryl R_2SnCl_2 and $RSnCl_3$ compounds in alcohol according to the following equations (196, 412, 414, 419, 665):

$$R_2SnCl_2 + 2HgCl_2 \rightarrow 2RHgCl + SnCl_4$$
$$RSnCl_3 + HgCl_2 \rightarrow RHgCl + SnCl_4$$
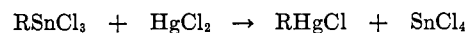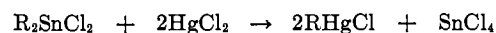
Similarly, organothallium compounds can be prepared from organotin halides (423, 424):

$$R_2SnCl_2 + TlCl_3 \rightarrow R_2TlCl + SnCl_4$$
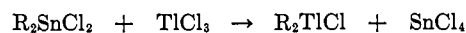
Incidental to the study of arylation agents, Freïdlina and Nesmeyanov (221) have found that phenyltin trichloride reacts energetically with iodine trichloride in dilute hydrochloric acid with the formation of a quantitative yield of $(C_6H_5)_2ICl$. Similarly, $C_6H_5ICl_2$ (221) and $CHCl=CHICl_2$ (80) can be arylated by phenyltin trichloride.

$$ICl_3 + 2C_6H_5SnCl_3 \rightarrow (C_6H_5)_2ICl + 2SnCl_4$$
$$C_6H_5ICl_2 + C_6H_5SnCl_3 \rightarrow (C_6H_5)_2ICl + SnCl_4$$
$$CHCl=CHICl_2 + C_6H_5SnCl_3 \rightarrow$$
$$CHCl=CHI(C_6H_5)Cl + SnCl_4$$

Benzenediazonium nitrate was obtained by the action of a mixture of N_2O_3 and NO on triphenyltin chloride, diphenyltin dichloride, and phenyltin trichloride (556). Aronheim (40) has reported that triphenyltin chloride is obtained when an acetic acid solution of diphenyltin dichloride is treated with sodium nitrate; diphenyltin dichloride also has been converted into triphenyltin chloride by the use of moist sodium amalgam (40).

trans-Tris(2-chlorovinyl)tin chloride, on being heated in xylene with benzoyl peroxide, is converted to the cis isomer (918). Diphenyltin dichloride, when heated with benzoyl chloride and aluminum chloride, forms benzophenone (785).

Organotin halides exhibit a strong tendency to form many complex compounds with amines or with organotin oxides and hydroxides (table 21).

### D. ORGANOTIN HYDROXIDES, OXIDES, AND RELATED COMPOUNDS

1. General

The organotin compounds reviewed in this subsection are among the most complex in organotin chemistry. They may be liquids or solids; they exist as monomers, as cyclic trimers, and as linear polymers of high molecular weight. As will become apparent in Sections V and VI, some of the organotin compounds contained in this group are commercially important and much of the future growth of industrial organotin chemistry will take place in this area.

2. Preparation

(a) R_3SnOH and R_2SnO compounds

These compounds (tables 14 and 15) are prepared from the organotin halides by treatment with aqueous alkali (39, 45, 101, 106, 107, 125, 126, 175, 196, 218, 222, 290, 293, 305, 327, 388, 402, 413, 416, 418, 422, 443, 468, 472, 474, 475, 477, 482, 530, 599, 621, 624, 650, 659, 661, 663, 665, 701, 724, 725, 761, 769, 794, 795, 802, 834, 850, 859, 886, 901).

$$R_3SnX + MOH \rightarrow R_3SnOH + MX$$
$$R_2SnX_2 + 2MOH \rightarrow R_2SnO + 2MX + H_2O$$
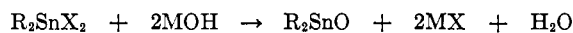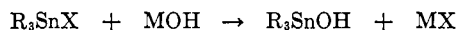
These reactions are carried out conveniently by shaking an ether solution of the organotin halide with an aqueous solution of potassium, sodium, or ammonium hydroxide. The ether is omitted in large-scale preparations if the organotin halide is a liquid or a low-melting solid, but heating is required. The dihydroxides, $R_2Sn(OH)_2$, except for a few compounds, are dehydrated immediately to amphoteric, polymeric R_2SnO compounds. The R_3SnOH compounds are more stable and are less readily dehydrated to $(R_3Sn)_2O$ compounds. The trihydroxides, $RSn(OH)_3$, are un-

known and are apparently dehydrated spontaneously to organostannonic acids.

When organostannonic acids are heated in an alkaline solution, the corresponding organotin oxide is formed (174, 175, 650, 673).

$$2RSnOOK \rightarrow R_2SnO + K_2SnO_3$$

Oxidation of R_2Sn compounds in organic solvents leads to the formation of R_2SnO compounds (126, 466, 651, 914). Alkaline hydrolysis of (carbethoxymethyl)tripropyltin and of (cyanomethyl)triphenyltin results in cleavage of the carbon–tin bond and formation of the corresponding R_3SnOH compound (388). Diaryltin oxides and triaryltin hydroxides are obtained from the reaction of aryldiazonium salts with tin(II) chloride (627).

(b) $(R_3Sn)_2O$ compounds

These compounds (table 14) are prepared by two general methods. The bis-oxides that are sensitive to moisture are prepared from the corresponding hydroxides by the removal of a molecule of water. This may be accomplished, in most cases, by distilling the organotin hydroxide under reduced pressure or by heating under reduced pressure in a vacuum desiccator, using calcium chloride or phosphorus pentoxide as the drying agent (39, 101, 103, 293, 305, 381, 468, 479, 579, 724). Bis(trimethyltin) oxide, because of its extreme sensitivity to moisture, is prepared from trimethyltin hydroxide and sodium in anhydrous benzene (300).

$$4(CH_3)_3SnOH + 2Na \rightarrow$$
$$2[(CH_3)_3Sn]_2O + H_2 + 2NaOH$$
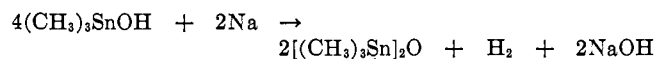
The bis-oxides that are not easily hydrolyzed may be prepared by reaction of the appropriate organotin halide with aqueous alkali. Bis(tributyltin) oxide is prepared by heating a well-stirred mixture of tributyltin chloride and aqueous sodium hydroxide (530) or by refluxing the chloride with sodium hydroxide in ethanol (859).

The bis(triorganotin) oxides and their corresponding hydroxides may also be prepared by the oxidation of hexaalkylditin compounds (45, 443, 462). The reaction of R_3SnX or $(R_3Sn)_2S$ compounds with silver oxide yields $(R_3Sn)_2O$ compounds (13). 1-Cyclopentadienyltriphenyltin is hydrolyzed by water to bis(triphenyltin) oxide (239). The thermal decomposition of triethyltin hydroxide is reported to yield diethyltin oxide and bis(triethyltin) oxide; diethyltin oxide is similarly transformed to bis(triethyltin) oxide (297).

(c) R_2SnS and $(R_3Sn)_2S$ compounds

The reaction of organotin halides with hydrogen sulfide in an alcoholic solution serves as a convenient

TABLE 14

Organotin oxides

[Compounds of the types R_2SnO, $RR'SnO$, $(R_3Sn)_2O$, and $(R_2R'Sn)_2O$]

Compound	Melting Point	Boiling Point*	References
	°C.	°C.	
Bis(acetoxybutylphenyltin)oxide			(724)
Bis(acetoxydibutyltin)oxide			(724)
Bis(p-bromophenyl)tin oxide			(418, 622, 624, 627)
Bis(butyldiethyltin) oxide			(381)
Bis(butyldimethyltin) oxide			(381)
Bis(m-carbethoxyphenyl)tin oxide			(679)
Bis(p-carbethoxyphenyl)tin oxide			(196, 679)
Bis(o-carbomethoxyphenyl)tin oxide			(627)
Bis(chloromethyl)tin oxide	180		(901)
Bis(p-chlorophenyl)tin oxide			(418, 622, 624, 627)
Bis(diamylethyltin) oxide			(381)
Bis[dibutyl(dodecyloxy)tin] oxide			(612)
Bis[dibutyl(hexyloxy)tin] oxide			(884)
Bis(diethylhexyltin) oxide			(381)
Bis(diethyloctyltin) oxide			(381)
Bis(dimethyloctyltin) oxide			(381)
Bis(1,2-diphenylvinyl)tin oxide	Above 300		(620)
Bis(dodecyldiethyltin) oxide			(381)
Bis(dodecyldimethyltin) oxide			(381)
Bis(p-ethoxyphenyl)tin oxide	134.5–135		(834)
Bis(2-ethylhexyl)tin oxide			(151, 384)
Bis(p-iodophenyl)tin oxide			(418, 622)
Bis(p-methoxyphenyl)tin oxide			(834)
Bis(p-nitrophenyl)tin oxide			(627)
Bis(triamyltin) oxide			(530)
Bis(tribenzyltin) oxide	120		(51)
Bis(tributyltin) oxide		220–230/10 mm. $n_D^{20°} = 1.8472$	(148, 200, 269, 380, 530, 579, 590, 591, 629, 630, 859)
Bis(tricyclohexyltin) oxide			(468)
Bis(triethyltin) oxide		100/1 mm. 272/760 mm, 154/10 mm. $n_D^{20°} = 1.5010$ or 1.4975	(12, 13, 71, 101, 293, 295, 297, 477, 479, 630, 744, 746)
Bis(trihexyltin) oxide			(380, 530)
Bis(triisobutyltin) oxide		197–198/12 mm. $n_D^{21°} = 1.4850$	(907)
Bis(triisopropyltin) oxide			(380, 530)
Bis(3,5,5-trimethylhexyl)tin oxide			(384)
Bis(trimethylsilylmethyl)tin oxide	145–160		(761)
Bis(trimethyltin) oxide		86/24 mm.	(297, 300, 443, 462)
Bis(trioctyltin) oxide			(380, 530)
Bis(triphenyltin) oxide	124		(239, 468, 629, 753)
Bis(tripropyltin) oxide		195–198/21 mm. 142–144/1 mm.	(103, 303, 380, 388, 530, 631, 634, 746)
Bis[tris(o-bromobenzyl)tin] oxide	158–159		(51)
Bis[tris(o-chlorobenzyl)tin] oxide	133.5		(51)
Bis[tris(o-fluorobenzyl)tin] oxide	113		(51)
Bis[tris(p-fluorophenyl)tin] oxide			(222)
Bis(tri-2-thienyltin) oxide			(629)
Butylphenyltin oxide			(115, 274, 275)
Diallyltin oxide			(435)
Dibenzyltin oxide	254–260 (d.)		(795)
Di-p-biphenylyltin oxide	Does not melt below 250		(834)
Dibutyltin oxide			(53, 109, 115, 132, 133, 134, 137, 168, 169, 188, 207, 262, 274, 275, 395, 496, 504, 658, 660, 703, 733, 869, 877, 884)
Dicyclohexyltin oxide			(629)
Didodecyltin oxide	110 (d.)		(135, 624, 802, 884)
Diethyltin oxide			(101, 174, 218, 293, 297, 527, 650, 651, 914)
Dihexyltin oxide			(384)
Diisoamyltin oxide			(282, 660)
Diisobutyltin oxide			(107)
Diisopropyltin oxide			(175)
Dimethyltin oxide			(101, 133, 293, 443, 658, 659, 673, 721, 766)
Di-1-naphthyltin oxide	315 (d.)		(665, 683)
Di-2-naphthyltin oxide			(627)
Dioctyltin oxide			(384)
Diphenyltin oxide	38		(39, 125, 126, 130, 132, 133, 134, 321, 395, 417, 435, 522, 621, 627, 628, 679, 683, 753, 795, 870, 884, 896)

TABLE 14—*Concluded*

Compound	Melting Point	Boiling Point	References
	°C.	°C.	
Dipropyltin oxide			(106, 176, 305, 327, 660)
Di-*o*-tolyltin oxide			(417, 624, 627, 679)
Di-*m*-tolyltin oxide			(413)
Di-*p*-tolyltin oxide			(417, 621, 627, 795)
Divinyltin oxide	Above 345		(701, 725, 769)
Ethylmethyltin oxide			(94)
Ethylphenyltin oxide			(481, 482)
5-Oxo-10,11-dihydrodibenzo[b,f]stanniepin			(477)
(Triethyltin)(trimethyltin) oxide			(629)

* A few values of the refractive index are included in this column.

method of preparation for these compounds (table 16) (196, 258, 408, 418, 622).

$$R_2SnX_2 + H_2S \rightarrow R_2SnS + 2HX$$
$$2R_3SnX + H_2S \rightarrow (R_3Sn)_2S + 2HX$$
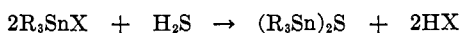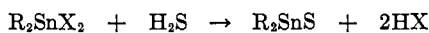
Triethyltin hydroxide has been used in this reaction for the preparation of triethyltin sulfide (479); (R₃Sn)₂O (744) and R₃SnOR′ (530) compounds also have been employed. These methods have been combined by treating the organotin dichloride with potassium hydroxide in ethanol saturated with hydrogen

sulfide (834). Sodium sulfide and potassium bisulfide may also be used in the preparation of organotin sulfides (301, 302).

Instead of the expected (3-mercaptopropyl)triphenyltin, the reaction of triphenyltin hydride with allyl mercaptan gives propene, hydrogen sulfide, and bis(triphenyltin) sulfide (635).

$$2(C_6H_5)_3SnH + 2CH_2=CHCH_2SH \rightarrow$$
$$[(C_6H_5)_3Sn]_2S + H_2S + 2CH_2=CHCH_3$$
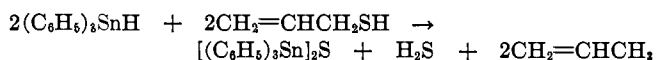
R₂Sn compounds react with sulfur to produce the corresponding R₂SnS derivatives (477).

TABLE 15

Organotin hydroxides

[Compounds of the types R₃SnOH, R₂R′SnOH, RR′R″SnOH, and R₂Sn(OH)₂]

Compound	Melting Point	Boiling Point	References
	°C.	°C.	
Benzylbutylphenyltin hydroxide	135–137		(402)
Benzylphenyl-*p*-tolyltin hydroxide	136–137		(402)
Di-*tert*-amyltin dihydroxide	200		(475)
Dianhydrotri(dibenzyltin dihydroxide)	250–260		(795)
Di-*tert*-butyltin bromide hydroxide	152		(475)
Di-*tert*-butyltin chloride hydroxide	170		(475)
Di-*tert*-butyltin dihydroxide			(475)
Dicyclohexyltin dihydroxide	291 (d.)		(468)
Diphenyltin chloride hydroxide	187		(39, 402)
Ethyldimethyltin hydroxide			(96)
Methyltin hydroxide sulfate·*x*H₂O			(659)
Tribenzyltin hydroxide	122–124		(51, 472, 599, 660)
Tributyltin hydroxide		186–190/5 mm.	(130, 436, 733, 856, 888)
Tri-*tert*-butyltin hydroxide	153		(475)
Triethyltin hydroxide	44–45 49–50	272/760 mm.	(71, 101, 171, 216, 293, 297, 380, 409, 422, 479, 484, 530, 625, 626, 630, 821, 859)
Triisoamyltin hydroxide		335–338/760 mm.	(107, 282)
Triisobutyltin hydroxide		311–314/760 mm.	(104, 107)
Triisopropyltin hydroxide			(106, 205)
Trimethyltin hydroxide	118 Sublimes above 80		(25, 101, 151, 291, 304, 380, 436, 443, 530)
Tri-2-naphthyltin hydroxide			(627)
Triphenyltin hydroxide	119–120		(39, 45, 126, 388, 416, 436, 462, 468, 599, 733, 905, 918)
Tripropyltin hydroxide	34–35		(103, 105, 106, 303, 530)
Tris(*p*-bromophenyl)tin hydroxide			(627)
Tris(*o*-carbomethoxyphenyl)tin hydroxide			(627)
Tris(*p*-chlorophenyl)tin hydroxide			(474, 627)
Tris(*p*-nitrophenyl)tin hydroxide			(627)
Tri-*o*-tolyltin hydroxide			(627)
Tri-*p*-tolyltin hydroxide	108–109		(416, 599, 627)
Trivinyltin hydroxide	67.5–69.0		(702, 725)

TABLE 16

Organotin sulfides

[Compounds of the types R_2SnS, $(R_3Sn)_2S$, and $(RSn)_2S_3$]

Compound	Melting Point	Boiling Point*	References
	°C.	°C.	
Bis(p-bromophenyl)tin sulfide	228–229		(418, 622)
Bis(p-bromophenyltin) trisulfide			(418, 622)
Bis(p-carbethoxyphenyl)tin sulfide	141.5–142.5		(196)
Bis(1-chloroethyl)tin sulfide	180		(903)
Bis(p-chlorophenyl)tin sulfide	179		(418, 622)
Bis(p-chlorophenyltin) trisulfide	295 (d.)		(418, 622)
Bis(p-ethoxyphenyl)tin sulfide	127		(834)
Bis(p-iodophenyl)tin sulfide	248		(418, 622)
Bis(p-iodophenyltin) trisulfide			(418, 622)
Bis(p-methoxyphenyl)tin sulfide	95		(834)
Bis(methyltin) trisulfide			(655, 658, 659, 660)
Bis(o-tolyltin) trisulfide			(412, 414)
Bis(tributyltin) sulfide		$n_D^{21°} = 1.518$	(800)
Bis(triethyltin) sulfide		113–137/1 mm.	(12, 301, 479, 530, 746)
		187–188/20 mm.	
		$n_D^{20°} = 1.5468$	
Bis(trimethylsilylmethyl)tin sulfide	150–165		(761)
Bis(trimethyltin) sulfide		233.5–235.5/759 mm.	(301, 462, 655)
		118/18 mm.	
Bis(triphenyltin) sulfide	141.5–143		(631, 634, 635)
Bis(tripropyltin) sulfide		215–219/19 mm.	(301, 303)
		254/16 mm.	
Bis[tris(p-carbethoxyphenyl)tin] sulfide	132–133		(599)
Di-p-biphenylyltin sulfide	134.5–135		(834)
Dibutyltin sulfide			(22, 188, 395, 557, 881, 882, 883, 884)
Didodecyltin sulfide			(881, 883)
Diethyltin sulfide	24	219–221/760 mm.	(302)
Dimethyltin sulfide	149		(22, 258, 302, 408, 577, 655, 660, 881, 882, 883)
Di-1-naphthyltin sulfide	215		(665)
Diphenyltin sulfide	183–184		(196, 395, 577, 882, 883, 884)
Dipropyltin sulfide		254/16 mm. (with slight decomposition)	(303, 305)
Di-m-tolyltin sulfide	121.5–122		(413)
5-Thio-10,11-dihydrodibenzo[b,f]stanniepin	274–275		(477)

* Two values of the refractive index are given in this column.

(d) R_3SnOR', $R_2Sn(OR')_2$, R_3SnSR', $R_2Sn(SR')_2$, and $RSn(SR')_3$ compounds

These compounds (table 17) are prepared by treating an organotin halide with a sodium alkoxide, phenoxide, or mercaptide, or by the reaction of an organotin hydroxide, halide, ester, or oxide with an alcohol, phenol, or mercaptan (34, 39, 43, 53, 98, 143, 168, 169, 196, 207, 480, 484, 496, 497, 504, 506, 530, 543, 546, 689, 692, 696, 697, 744, 746, 760, 777, 873); the reaction of an organotin oxide with an alcohol or a mercaptan is frequently run in benzene or toluene and is assisted by the removal of water by azeotropic distillation.

Tetraalkyltin compounds are cleaved by mercaptans to give, usually, the R_3SnSR' derivatives (745, 747); vinyl groups are especially easily cleaved (760, 765).

$$R_4Sn + R'SH \rightarrow R_3SnSR' + RH$$
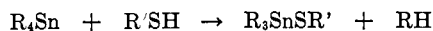
Tetraethyltin is similarly cleaved by phenol to give triethylphenoxytin (747).

Organotin alkoxides and mercaptides can undergo reactions of the ester-exchange type (548, 746).

$$R_2Sn(OR)_2 + 2R'OH \rightleftharpoons R_2Sn(OR')_2 + 2ROH$$
$$R_3SnSR + R'SH \rightleftharpoons R_3SnSR' + RSH$$
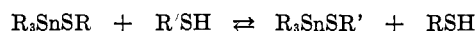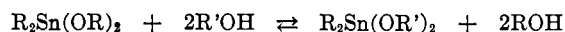
On heating organostannonic acids with mercaptans, organotin trimercaptides are obtained (818).

$$RSnOOH + 3R'SH \rightarrow RSn(SR')_3 + 2H_2O$$
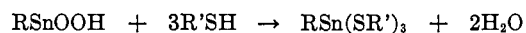
(e) $R_3SnOCOR'$ and $R_2Sn(OCOR')_2$ compounds

A variety of methods has been applied to the preparation of organotin esters (table 18). The oldest and most frequently used procedure involves the reaction of organotin hydroxides, oxides, or halides with organic acids or acid anhydrides (11, 14, 101, 220, 258, 268, 381, 422, 426, 479, 530, 553, 683, 724, 744, 769, 777, 792, 794, 850).

$$R_3SnOH + R'COOH \rightarrow R_3SnOCOR' + H_2O$$
$$R_2SnO + (R'CO)_2O \rightarrow R_2Sn(OCOR')_2$$
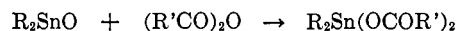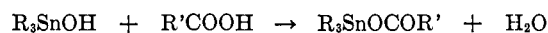
In addition, they can be prepared from organotin halides and organic acid salts (11, 184, 488, 552, 660, 669, 670, 774). Other methods include the reaction of silver salts of organic acids with organotin halides,

TABLE 17

Organotin compounds of the types R_3SnOR', R_3SnSR', $R_2Sn(OR')_2$, $R_2Sn(SR')_2$, $RSn(OR')_3$, $RSn(SR')_3$, $R_2Sn(OR')(OR'')$, *and* $R_2Sn(OR')(SR'')$

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
(Benzyloxy)tributyltin..		90–95/1 mm.		(536)
(Benzylthio)triethyltin...		138–140/1 mm.	1.5682	(744, 747)
			1.5675	
(Benzylthio)triisopropyltin.......................................		167–170/1 mm.	1.5497	(745)
(Benzylthio)tripropyltin..		165–167/1 mm.	1.5558	(745)
Bis(allyloxy)dibutyltin...				(546)
Bis(o-aminophenylthio)dibutyltin.................................				(353, 354, 697)
Bis(amylthio)dibutyltin...				(353, 354, 697)
Bis(amylthio)didodecyltin..				(353, 354, 697)
Bis(2-benzothiazolylthio)dibutyltin...............................				(353, 354, 697)
Bis(benzyloxy)dibutyltin..				(97)
Bis(benzyloxy)diethyltin..				(114, 548)
Bis(benzylthio)didodecyltin.......................................				(353, 354, 697)
Bis(benzylthio)diphenyltin..				(353, 354, 697)
Bis{2-[2-(2-butoxyethoxy)ethoxy]ethoxy} dibutyltin................				(548)
Bis(p-carbethoxyphenyl)bis(8-quinolyloxy)tin......................	216–217			(196)
Bis(carbobutoxymethylthio)dioctyltin..............................				(532)
Bis(1-carboxyethoxy)diethyltin, dibutyl ester.....................			1.4652	(114, 548)
Bis(dodecylthio)dimethyltin.......................................				(353, 354, 697)
Bis(dodecylthio)diphenyltin.......................................				(26, 353, 354, 505, 697)
Bis(furfuryloxy)diphenyltin.......................................				(114, 548)
Bis(phenylthio)dipropyltin..		226–230/1 mm.	1.6298	(746)
(O,O)-Bis(triethyltin)ethylene glycol.............................		184–185/4.5 mm.	1.4975	(777)
Butoxydibutyl(octylthio)tin.......................................				(44)
Butoxytributyltin...		124–128/3 mm.	1.4688	(143, 168, 169, 207)
tert-Butoxytributyltin..				(536)
(Butylthio)triethyltin..		88–91/1 mm.	1.5133	(744)
(tert-Butylthio)triethyltin..		84–86/1 mm.	1.5060	(744)
Butyltin-(S,S,S)-tris(decyl mercaptoacetate)......................				(879)
Butyltin-(S,S,S)-tris(mercaptoacetic acid)........................				(879, 880)
Butyltris(butylthio)tin...			1.5420	(818)
Butyltris(p-carbomethoxyphenylthio)tin...........................				(818)
Butyltris(p-cresylthio)tin..			1.6540	(818)
Butyltris(dodecylthio)tin...				(697)
Butyltris(tert-dodecylthio)tin.....................................				(818)
tert-Butyltris(2-hydroxyethylthio)tin..............................				(503)
(Carbethoxymethylthio)triethyltin.................................		107–109/1.0 mm.	1.5101 (at 25°)	(760)
(Decylthio)triisopropyltin...		192–195/1 mm.	1.5010	(745)
(Decylthio)tripropyltin...		180–183/1 mm.	1.4998	(745)
Diamylbis(dodecylthio)tin...				(353, 354)
Diamyldibutoxytin..				(539)
Diamyldipropoxytin...				(539)
Dibutoxydibutyltin..	110–115			(98, 108, 142, 143, 539, 546, 951)
Dibutylbis(amylcarbamoylmethylthio)tin..........................				(28, 31, 497)
Dibutylbis(butylthio)tin..				(353, 354, 697)
Dibutylbis(sec-butylthio)tin.......................................				(353, 354, 697)
Dibutylbis(o-carbomethoxyphenoxy)tin............................				(114, 548, 873)
Dibutylbis(carboxymethylthio)tin, dinonyl ester...................				(878)
Dibutylbis(decylthio)tin..				(353, 354, 697)
Dibutylbis(dodecyloxy)tin...			1.4730	(114, 548, 549)
Dibutylbis(dodecylthio)tin..		160/0.0001 mm.	1.5011	(26, 353, 354, 505, 506, 548, 697, 819, 884, 892)
Dibutylbis(ethylthio)tin..				(353)
Dibutylbis(heptylthio)tin...				(353, 354, 697)
Dibutylbis(hexadecylthio)tin......................................				(353, 354, 697)
Dibutylbis(hexylthio)tin..				(353, 354, 697)
Dibutylbis(tert-hexylthio)tin......................................				(353, 354, 697)
Dibutylbis(2-hydroxyethoxy)tin...................................	120–130			(97)
Dibutylbis(2-hydroxyethylthio)tin.................................				(689, 695)
Dibutylbis(2-hydroxyethylthio)tin, adipate........................				(30, 34, 502)
Dibutylbis(2-hydroxyethylthio)tin, dilaurate......................				(692)
Dibutylbis(isobutylthio)tin.......................................				(353, 354, 697)
Dibutylbis(2-methyl-1,3-dioxolan-4-ylmethoxy)tin.................				(114, 548)
Dibutylbis(morpholinocarbonylmethylthio)tin......................				(28, 31, 497)
Dibutylbis(nonylthio)tin..				(353, 354, 697)
Dibutylbis(octylcarbamoylmethylthio)tin..........................				(31, 497)
Dibutylbis(octyloxy)tin...				(142, 143)
Dibutylbis(octylthio)tin..				(353, 354, 697)

TABLE 17—*Continued*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Dibutylbis(phenylthio)tin				(353, 354, 697)
Dibutylbis(3-propyl-2-oxaziridinyl)tin				(114, 548)
Dibutylbis(tetradecylthio)tin				(353, 354, 697)
Dibutylbis(p-tolylthio)tin				(353, 354, 697)
Dibutyl(N-butylbenzenesulfonamido)methoxytin				(114, 548)
Dibutyldiethoxytin				(142, 143)
Dibutyldimethoxytin		136–139/1.2 mm.	1.4831	(142, 143, 539, 546)
2,2-Dibutyl-1,3,2-dioxastannolane				(696, 851)
Dibutyldiphenoxytin				(53)
Dibutyldipropoxytin				(53)
Dibutyldisuccinimidotin				(114, 548)
Dibutyl-3-indenylmethoxytin				(114, 548)
(Dibutylmethoxystannyl)phenylacetic acid, 2-ethylhexyl ester				(114, 548)
2,2-Dibutyl-4-methyl-1,3,2-dioxastanninane				(696)
2,2-Dibutyl-4-methyl-1,3,2-dioxastannolane	182			(76, 696)
2,2-Dibutyl-1,3,2-oxathiastannolane				(689, 695)
Dibutyltin-(S,S)-bis(butyl 2-mercaptocaproate)				(879)
Dibutyltin-(S,S)-bis(butyl 8-mercaptocaprylate)				(879)
Dibutyltin-(S,S)-bis(butyl 2-mercaptoenanthate)				(879)
Dibutyltin-(S,S)-bis(butyl 2-mercaptolaurate)				(879)
Dibutyltin-(S,S)-bis(butyl 12-mercaptolaurate)				(879)
Dibutyltin-(S,S)-bis(butyl 2-mercaptopalmitate)				(879)
Dibutyltin-(S,S)-bis(butyl 2-mercaptopelargonate)				(879)
Dibutyltin-(S,S)-bis(butyl 2-mercaptostearate)				(879)
Dibutyltin-(S,S)-bis(2-butyloctyl 3-mercaptopropionate)				(879)
Dibutyltin-(S,S)-bis(cyclohexyl mercaptoacetate)				(879)
Dibutyltin-(O,O)-bis(dibutyl tartrate)				(873)
Dibutyltin-(S,S)-bis(diethylene glycol laurate mercaptoacetate)				(879)
Dibutyltin-(O,O)-bis(diethylene glycol diricinoleate)				(872, 873)
Dibutyltin-(S,S)-bis(dihydroabietyl mercaptoacetate)				(879)
Dibutyltin-(S,S)-bis(ethylene glycol ricinoleate mercaptoacetate)				(879)
Dibutyltin-(O,O)-bis(ethyl 2-hydroxyisobutyrate)				(872, 873)
Dibutyltin-(O,O)-bis(ethyl lactate)				(872, 873)
Dibutyltin-(S,S)-bis(ethyl 2-mercapto-2-ethylcaproate)				(879)
Dibutyltin-(S,S)-bis(ethyl mercaptodiphenylacetate)				(879)
Dibutyltin-(S,S)-bis(ethyl mercaptolaurate)				(704)
Dibutyltin-(O,O)-bis(glyceryl dilaurate)				(851)
Dibutyltin-(S,S)-bis(hexyl 3-mercaptopropionate)				(27, 495)
Dibutyltin-(S,S)-bis(isoöctyl mercaptoacetate)				(884)
Dibutyltin-(S,S)-bis(4-mercaptobutyl pelargonate)				(500)
Dibutyltin-(S,S)-bis(4-mercaptobutyl trimethylhexanoate)				(501)
Dibutyltin-(S,S)-bis(2-mercaptoethyl abietate)				(501)
Dibutyltin-(S,S)-bis(2-mercaptoethyl arachidate)				(500)
Dibutyltin-(S,S)-bis(mercaptoethylene glycol adipate)				(501)
Dibutyltin-(S,S)-bis(2-mercaptoethyl laurate)				(500, 501)
Dibutyltin-(S,S)-bis(2-mercaptoethyl pelargonate)				(500)
Dibutyltin-(S,S)-bis(2-mercaptoethyl trimethylhexanoate)				(501)
Dibutyltin-(O,O)-bis(methyl ricinoleate)				(851)
Dibutyltin-(S,S)-bis(phenoxyethyl mercaptoacetate)				(879)
Dibutyltin-(S,S)-bis(thiomalic acid)				(879)
Dibutyltin-(O,O)-bis(tributyl citrate)				(872, 873)
Dibutyltin-(O,O)-bis(triethyl citrate)				(872, 873)
Dibutyltin-(S,S)-bis(3,5,5-trimethylhexyl mercaptoacetate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 2-mercaptobutyrate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 2-mercaptocaproate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 6-mercaptocaproate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 2-mercaptodiethylacetate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 2-mercaptopropionate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 3-mercaptopropionate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 2-mercaptovalerate)				(879)
Dibutyltin-(S,S)-bis(trimethylhexyl 5-mercaptovalerate)				(879)
Dibutyltin-(S,S)-bis(trimethylnonyl mercaptoacetate)				(879)
Dibutyltin dicyclohexyl thioglycolate				(316)
Dibutyltin-(O,O)-(glyceryl monolaurate)				(690)
Dibutyltin-(O,O)-(glyceryl monoöleate)				(690)
Dibutyltin-(O,O)-(glyceryl monoricinoleate)				(690)
Dibutyltin-(O,O)-(glyceryl monostearate)				(690)
Didodecylbis(dodecylthio)tin				(353, 354, 697)
Didodecyltin-(S,S)-bis(butyl mercaptoacetate)				(879)
Didodecyltin-(S,S)-bis(butyl 4-mercaptobutyrate)				(27, 495)
Diethoxydiphenyltin	Decomposes at 124			(39, 348, 349)
Diethylbis(2-ethylhexyloxy)tin				(539, 543)
Diethyldimethoxytin		124–126/3 mm.	1.4206	(546)
Dimethoxydiphenyltin	270 (d.)			(546)
Dimethyltin-(S,S)-bis(octadecyl 2-mercaptopropionate)				(575)

TABLE 17—*Continued*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Diphenylbis(phenylthio)tin	65–65.5			(43)
Diphenyltin-(O,O)-(glyceryl monoricinoleate)				(690)
Dipropyltin-(S,S)-bis(2-mercaptoethyl trimethylhexanoate)				(501)
(Dodecylthio)trimethyltin				(353, 354, 697)
(Dodecylthio)triphenyltin				(353, 354, 697)
Ethoxydiethyltin fluoride	90–91			(902)
Ethoxytriethyltin		82/13 mm.	1.4842 (at 15°)	(25, 286, 480,
		82–84/11 mm.		484, 536, 856,
		190–192/760 mm.		888)
Ethoxytrimethyltin		65–66/760 mm.		(484)
(Heptylthio)triisopropyltin		155–157/1 mm.	1.5045	(745)
(Heptylthio)tripropyltin		158–160/1 mm.	1.4981	(745)
Isopropyltin-(S,S,S)-tris(mercaptoethyl pelargonate)				(500)
Methoxytrioctyltin			1.4781	(143, 168, 169,
				207)
Methoxytripropyltin		87–88/3 mm.		(626)
(Methylthio)triethyltin		224/760 mm,	1.5290	(13)
Methyltris(1-naphthylthio)tin			1.71	(818)
Methyltris(octadecylthio)tin	50–60			(818)
Methyltris(α-pinylthio)tin			1.5449	(818)
Phenoxytripropyltin		145–147/1 mm.	1.5284	(746)
(Phenylthio)triisopropyltin		138–139/1 mm.	1.5676	(745)
(Phenylthio)tripropyltin		157–159/1 mm.	1.5626	(746)
Tribenzyl(4-hydroxybutylthio)tin, diester with azelaic acid				(30, 34, 502)
Tributyl[2-(amylcarbamoyl)ethylthio]tin				(28, 31, 497)
Tributyl(carboxymethylthio)tin, decyl ester				(878)
Tributyl(cyclohexyloxy)tin				(536)
Tributyl(1,1-dimethyl-3-oxobutoxy)tin				(114, 548)
Tributyl(dodecyloxy)tin				(114, 548)
Tributyl(dodecylthio)tin				(353, 354, 697)
Tributylmethoxytin		101–102/2 mm.	1.4745	(143, 536, 626)
Tributyltin-S-(decyl mercaptoacetate)				(879)
Tributyltin-S-(mercaptoacetic acid)				(879)
Triethyl(ethylthio)tin		125–126/12 mm.	1.5150	(744)
Triethyl(heptylthio)tin		134–135/1 mm.	1.5006	(747)
Triethyl(isobutylthio)tin		86–88/1 mm.	1.5122	(744, 746)
Triethyl(isopropylthio)tin		78–80/1 mm.	1.5132	(744, 746)
Triethylmethoxytin		73–74/13 mm,	1.4760	(626)
Triethyl(3-methylbutylthio)tin		95–97/1 mm.		(746)
Triethyl(2-naphthylthio)tin		189–190/1 mm.	1.3231	(747)
Triethyl(p-nitrophenoxy)tin				(380, 530)
Triethylphenoxytin		115–126/1 mm.	1.5422	(380, 530, 744,
		115/1 mm.	1.5415	746, 747)
		147.5–148/12 mm.		
Triethyl(phenylthio)tin		138–140/1 mm.	1.5828	(747)
Triethyltin-S-(decyl mercaptoacetate)				(879)
Triethyltin-S-(mercaptoacetic acid)				(879)
Triethyl(p-tolyloxy)tin		124–127/1 mm.	1.5365	(744, 747)
			1.5360	
Triethyl(o-tolylthio)tin		132–135/1 mm.	1.5704	(744, 747)
			1.5720	
Triethyl(m-tolylthio)tin		132–134/1 mm.	1.5705	(744)
Triethyl(p-tolylthio)tin		125–126/1 mm.	1.5712	(744, 746, 747)
		129–132/1 mm.		
Triisopropyl(p-tolylthio)tin		157–158/1 mm.	1.5648	(745)
Trimethylphenoxytin		109/8 mm.		(458)
		222–224/760 mm.		
Trimethyltin-O-(tributyl citrate)				(873)
Triphenyltin-S-(decyl mercaptoacetate)				(879)
Triphenyl(triphenylsiloxy)tin	138–139			(641)
Tripropyl(p-tolylthio)tin		157–159/1 mm.	1.5516	(744, 745, 746)
			1.5602	
Tris(sec-amylthio)methyltin			1.5452	(818)
Tris[3-(butylcarbamoyl)propylthio]isopropyltin				(28, 31, 497)
Tris(butylthio)methyltin			1.5541	(818)
Tris(butylthio)phenyltin			1.5710	(818)
Tris(p-carbomethoxyphenylthio)methyltin			1.6579	(818)
Tris(p-chlorobenzylthio)methyltin			1.6523	(818)
Tris(p-cresylthio)methyltin	143–145			(818)
Tris(p-cresylthio)phenyltin			1.6890	(818)
Tris(dodecylthio)ethyltin				(353, 354, 697)
Tris(dodecylthio)methyltin				(353, 354, 697)
Tris(tert-dodecylthio)methyltin				(818)
Tris(2-hydroxyethylthio)isopropyltin, terephthalate				(30, 34, 502)
Tris(2-hydroxyethylthio)methyltin			1.6168	(818)
Tris(p-mercaptophenoxyphenylthio)methyltin				(818)

TABLE 17—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
$(C_4H_9)_2SnSCH_2COOCH_2CH_2OCOCH_2S$				(35, 507)
$(C_4H_9)_2SnSCH_2COOCH_2CH(CH_3)OCOCH_2S$				(35, 507)
$(C_6H_5CH_2)_3SnS(CH_2)_2COO(CH_2)_4OCO(CH_2)_2SSn(CH_2C_6H_5)_3$				(35, 507)
$[(C_6H_5CH_2)_3SnS(CH_2)_4OCO(CH_2)_3]_2CH_2$				(503)
$[(C_{11}H_{23}COO)(C_4H_9)_2SnS(CH_2)_4]_2O$				(44)
$[(CH_3CH=CHCOO)(C_4H_9)_2SnS(CH_2)_4]_2O$				(44)
$HO(CH_2)_2[OSn(C_4H_9)_2O(CH_2)_2]_2OH$	215–218			(696)
$[(C_4H_9)(C_2H_5)CHCH_2OCOCH_2SSn(C_4H_9)_2]_2O$		80–90/5 mm.	1.5128	(163, 164, 551)
$(C_4H_9)(C_2H_5)CHCH_2OCOCH_2S[Sn(C_4H_9)_2O]_3OCC_{11}H_{23}$			1.5069	(163, 164, 551)
$(C_4H_9)(C_2H_5)CHCH_2OCOCH_2S[Sn(C_4H_9)_2O]_3OCCH=CHCOOC_{18}H_{35}$			1.5037	(163, 164, 551)
$(C_4H_9)(C_2H_5)CHCH_2OCOCH_2S[Sn(C_4H_9)_2O]_3OCCH=CHCOOCH_2CH(CH_3)OH$				(163, 164, 551)
$(C_4H_9)_2\{CH_3[CH(CH_3)]_3CH_2COOCH_2CH_2S\}_2Sn$				(32)
$(C_4H_9)_2Sn[SCH_2CH(OCOC_{11}H_{23})(CH_2OCOC_{11}H_{23})]_2$				(501)
$C_{12}H_{25}S[Sn(C_4H_9)_2O]_3Sn(C_4H_9)_2SC_{12}H_{25}$				(163, 164, 551)
$(C_4H_9)_2Sn(OCH_2CH_2O)_2Sn(C_4H_9)_2$	223–229 (d.)			(76)
$[(CH_3)_2Sn]_3[B(OC_6H_4S-p)_3]_2$				(688)
$[(C_4H_9)_2Sn]_3[B(OCH_2CH_2S)_3]_2$				(688)
$[(C_{12}H_{25})_2Sn]_3[B(OCH_2CH_2S)_3]_2$				(688)
$[(C_6H_5)_2Sn]_3[B(OCH_2CH_2S)_3]_2$				(688)
$[(C_6H_5)_2Sn]_3\{B[OCH_2CH(C_6H_5)S]_3\}_2$				(688)

Related compounds

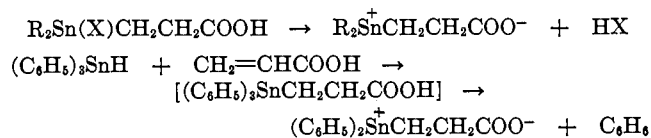| Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
(*tert*-Butylperoxy)tributyltin		105–110/1 mm. (with decomposition)		(717)
(*tert*-Butylperoxy)triethyltin		56–57/12 mm.		(717)
(*tert*-Butylperoxy)trimethyltin		56/12 mm.		(717)
(Cumylperoxy)triethyltin		105–110/1–2 mm.		(717)

sulfides, and oxides (13); transesterification reactions (14, 746); the reaction of organic esters with organotin oxides (10, 11); and the reaction of an organotin sulfate with a barium salt of an organic acid or an organotin carbonate with an acid (479).

A recent method involves the cleavage of organic groups from tetraorganotin compounds (222, 511, 724, 739, 745, 747, 760, 761, 765). The cleavage of one or

$$R_4Sn + R'COOH \rightarrow R_3SnOCOR' + RH$$
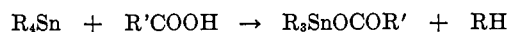
more vinyl groups by organic acids, hydrogen halides, or mercaptans occurs in preference to addition to the vinyl double bond; vinyl groups are cleaved more readily than normal alkyl groups but less readily than phenyl groups (739, 760).

Organotin inner salts may be formed from the hydrolysis of bromo(carboxyethyl)-substituted tin compounds (388, 390) or by the reaction of triphenyltin hydride with acrylic acid (385).

$$R_2Sn(X)CH_2CH_2COOH \rightarrow R_2\overset{+}{S}nCH_2CH_2COO^- + HX$$
$$(C_6H_5)_3SnH + CH_2=CHCOOH \rightarrow$$
$$[(C_6H_5)_3SnCH_2CH_2COOH] \rightarrow$$
$$(C_6H_5)_2\overset{+}{S}nCH_2CH_2COO^- + C_6H_6$$

(2-Carboxyethyl)triphenyltin is unstable at room temperature; other $R_3SnCH_2CH_2COOH$ compounds can be thermally decomposed to the corresponding inner salts (388).

Organotin thio esters have been prepared by the reaction of organic thio acids with R_3SnOH and R_2Sn compounds (801).

(f) RSnOOH compounds

The organostannonic acids (table 19) are usually prepared by one of two methods. The reaction of tin(II) chloride, sodium or potassium hydroxide, and an organic halide is employed in the preparation of the alkanestannonic acids (173, 174, 175, 176, 178, 185, 212, 485, 508, 513, 585, 658, 660, 673, 803).

$$SnCl_2 + 3MOH \rightarrow MHSnO_2 + 2MCl + H_2O$$
$$MHSnO_2 + RX + MOH \rightarrow$$
$$RSnOOM + MX + H_2O$$
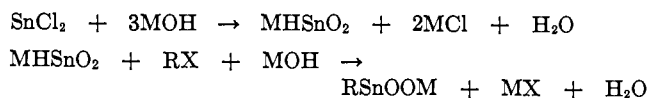
Hydrolysis of aryltin trichlorides is used most commonly for the preparation of the aromatic stannonic acids (406, 412, 413, 414, 418, 665, 673); the method has also been applied to the preparation of aliphatic stannonic acids (844). Warming $RSnX_3$ compounds

$$RSnCl_3 + 4MOH \rightarrow RSnOOM + 3MX + H_2O$$

with water alone often brings about the desired hydrolysis.

2-Propene-1-stannonic acid has been prepared by heating tetraallytin in an ampoule at 170°C. (435).

(g) $(RSnS)_2S$ compounds

These compounds (table 16) are prepared from

TABLE 18

Carboxylic acid derivatives of organotin compounds

[Compounds of the types R_3SnO_2CR', $R_2R'SnO_2CR''$, $R_2Sn(O_2CR')_2$, and $R_2Sn(O_2CR')(O_2CR'')$]

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Allyldiphenyltin acetate	Decomposes at 260			(724)
5-Amino-2,2-dibutyl-1-oxa-2-stanna-3-thiacyclohexan-6-one	205-207			(280)
Benzyltin tris(butylxanthate)				(29, 33)
Bis(dibutyltin monobehenate) maleate				(263)
Bis(2-ethylhexyl)tin dilaurate				(384, 532)
Bis(tributyltin) thiomalate				(801)
Bis(3,5,5-trimethylhexyl)tin dilaurate				(384, 532)
(5-Bromoamyl)diethyltin acetate	68-69			(380)
(p-Bromophenyl)diethyltin acetate	108-109			(380, 530)
Butoxydiphenyltin oleate				(552)
Butyldiethyltin acetate	71-73			(381, 530)
Butyldimethyltin acetate	106-108			(381, 530)
(2-Carboxyethyl)diphenyltin (inner salt)	Does not melt below 320			(385, 388, 391, 631, 634)
(2-Carboxyethyl)dipropyltin (inner salt)	158-160			(390, 631, 634)
(o-Carboxyphenyl)diphenyltin (inner salt)				(234)
(p-Chlorophenyl)diethyltin acetate	100-101			(380, 530)
(3-Cyanopropyl)dipropyltin acetate	71-72			(390)
Decyldimethyltin acetate	96-98			(724)
Decyldivinyltin acetate				(724)
Diamylethyltin acetate	50-53.5			(381, 530)
Dibenzyltin diacetate	136-137			(794)
Dibenzyltin dilaurate	88-92			(774)
Dibenzyltin distearate	99-100			(774)
Dibenzyltin ricinoleate				(774)
Dibutyl(2-carboxyethyl)tin (inner salt)	110-113			(388, 631, 634)
Dibutyl(dodecylthio)tin acrylate				(44)
Dibutyl(dodecylthio)tin crotonate				(44)
Dibutyl(dodecylthio)tin laurate				(44)
Dibutyl(dodecylthio)tin methacrylate				(44)
Dibutyl(dodecylthio)tin methyl maleate				(44)
Dibutyl(dodecylthio)tin oleate				(44)
Dibutylmethoxytin acetate				(4, 552, 553)
Dibutylmethoxytin allyl maleate			1.5011	(4, 552, 553)
Dibutylmethoxytin butyl maleate			1.5068	(4, 552, 553)
Dibutylmethoxytin laurate			1.4860	(4, 552, 553)
Dibutylmethoxytin methyl maleate			1.5103	(4, 114, 548, 552, 553)
Dibutylmethoxytin methyl phthalate			1.5448	(4, 552, 553)
Dibutylmethoxytin sorbate				(114, 548)
Dibutylmethoxytin methyl succinate			1.4980	(4, 552, 553)
Dibutylmethoxytin tetrahydrofurfuryl maleate			1.5036	(4, 552, 553)
2,2-Dibutyl-1-oxa-2-stanna-3-thiacyclopentan-5-one	185-187			(280)
Dibutyltin acrylate thioacetate				(44)
Dibutyltin adipate	136-137			(14)
Dibutyltin bis(amyl maleate)			1.4906	(425, 426)
Dibutyltin bis(butyl maleate)			1.4927	(425, 426)
Dibutyltin bis(dodecylmercaptoisobutyrate)				(496)
Dibutyltin bis(9,10-epoxy-12-hydroxystearate)				(792)
Dibutyltin bis(9,10-epoxystearate)				(735, 792)
Dibutyltin bis(2-ethylhexyl thioacetate)				(578)
Dibutyltin bis(ethyl maleate)			1.5005	(425, 426)
Dibutyltin bis(ethyl malonate)				(550)
Dibutyltin bis(isoöctyl maleate)				(884)
Dibutyltin bis(isoöctyl thioacetate)				(578)
Dibutyltin bis(isopropyl maleate)	37		1.4982	(425, 426)
Dibutyltin bis(isopropylxanthate)				(29, 33)
Dibutyltin crotonate thioacetate				(44)
Dibutyltin diacetate		142-145/10 mm.		(21, 81, 109, 151, 184, 226, 306, 373, 395, 682, 729, 733, 790, 856, 884, 888, 906)
Dibutyltin dihendecanoate				(888)
Dibutyltin dilaurate				(1, 108, 137, 151, 187, 217, 324, 394, 395, 532, 680, 729, 733, 789, 790, 805, 856, 884, 888, 906)
Dibutyltin diphthalate				(137)
Dibutyltin disalicylate				(731)
Dibutyltin fumarate				(306, 681, 805)
Dibutyltin itaconate				(14)
Dibutyltin maleate				(137, 188, 268, 395, 532, 680, 789, 790, 861, 884)
Dibutyltin 3-methyladipate	143-144.5			(14)

TABLE 18—*Continued*

Compound	Melting Point	Boiling Point	n_D^{2} °	References
	°C.	°C.		
Dibutyltin thioacetate methyl maleate...............................				(44)
Dibutyltin oxalate..	195 (d.)			(14)
Dibutyltin phthalate...				(137)
Dibutyltin sebacate..	78–82			(14)
Dibutyltin succinate...	187–187.5			(14)
Dibutyltin terephthalate...	Above 245			(14)
Dibutyltin thiomalate..				(801)
Dibutyl(trimethylsilylmethyl)tin trifluoroacetate....................	62.0–63.4			(761)
Dibutylvinyltin acetate..				(744)
Diethylhexyltin acetate..	64–65			(381, 530)
Diethyloctyltin acetate..	67–69			(381, 530)
Diethylphenyltin acetate...	93.5–94.5			(380, 530)
Diethyltin citrate...				(101)
Diethyltin diacetate...				(101)
Diethyltin dibutyrate..				(101)
Diethyltin diformate...				(101)
Diethyltin oxalate...				(101)
Diethyltin tartrate..				(101)
Dihexyltin dilaurate...	About 13			(384, 532)
Dihexyltin maleate...				(384, 532)
Diisopropyltin bis(chloroacetate)....................................	54–55			(745)
Diisopropyltin bis(dichloroacetate)..................................	69–71			(745)
Dimethyloctyltin acetate...	95–97			(381, 530, 724)
	96–97.8			
Dimethyltin bis(bromoacetate)..	159–160			(739)
Dimethyltin bis(chloroacetate).......................................	162–165			(739)
Dimethyltin bis(dichloroacetate).....................................	226–228			(739)
Dimethyltin bis(trichloroacetate)....................................	190–191			(739)
Dimethyltin bis(trifluoroacetate)....................................	240–243			(739)
Dimethyltin dibenzoate...				(258, 722)
Dimethyltin diacetate..				(101)
Dimethyltin dibutyrate...				(101)
Dimethyltin dicaprylate..				(101)
Dimethyltin diformate..				(101, 327, 328)
Dimethyltin dimethacrylate...	140–144			(739)
Dimethyltin disalicylate...	205–206			(258, 722)
Dimethyltin divalerate...				(101)
Dimethyltin oxalate..				(258, 660, 722)
Dimethyltin phthalate..	360 (d.)			(258, 722, 766)
Dimethyltin succinate..	314 (d.)			(258, 722)
Dimethylvinyltin 2-bromopropionate...................................	78–81			(760)
Dimethylvinyltin chloroacetate.......................................	104–107			(739)
Dioctyltin bis(butyl maleate)..				(384, 532)
Dioctyltin bis(2-ethylhexanoate).....................................				(384, 532)
Dioctyltin diacetate...				(384)
Dioctyltin dibutyrate..				(384, 532)
Dioctyltin diformate...				(384)
Dioctyltin dilaurate...				(116, 384, 532)
Dioctyltin distearate..				(384, 532)
Dioctyltin maleate...				(384)
Diphenyloctyltin acetate...	99.5–100.5			(530)
Diphenyltin diacetate..				(395, 532)
Diphenyltin maleate..				(395)
Diphenyltin tartrate...	114			(683)
Dipropyl[2-(4-pyridyl)ethyl]tin acetate..............................	96–97			(390, 631, 634)
Divinyltin phthalate...	283 (d.)			(769)
Dodecyldiethyltin acetate..	68–72			(381, 530)
Dodecyldimethyltin acetate...	99–102			(381, 530, 724)
	97–98.6			
Ethoxydiethyltin ethyl sebacate......................................				(552)
(2-Ethoxyethoxy)diethyltin crotonate.................................				(552)
Ethyldiphenyltin acetate...	125–127			(530)
Hexyldiphenyltin acetate...				(724)
Hexyldivinyltin acetate..				(724)
Methoxydiphenyltin butyl itaconate...................................				(552)
Octyldivinyltin acetate..				(724)
(2-Phenylethyl)dipropyltin acetate...................................	79–80			(390, 631, 634)
Tetrabutylditin dilaurate maleate....................................				(59)
Triamyltin acetate...	66–67.5			(530)
Tribenzyltin acetate...	117–118			(774)
Tribenzyltin benzoate..	99–100			(774)
Tribenzyltin laurate...	90–91			(774)
Tribenzyltin methyl maleate..	114–117			(774)
Tribenzyltin ricinoleate...				(774)
Tribenzyltin stearate..	99–100			(774)
Tributyltin acetate..	84.5–85			(151, 184, 378, 380, 530)
Tributyltin cyanoacetate...				(382, 530)

TABLE 18—*Continued*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Tributyltin methacrylate..	20–22			(436)
Tricyclohexyltin acetate...	61–63			(530)
Triethyltin acetate..	130–131	224/760 mm.		(10, 13, 71, 101, 220, 378, 380, 381,
	132–134			422, 479, 530, 631, 634, 744, 746,
	119			760)
	121			
	134–135			
Triethyltin acrylate...	116–117			(11, 71, 631, 634)
Triethyltin benzoate..	80	133–134/1 mm.		(10, 71, 380, 479, 530, 744, 747)
	74–74.5			
	71			
Triethyltin bis(p-chlorophenyl)acetate.............................				(71)
Triethyltin bitartrate·2H2O..				(479)
Triethyltin bromoacetate..	99.5			(11)
Triethyltin 2-bromopropionate.....................................	88–89			(11)
Triethyltin 3-bromopropionate.....................................	84.5			(11)
Triethyltin butyrate...	92	96–98/1 mm.		(101, 479, 744)
Triethyltin caproate...	80.5–81			(101, 530)
Triethyltin caprylate..				(101)
Triethyltin chloroacetate..	111–112	118–119/1 mm.		(747)
Triethyltin 2-chloropropionate.....................................	90.5–91			(11)
Triethyltin 3-chloropropionate.....................................	87.5–88			(11)
Triethyltin d-trans-chrysanthemumate..............................				(71)
Triethyltin cinnamate...	107–108			(11)
Triethyltin 2,3-dibromopropionate.................................	99.5–100			(11)
Triethyltin dichloroacetate..	132–133	121–123/1 mm.		(747)
Triethyltin fluoroacetate..	155–156			(11)
Triethyltin formate...	50–60			(71, 101, 479)
Triethyltin glycolate..	106.5–107			(11)
Triethyltin heptafluorobutyrate....................................	75.5	224/760 mm.		(11)
Triethyltin iodoacetate..	94.5			(11)
Triethyltin laurate..	73–74			(530)
Triethyltin maleate...				(530)
Triethyltin malonate..	175–175.5 (d.)			(530)
Triethyltin methacrylate...	75.5			(11, 436, 771)
Triethyltin oxalate..				(101, 479)
Triethyltin pentafluoropropionate..................................	94.5	216.5/760 mm.		(11)
Triethyltin propionate...	103	226–238/760 mm.		(744)
Triethyltin tartrate·2H2O..				(479)
Triethyltin trifluoroacetate..	107	218/760 mm.		(10, 744, 747)
	122–123			
Triethyltin valerate...				(101)
Trihexyltin acetate..	68–69			(378, 380, 530)
Triisoamyltin acetate..				(107)
Triisoamyltin formate..				(107)
Triisobutyltin acetate..				(107)
Triisobutyltin formate...				(107)
Triisopropyltin acetate..				(378, 530)
Triisopropyltin acetate·H2O..	51.5–52			(380, 530)
Triisopropyltin butylxanthate......................................				(29, 33)
Trimethyltin acetate...	196.5–197.5			(101, 378, 380, 530)
Trimethyltin butyrate..				(101)
Trimethyltin caproate..				(101)
Trimethyltin caprylate...				(101)
Trimethyltin formate..				(101)
Trimethyltin methacrylate..	100			(436, 488)
	122			
Trimethyltin valerate..				(101)
Trioctyltin acetate..	47–48			(378, 380, 530)
Triphenyltin acetate...	121–122			(378, 380, 530, 631, 634, 663)
Triphenyltin benzoate...	82.5–84.0			(237)
Triphenyltin butyrate..				(534)
Triphenyltin cyanoacetate..	140–142			(382, 530)
Triphenyltin 2-cyanopropionate.....................................	139–141			(631, 634)
Triphenyltin laurate...				(733)
Triphenyltin methacrylate..	91–92			(436)
Tripropyltin acetate...	82	81–83/1 mm.		(103, 378, 380, 388, 530, 631, 634,
	100			739, 746)
	34–35			
Tripropyltin acrylate..	94–95			(631, 634)
Tripropyltin benzoate...	45–46	158–162/1 mm.		(744, 746)
Tripropyltin bromoacetate...	77–78			(739)
Tripropyltin 2-bromopropionate....................................	88–89			(739)
Tripropyltin butyrate..	66	102–104/1 mm.		(103, 746)
Tripropyltin chloroacetate...	78–79	135–140/1 mm.		(739, 745)
Tripropyltin cyanoacetate..	91–92			(739)

TABLE 18—*Concluded*

Compound	Melting Point	Boiling Point	$n_D^{20°}$	References
	°C.	°C.		
Tripropyltin dichloroacetate...................................	83–84			(739, 745)
	84–85			
Tripropyltin formate...				(103)
Tripropyltin propionate..	70	88–89/1 mm.		(746)
Tripropyltin trichloroacetate...................................	96–97			(739)
Tripropyltin trifluoroacetate...................................	94–95	88–90/1 mm.		(739, 746)
	80			
Tris(p-chlorophenyl)tin acetate................................	148.5–149.5			(380, 530)
Tris(p-fluorophenyl)tin heptafluorobutyrate......................	276–278 (d.)			(222)
Tris(p-fluorophenyl)tin trifluoroacetate..........................	318–322 (d.)			(222)
CH₃COOSn(C₄H₉)₂OCOCH=CHCOOSn(C₄H₉)₂OCOCH₃...........				(263)
C₁₁H₂₃COOSn(C₄H₉)₂OCOCH=CHCOOSn(C₄H₉)₂OCOC₁₁H₂₃........				(263)
(C₈H₁₇OCOCH=CHCOO)₂(OCOCH=CHCOO)(C₄H₉Sn)₂(H₂O)ₓ......				(875)

organotin trihalides and hydrogen sulfide in aqueous solution (412, 414, 418, 622, 658, 659, 660). Organotin

$$2RSnX_3 + 3H_2S \rightarrow (RSnS)_2S + 6HX$$
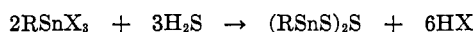
chlorides, bromides, and iodides have been used in this reaction. Alkanestannonic acids react with hydrogen selenide to give $(RSnSe)_2Se$ compounds (844).

$$2RSnOOH + 3H_2Se \rightarrow (RSnSe)_2Se + 4H_2O$$
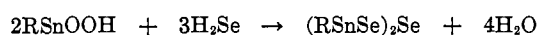
(h) Miscellaneous salts

For convenience, the nitrates, cyanides, cyanates, phosphates, platinates, sulfates, arsenates, etc. (table 20) are discussed as a group, since their methods of preparation are essentially the same. The reactions of an organotin oxide, hydroxide, halide, or acetate with an acid and of an organotin halide or mercaptide with a silver or alkali metal salt are used for the preparation of these compounds (13, 101, 102, 130, 135, 197, 258, 282, 380, 412, 479, 530, 535, 576, 722, 769, 843, 860, 886, 910).

Organotin oxides, hydroxides, and halides react with phosphorus pentoxide and with phosphoryl chloride to give organotin phosphate esters (130, 136). Frankland and Lawrence (220) obtained triethyltin sulfate by the action of sulfur dioxide on tetraethyltin in the presence of air. Triethyltin sodium reacts, in liquid ammonia, with p-toluenesulfonyl chloride to form p-(triethylstannylsulfonyl)toluene (530). Attempts to prepare triphenyltin cyanide from triphenyltin hydroxide and hydrocyanic acid or from triphenyltin chloride and potassium cyanide were unsuccessful; the cyanide can be prepared from triphenyltin hydroxide and anhydrous hydrogen cyanide (918).

Arbuzov and Pudovic (25) have reported that triethyltin iodide reacts with triethyl phosphite to give diethyl triethyltinphosphonate; later reports indicate the product to be triethyltin (ethyl ethylphosphonate) (24, 558). Similarly, diethyltin diiodide and triethyl

$(C_2H_5)_3SnI + P(OC_2H_5)_3 \rightarrow$
$(C_2H_5)_3SnOP(O)(C_2H_5)(OC_2H_5)$
not
$(C_2H_5)_3SnP(O)(OC_2H_5)_2$
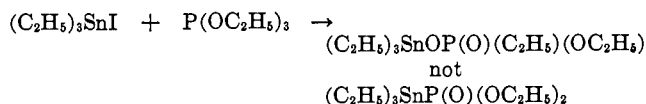
phosphite give diethyl bis(ethyl ethylphosphonate) (23, 24, 558).

3. Physical properties

The organotin hydroxides, R_3SnOH, usually are solids with well-defined melting points. They are soluble in the common organic solvents, and the low-molecular-weight hydroxides are soluble in water. In water and methyl alcohol, the organotin hydroxides are weaker bases than the corresponding compounds of mercury, thallium, and lead; all of these are stronger than their corresponding normal inorganic hydroxides (82, 322). It has also been reported that while triethyltin hydroxide is basic, triisopropyltin hydroxide is only faintly basic, and triphenyltin hydroxide is acidic (678). Determinations of the molecular weights of trimethyltin and tribenzyltin hydroxides have shown that these compounds are somewhat associated in refluxing benzene (443, 795). Triethyltin hydroxide is associated in refluxing benzene; the molecular weight is dependent on the concentration of the solution, but a value of 1000 was found as compared to the calculated value of 223 for the molecular weight (293). Kipping (402) attempted to resolve benzylphenyl-p-tolyltin hydroxide, benzylbutylphenyltin hydroxide, and benzylbutylethyltin hydroxide with the aid of two different optically active camphor derivatives and d-tartaric acid. These salts, except two of the tartrates, were oils which could not be solidified. The d-tartrates of the first two hydroxides were solids, but the regenerated hydroxides and fluorides were optically inactive. Bond-refraction data have been reported for R_3SnOH, R_3SnOR', and $R_2Sn(OCOR')_2$ compounds (856, 888). The infrared spectrum of triethyltin hydroxide has been reported (171).

The organotin oxides, R_2SnO, are all solids which, in most cases, do not melt but decompose at high temperatures. Usually they are insoluble in the common organic solvents and in water. Although the formulas of these organotin oxides are written as

TABLE 19

Organostannonic acids

(Compounds of the type RSnOOH)

Compound	Melting Point	References
	°C.	
Benzenestannonic acid..................		(406, 407, 417, 513, 621)
p-Bromobenzenestannonic acid..........		(81, 418, 622)
2-Bromoethanestannonic acid...........		(513)
1,4-Butanedistannonic acid.............		(803)
p-Chlorobenzenestannonic acid.........		(81, 418, 622)
Dichloromethanestannonic acid.........		(513)
1,2-Diphenylethenestannonic acid.......	157–160	(620)
1-Dodecanestannonic acid..............		(803)
1,2-Ethanedistannonic acid............		(803)
Ethanestannonic acid..................		(174)
Ethenestannonic acid..................		(803)
p-Iodobenzenestannonic acid...........		(418, 622)
2-Keto-1-propanestannonic acid.........		(513)
Methanedithiostannonic acid...........		(658)
Methanestannonic acid................		(173, 185, 212, 485, 585, 658, 660, 673)
1-Naphthalenestannonic acid...........		(513, 665)
Phenylmethanestannonic acid..........		(513)
1-Propanestannonic acid...............		(176)
2-Propanestannonic acid...............		(175)
2-Propene-1-stannonic acid.............		(435, 513, 803)
o-Toluenestannonic acid...............	295 (d.)	(412, 414)
m-Toluenestannonic acid...............	295 (d.)	(413)
p-Toluenestannonic acid...............		(412, 414, 417, 621)

Derivatives of methanestannonic acid

Hexabutyrate........................	180	(486)
Hexaisobutyrate......................	260	(486)
Hexapropionate......................	246 (d.)	(486)
Pentaacetate.........................	250 (d.)	(485)
Pentabenzoate.......................	272	(485)
Pentabutyrate........................	105	(486)
Pentaformate........................	240–280 (d.)	(485)
Pentaisobutyrate.....................	194	(486)
Pentakis(chloroacetate)................	214–224 (d.)	(485)
Pentakis(dichloroacetate)..............	235–240 (d.)	(486)
Pentapropionate.....................	156–157 240	(486)
Triacetate...........................	280 (d.)	(485)
Triformate...........................	270 (d.)	(485)

Other compounds

γ-Aceto-α,β-didodecylstannonin.........		(803)
Ethylenebis(stannonyl chloride)..........		(803)
Tridodecylstannonin...................		(803)
CH₃SnOOCOOK·H₂O...............		(660)
(CH₂=CHSnOOCOCH₃)₃.............	240 (d.)	(765)

R_2SnO, their structures are represented more correctly by the formula $(R_2SnO)_n$. Smith and Kipping (795) have studied the properties of a dibenzyltin oxide derivative, $HOSn(CH_2C_6H_5)_2[OSn(CH_2C_6H_5)_2]_n$-$OSn(CH_2C_6H_5)_2OH$. The analyses indicate that n is equal to 1, but molecular-weight determinations show that n is actually 6 or 7. It has been noted in a few cases that freshly prepared oxides are soluble in alkali; however, after standing they become insoluble. This may be due to the formation of a polymeric structure,

as proposed by Smith and Kipping. Solerio has reported that R_2SnO compounds are monomeric if the R group is large, e.g., $C_{12}H_{25}$, but polymeric if R is smaller (802).

The bis(trialkyltin) oxides, $(R_3Sn)_2O$, are liquids which can be distilled under reduced pressure. They are soluble in the common organic solvents and are decomposed, in most cases, by water and alcohol. Bis(triaryltin) oxides are reported only briefly; they are solids which are insoluble in organic solvents. The basicity of organotin oxides decreases progressively as the oxygen content increases: $R_4Sn > (R_3Sn)_2O > (R_2SnO)_n > [(RSnO)_2O]_n > SnO_2$ (10).

The organotin sulfides, R_2SnS, are usually solids with definite melting points. These compounds are soluble in the common organic solvents. The sulfides of higher molecular weight, however, are only slightly soluble in methyl alcohol, ethyl alcohol, and petroleum ether. From molecular-weight determinations Harada (301, 302) has concluded that the sulfides are trimers of the structure

$$R_2SnSSn(R_2)SSn(R_2)S$$
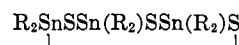
i.e., a six-membered heterocycle.

The bis(trialkyltin) sulfides, $(R_3Sn)_2S$, are similar to the bis(trialkyltin) oxides. Bis(trimethyltin) sulfide, monomeric in structure, is a distillable liquid (301, 302).

The organotin alkoxides and aryloxides, R_3SnOR' and $R_2Sn(OR')_2$, and the organotin mercaptides, R_3SnSR' and $R_2Sn(SR')_2$, are either distillable liquids or solids with definite melting points. Diethoxydiphenyltin is soluble in ethanol but insoluble in ether; methyl alcohol is used as the solvent for the recrystallization of diphenylbis(phenylthio)tin. Kraus and Neal (458) found that the molecular weight of trimethylphenoxytin was normal.

The organotin carboxylates, $R_3SnOCOR'$ and $R_2Sn(OCOR')_2$, are solids which melt or sublime when heated. Partial decomposition accompanies sublimation in some cases. In general, these compounds are soluble in alcohol. The crystal structures of several of these compounds have been investigated (257, 327, 328). Molecular weights of the $R_2Sn(OCOR')_2$ compounds vary from that of a dimer to 3000 (14).

The organostannonic acids, RSnOOH, are all solids which do not melt but decompose, usually at temperatures above 300°C. The low-molecular-weight acids are insoluble in the common organic solvents and in water; the higher-molecular-weight compounds are soluble in most organic solvents but insoluble in petroleum ether and water. The stannonic acids are amphoteric; they dissolve in sodium or potassium hydroxide and may dissolve in halogen acids if the

TABLE 20

Miscellaneous organotin salts

[Compounds of the types R_3SnE, $RR'R''SnE$, and R_2SnE_2 (E = anion other than halide, oxide, sulfide, —OR, —SR, or —OCOR)]

Compound	Melting Point	Boiling Point*	References
	°C.	°C.	
Bis(diphenyltin) pyrophosphate			(130)
Bis(ethyltin) triselenide			(844)
Bis(methyltin) triselenide			(844)
Bis(triethyltin) sulfate			(7, 746)
N,N-(Dibutylstannylene)bis(benzenesulfonamide)	135–137		(542, 545, 790)
N,N-(Dibutylstannylene)bis(N-butylbenzenesulfonamide)			(542, 545)
N,N-(Dibutylstannylene)bis(N-ethylbenzenesulfonamide)			(545)
N,N-(Dibutylstannylene)bis(1-hexanesulfonamide)			(542, 545)
N,N-(Dibutylstannylene)bis(toluenesulfonamide)			(542, 545)
Dibutyltin p-aminobenzenearsonate	175–185 (d.)		(860)
Dibutyltin bis(S-benzyl-N-benzylisodithiocarbamate)			(580)
Dibutyltin bis(S-benzyl-N-butylisodithiocarbamate)		100/760 mm.	(580)
Dibutyltin bis(S-benzyl-N-cyclohexylisodithiocarbamate)			(580)
Dibutyltin bis[bis(methylcyclohexyl) dithiophosphate]			(197, 535)
Dibutyltin bis[bis(octylphenyl) dithiophosphate]			(197, 535)
Dibutyltin bis(butyl dithiocarbonate)			(197)
Dibutyltin bis(diamyl dithiocarbamate)			(197, 535)
Dibutyltin S,S-bis(di-2-butyloctyl 2-mercaptoethyl borate)			(691)
Dibutyltin S,S-bis(di-2-ethylhexyl 2-mercaptoethyl borate)			(691)
Dibutyltin S,S-bis(dihydroabietyl 2-mercaptoethyl borate)			(691)
Dibutyltin S,S-bis(ethylene 2-mercaptoethyl borate)			(691)
Dibutyltin bis(3-nitro-4-aminobenzenearsonate)	189–193 (d.)		(860)
Dibutyltin bis(p-nitrobenzenearsonate)	165–172 (d.)		(860)
Dibutyltin bis(3-nitro-4-hydroxybenzenearsonate)	164–170 (d.)		(860)
Dibutyltin bis(p-toluenesulfonate)	Above 320		(769)
Dibutyltin borate			(576, 584)
Dibutyltin dioctyl borate			(576, 584, 693)
Dibutyltin hydrogen phosphate			(884)
Dibutyltin 3-nitro-4-aminobenzenearsonate	262 (d.)		(860)
Dibutyltin p-nitrobenzenearsonate	249 (d.) 256 (d.)		(860)
Dibutyltin 3-nitro-4-hydroxybenzenearsonate	191 (d.)		(860)
Dibutyltin sulfite			(884)
Dibutyltin tris(tributyltin) triphosphate			(130)
Didodecyltin bis(dibutyl dithiocarbamate)			(197, 535)
Didodecyltin bis(diisopropyl dithiophosphate)			(197, 535)
Didodecyltin bis(isopropyl dithiocarbonate)			(197)
Diethyltin bis(diphenylphosphinate)	346–349		(24)
Diethyltin bis(ethyl ethylphosphonate)	234.5		(558)
Diethyltin bis(ethylphenylphosphinate)	292–294 (d.)		(24)
Diethyltin chloroplatinate			(327)
Diethyltin cyanide iodide			(102)
Diethyltin dinitrate			(101, 527)
Diethyltin dithiocyanate			(102)
Diethyltin hydrogen phosphate			(886)
Diethyltin sulfate			(101, 527, 886)
Diethyl triethyltinphosphonate		210–220/2.5 mm. $n_D^{14°}$ = 1.4858	(25)
Dihexyl diphenyltinpyrophosphate			(130, 135, 136)
Diisoamyltin sulfate			(282)
Dimethylbis(trimethylsiloxy)tin			(843)
Dimethyltin antimonate			(258, 722)
Dimethyltin arsenate			(258, 722)
Dimethyltin bis(S-benzyl-N-butylisodithiocarbamate)		120/5 mm.	(580)
Dimethyltin bis(phenylphosphonite)	260 (d.)		(739, 769)
Dimethyltin chloroplatinate			(327)
Dimethyltin diazide			(722)
Dimethyltin dicyanate			(258, 722)
Dimethyltin dihypophosphite	213 (d.)		(769)
Dimethyltin diiodate			(258, 722)
Dimethyltin dimetaborate			(722)
Dimethyltin dinaphthionate			(722)
Dimethyltin ferricyanide	335–360 (d.)		(258, 722)
Dimethyltin ferrocyanide			(258, 722)
Dimethyltin molybdate	343 (d.)		(258, 722)
Dimethyltin phenylphosphonate	Above 350		(769)
Dimethyltin phosphate	Above 345		(722, 769)
Dimethyltin sulfate			(101, 327, 328)
Dimethyltin tungstate	330 (d.)		(258, 722)
Dimethyltin vanadate			(258, 722)
Dimethyl trimethyltinphosphonate	96		(25)
Dioctyl tris(tributyltin) triphosphate			(135)
Diphenyltin bis(butanearsonate)	296 (d.)		(860)

TABLE 20—*Concluded*

Compound	Melting Point	Boiling Point*	References
	°C.	°C.	
Diphenyltin S,S-bis(diphenyl mercaptoethyl borate)			(691)
Diphenyltin butanearsonate	297 (d.)		(860)
Dipropyltin dicyanide			(177)
Divinyltin dithiocyanate	163.5–165 (d.)		(769)
Divinyltin phenylphosphonate	Above 355		(769)
(+)-Ethylmethylpropyltin bromocamphorsulfonate	194–197		(670)
(+)-Ethylmethylpropyltin camphorsulfonate	125–126		(669)
Hexamethyl methyltintriphosphonate			(23)
Tetraethyl diethyltindiphosphonate	249–251		(23)
Tetraethyl dimethyltindiphosphonate			(23)
Tetramethyl diethyltindiphosphonate	263.5–265		(23)
Tetramethyl dimethyltindiphosphonate	245–247		(23)
Tetrapropyl diethyltindiphosphonate	262–264		(23)
Tetrapropyl dipropyltindiphosphonate	251–253		(23)
N-(Tributylstannyl)-N-ethylbenzenesulfonamide			(545)
Tributyltin cyanide	90–93		(530)
Tributyltin dioctyl phosphate			(136)
Tributyltin dioctyl triphosphate			(136)
N-Triethylstannylsaccharin	113.5–114		(530)
p-Triethylstannylsulfonyltoluene	91.5–92		(530)
N-Triethylstannyltoluenesulfonamide	69.5–71		(530)
Triethyltin arsenate			(479)
Triethyltin carbonate	120		(479, 530, 661, 910)
	138–139 (d.)		
Triethyltin chloroplatinate			(327, 479)
Triethyltin cyanate	214		(10, 102, 479)
Triethyltin cyanide	163.5–164	130/760 mm.	(10, 13, 101, 102,
	153	249/760 mm. (with	380, 479, 530)
		decomposition)	
Triethyltin (ethyl ethylphosphonate)	261–263	$n_D^{14°} = 1.4902$	(24, 558)
Triethyltin isocyanate	48	239/760 mm.	(13)
		162–163/80 mm.	
		120–121/11 mm,	
Triethyltin isothiocyanate	33	130/1 mm.	(13)
		282/760 mm. (with	
		decomposition)	
		$n_D^{20°} = 1.5825$	
Triethyltin methanesulfonamide	38		(380, 530)
Triethyltin nitrate			(479, 527)
Triethyltin phosphate			(479)
Triethyltin phthalimide	71–73		(380, 530)
Triethyltin selenate			(328)
Triethyltin sulfate			(90, 101, 220, 327,
			328, 479, 527, 530)
Triethyltin thiocyanate		160/70 mm.	(10, 102)
Triethyltin urea			(479)
Triisoamyltin sulfate			(282)
Triisobutyltin nitrate			(104)
Triisobutyltin sulfate			(104)
Trimethyltin amide			(459)
Trimethyltin nitride			(95)
Trimethyltin sulfate			(101, 327, 328, 462)
(Triphenylsiloxy)triphenyltin	141–142		(723)
N-Triphenylstannylbenzenesulfonamide			(534)
Triphenyltin cyanide			(918)
Triphenyltin dodecyl trithiocarbonate			(197)
Triphenyltin p-nitrobenzenearsonate	272 (d.)		(860)
Tripropyltin cyanide			(103)
Tris(tributyltin) phosphate			(130)
$(C_4H_9)_2Sn(ON=CHC_3H_7)_2$			(114, 548)

*Three values of the refractive index are given in this column.

organotin trihalide formed is water soluble. Like phenols, these compounds may be precipitated from alkaline solutions by carbon dioxide and they are insoluble, in most cases, in ammonium hydroxide. Lambourne (485, 486) studied the structure of methanestannonic acid and found that it is not correctly represented by the simple formula CH_3SnOOH, but by a more complex cyclic formula containing three atoms of tin in the ring:
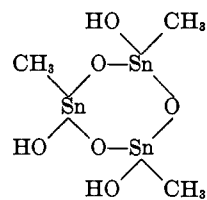
The RSnOOH compounds show no crystal structure by x-ray examination (803).

The thio anhydrides of organothiostannonic acids, $(RSnS)_2S$, commonly referred to as organotin trisulfides, are solids which do not melt but decompose at high temperatures. They are insoluble in most organic solvents and in water; the p-halophenyl derivatives are soluble in pyridine, aniline, and nitrobenzene. In general, these compounds are soluble in ammonium sulfide, alkali, and mineral acids, owing to the formation of water-soluble reaction products. The following structure has been proposed for these compounds:

$$R\!-\!\overset{\overset{S}{\uparrow}}{Sn}\!-\!S\!-\!\overset{\overset{S}{\uparrow}}{Sn}\!-\!R$$
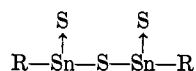
The miscellaneous salts usually are solids which decompose on heating. In general, they are soluble in water and alcohol. In water solution, diethyltin sulfate and many similar salts are largely dissociated into ions (886).

$$(C_2H_5)_2SnSO_4 \xrightarrow{\text{H}_2\text{O}} (C_2H_5)_2Sn^{+2} + SO_4^{-2}$$
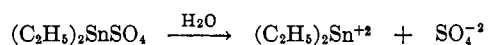
Hjortdahl (327, 328) has studied the crystal structure of several of these compounds.

4. Chemical properties

Some of the chemical properties of these compounds have been discussed previously in connection with the preparation of other organotin derivatives. In general, it may be stated that organotin hydroxides, oxides, sulfides, alkoxides, mercaptides, and carboxylates will react with halogen acids to form the appropriate organotin halide. Most of the bis(triorganotin) oxides are sensitive toward basic hydrolysis, forming organotin hydroxides. The sulfides, alkoxides, mercaptides, and carboxylates can be hydrolyzed by base to form the appropriate organotin oxide, hydroxide, or bisoxide.

In liquid ammonia, trimethyltin hydroxide reacts with sodium to form hexamethylditin (290, 291); hexamethylditin is also formed in the reaction of

$$2(CH_3)_3SnOH + 2Na \rightarrow (CH_3)_3SnSn(CH_3)_3 + 2NaOH$$

trimethylphenoxytin with sodium (458). Vinylmagnesium chloride reacts with dibutyltin oxide and bis(tributyltin) oxide to form dibutyldivinyltin and tributylvinyltin, respectively (728).

$$2CH_2\!=\!CHMgCl + (C_4H_9)_2SnO \rightarrow$$
$$(C_4H_9)_2Sn(CH\!=\!CH_2)_2 + (MgCl)_2O$$
$$2CH_2\!=\!CHMgCl + [(C_4H_9)_3Sn]_2O \rightarrow$$
$$2(C_4H_9)_3SnCH\!=\!CH_2 + (MgCl)_2O$$
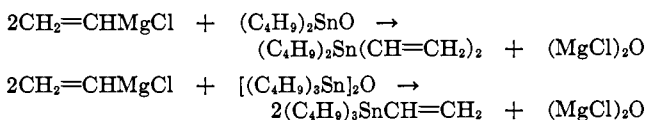
Diethyltin oxide reacts with phosphorus(V) chloride to form diethyltin dichloride and phosphoryl chloride (101).

$$(C_2H_5)_2SnO + PCl_5 \rightarrow (C_2H_5)_2SnCl_2 + POCl_3$$
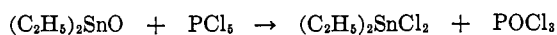
Tin(IV) chloride reacts with bis(triethyltin) oxide to form triethyltin chloride and tin(IV) oxide (10);

silicon tetrabromide reacts similarly. The bis(trialkyltin) oxides reduce iodine in benzene and permanganate in acetone solutions (51). Aryltin oxides react nearly quantitatively with mercury(II) oxide in alkaline alcohol solution to form the corresponding organomercury compound (486, 665).

$$R_2SnO + HgO + 2NaOH \rightarrow$$
$$R_2Hg + Na_2SnO_3 + H_2O$$
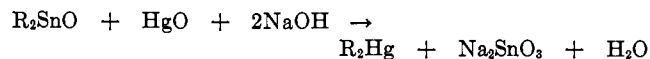
Pope and Peachey (673) reported that methane, trimethyltin hydroxide, and dimethyltin oxide are formed when methanestannonic acid is refluxed with aqueous alkali. Lesbre and Glotz (513) found that the conversion of organostannonic acids to organotin oxides takes place more readily the shorter the alkyl group, and that aromatic stannonic acids do not undergo this reaction. Organostannonic acids react with halogen acids to form organotin trihalides (174, 175, 513, 673, 803); heating with halogen acids may

$$RSnOOH + 3HX \rightarrow RSnX_3 + 2H_2O$$
$$RSnOOH + 4HX \rightarrow RH + SnX_4 + 2H_2O$$
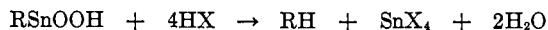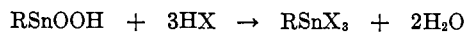
result in the formation of the corresponding hydrocarbon and the tin(IV) halide (665). Glyceryl esters and acid chloride derivatives of organostannonic acids have been reported (803). Attempts to hydrolyze triphenyltin cyanide to the carboxylic acid were unsuccessful (918).

Chambers and Scherer (126) found that the thermal decomposition of triphenyltin hydroxide leads to the formation of tetraphenyltin, diphenyltin oxide, and water; Schmitz-Dumont (753) obtained the same

$$2(C_6H_5)_3SnOH \rightarrow (C_6H_5)_4Sn + (C_6H_5)_2SnO + H_2O$$
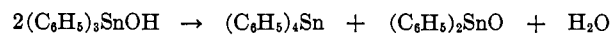
products and proposed bis(triphenyltin) oxide as an intermediate. Similar results were obtained by Krause and Bullard (443) with trimethyltin hydroxide. The thermal decomposition of triethyltin hydroxide, however, follows a different course (293, 295, 297).

$$(C_2H_5)_3SnOH \rightarrow (C_2H_5)_2SnO + C_2H_6$$
$$3(C_2H_5)_2SnO \rightarrow [(C_2H_5)_3Sn]_2O + SnO_2$$
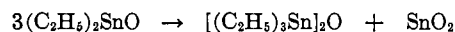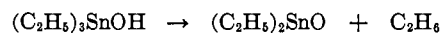
Thermal decomposition of dimethyltin oxide at elevated temperatures leads to the formation of tetramethyltin, ethane, tin(II) oxide, and tin(IV) oxide (443). Under diminished pressure, diethyltin oxide undergoes thermal decomposition with the formation of bis(triethyltin) oxide and tin(IV) oxide (293). Thermal decomposition of bis(trimethyltin) oxide leads to the formation of tetramethyltin and dimethyltin oxide (443). When methanestannonic acid is heated in the absence of air, methane is formed; carbon dioxide, water, and tin(IV) oxide are formed when this compound is heated with ammonium nitrate (173). The thermal decomposition of ethanestannonic acid follows two courses simultaneously (174).

$$C_2H_5SnOOH \begin{cases} C_2H_4 + SnO_2 \\ C_2H_5OH + SnO \end{cases}$$
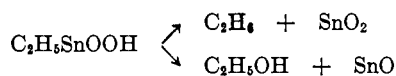
Complex compounds, such as $R_2SnO \cdot R_2SnX_2$, may occur as troublesome by-products in the preparation of organotin compounds; a large number of these compounds (table 21) have been described by Harada (293, 297, 304). Exposure of a trialkyltin–dithizone complex in chloroform to sunlight causes photochemical decomposition to a dialkyltin–dithizone complex (8).

E. ORGANOTIN HYDRIDES

1. General

Among the Group IVA elements the hydrides (table 22) become increasingly unstable as the group is descended. The first successful preparation of an organolead hydride was only recently announced (180). Tin hydride, SnH_4, is a very unstable substance, but progressive substitution of alkyl or aryl groups results in greatly increased stability (167, 211). Because of their instability, the organotin hydrides have received little attention; recent studies of these compounds indicate that they may have some promise as selective reducing agents (12, 478, 635) and for the preparation of organotin compounds containing functional groups (385, 387, 509, 632, 635).

2. Preparation

Two general methods for the preparation of organotin hydrides appear in the literature. The first of these methods was introduced by Kraus and Greer (451) and involves the reaction of an organotinsodium compound with ammonium chloride or bromide in

$$R_3SnNa + NH_4X \xrightarrow{NH_3} R_3SnH + NaX + NH_3$$

$$R_2SnNa_2 + 2NH_4X \xrightarrow{NH_3} R_2SnH_2 + 2NaX + 2NH_3$$
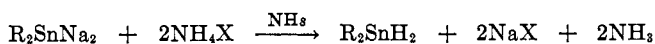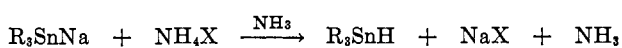
liquid ammonia. This was the sole method employed (96, 126, 451, 896) until a more convenient synthesis was reported in 1947.

This second method, developed by Finholt, Bond, and Schlesinger (210, 211), involves the reduction of organotin halides with lithium aluminum hydride. The method has been widely used in recent years (12, 167, 211, 237, 392, 398, 509, 520, 631, 896); dioxane, ethyl ether, and tetrahydrofuran have been used as solvents. Under comparable conditions, no

$$4R_3SnX + LiAlH_4 \rightarrow 4R_3SnH + LiX + AlX_3$$

$$2R_2SnX_2 + LiAlH_4 \rightarrow 2R_2SnH_2 + LiX + AlX_3$$

$$4RSnX_3 + 3LiAlH_4 \rightarrow 4RSnH_3 + 3LiX + 3AlX_3$$
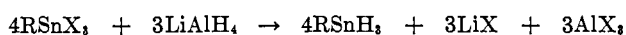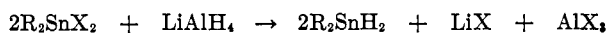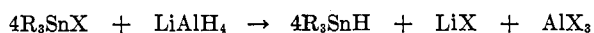
reduction occurs when lithium hydride is substituted for lithium aluminum hydride (211). When 1,1,2,2-tetrabutylditin 1,2-dichloride is treated with lithium

aluminum hydride, reductive cleavage of the tin–tin bond occurs and dibutyltin dihydride is formed (631). Triphenyltin hydride has been prepared by the reaction of triphenyltin bromide with lithium in liquid ammonia followed by treatment with ammonium bromide (896).

In searching for a less expensive reagent than lithium aluminum hydride for the preparation of organotin hydrides, van der Kerk, Noltes, and Luijten found that organotin halides can be reduced in good yields with amalgamated aluminum (393, 631). It is reported that silicon or magnesium in the aluminum–mercury alloy have a deleterious effect and that zinc cannot be used to replace aluminum. Attempts to reduce dipropyltin dichloride by this method were not successful. Triphenylgermanium bromide is readily reduced to triphenylgermane with zinc and hydrochloric acid; an attempted reduction of triphenyltin halides by this method was unsuccessful (887).

Eméleus and Kettle have prepared alkyltin trihydrides by the reaction of alkyl iodides with H_3SnNa

$$2SnH_4 + 2Na \xrightarrow{NH_3} 2H_3SnNa + H_2$$

$$H_3SnNa + RI \rightarrow RSnH_3 + NaI$$
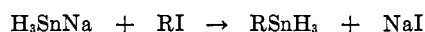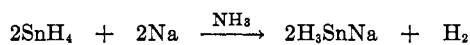
in liquid ammonia (193). Methylene chloride did not react with H_3SnNa.

3. Physical properties

With the exception of diphenyltin dihydride and tribenzyltin hydride, the organotin hydrides are distillable liquids; diphenyltin dihydride is reported to be a solid which decomposes on heating (126, 392) and methyltin trihydride is a gas at room temperature. Organotin hydrides are soluble in the common organic solvents. Molecular-weight determinations indicate that the compounds are monomeric, nonionized substances (12, 96, 126, 451). The application of Egloff's boiling-point equation to organotin hydrides gives good results (195).

Vapor-pressure constants have been reported for the methyltin hydrides (211, 398) and for the ethyltin hydrides (167). The infrared spectra of a number of the alkyltin hydrides have been determined (193, 398, 520, 568). The microwave spectrum of methyltin trihydride between 25,500 and 29,000 mc. has been reported; in this compound the carbon–tin distance is estimated as 2.143 ± 0.002 A. The dipole moment of methyltin trihydride is 0.68 ± 0.03 Debye unit (520); dipole moments of "hydrates" of triethyltin hydride and triphenyltin hydride have been reported (557).

4. Chemical properties

Most organotin hydrides decompose slowly at room temperature, especially in the presence of atmospheric oxygen, and a white-to-gray precipitate usually is formed (12, 167, 211, 237). Stability usually increases

TABLE 21

Some organotin complex compounds

Compound	Melting Point °C.	References
RSnX₃ compounds:		
CH₃SnBr₃·2C₅H₅N	203	(410, 654)
CH₃SnBr₃·2(C₅H₅N·HBr)	165–172 (d.)	(655)
CH₃SnBr₃·2(C₉H₇N·HBr)	145 (d.)	(655)
CH₃SnCl₃·2C₅H₅N		(410, 654)
CH₃SnCl₃·2(C₅H₅N·HCl)	300	(173, 655)
CH₃SnCl₃·2(C₆H₅NH₂·HCl)	214	(173)
CH₃SnCl₃·2(C₆H₅NHCH₃·HCl)	194	(173)
CH₃SnCl₃·2(C₉H₇N·HCl)	200 (d.)	(655)
CH₃SnCl₃·2(p-BrC₆H₄N₂Cl)	147 (d.)	(713)
CH₃SnCl₃·2(o-NO₂C₆H₄N₂Cl)	106 (d.)	(713)
CH₃SnCl₃·2(p-CH₃C₆H₄N₂Cl)	112 (d.)	(713)
CH₃SnCl₃·2(p-CH₃OC₆H₄N₂Cl)	165 (d.)	(713)
CH₃SnCl₃·2(p-C₂H₅OC₆H₄N₂Cl)	108 (d.)	(713)
CH₃SnI₃·4C₅H₅N		(654)
C₂H₅SnCl₃·2(C₆H₅NH₂·HCl)		(174)
iso-C₃H₇SnBr₃·2(C₅H₅N·HBr)		(175)
iso-C₃H₇SnBr₃·2(C₅H₅N·HCl)		(175)
C₆H₅SnCl₃·2C₅H₅N		(410)
o-CH₃C₆H₄SnCl₃·2C₅H₅N		(410)
p-CH₃C₆H₄SnCl₃·2C₅H₅N		(410, 412, 414)
R₂SnX₂ compounds:		
(CH₃)₂SnBr₂·4NH₃		(652)
(CH₃)₂SnBr₂·2C₅H₅N	172 (d.)	(410, 654)
(CH₃)₂SnBr₂·2(C₅H₅N·HBr)	108–112	(655)
(CH₃)₂SnBr₂·2C₉H₇N	80–115	(652)
(CH₃)₂SnBr₂·2(C₉H₇N·HBr)	134	(655)
(CH₃)₂SnCl₂·4NH₃		(652)
(CH₃)₂SnCl₂·2C₅H₅N	163 143	(410, 453, 652, 654, 848)
(CH₃)₂SnCl₂·2(C₅H₅N·HCl)	143–144	(654, 655)
(CH₃)₂SnCl₂·2C₆H₅NH₂		(652)
(CH₃)₂SnCl₂·2C₉H₇N	40–60	(655)
(CH₃)₂SnCl₂·2(C₉H₇N·HCl)	167	(655)
(CH₃)₂SnI₂·4NH₃		(652)
(CH₃)₂SnI₂·2C₅H₅N	151–152	(370, 654, 658)
(CH₃)₂SnI₂·2C₆H₅NH₂	109–110	(370, 652)
(CH₃)₂SnI₂·2CH₃C₅H₄N		(370)
(CH₃)₂SnI₂·2(o-CH₃C₆H₄NH₂)	69–70	(370)
(CH₃)₂SnI₂·2C₆H₄N(C₂H₅)₂	88–90	(370)
(CH₃)₂SnI₂·2(α-CH₃C₉H₆N)	110–111	(370)
(C₂H₅)₂SnBr₂·4NH₃		(652)
(C₂H₅)₂SnBr₂·2C₅H₅N	140	(410, 652, 886)
(C₂H₅)₂SnBr₂·2(C₅H₅N·HBr)	90–99	(655)
(C₂H₅)₂SnBr₂·C₆H₅NH₂		(652)
(C₂H₅)₂SnBr₂·2C₆H₅NH₂		(652)
(C₂H₅)₂SnBr₂·2(C₉H₇N·HBr)	120–124	(655)
(C₂H₅)₂SnCl₂·2NH₃		(886)
(C₂H₅)₂SnCl₂·3NH₃		(652)
(C₂H₅)₂SnCl₂·2C₅H₅N	135	(654, 886)
(C₂H₅)₂SnCl₂·2(C₅H₅N·HCl)	118–122	(655)
(C₂H₅)₂SnCl₂·2C₆H₅NH₂		(652)
(C₂H₅)₂SnCl₂·2(C₆H₅N₂Cl)	80–81 (d.)	(713)
(C₂H₅)₂SnCl₂·2(p-BrC₆H₄N₂Cl)	110 (d.)	(713)
(C₂H₅)₂SnCl₂·2(p-ClC₆H₄N₂Cl)	98–99 (d.)	(713)
(C₂H₅)₂SnCl₂·2(p-CH₃C₆H₄N₂Cl)	88–89 (d.)	(713)
(C₂H₅)₂SnCl₂·2(p-C₂H₅OC₆H₄N₂Cl)	80 (d.)	(713)
(C₂H₅)₂SnCl₂·2(C₉H₇N·HCl)	134–135	(655)
(C₂H₅)₂SnI₂·2NH₃		(886)
(C₂H₅)₂SnI₂·4NH₃		(652)
(C₂H₅)₂SnI₂·2C₅H₅N	117	(370, 654, 886)
(C₃H₇)₂SnBr₂·4NH₃		(652)
(C₃H₇)₂SnBr₂·2C₅H₅N	128	(410, 654)
(C₃H₇)₂SnBr₂·2(C₅H₅N·HBr)	100–114	(655)
(C₃H₇)₂SnBr₂·2C₆H₅NH₂		(652)
(C₃H₇)₂SnCl₂·4NH₃		(652)
(C₃H₇)₂SnCl₂·2C₅H₅N	114	(654)
(C₃H₇)₂SnCl₂·2(C₅H₅N·HCl)	114	(655)
(C₃H₇)₂SnCl₂·2(C₉H₇N·HCl)	77	(655)
(C₃H₇)₂SnI₂·2C₅H₅N	64–65	(370)
(C₃H₇)₂SnI₂·2C₆H₅NH₂		(370)
(C₃H₇)₂SnI₂·2C₅H₅N(C₂H₅)₂	63–64	(370)
(C₃H₇)₂SnI₂·2CH₃C₉H₆N	71–72	(370)

Compound	Melting Point °C.	References
R₂SnX₂ compounds (Continued):		
(iso-C₃H₇)₂SnBr₂·2(C₅H₅N·HBr)	230 (d.)	(175)
(iso-C₃H₇)₂SnCl₂·2(C₅H₅N·HCl)	270 (d.)	(175)
(C₄H₉)₂SnBr₂·2C₅H₅N	77–78	(654)
(C₄H₉)₂SnCl₂·2C₅H₅N	65–66	(654)
(iso-C₄H₉)₂SnI₂·2C₅H₅N(C₂H₅)₂		(370)
(C₆H₅)₂SnBr₂·2C₅H₅N	165	(654)
(C₆H₅)₂SnBr₂·4C₅H₅N	160	(655)
(C₆H₅)₂SnBr₂·2(C₅H₅N·HBr)	195	(655)
(C₆H₅)₂SnBr₂·2(C₉H₇N·HBr)	119–129	(655)
(C₆H₅)₂SnCl₂·2C₅H₅N	151	(654)
(C₆H₅)₂SnCl₂·4C₅H₅N	155–156	(654)
(C₆H₅)₂SnCl₂·2(C₅H₅N·HCl)	186	(655)
(C₆H₅)₂SnCl₂·2(C₉H₇N·HCl)	133–140	(655)
(p-CH₃C₆H₄)₂SnBr₂·2C₅H₅N	172–176	(654)
R₃SnX compounds:		
(CH₃)₃SnBr·NH₃		(460, 461, 462)
(CH₃)₃SnCl·NH₃		(453)
(CH₃)₃SnCl·2NH₃		(453)
(CH₃)₃SnCl·C₅H₅N	37	(453)
(CH₃)₃SnCl·C₆H₅NH₂	84.5	(453)
(CH₃)₃SnI·NH₃		(453)
(CH₃)₃SnI·2NH₃		(102, 453)
(CH₃)₃SnI·2C₅H₅N	60.5	(453)
(CH₃)₃SnI·2C₆H₅NH₂	95.2	(102, 453)
(C₂H₅)₃SnBr·2NH₃		(422)
(C₂H₅)₃SnI·2NH₃		(102, 886)
(C₂H₅)₃SnI·2(iso-C₅H₁₁NH₂)		(102, 886)
(C₂H₅)₃SnI·2C₅H₅N	−17	(453)
(C₂H₅)₃SnI·2C₆H₅NH₂	58	(102, 886)
(C₆H₅)₃SnBr·2C₅H₅N	78–84	(654)
(C₆H₅)₃SnBr·2(C₅H₅N·HBr)	146–153	(655)
(C₆H₅)₃SnCl·2C₅H₅N	81–84	(654)
(C₆H₅)₃SnCl·2(C₅H₅N·HCl)	169–170	(654, 655)
(C₆H₁₁)₃SnCl·2NH₃	128	(468)
R₂SnO·R₂SnX₂ compounds:		
(CH₃)₂SnO·(C₂H₅)₂SnI₂	102–103	(303)
(CH₃)₂SnO·(C₃H₇)₂SnBr₂	68–70	(303)
(C₂H₅)₂SnO·(CH₃)₂SnI₂	100–106	(303)
(C₂H₅)₂SnO·(C₂H₅)₂SnBr₂	170–171	(653)
(C₂H₅)₂SnO·(C₂H₅)₂SnCl₂	175.5	(653)
(C₂H₅)₂SnO·(C₂H₅)₂SnI₂		(824)
(C₂H₅)₂SnO·(C₃H₇)₂SnBr₂	85–87	(303)
(C₃H₇)₂SnO·(C₂H₅)₂SnBr₂	104–105	(303)
(C₃H₇)₂SnO·(C₃H₇)₂SnBr₂	108	(303, 653)
(C₃H₇)₂SnO·(C₃H₇)₂SnCl₂	122	(653)
R₂SnO·R₂SnIOH compounds:		
(CH₃)₂SnO·(CH₃)₂SnIOH		(371)
(C₂H₅)₂SnO·(C₂H₅)₂SnIOH	140–141	(371)
(iso-C₃H₇)₂SnO·(iso-C₃H₇)₂SnIOH	187	(371)
(iso-C₄H₉)₂SnO·(iso-C₄H₉)₂SnIOH	215	(371)
(iso-C₅H₁₁)₂SnO·(iso-C₅H₁₁)₂SnIOH		(371)
R₂SnO·R₂Sn(OCOCH₃)₂ compounds:		
(CH₃)₂SnO·(CH₃)₂Sn(OCOCH₃)₂	231	(293)
(R₂SnO)₂·R₂SnX₂ compounds:		
[(CH₃)₂SnO]₂·(CH₃)₂SnCl₂		(293)
H(R₂SnO)₃OH·R₂SnX₂ compounds:		
H[(CH₃)₂SnO]₃OH·(CH₃)₂SnBr₂		(294)
H[(CH₃)₂SnO]₃OH·(CH₃)₂SnI₂		(294)
H[(C₂H₅)₂SnO]₃OH·(C₂H₅)₂SnBr₂	210 206–218 (d.)	(293, 303, 304)
H[(C₂H₅)₂SnO]₃OH·(C₂H₅)₂SnCl₂	218 215–217 (d.)	(293, 303, 304, 540)
H[(C₂H₅)₂SnO]₃OH·(C₂H₅)₂SnI₂	205–213 (d.)	(293)
H[(C₃H₇)₂SnO]₃OH·(C₃H₇)₂SnI₂	188–205 (d.)	(303)
H[(C₂H₅)₂SnO]₃OH·(CH₃)₂SnI₂	180–198 (d.)	(303)

TABLE 21 (Concluded)

Compound	Melting Point	References			
	°C.				
R'(R2SnO)3OR'·R2SnX2 compounds:			(R3SnOH)2·R3SnX compounds (Continued)		
CH3[(CH3)2SnO]3OCH3·(CH3)2SnBr2....		(294)	[(C2H5)3SnOH]2·(C2H5)3SnCl·H2O......	77	(293)
CH3[(CH3)2SnO]3OCH3·(CH3)2SnI2......		(294)	[(C2H5)3SnOH]2·(C2H5)3SnI·H2O.......	108–110	(293)
C2H5[(CH3)2SnO]3OC2H5·(CH3)2SnBr2...	210–215 (d.)	(293, 294)			
C2H5[(CH3)2SnO]3OC2H5·(CH3)2SnI2....	215–218 (d.)	(293, 294)	Other compounds:		
C2H5[(C2H5)2SnO]3OC2H5·(C2H5)2SnBr2.	137–187 (d.)	(293)	[(C6H5)2Br]2SnCl6....................	178–180	(628)
C2H5[(C2H5)2SnO]3OC2H5·(C2H5)2SnCl2..	135–190 (d.)	(293)	[(C6H5)2Cl]2SnCl6....................	155–156	(628)
C2H5[(C2H5)2SnO]3OC2H5·(C2H5)2SnI2 ..	137–198 (d.)	(293)	[(C6H5)3O]2SnCl6.....................	247–248	(628)
C2H5[(C3H7)2SnO]3OC2H5·(C3H7)2SnI2 ..	122–140 (d.)	(303)	(C6H5)3SnHAl(OC2H5)3...............		(754, 755)
C3H7[(CH3)2SnO]3O(C3H7)·(CH3)2SnI2...	230–235	(294)	(C6H5)2Sn[HAl(OC2H5)3]2............		(754, 755)
C3H7[(C3H7)2SnO]3O(C3H7)·(C3H7)2SnI2.	151–178 (d.)	(303)	C6H5Sn[HAl(OC2H5)3]3...............		(754, 755)
C4H9[(CH3)2SnO]3O(C4H9)·(CH3)2SnI2...	200–209	(294)	(C6H11)3SnHAl(OC2H5)3...............		(754, 755)
C2H5[(CH3)2SnO]3OC2H5·(C2H5)2SnI2...	127–162 (d.)	(303)	(CH3)2Sn[Co(CO)4]2..................		(323)
			(C4H9)2Sn[Co(CO)4]2.................		(323)
(R3Sn)2O·R3SnX compounds:			(C4H9)2Sn[Co(CO)3P(C6H5)3]2.........		(323)
[(CH3)3Sn]2O·(CH3)3SnBr..............	88 (d.)	(298)	(C4H9)3SnCo(CO)4...................		(323)
[(CH3)3Sn]2O·(CH3)3SnI...............	94 (d.)	(298)	[(C6H5)3PCH2Sn(CH3)3][(CH3)3SnBr2]...	About 152 (d.)	(281)
			[(C6H5)3PCH2Sn(CH3)3]-		
R3SnOH·R3SnX·H2O compounds:			[Cr(CH3)2(SCN)4]....................	123–125	(281)
(CH3)3SnOH·(CH3)3SnBr·H2O.........	210–211 (d.)	(455)	[(C6H5)3PCH2Sn(CH3)2CH2P(C6H5)3]-		
(CH3)3SnOH·(CH3)3SnCl·H2O.........	81–95 (d.)	(293, 296, 455)	[(CH3)2SnBr4]......................	About 135 (d.)	(281)
(CH3)3SnOH·(CH3)3SnI·H2O...........	221 (d.)	(455)	[(C6H5)3PCH2Sn(CH3)2CH2P(C6H5)3]-		
			[Cr(NH3)2(SCN)4]2..................	115–119	(281)
(R3SnOH)2·R3SnX compounds:			[(C6H5)3PCH2Sn(CH3)2CH2P(C6H5)3]-		
[(CH3)3SnOH]2·(CH3)3SnBr.............	113–115 (d.)	(444, 455)	[B(C6H5)4]2.......................	78–81	(281)
[(CH3)3SnOH]2·(CH3)3SnCl.............	85–91	(296, 455)	[(C6H5)3PCH2Sn(CH3)2CH2P(C6H5)3]-		
[(CH3)3SnOH]2·(CH3)3SnI..............	143–153 (d.)	(292, 455)	[HgBr2Cl2]2.......................	139–140	(281)
[(C2H5)3SnOH]2·(C2H5)3SnBr·H2O......	103	(293)			

as the number of alkyl or aryl groups is increased (167, 211, 451); however, among the alkyl compounds stability decreases as larger groups are substituted (193). On standing at room temperature in a glass tube, methyltin trihydride is less than 2 per cent decomposed after sixteen days; dimethyltin dihydride showed no appreciable change at the end of three weeks; and trimethyltin hydride did not change within three months (211). Another report states that methyltin trihydride showed no noticeable decomposition on standing in a glass bulb for one month (520). No deposit appeared when triethyltin hydride was allowed to stand for one month, but a small amount of pressure developed (12).

The nature of the decomposition of the organotin hydrides has not been determined. One author states that disproportionation does not occur (211). When triethyltin hydride was refluxed, the odor of hexaethylditin was observed (12). Diphenyltin dihydride decomposes above −33°C. to diphenyltin (126); diphenyltin dihydride has been reported to decompose to tetraphenyltin and metallic tin when heated above 100°C. in vacuo (392). This latter reaction may be explained by assuming decomposition to diphenyltin and subsequent disproportionation of this compound. Triphenyltin hydride reacts with atmospheric oxygen

$$(C_6H_5)_2SnH_2 \rightarrow (C_6H_5)_2Sn + H_2$$

$$2(C_6H_5)_2Sn \rightarrow (C_6H_5)_4Sn + Sn$$
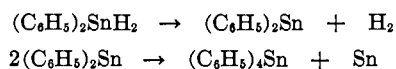
to give hexaphenylditin (126), while ethyldimethyltin hydride (96) and triethyltin hydride (12) are reported

$$4(C_6H_5)_3SnH + O_2 \rightarrow 2(C_6H_5)_3SnSn(C_6H_5)_3 + 2H_2O$$

$$2R_3SnH + O_2 \rightarrow 2R_3SnOH$$
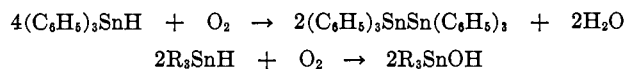
to give the corresponding hydroxides with oxygen. On standing in sunlight, triphenyltin hydride decomposes to tetraphenyltin and metallic tin. When a small amount of benzoyl peroxide is added to triphenyltin hydride in hexane, tetraphenyltin is obtained with no accompanying metallic tin, while with larger amounts of benzoyl peroxide, triphenyltin benzoate is formed with no evidence of tetraphenyltin or metallic tin (237).

Alkyltin hydrides react slowly with water to form white gels (211). Triphenyltin hydride in ethyl ether remains unchanged on addition to water or sodium hydroxide solutions (896); tripropyltin hydride reacts with a dilute aqueous-alcoholic sodium hydroxide solution to form tripropyltin hydroxide and hydrogen (748). Triphenyltin hydride (896) and trimethyltin hydride (451) react with concentrated hydrochloric acid to yield the corresponding tin chlorides; organic

$$R_3SnH + HCl \rightarrow R_3SnCl + H_2$$

acids react in a similar manner (631). Organotin hydrides react vigorously with the halogens, hydrogen being displaced by the more electronegative halogen atom (631).

$$(C_3H_7)_3SnH + Br_2 \rightarrow (C_3H_7)_3SnBr + HBr$$
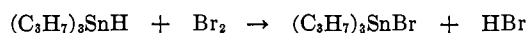
Trimethyltin hydride (451) and triphenyltin hydride (126) were found to react with sodium in liquid

TABLE 22

Organotin hydrides

Compound	Melting Point	Boiling Point*	References
	°C.	°C.	
RSnH₃ compounds:			
Butyltin trihydride		99–101/760 mm.	(392, 631, 634)
Ethyltin trihydride		35/760 mm.	(167, 193)
		25/760 mm.	
Methyltin trihydride		0/760 mm.	(193, 211, 520)
		1.4/760 mm.	
Propyltin trihydride			(193, 631, 634)
Vinyltin trihydride			(82a)
R₂SnH₂ compounds:			
Diamyltin dihydride		58–59/0.45 mm.	(631, 634)
Dibutyltin dihydride		55–59/5 mm.	(392, 476, 568, 631,
		75–76/12 mm.	634)
Diethyltin dihydride		80/760 mm.	(167, 631, 634)
		96–97/760 mm.	
10,11-Dihydrodibenzo[b,f]stanniepin		Not isolated	(477)
Dimethyltin dihydride		35/760 mm.	(195, 211, 398)
		$n_D^{20°} = 1.4480$	
Diphenyltin dihydride		Decomposes above 100 in vacuo	(126, 392, 478, 631, 634)
Dipropyltin dihydride		39–40.5/12 mm.	(392, 568, 631, 634)
R₃SnH compounds:			
Tribenzyltin hydride	52–53		(631, 634)
Tributyltin hydride		76–81/0.7–0.9 mm.	(392, 568, 631, 634)
Triethyltin hydride		69–70/47 mm.	(12, 124, 167, 392,
		79–81/92 mm.	393, 557, 631, 634)
		142/760 mm.	
		$n_D^{20°} = 1.4725; 1.4700$	
Trihexyltin hydride		124–127/0.015 mm.	(631, 634)
Trimethyltin hydride		60/750 mm.	(195, 211, 451)
		59/760 mm.	
Trioctyltin hydride		143/0.0005 mm.	(631, 634)
Triphenyltin hydride	26–28	173–174/6 mm.	(126, 237, 247, 252,
		164–165/0.3 mm.	392, 393, 557, 631,
		151/0.005 mm.	634, 635, 896)
Tripropyltin hydride		80–81/12 mm.	(124, 392, 393, 568, 631)
R₂R'SnH compounds:			
Ethyldimethyltin hydride		90/760 mm.	(96, 195)

* Two values for the refractive index are included in this column.

ammonia to form the corresponding organotinsodium compounds and hydrogen. Triphenyltin hydride was

$$2R_3SnH + 2Na \rightarrow 2R_3SnNa + H_2$$
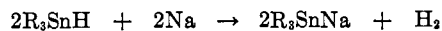
reported to react with methyllithium to give triphenyltinlithium and methane (896); another paper reported methyltriphenyltin and lithium hydride as the products of this reaction (252). Triphenyltin

$$(C_6H_5)_3SnH + CH_3Li \longrightarrow \begin{cases} (C_6H_5)_3SnLi + CH_4 \\ (C_6H_5)_3SnCH_3 + LiH \end{cases}$$
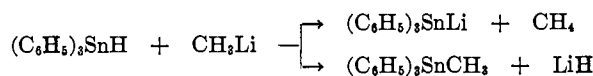
hydride similarly gives tetraphenyltin and lithium hydride when treated with phenyllithium (247).

Recently, two methods which utilize organotin hydrides for the preparation of organotin compounds containing functional groups have been reported. The first of these involves the reaction of diazo compounds with trialkyltin hydrides (509). Compounds in which

$$R_3SnH + N_2CHR' \rightarrow R_3SnCH_2R' + N_2$$
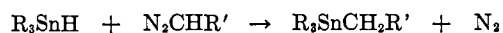
R = —C₃H₇ or —C₄H₉ and R' = —H, —COOC₂H₅, —COCH₃, —COC₆H₅, and —CN have been synthesized by this method.

In the second of the methods mentioned above, trisubstituted organotin hydrides are added to olefinic compounds (385, 387, 391, 631, 635). Compounds

$$R_3SnH + R'CH=CHR'' \rightarrow R_3SnCHR'CH_2R''$$
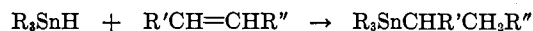
prepared in this manner include those in which R = —C₃H₇, —C₄H₉, or —C₆H₅; R' = —H, —CH₃, or —CN; and R'' = —CN, —(CH₂)₅CH₃, —CH₂OH, —CH₂CN, —CH₂OCH₂CH₂CN, —CH₂NHCOCH₃, —CH₂CH₂COCH₃, —CH₂OCOCH₃, —CH(OC₂H₅)₂, —CH₂COOC₂H₅, —CH₂Sn(C₆H₅)₃, —C₆H₅, —C₅H₄N, —C₁₂H₈N, —C₆H₄NHCOCH₃, —CONH₂, —OC₆H₅, —OCOCH₃, —COOH, —COOCH₃, or —COOC₂H₅. The reaction product usually is not contaminated with undesirable by-products as is often the case with other methods of synthesis of the tin–carbon bond. The functional groups thus introduced will often undergo

reaction with alkali, lithium aluminum hydride, and Grignard reagents without cleavage of carbon–tin bonds (385, 388).

Although triphenylsilane and other similar compounds have been shown to add to olefins via a free-radical mechanism, there is evidence that the reactions of organotin hydrides with olefins are ionic (385, 387, 476, 632). The presence of small amounts of hydroquinone has no detectable influence on the yields of these reactions; neither platinum nor hexachloroplatinic acid has any catalytic effect. With triphenyltin hydride the reaction is more facile than with the aliphatic tin hydrides, but the latter often still react without the assistance of catalysts. Attempts to add tripropyltin hydride to allyl alcohol failed, whereas triphenyltin hydride reacts quantitatively with this compound under very mild conditions (632). It has been reported (223) that triphenyltin hydride does not add to 1-octene but gives a redistribution product, tetraphenyltin; other workers (631, 632, 634) report obtaining the normal addition product from this reaction.

In some cases, reactions other than addition may occur. Triphenyltin hydride reacts with vinyl ketones giving hexaphenylditin and an α,β-unsaturated alcohol (635). Diphenyltin dihydride similarly reduces α,β-

$$2(C_6H_5)_3SnH + CH_2=CHCOR \rightarrow$$
$$(C_6H_5)_3SnSn(C_6H_5)_3 + CH_2=CHCHOHR$$

$$(C_6H_5)_2SnH_2 + CH_2=CHCOR \rightarrow$$
$$(C_6H_5)_2Sn + CH_2=CHCHOHR$$
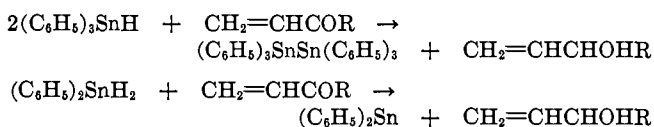
unsaturated aldehydes and ketones to the corresponding unsaturated alcohols (19, 478). This reaction may prove quite useful for such reductions; the yields are usually good, no hydrolysis step is necessary, and a substantial degree of stereoselectivity is reported. Divinyl sulfone, divinyl sulfoxide, and p-nitrostyrene also are reported to undergo reduction rather than addition (635). Compounds in which the keto group is not conjugated with the double bond undergo the usual addition reactions (387, 635).

$$(C_6H_5)_3SnH + CH_2=CHCH_2CH_2COCH_3 \rightarrow$$
$$(C_6H_5)_3SnCH_2CH_2CH_2CH_2COCH_3$$
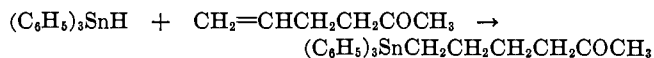
Allyl bromide and triphenyltin hydride react to give triphenyltin bromide and propene; 2-methylpropene in like manner is obtained from methallyl chloride

$$(C_6H_5)_3SnH + CH_2=CHCH_2Br \rightarrow$$
$$CH_2=CHCH_3 + (C_6H_5)_3SnBr$$
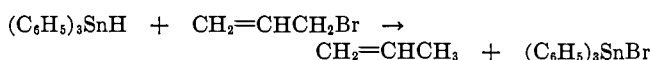
(635). Saturated alkyl halides (386) and bromobenzene (730) also undergo hydrogenolysis with triphenyltin hydride. The reaction of triphenyltin hydride with allylamine yields hexaphenylditin and propene, but with 3-acetamidopropene and triphenyl-

$$2(C_6H_5)_3SnH + CH_2=CHCH_2NH_2 \rightarrow$$
$$(C_6H_5)_3SnSn(C_6H_5)_3 + CH_2=CHCH_3 + NH_3$$

$$(C_6H_5)_3SnH + CH_2=CHCH_2NHCOCH_3 \rightarrow$$
$$(C_6H_5)_3SnCH_2CH_2CH_2NHCOCH_3$$
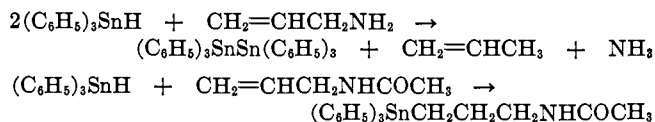
tin hydride, (3-acetamidopropyl)triphenyltin is obtained. Butylamine and hexylamine react with triphenyltin hydride to give hexaphenylditin and the saturated hydrocarbon (635). Allyl mercaptan similarly reacts to give propene and bis(triphenyltin) sulfide; the reaction offers a direct method of converting mercaptans into the corresponding hydro-

$$2(C_6H_5)_3SnH + 2CH_2=CHCH_2SH \rightarrow$$
$$2CH_2=CHCH_3 + [(C_6H_5)_3Sn]_2S + H_2S$$
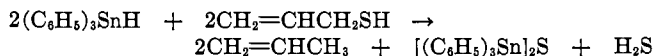
carbons (635). Triphenyltin hydride adds to acrylic acid but the addition compound is not stable, losing benzene to give an interesting polymeric product (632).

$$(C_6H_5)_3SnH + CH_2=CHCOOH \rightarrow$$
$$[(C_6H_5)_3SnCH_2CH_2COOH] \xrightarrow{-C_6H_6}$$
$$[-(C_6H_5)_2SnCH_2CH_2COO-]_n$$
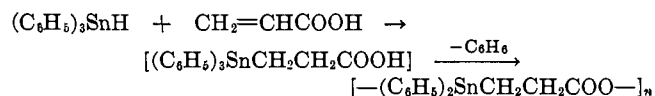
Triphenyltin hydrides also add to diolefinic compounds (387). Products have been obtained where R = $-C_6H_4-$, $-COOCO-$, $-COOCH_2OCO-$, and

$$2(C_6H_5)_3SnH + CH_2=CHRCH=CH_2 \rightarrow$$
$$(C_6H_5)_3SnCH_2CH_2RCH_2CH_2Sn(C_6H_5)_3$$
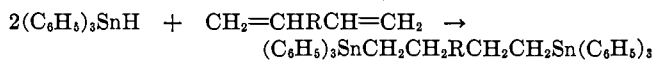
$-CH_2OCH_2-$. Attempts to prepare a mono-addition product were unsuccessful. With acetylenic compounds either mono- or di-addition products can be obtained (387). That the addition to alkynes takes place more

$$R_3SnH + CH\equiv CR' \rightarrow R_3SnCH=CHR'$$
$$R_3SnCH=CHR' + R_3SnH \rightarrow R_3SnCH_2CHR'SnR_3$$
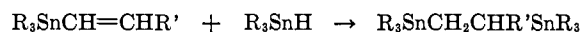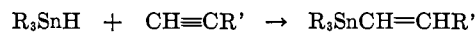
readily than addition to olefins is indicated by the failure of tripropyltin hydride to react with 1-octene but its facile addition to 1-hexyne. Triphenyltin hydride reacts with 2-propyn-1-ol to give a mixture of the cis and trans addition products; however, with phenylacetylene, which has a larger group adjacent to the triple bond, only the trans isomer is obtained (387). The reactivity of organotin hydrides toward carbon–carbon triple bonds offers a general method for the preparation of organotin compounds containing a substituted vinyl group.

Di- and trihydrides may add to olefinic compounds (387, 476), as illustrated by the following examples:

$$(C_4H_9)_2SnH_2 + 2CF_2=CF_2 \rightarrow (C_4H_9)_2Sn(CF_2CF_2H)_2$$

$$(C_3H_7)_2SnH_2 + 2CH_2=CHCOOCH_3 \rightarrow$$
$$(C_3H_7)_2Sn(CH_2CH_2COOCH_3)_2$$

$$C_4H_9SnH_3 + 3CH_2=CHCOOCH_3 \rightarrow$$
$$C_4H_9Sn(CH_2CH_2COOCH_3)_3$$
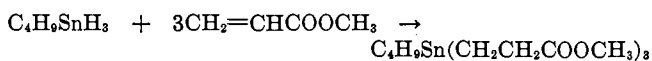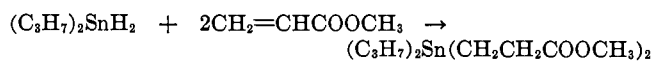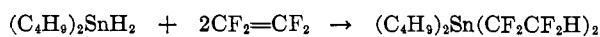
Because of the decreased stability of the di- and trihydrides, the reaction is limited to the more reactive

olefinic substances; the yields of pure adducts are usually lower than in the corresponding mono-addition reactions (387). The reaction of dialkyltin dihydrides with diolefinic or acetylenic compounds may result in polymer formation (386, 632). With diphenyltin

$$(C_3H_7)_2SnH_2 \ + \ CH_2{=}CHC_6H_4CH{=}CH_2 \ \rightarrow$$

$$\left[\begin{array}{c} C_3H_7 \\ / \\ -SnCH_2CH_2C_6H_4CH_2CH_2- \\ \backslash \\ C_3H_7 \end{array} \right]_n$$

$$(C_3H_7)_2SnH_2 \ + \ CH_2{=}CHCOOCH_2CH_2OCOCH{=}CH_2 \ \rightarrow$$
$$[-(C_3H_7)_2SnCH_2CH_2COOCH_2CH_2OCOCH_2CH_2-]_n$$

$$(C_3H_7)_2SnH_2 \ + \ CH{\equiv}CC_6H_5 \ \rightarrow \ \left[\begin{array}{c} C_3H_7 \\ | \\ -SnCH_2CH- \\ | \quad\ | \\ C_3H_7 \ \ C_6H_5 \end{array} \right]_n$$
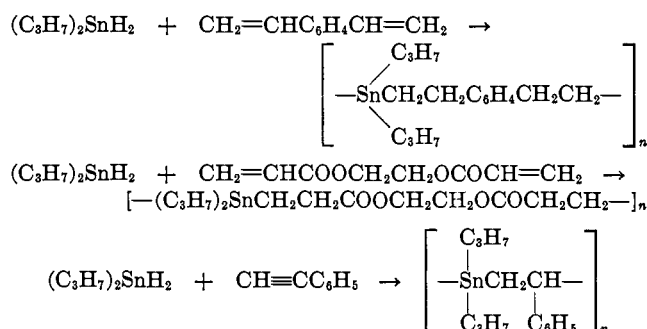
dihydride and phenylacetylene, a dimeric cyclic product, 1,1,2,4,4,5-hexaphenyl-1,4-distannacyclohexane, was obtained instead of the expected polymer (632).

The reaction of triphenyltin hydride or diphenyltin dihydride with vinyl-substituted germanium or silicon compounds leads to products containing two or more Group IVA atoms (632).

$$(C_6H_5)_3SnH \ + \ CH_2{=}CHGe(C_6H_5)_3 \ \rightarrow$$
$$(C_6H_5)_3SnCH_2CH_2Ge(C_6H_5)_3$$

$$(C_6H_5)_2SnH_2 \ + \ (CH_2{=}CH)_2Si(C_6H_5)_2 \ \rightarrow$$

$$\begin{array}{ccc} C_6H_5 & CH_2CH_2 & C_6H_5 \\ \diagdown\;\diagup & & \diagdown\;\diagup \\ Sn & & Si \\ \diagup\;\diagdown & & \diagup\;\diagdown \\ C_6H_5 & CH_2CH_2 & C_6H_5 \end{array}$$
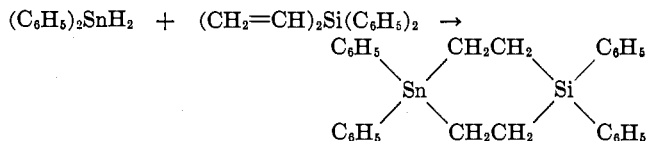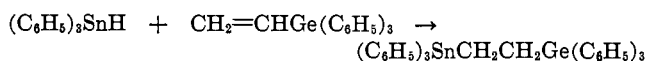
Triethyltin hydride reduces certain halides and oxides of at least thirteen transitional elements and seven regular group elements either to a lower oxidation state or sometimes to the free element (12). Both aluminum chloride and boron trifluoride are readily reduced by tripropyltin hydride (631).

$$6(C_3H_7)_3SnH \ + \ 2AlCl_3 \ \rightarrow \ 6(C_3H_7)_3SnCl \ + \ 2Al \ + \ 3H_2$$
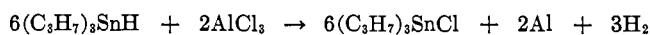
F. ALKALI METAL DERIVATIVES

1. General

The organotin–alkali metal derivatives (table 23) may be formulated as $M^+(R_3Sn)^-$ and $2M^+(R_2Sn)^=$, as indicated by conductivity data. The R_3Sn^- ion would then be analogous to a carbanion and would be a strong nucleophilic reagent. This is the essential chemical nature of these substances, which are useful for the formation of a tin–carbon bond by nucleophilic displacement on carbon. Used in this way, these tin-containing anions can complement the tin-containing cations of the organotin halides. Syntheses which would be very difficult through one type of reagent may sometimes be accomplished easily through the other.

TABLE 23
Alkali metal derivatives

Compound	References
Dibutyltindisodium	(199)
Dimethyltindisodium	(95, 199, 398, 454)
Diphenyltindisodium	(95, 126, 199)
Ethylmethyltindisodium	(94)
Hexamethyltritin-1,3-disodium	(454)
Tetraethylditin-1,2-disodium	(293)
Tetramethylditin-1,2-disodium	(398, 454, 458)
Tributyltinlithium	(251)
Triethyltinlithium	(251)
Triethyltinsodium	(293)
Trimethyltinsodium	(95, 234, 442, 456, 458, 462)
Triphenyltinlithium	(159, 241, 246, 249, 253, 254, 256, 895, 896)
Triphenyltinsodium	(95, 126, 449, 457)
Tri-o-tolyltinlithium	(254)
Tri-m-tolyltinlithium	(254)
Tri-p-tolyltinlithium	(254)

Other compounds containing a tin–metal bond	
$(CH_3)_2SnHNa$	(398)
$(CH_3)_2(NH_2)SnNa$	(398)
$(C_3H_7)_3SnSb(C_7H_7OH)_2$	(808)
$(C_3H_7)_3SnSb[C_6H_3(OH)CH_3]_2$	(808)
$(C_2H_5)_3SnBi(C_6H_5)_2$	(808)
$(iso{-}C_3H_7)_3SnBi(C_6H_5)_2$	(808)
$(C_6H_5)_2BiSn(iso{-}C_3H_7)_2As[C_6H_3(OH)CH_3]_2$	(808)
$(CH_3)_3SnPb(C_6H_5)_3$	(808)
$(CH_3)_3SnTl(C_6H_5)_2$	(808)

2. Preparation

Several methods have been reported for the preparation of these compounds. The method exploited first was the reaction of an organotin halide with sodium in liquid ammonia (94, 95, 126, 199, 234, 454, 462).

$$R_3SnX \ + \ 2Na \ \rightarrow \ R_3SnNa \ + \ NaX$$
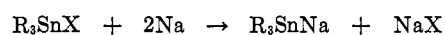
When dimethyltin dibromide is treated with sodium, an intermediate product, $(CH_3)_2Sn(Na)Sn(Na)(CH_3)_2$, is obtained which is converted into dimethyltindisodium by further reaction with sodium (454).

$$2(CH_3)_2SnBr_2 \ + \ 6Na \ \rightarrow$$
$$(CH_3)_2Sn(Na)Sn(Na)(CH_3)_2 \ + \ 4NaBr$$
$$(CH_3)_2Sn(Na)Sn(Na)(CH_3)_2 \ + \ 2Na \ \rightarrow \ 2(CH_3)_2SnNa_2$$
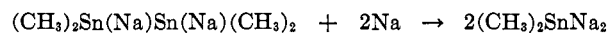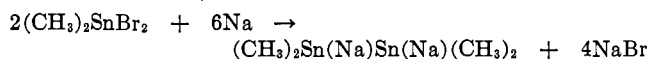
This ditin intermediate may be obtained from dimethyltin and dimethyltindisodium (454). The R_3SnNa and R_2SnNa_2 compounds are also prepared from the corresponding R_3SnSnR_3 and R_2Sn compounds by reaction with sodium in liquid ammonia (293, 449, 454, 456, 462).

$$R_3SnSnR_3 \ + \ 2Na \ \rightarrow \ 2R_3SnNa$$
$$R_2Sn \ + \ 2Na \ \rightarrow \ R_2SnNa_2$$
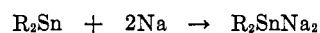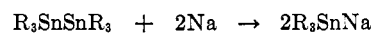
Actually, these reactions are intermediate steps in the preparation of organotinsodium compounds from organotin halides.

$$2R_3SnX + 2Na \rightarrow R_3SnSnR_3 + 2NaX$$
$$R_2SnX_2 + 2Na \rightarrow R_2Sn + 2NaX$$
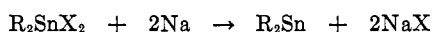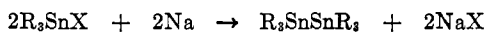
In liquid ammonia R_4Sn compounds react with sodium to form R_3SnNa compounds (52, 126, 293, 462).

$$R_4Sn + 2Na + NH_3 \rightarrow R_3SnNa + RH + NaNH_2$$

With tetraphenyltin, some diphenyltindisodium is formed. It has been shown that triphenyltinsodium reacts with sodium in liquid ammonia to form diphenyltindisodium (126). Organotin ethers and hydrides react with sodium in liquid ammonia to form these derivatives (126, 451, 458).

Conductometric titration of a solution of sodium in liquid ammonia with dimethyltin dihydride shows the formation of $(CH_3)_2SnNa_2$, $(CH_3)_2SnHNa$, and $(CH_3)_2Sn(Na)Sn(Na)(CH_3)_2$; under suitable conditions $(CH_3)_2(NH_2)SnNa$ also is formed (398).

More recently, organotin alkali derivatives have been prepared in solvents other than liquid ammonia. Wittig (895, 896) has prepared triphenyltinlithium from diphenyltin and phenyllithium in ethyl ether.

$$(C_6H_5)_2Sn + C_6H_5Li \rightarrow (C_6H_5)_3SnLi$$

Later it was shown (249) that this derivative can be prepared directly from phenyllithium and tin(II) chloride and that the reaction appears to be general; the organic group may be alkyl or aryl (251, 253, 254).

$$3RLi + SnCl_2 \rightarrow R_3SnLi + 2LiCl$$
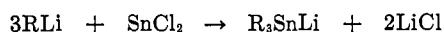
Triphenyltin hydride has been reported to react with methyllithium to give triphenyltinlithium and methane (896); a more recent paper lists methyltriphenyltin and lithium hydride as the products of this reaction (252).

Triphenyltinlithium can be prepared in better than 75 per cent yield by the reaction of triphenyltin chloride with lithium metal in tetrahydrofuran (246). Low

$$(C_6H_5)_3SnCl + 2Li \rightarrow (C_6H_5)_3SnLi + LiCl$$
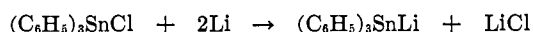
yields of triphenyltinlithium also can be obtained by the cleavage of hexaphenylditin or tetraphenyltin with lithium in tetrahydrofuran (246).

3. Physical properties

Trimethyltinsodium (462) and triphenyltinsodium (126) are pale yellow solids which readily decompose. They dissolve in liquid ammonia with the formation of yellow to deep red solutions. Triphenyltinsodium is slightly soluble in ether. Triphenyltinlithium may be crystallized solvent-free from dioxane to yield brilliant yellow needles (895). It is possible to obtain diphenyltindisodium in the dry state and to redissolve it without apparent decomposition (199).

Conductivity measurements have shown that triphenyltinsodium and trimethyltinsodium are strong electrolytes in liquid ammonia. The dissociation constant of triphenyltinsodium is approximately four times greater than that of sodium bromate (456, 457).

4. Chemical properties

Many of the reactions of the organotinalkali derivatives have been discussed previously in connection with the preparation of various other types of organotin compounds. Surveys have been written concerning some of the reactions of organotinsodium compounds in liquid ammonia (441, 866). The organotinsodium compounds react with organic halides in liquid ammonia to form R_4Sn, R_3SnR', R_2SnR_2' (94, 95, 96, 126, 442), R_3SnSnR_3, $R_2R'SnSnR'R_2$ (449, 460, 462),

$$R_xSnNa_y + yR'X \rightarrow R_xSnR_y' + yNaX$$
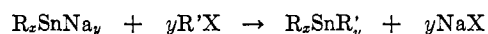
$R_3SnCH_2SnR_3$ (449, 459), $R_3SnC_6H_4SnR_3$ (462), $(R_3Sn)_3CH$ (449), and $R_2R'Sn(SnR_2)_nSnR'R_2$ (454). In a similar manner, these compounds react with organotin halides in liquid ammonia to form R_3SnSnR_3' (442, 450, 462) and $R_3Sn(SnR_2)_nSnR_3$ (454, 458) compounds. Treatment of a solution of an R_3SnNa or R_2SnNa_2 compound in liquid ammonia with ammonium chloride or bromide leads to the formation of the corresponding organotin hydride (96, 126, 451, 896); triphenyltinlithium similarly gives triphenyltin hydride (896).

Oxidation of an R_3SnNa derivative leads to the formation of the corresponding R_3SnONa intermediate, which is readily hydrolyzed to the organotin hydroxide or the bis-oxide (126, 293). Bullard and Robinson (95) reported that trimethyltinsodium reacts with bromobenzene in liquid ammonia, probably according to the following equation:

$$3(CH_3)_3SnNa + 3C_6H_5Br + NH_3 \rightarrow [(CH_3)_3Sn]_3N + 3C_6H_6 + 3NaBr$$
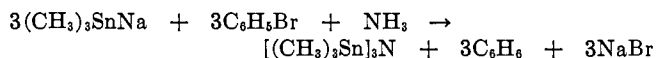
Triphenyltinsodium reacts with phenylmercury iodide to form hexaphenylditin, sodium iodide, mercury, and phenylmercury amine (126). Disubstituted organotindisodium compounds react with dichloromethyl derivatives to give polymeric substances (199, 454).

$$R_2SnNa_2 + R_2'CCl_2 \rightarrow [R_2SnCR_2']_n$$

In an attempt to explain the observation that triphenyltinlithium reacts with bromine to give diphenyltin dibromide, the existence of the equilibrium

$$(C_6H_5)_3SnLi \rightleftarrows (C_6H_5)_2Sn + C_6H_5Li$$
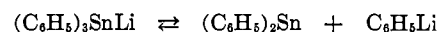
was proposed (159). Triphenyltinlithium reacts with fluorene in ether to give, subsequent to carbonation, a 21.5 per cent yield of 9-fluorenecarboxylic acid; thus, it was suggested that triphenyltinlithium is approximately 20 per cent dissociated. However, it was then

reported (253, 254) that triphenyltinlithium does not react with Dry Ice, gaseous carbon dioxide, benzophenone, benzalacetophenone, or trans-stilbene; from these results it was concluded that triphenyltinlithium is not part of an equilibrium system in ethyl ether. Presumably, the metalation of fluorene must result from the action of triphenyltinlithium and not from the presence of phenyllithium. Triphenyltinlithium does not metalate fluorene in tetrahydrofuran (934).

Triorganotinlithium compounds in ether react with organic halides, with organic sulfates, and with organotin chlorides to form R_4Sn, R_3SnR', and R_3SnSnR_3 compounds (246, 249, 251, 253, 254, 256, 896, 915). Under these conditions triphenyltinlithium does not react with chlorobenzene. In reactions between triphenyltinlithium and o-substituted iodobenzene compounds, a halogen–metal interconversion accompanies the normal nucleophilic coupling reaction (253, 254). The triphenyltinalkali derivatives react with epoxides to give, following hydrolysis, the β-hydroxyalkyl derivatives (234, 254). The reaction of triphenyltin-

$$(C_6H_5)_3SnM + CH_2\!\!-\!\!CHR \xrightarrow{\text{hydrolysis}}$$
$$\diagdown \!\! O \!\! \diagup$$
$$(C_6H_5)_3SnCH_2CHOHR$$
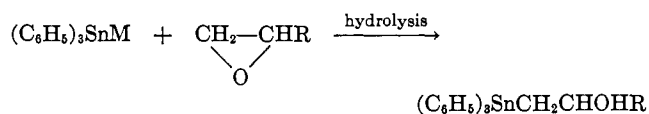
lithium with water gives a mixture of tetraphenyltin and hexaphenylditin (254, 895); triphenyltin hydride has been proposed as an intermediate in this reaction (895). Tetraphenyltin and hexaphenylditin are also formed when ethyl carbonate or ethyl chloroformate is treated with triphenyltinlithium (241).

G. HEXAALKYL- AND HEXAARYLDITIN COMPOUNDS

1. General

Catenation is most important with carbon; although this property becomes decreasingly important as one departs from carbon either within the family or within the period, a number of chain or ring-type compounds have been reported for other elements of Group IVA. Organic derivatives of tin containing from two to five tin–tin bonds per molecule have been reported (table 24). The most widely studied of these derivatives are those conforming to the general formula R_3SnSnR_3, and much of the information reported on the structure of the higher homologs is of a speculative nature.

The hexaarylditins are crystalline solids; the low-molecular-weight hexaalkylditins are liquids and the higher-molecular-weight compounds are solids. The R groups may be the same or different, and mixed alkyl-arylditins are known.

2. Preparation

The most direct method for the preparation of ditin compounds is the reaction of a trisubstituted organotin

halide with sodium in organic solvents or liquid ammonia (48, 87, 284, 293, 299, 442, 462, 466, 468, 474,

$$2R_3SnX + 2Na \rightarrow R_3SnSnR_3 + 2NaX$$
$$2R_2R'SnX + 2Na \rightarrow R_2R'SnSnR'R_2 + 2NaX$$
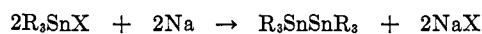
480, 484, 490, 625). Hexamethylditin has been prepared from trimethyltin hydroxide and sodium in liquid ammonia (291).

Several R_3SnSnR_3 compounds have been obtained as by-products in the preparation of other organotin compounds. Hexaethylditin was obtained as one of several products from the reaction of ethyl iodide and a sodium–tin alloy (100), and hexabutylditin was a by-product in the preparation of tetrabutyltin from the reaction of a mixture of dibutyltin dichloride and butyl chloride with sodium (530). Hexaphenylditin was produced in the preparation of tetraphenyltin from phenylmercury chloride and a sodium–tin alloy; hexakis(p-chlorophenyl)ditin was similarly obtained (599). The preparation of tetracyclohexyltin from cyclohexylmagnesium bromide and tin(IV) chloride is accompanied by the formation of hexacyclohexylditin (468). Hexamethylditin, hexaethylditin, and hexaphenylditin were obtained when the corresponding R_3SnNa compounds were treated with carbon tetrachloride in liquid ammonia in efforts to prepare $(R_3Sn)_4C$ compounds (449, 460, 462). Phenylazotriphenylmethane reacts with diphenyltin in benzene or in carbon tetrachloride to form hexaphenylditin (707). Hexaphenylditin is one of the products of the reaction of triphenyltinlithium with 2,6-dimethyliodobenzene (253), and hexa-o-tolylditin is the principal product of the reaction of tri-o-tolyltinlithium with o-iodotoluene (254).

Hexaphenylditin has been prepared from phenylmagnesium bromide and tin(II) chloride at reflux (74, 466). This method is used extensively for the

$$2C_6H_5MgBr + SnCl_2 \rightarrow (C_6H_5)_2Sn + 2MgBrCl$$
$$3(C_6H_5)_2Sn \rightarrow (C_6H_5)_3SnSn(C_6H_5)_3 + Sn$$
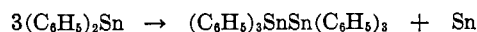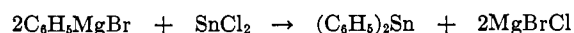
preparation of dilead compounds. Hexa-2-biphenylylditin has been prepared from 2-biphenylylmagnesium bromide and tin(II) chloride as well as by the reaction of tri-2-biphenylyltin bromide with sodium (48); the former method gave a solid melting at 170°C., while the latter method produced a form melting at 288–289°C. Good yields of hexaphenylditin are obtained from the reaction of triphenyltinlithium with triphenyltin halides (249, 253, 896). Triphenyltin bromide, when treated with lithium in liquid ammonia followed by treatment with ammonium bromide, gives a mixture of hexaphenylditin and triphenyltin hydride (896).

The $R_3SnSnR'_3$ and $R_3SnMR'_3$ compounds can be prepared in liquid ammonia by the reaction of R_3SnX

TABLE 24

Hexaalkyl- and hexaarylditin compounds

Compound	Melting Point	Boiling Point	References
	°C.	°C.	
Hexabenzylditin...	147–148		(490)
Hexa-2-biphenylylditin..	170		(48)
	288–289		
Hexabutylditin...			(530)
Hexacyclohexylditin...		Decomposes above 300	(468)
Hexaethylditin...		161–162/23 mm.	(100, 284, 293, 297, 299, 422, 480,
		153–155/17 mm.	483, 484, 625, 732, 856, 888, 917)
Hexaisobutylditin..	43.8	179/3.5 mm.	(284, 856, 888)
Hexaisopropylditin...			(123)
Hexakis(p-chlorophenyl)ditin....................................	224–226		(474, 599)
Hexamethylditin..	23	182/756 mm.	(87, 291, 398, 442, 460, 462, 596,
		85–88/45 mm.	647)
Hexaphenylditin..	237		(74, 249, 253, 254, 466, 599, 631,
	229–231		634, 635, 707, 808, 895, 896)
Hexapropylditin..		143.6/15 mm.	(284, 856, 888)
Hexa-o-tolylditin...	298–300		(254, 595, 723)
	208–210		
Hexa-p-tolylditin...	251–252		(87, 466)
	145		
Hexa-2,5-xylylditin...	196		(466)
1,1,2,2-Tetraethyl-1,2-diisobutylditin		179/15.5 mm.	(284, 856, 888)
1,1,2,2-Tetraethyl-1,2-dipropylditin.............................		165.8/15 mm.	(284, 856, 888)
1,1,1-Triethyl-2,2,2-trimethylditin..............................		235/748 mm.	(442, 462)
1,1,1-Trimethyl-2,2,2-triphenylditin.............................	106		(442, 808, 809)
1,1,1-Trimethyl-2,2,2-tri-p-tolylditin............................	139.5–141		(87)

Polytin compounds

Compound	Melting Point	Boiling Point	References
Decamethyltetratin..			(458)
1,3-Diethyl-1,1,2,2,3,3-hexamethyltritin..........................	Not stable in air		(454)
Dodecamethylpentatin...			(454)
Dodecaphenylpentatin...			(74)

Related compounds

Compound	Melting Point	Boiling Point	References
Bis(dimethylchlorosilyl)diphenyltin...............................			(199)
Trimethyl(triphenylsilyl)tin.....................................			(448)
(Triphenylgermyl)trimethyltin...................................	88		(450)
(Triphenylgermyl)triphenyltin...................................	284–286		(238)
(Triphenylsilyl)triphenyltin.....................................	289–291		(249, 253, 900)

compounds with R'_3SnNa and R'_3MNa intermediates (442, 450, 462). Bis(dimethylchlorosilyl)diphenyltin

$$R_3SnX + R'_3SnNa \rightarrow R_3SnSnR'_3 + NaX$$
$$R_3SnX + R'_3MNa \rightarrow R_3SnMR'_3 + NaX$$
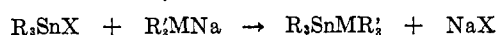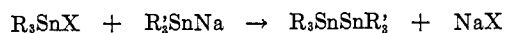
has been prepared by the reaction of dichlorodimethylsilane with diphenyltindisodium (199). In the preparation of trimethyl(triphenylsilyl)tin, triphenylsilyllithium was used (448). (Triphenylsilyl)triphenyltin has been prepared by the reaction of triphenylchlorosilane with triphenyltinlithium (249, 253) and of triphenylsilylpotassium with triphenyltin chloride (900). Similarly, (triphenylgermyl)triphenyltin has been obtained from the reaction of triphenylgermylpotassium and triphenyltin chloride (238). Two attempts to prepare tin–lead compounds have not been successful (90, 900); apparently these compounds are unstable, although (trimethylstannyl)triphenyllead has been reported in the patent literature (808).

Aliphatic amines react with triphenyltin hydride to form the corresponding hydrocarbons and hexaphenylditin (635); this two-step reaction allows the direct replacement of a primary aliphatic amine group by hydrogen. Triphenyltin hydride also reacts with α,β-unsaturated aldehydes and ketones to produce hexaphenylditin and an α,β-unsaturated alcohol (635). These reactions are discussed in Section II,E. Aliphatic tin dihalides react with sodium ethoxide in ethanol (360) or with the more basic amines (361) to form tetraalkylditin dihalides.

3. Physical properties

The lower-molecular-weight compounds of these types are liquids and the higher-molecular-weight derivatives are solids, which, in most cases, have definite melting points. Although their solubilities vary somewhat, these compounds are, in general, soluble in the common organic solvents excepting methyl and ethyl alcohol.

The extent to which the ditin compounds undergo dissociation has been the subject of several conflicting reports. Numerous molecular-weight determinations have been carried out with ditin compounds (74, 284, 442, 448, 450, 462, 466, 468, 732). Some reports indicate that in dilute solutions the compounds are dissociated, while in more concentrated solutions they exist in the completely associated form; other reports indicate no evidence for dissociation. For example, Kraus and Sessions (462) state that cryoscopic measurements indicate that hexamethylditin is almost completely dissociated into the trimethyltin radical in dilute solution. As supporting evidence for dissociation, Bullard (91) prepared 1,1,1-triethyl-2,2,2-trimethylditin by refluxing a mixture of hexamethylditin and hexaethylditin in benzene. The results obtained from studying the magnetic properties indicate that the organoditin compounds are not dissociated. Morris and Selwood (596) report that hexamethylditin is diamagnetic at 40°C. and at 90°C. Similarly, hexa-o-tolylditin (595) is reported to be diamagnetic. Diamagnetism in these compounds would appear to exclude homolytic dissociation into radicals, while heterolytic dissociation into ions R_3Sn^+ and $R_3Sn:^-$ seems excluded by the absence of color (144). A reëxamination of the entire subject is necessary before the existing discrepancies can be resolved.

Bond-refraction data for numerous organotin compounds, including various hexaalkylditins, have been reported (856, 888). A study of the Raman and infrared spectra of hexamethylditin is in progress but has not yet been published (87).

4. Chemical properties

The organoditin compounds are more reactive than their germanium analogs but less reactive than the corresponding dilead compounds. Halogens readily cleave the ditin compounds to the triorganotin halides (74, 100, 238, 448, 450, 462, 466, 468, 474, 480, 490, 599).

$$R_3SnSnR_3 + X_2 \rightarrow 2R_3SnX$$
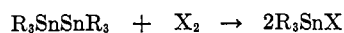
The hexaalkylditins are slowly oxidized in air to the bis-oxides, $(R_3Sn)_2O$, which are converted to the hydroxide, when this is the more stable form, by the moisture in air (87, 293, 442, 462). Similarly, hexa-

$$2R_3SnSnR_3 + O_2 \rightarrow 2(R_3Sn)_2O$$
$$(R_3Sn)_2O + H_2O \rightarrow 2R_3SnOH$$
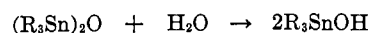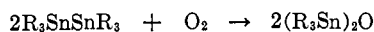
methylditin is cleaved by sulfur with the formation of bis(trimethyltin) sulfide (462). In the presence of air hexamethylditin, in organic solvents, reacts with calcium chloride to form trimethyltin chloride (462). The hexaarylditins and mixed alkyl-arylditins are stable in air (442, 468).

Hexaethylditin and mercury (II) chloride or bromide react to form triethyltin halide and mercury (284, 462, 625). When phenylmercury chloride is used in place of a mercury(II) halide, triethylphenyltin, triethyltin chloride, and mercury are formed (625). Triethylphenyltin and mercury are formed when diphenylmercury reacts with hexaethylditin; other

$$R_3SnSnR_3 + HgCl_2 \rightarrow 2R_3SnCl + Hg$$
$$R_3SnSnR_3 + R'HgCl \rightarrow R_3SnR' + R_3SnCl + Hg$$
$$R_3SnSnR_3 + R_2'Hg \rightarrow 2R_3SnR' + Hg$$
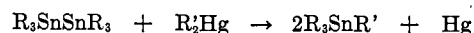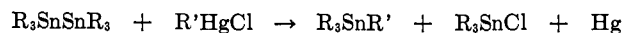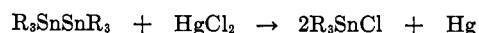
R_2Hg compounds undergo this reaction (625). These reactions may prove useful for preparing mixed alkyl and aryl tin compounds containing groups which cannot be introduced via a Grignard reagent.

Sodium in liquid ammonia cleaves these compounds to the corresponding R_3SnNa compounds (448, 462). The ditin compounds are also readily cleaved by

$$R_3SnSnR_3 + 2Na \rightarrow 2R_3SnNa$$
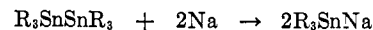
sodium–potassium alloy in ether solutions to produce R_3SnK compounds (87, 238). Low yields of triphenyltinlithium are obtained by the cleavage of hexaphenylditin with lithium in tetrahydrofuran (246).

Ditin compounds are cleaved by a variety of other reagents: methyl and ethyl iodide (284, 483), chloroacetic acid and ethyl chloroacetate (483), alcoholic silver nitrate (293, 466, 474), anhydrous bismuth bromide (284), sodium amide in liquid ammonia (459), organolithium reagents (238, 253), and N-nitrosoacetanilide (707).

III. ORGANOTIN COMPOUNDS OF TWO-COVALENT TIN

A. GENERAL

The first report of an R_2Sn compound was made by Löwig (527), who treated a sodium–tin alloy with ethyl iodide and obtained diethyltin as well as triethyltin iodide and hexaethylditin. A number of R_2Sn compounds have now been reported (table 25). These compounds are usually polymeric substances; in a few cases, monomeric compounds which slowly polymerize on standing have been obtained.

The two-covalent state of the Group IVA elements has been discussed (493), but a review of this topic seems appropriate. This state has been described (493, 720) as arising from the s^2p^2 ^3P ground state of the atom (structure III); the expected bond angle
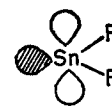
III   IV

would be approximately 90° (for p^2 bonding). Indeed, electron-diffraction measurements on tin(II)

TABLE 25

R₂Sn *compounds*

Compound	Melting Point	References
	°C.	
Bis(methylcyclopentadienyl)tin		(159a)
Di-2-biphenylyltin		(50)
Dibutyltin	Not isolated	(914)
Di-*tert*-butyltin		(475)
Dicyclohexyltin	176–178	(468)
Dicyclopentadienyltin	104–105 (under nitrogen)	(159a, 215, 885)
Diethyltin	Decomposes above 150/760 mm.	(90, 100, 218, 293, 297, 304, 369, 527, 651, 914)
10,11-Dihydrodibenzo[b,f]stannoepin	Indefinite	(477)
Dimethyltin		(398, 454, 651)
Di-1-naphthyltin	200	(466)
Di-9-phenanthryltin	179–180	(49)
Diphenyltin	126–130	(74, 126, 159, 350, 466, 707, 896)
Dipropyltin		(651)
Di-2-thienyltin		(191)
Di-*p*-tolyltin	111.5	(466)
Di-2,5-xylyltin	157	(466)

chloride in the vapor state indicate the molecule to be angular (525). However, structure IV, a molecule having sp^2 hybridization and a vacant p orbital, seems more probable (231, 898). It is particularly to be noted that these molecules exist in a singlet state with their nonbonding electrons paired. Since the central tin atom in either structure III or IV has only six electrons in the valence shell, polymerization to form the stable octet would be expected. The careful measurements of Jensen and Clauson-Kass (350) on diphenyltin are especially illuminating. When freshly prepared, diphenyltin is monomeric; it readily polymerizes to reach the molecular weight of a pentamer or greater, and it is diamagnetic at all stages. The dipole moment is about 1.0 Debye unit at all stages of polymerization. Jensen and Clauson-Kass suggest the presence of a biradical to explain these observations. A more likely interpretation for the polymerization of diphenyltin might be pictured as follows:

$$C_6H_5Sn\colon + \colon SnC_6H_5 \rightarrow C_6H_5\overset{+}{Sn}\text{---}\overset{\cdot\cdot}{Sn}C_6H_5 \rightarrow \text{ higher polymers}$$
$$\underset{C_6H_5}{|} \quad \underset{C_6H_5}{|} \quad \quad \underset{C_6H_5}{|} \quad \underset{C_6H_5}{|}$$

V
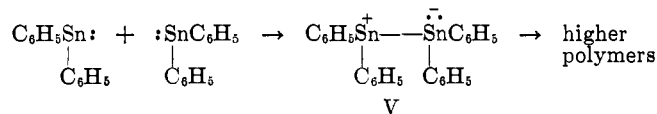
Compounds such as structure V would be expected to be diamagnetic; in this structure the formal charge separation should result in a large dipole moment. Presumably, the first tin atom in structure V possesses a planar configuration, while the configuration around the other tin atom would be pyramidal. Since the two tin atoms would not be configurationally identical, complete hybridization would be prevented; however, some hybridization might occur. The result would

be a lowering of the dipole moment, without complete obliteration, as was observed.

B. PREPARATION

The most used method for preparing R₂Sn compounds is the reaction of a Grignard reagent with tin(II) chloride (49, 466, 468, 651); ethyl ether, an ether–benzene solvent pair, and tetrahydrofuran have been employed as solvents. Diphenyltin prepared in this manner was found to be monomolecular when

$$2RMgX + SnCl_2 \rightarrow R_2Sn + MgX_2 + MgCl_2$$

freshly precipitated; it polymerized slowly on standing. Heating diphenyltin with an excess of the Grignard reagent caused disproportionation to give hexaphenylditin and metallic tin (466). Other R₂Sn compounds do not undergo this disproportionation as

$$3(C_6H_5)_2Sn \rightarrow (C_6H_5)_3SnSn(C_6H_5)_3 + Sn$$
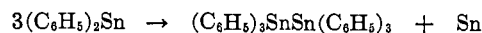
smoothly as diphenyltin; with dicyclohexyltin (468) and di-9-phenanthryltin (49) the reaction apparently does not take place and an excess of the Grignard reagent can be used in their preparation.

There are three references in the literature to the preparation of R₂Sn compounds by the reaction of Grignard reagents with tin(IV) chloride (74, 126, 475); the first two articles refer to the work of Krause (466), and thus it appears that tin(II) chloride actually was used. Organolithium reagents can be used to prepare R₂Sn compounds, but an excess of the

$$2RLi + SnCl_2 \rightarrow R_2Sn \xrightarrow{RLi} R_3SnLi$$
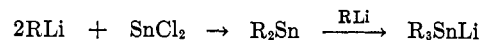
organolithium reagent converts the R₂Sn compound to R₃SnLi (see Section II,F).

The reaction of an organotin dihalide with a reactive metal was first employed by Frankland (218), who obtained diethyltin from diethyltin dichloride and zinc. In a similar reaction, Pfeiffer (651) used sodium

$$(C_2H_5)_2SnCl_2 + Zn \rightarrow (C_2H_5)_2Sn + ZnCl_2$$
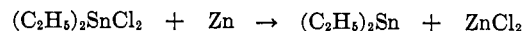
amalgam rather than zinc. More recently, sodium in liquid ammonia has been used for these reduction reactions (126, 293, 454). An excess of sodium may further react with the dialkyltin (293, 454) to give

$$R_2SnX_2 + 2Na \rightarrow R_2Sn + 2NaX$$
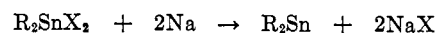
tin–metal compounds (see Section II,F). The procedure has been used for the preparation of both dialkyltins and diaryltins; diphenyltin, when prepared in this manner, was found to be polymerized even when freshly prepared (126).

The reaction of an alkyl halide with a sodium–tin alloy produces the dialkyltin, as well as the trialkyltin halide, tetraalkyltin, and hexaalkylditin (100, 297, 304, 527, 914). The trialkyltin halide is usually

the major product, especially at higher temperatures and if a small amount of zinc is added to the alloy (297, 914). A similar reaction of a sodium–lead alloy with ethyl chloride is of considerable economic importance for the synthesis of tetraethyllead.

Chambers and Scherer (126) have prepared diphenyltin in the monomolecular form by warming diphenyltin dihydride to room temperature. This

$$(C_6H_5)_2SnH_2 \rightarrow (C_6H_5)_2Sn + H_2$$
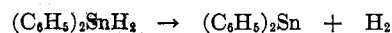
reaction has been used recently to prepare 10,11-dihydrodibenzo[b,f]stannoepin from the corresponding tin dichloride by reduction with lithium aluminum hydride (477).
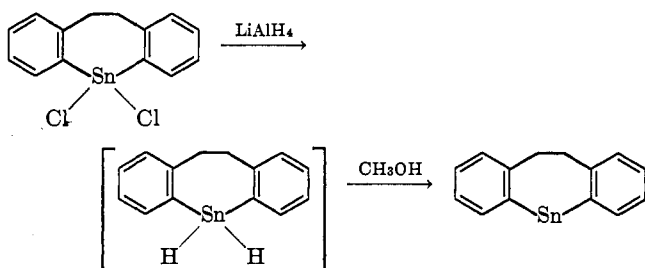
Dimethyltin has been prepared from dimethyltindisodium and dimethyltin dibromide (454). Diethyltin

$$(CH_3)_2SnNa_2 + (CH_3)_2SnBr_2 \rightarrow 2(CH_3)_2Sn + 2NaBr$$
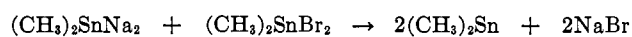
is obtained from the reaction of triethylaluminum with tin(IV) chloride in hexane (369).

C. PHYSICAL PROPERTIES

In general, R_2Sn compounds are yellow solids and form yellow-to-red solutions in organic solvents. In the monomolecular or slightly polymerized state they are soluble in the common organic solvents, except alcohol, and insoluble in water. When polymerized, they are insoluble in organic solvents and in water.

As mentioned above, diphenyltin can be prepared in the monomeric state but it readily polymerizes; it is diamagnetic and has a dipole moment of about 1.0 Debye unit at all stages of polymerization (350). Dicyclopentadienyltin also has a dipole moment of about 1.0 Debye unit (885). The R_2Sn compounds can be obtained in the monomeric state by the reaction of a Grignard reagent with tin(II) chloride or by the decomposition of an R_2SnH_2 compound; other methods apparently give a polymerized product.

R_2Sn compounds usually melt between 100° and 200°C.; the melting point may increase considerably as the compound ages (49, 456). At higher temperatures, usually 200–300°C., the compounds decompose with the deposition of metallic tin; di-9-phenanthryltin possesses unusual thermal stability, with no tin depositing even when heated to 360°C. (49).

Infrared, nuclear magnetic resonance, ultraviolet, and dipole-moment measurements indicate an angular sandwich structure for dicyclopentadienyltin and bis(methylcyclopentadienyl)tin (159a).

D. CHEMICAL PROPERTIES

The R_2Sn compounds are oxidized by air (74, 126, 218, 454, 466, 468, 527, 651). Oxidation proceeds more rapidly when these compounds are in solution and

$$2R_2Sn + O_2 \rightarrow 2R_2SnO$$
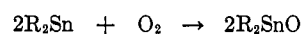
the reaction is accelerated by light. Hydrogen peroxide also has been used for this oxidation reaction (468); diphenyltin ignites when treated with fuming nitric acid (466). Di-m-tolyltin (466), di-2,5-xylyltin (466), and di-9-phenanthryltin (49) are reported to undergo oxidation less readily than diphenyltin; the last two of these compounds, when in the solid state, can be stored without particular precautions. Other R_2Sn solids may be stored in the dark in a nitrogen atmosphere without the occurrence of oxidation (466, 468). A silver nitrate solution is almost immediately reduced to metallic silver by R_2Sn compounds (49, 74, 466, 468, 651).

With halogens the R_2Sn compounds form the corresponding R_2SnX_2 compounds (126, 218, 454, 466, 468, 651). Dicyclohexyltin can be titrated with

$$R_2Sn + X_2 \rightarrow R_2SnX_2$$
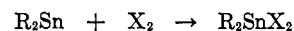
bromine in chloroform (468). Di-9-phenanthryltin does not add bromine, but some of the carbon–tin bonds are cleaved to give an unidentified mixture (49).

Diphenyltin, when refluxed with an excess of phenylmagnesium bromide, deposits metallic tin and forms hexaphenylditin (74, 466).

$$3(C_6H_5)_2Sn \rightarrow Sn + (C_6H_5)_3SnSn(C_6H_5)_3$$
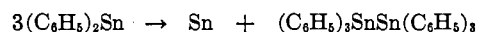
Dicyclohexyltin (468) and di-9-phenanthryltin (49) do not undergo this disproportionation. When diethyltin is heated above 150°C., tin and tetraethyltin are formed (73, 100, 218).

$$2(C_2H_5)_2Sn \rightarrow Sn + (C_2H_5)_4Sn$$
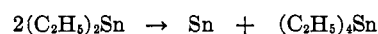
Triethyltin iodide is formed when diethyltin is heated with ethyl iodide (375). Under similar con-

$$(C_2H_5)_2Sn + C_2H_5I \rightarrow (C_2H_5)_3SnI$$

$$(C_6H_{11})_2Sn + 2C_6H_{11}Br \rightarrow (C_6H_{11})_2SnBr_2 + (C_6H_{11})_2$$
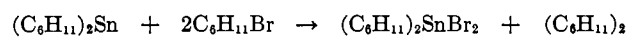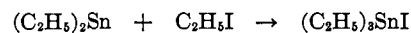
ditions, dicyclohexyltin and cyclohexyl bromide react to give dicyclohexyltin dibromide (468).

The reactions discussed in the previous two paragraphs have been employed to explain the products (tributyltin chloride and tetrabutyltin) obtained from the reaction of butyl chloride with sodium–tin alloy

(914). It is postulated that dibutyltin is first formed; this compound then may react with additional butyl chloride to form tributyltin chloride, or it may undergo disproportionation to yield tetrabutyltin. The products (tetraphenyltin and hexaphenylditin) from the reaction of phenylmercuric chloride with a sodium–tin alloy similarly have been postulated to arise from the disproportionation of initially formed diphenyltin (599).

Diphenyltin, when heated in benzene or carbon tetrachloride with phenylazotriphenylmethane, yields hexaphenylditin; when diphenyltin is heated in carbon tetrachloride with N-nitrosoacetanilide, tetraphenyltin is obtained (707).

Diethyltin reacts with mercury(II) chloride to give diethyltin dichloride and with diphenylmercury to give diethyldiphenyltin (422, 625). This reaction has

$$(C_2H_5)_2Sn + HgCl_2 \rightarrow (C_2H_5)_2SnCl_2 + Hg$$

$$(C_2H_5)_2Sn + (C_6H_5)_2Hg \rightarrow (C_2H_5)_2Sn(C_6H_5)_2 + Hg$$
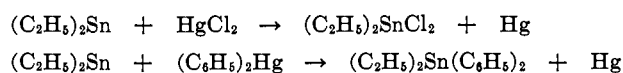
been suggested as a method for preparing mixed tetra-organotin compounds.

Kraus and Greer (454) found that dimethyltin reacts with sodium in liquid ammonia according to the following equations:

$$2(CH_3)_2Sn + 2Na \rightarrow \underset{\underset{Na}{|}\quad\underset{Na}{|}}{(CH_3)_2Sn-Sn(CH_3)_2}$$

$$\underset{\underset{Na}{|}\quad\underset{Na}{|}}{(CH_3)_2Sn-Sn(CH_3)_2} + 2Na \rightarrow 2(CH_3)_2SnNa_2$$
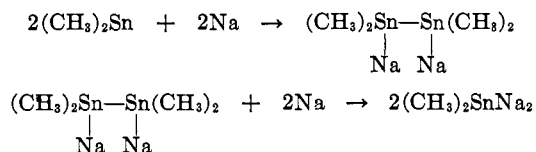
A similar reaction occurs with diethyltin and sodium (293). Incidental to the study of this reaction, it was shown (454) that dimethyltin reacts with dimethyltin-disodium in liquid ammonia according to the equation:

$$(CH_3)_2Sn + (CH_3)_2SnNa_2 \rightarrow \underset{\underset{Na}{|}\quad\underset{Na}{|}}{(CH_3)_2Sn-Sn(CH_3)_2}$$
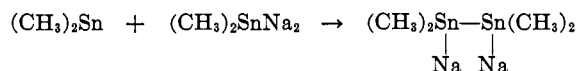
Diphenyltin reacts with phenyllithium to form triphenyltinlithium (896). It has been suggested that the reaction is reversible and that an equilibrium

$$(C_6H_5)_2Sn + C_6H_5Li \rightarrow (C_6H_5)_3SnLi$$

exists in solution (159); however, evidence against such an equilibrium has been presented (254) (see Section II,F).

IV. ANALYSIS OF ORGANOTIN COMPOUNDS

Quantitatively, tin in organotin compounds usually is determined as tin(IV) oxide. Pfeiffer (660) introduced a method which involves decomposition of the sample by the use of fuming nitric acid in a sealed tube, followed by evaporation of the product with concentrated sulfuric acid and ignition to tin(IV) oxide. This basic method has been refined through

the years by a number of researchers (66, 204, 244, 404, 466, 530, 570, 660, 823, 828) to a point where organotin compounds can be completely decomposed simply by treatment with concentrated sulfuric acid in a Vycor crucible on a Rogers ring burner, followed by ignition to tin(IV) oxide (252). Other reports (204, 530) suggest the desirability of a considerable excess of nitric acid, in addition to the concentrated sulfuric acid, especially with organotin compounds containing chlorine or with the more volatile organotin compounds.

Although the sulfuric acid and nitric–sulfuric acid procedures are reported to be suitable for the more volatile compounds, some investigators have resorted to aspiration of the vapor of the compound by means of a current of inert gas into the nitric–sulfuric acid mixture (674) or to passing oxygen through the weighed sample and igniting the vapor on asbestos (86). A preliminary treatment with bromine in carbon tetrachloride to form the less volatile bromides, followed by decomposition by sulfuric acid, also has been recommended (244). Decomposition using hydrogen peroxide and sulfuric acid has been suggested (823), but this procedure does not appear to have received many adoptions.

For routine analysis of a large number of samples, a colorimetric procedure recently has been proposed (204); this method employs combustion in a Parr bomb followed by photometric determination using the reagent dithiol (toluene-3,4-dithiol) (139, 140, 203, 400, 640), which produces a red-to-pink color with tin. It is reported that tin dithiol shows an interesting thermochromic effect (141). A procedure which involves decomposition with a nitric–sulfuric acid mixture, followed by reduction of the inorganic tin and subsequent titration of the tin(II) ion, is preferred by some workers (204, 641, 674). A colorimetric method based on optical density measurements on solutions of a green reduction compound of silico-molybdic acid has been developed for determining small amounts of tin; this method is especially useful for determining organotin compounds in textiles (734a).

Instrumental methods have been described for the determination of small amounts of tin found in certain tin-stabilized polyvinyl chloride compositions and biologically active products. These include a polarographic method (270, 277, 756), a photometric method (154, 640), a turbidimetric method (372), and a method based on radioactivation (118) by introducing a radioactive isotope of tin, Sn^{113}, into an organotin compound.

Several methods have been reported for the quantitative determination of the components of mixtures of trialkyltin and dialkyltin compounds. Colorimetric

methods have been based on the reagents diphenyl-thiocarbazone (dithizone) (9, 58, 127, 344) and sodium dimethyldithiocarbamate (674, 675). The combined researches of Costa (149) and Toropova (852) have shown that polarographic techniques may be used to analyze such mixtures over certain concentration ranges. A procedure for the simultaneous determination of triphenyltin compounds, diphenyltin compounds, and inorganic tin in mixtures has recently been reported (73). Quantitative determination using infrared spectra has been attempted (171).

The microdetermination of carbon and hydrogen in organotin compounds by ordinary combustion tube techniques offers difficulties. Silbert and Kirner (783) obtained satisfactory results when a portion of the copper oxide–lead chromate filling had been replaced by a cylinder of platinum gauze filled with granulated red lead. A semimicro method for the determination of carbon and hydrogen in organotin compounds has been reported by Colaitis and Lesbre (146); silver vanadate was used as a combustion catalyst. Nitrogen in organotin compounds may be determined by the modified Pregl–Dumas method (922). Halogen bonded directly to tin may be determined in dilute alcohol or acetone by precipitation with silver nitrate and weighing of the silver halide (287, 475); a potentiometric titration using 0.1 N silver nitrate solution and a calomel and platinum electrode has also been used (530, 531). Total halogen, including halogen bonded to carbon, may be determined by the Carius method (287). Safford and Stragand (737) have determined total halogen by combustion in a stream of oxygen over a platinum catalyst and absorption of the halogen by silver gauze. Silicon contained in organotin compounds may be determined by gravimetric (641, 723) and volumetric methods (641). The exceptionally low solubility of triphenyltin fluoride has been applied to the gravimetric analysis of the fluoride ion (55, 183).

The most convenient qualitative test for tin in organotin compounds, although not the most definitive, involves the ignition of a small sample on a clean spatula or crucible cover. The gray-white residue of tin(IV) oxide indicates the presence of tin. This test may be ineffective with volatile organotin compounds. Decomposition of a sample with bromine, followed by precipitation of the tin as the sulfide, can be used as an alternative test for the presence of tin. Another qualitative test for tin has been developed; the test involves cleavage of the organotin compound with bromine and subsequent reduction of tin from the tetravalent to the divalent state. A drop of the solution containing the tin(II) ion is placed upon a strip of ammonium phosphomolybdate paper; a blue spot on the test paper indicates a positive test (208, 242, 823).

V. Physiological Properties of Organotin Compounds

A. INTRODUCTION

A few references were made in the older literature to the toxic properties of organotin compounds. The earliest report came from White (890), who found triethyltin acetate, in contrast to inorganic tin salts, highly toxic to dogs, rabbits, and frogs. Collier (147) found organotin compounds to be toxic toward mice in the increasing order: tetraphenyltin, hexaphenylditin, triphenylpropyltin, triphenyltin bromide. In 1929 a patent (338) issued to I. G. Farbenindustrie suggested the use of tetraalkyltin and tetraaryltin compounds as mothproofing agents. This patent was extended to all organic compounds of quadrivalent tin containing one tin atom per molecule (310, 311, 337). A recent patent (636) dealing with sprays against insects other than moths claimed only the use of trialkyltin chlorides. This is indicative of the fact that the triorganotin compounds are very much more toxic than the other groups of organotin substances. In 1943 the use of certain organotin compounds as toxic agents in antifouling paints was patented (182). Complex tin compounds of proteins and nucleoproteins and their hydrolysis products have been stated to be effective against certain skin diseases (899) and blood diseases (734). So far as can be ascertained, no commercial application has been made of organotin compounds in any of these uses.

More recently, two new discoveries about the toxic properties of organotin compounds have led to commercial use of these substances. Kerr and Walde (394, 395) have shown that dibutyltin dilaurate is a very effective remedy for certain intestinal worm infections in chickens. van der Kerk and Luijten (530), in an investigation of the biocidal properties of organotin compounds, have discovered that triorganotin compounds are highly toxic toward a number of fungi.

B. MODE OF ACTION

White (890, 891) in 1881 and Ungar and Bodländer (853) in 1886 first demonstrated the toxic effects of certain organotin compounds on small mammals. In this century, except for a few minor studies (336), work was not resumed until the war-induced search for gases and vesicants brought on the studies of Seifter (759), Gilman (232), Glass (261), and McCombie and Saunders (534). These researches showed a definite relation between the structure of the organotin compound and its toxic action. Low-molecular-weight tetraalkyltin compounds exhibited an immediate reversible paralysis and a delayed encephalopathy. Dialkyltin and trialkyltin compounds showed vesicant action and lachrymatory properties. This action was

most prominent in the methyl- to butyl-substituted substances. None of the compounds investigated had severe enough toxic reactions to warrant their serious consideration as war gases.

When organotin compounds were made available commercially, about 1940–1942, toxicological studies were carried out, but publications did not result until the work sponsored by the Tin Research Institute was reported in 1955. Two groups prominent in this effort were the Medical Research Council Laboratories in England and the University of Toulouse in France. Stoner, Barnes, and Duff (821) examined the biological effects of a series of tetra-, tri-, di-, and mono-alkyltin compounds. They found that di- and triethyltin compounds behaved differently and that only the toxic effects of the former were antagonized by dimercaptol (BAL). In acute experiments the most active compound studied was based on triethyltin. This material produced muscular weakness followed by some recovery, followed in turn by tremors leading to convulsions and death. Muscular weakness was the outstanding sign of chronic poisoning. The main site of action for this compound appeared to be in the central nervous system. Meynier (586) conducted an extensive study of tetraalkyltin compounds via intravenous, intramuscular, oral, and intraperitoneal routes. She observed the general lessening of toxicity as the size of the alkyl group increased. Cajoulle, Lesbre, and Meynier (122) reported greater toxicity for tetraisopropyltin as compared with tetrapropyltin. The same authors (121) indicated the difficulty of obtaining accurate LD_{50} values, owing to delayed deaths. In mice at a dosage of 4 mg./kg., tetrahexyltin gave the following mortalities: 10 per cent, 1 day; 30 per cent, 2 days; 70 per cent, 6 days; 90 per cent, 10 days; 100 per cent, 20 days. Cremer (155, 156) reported that the *in vivo* conversion of tetraethyltin to a triethyltin species accounted for the latent toxicity with symptoms similar to those produced by triethyltin compounds. On injecting tetraalkyltin (labeled with Sn^{113}) into dogs (118, 119), the concentration of tin in the blood fell rapidly and then rose; the heaviest concentrations of tin were found in the central nervous system and in the lungs. Magee, Stoner, and Barnes (554) reported the experimental production of interstitial edemas in the white matter of the brain and spinal cord with triethyltin sulfate. There was no damage to the neurones and the lesions were reversible. In the rat and mouse, poisoning by dibutyltin salts is accompanied by damage to the biliary tract and the liver (60).

Aldridge and Cremer (7) defined toxic mechanisms for diethyltin and triethyltin compounds as follows: (*1*) Diethyltin is an inhibitor of α-keto acid oxidase, similar to phenylarsenious acid; (*2*) triethyltin showed no activity other than interference with oxidative phosphorylation. More recent work by Aldridge (6) and Stoner and Threlfall (822) shows that no real information exists as to what actually happens *in vivo*. Studies of the effect of organotin compounds on the levels of tissue phosphates in rats were inconclusive. A summary of the information available indicates that *in vivo* the only pathology is the generation of interstitial edemas in the white matter of the .brain and spinal cord. *In vitro* studies point to the inhibition of a step in the energy-transferring chain between electron transport and the formation of adenosine triphosphate. These studies further revealed that the action of trialkyltin compounds is at the same site as is the action of 2,4-dinitrophenol. A similarity in action to chloropromazine has likewise been cited.

Barnes and Stoner (61) recently reported on the comparative toxicity of dialkyltin and trialkyltin compounds. Elsea and Paynter (192) recently reported varied toxicity data on bis(tributyltin) oxide. Acute oral LD_{50} figures in rats were 194 mg./kg. in aqueous suspension and 148 mg./kg. in corn oil. An acute dermal LD_{50} was calculated to be 11.7 gm./kg. Thirty-day subacute feeding tests were run at 32, 100, and 320 p.p.m. Growth suppression was noted at all levels. No deaths were noted at 32 and 100 p.p.m. This study pointed to the possibility that this substance is a skin sensitizer. Tests results indicate that bis(tributyltin) oxide is even less toxic than the commercially important compound pentachlorophenol when taken by oral ingestion (201).

Very little work has been reported on the toxicity of triaryltin compounds. Stoner showed the LD_{100} value for triphenyltin compounds to be higher than for tributyltin compounds. Recent work puts the LD_{50} value of triphenyltin acetate at 150 mg./kg. for rats (374).

C. ANTHELMINTICS

Kerr and Walde (394, 395) have shown that dibutyltin dilaurate, dibutyltin maleate, and many other organotin esters of monobasic and dibasic organic acids are very effective agents for the control of helminthic and protozoal infections in poultry. These compounds are preventive and curative agents for coccidiosis caused by *Eimeria tenella* in the cecal area and *Eimeria necatrix* in the small intestines of fowl. Cestodes, tapeworms, nematodes, and roundworms, as exemplified by *Raillientina cesticillus* and *Ascaridia galli*, are controlled by these organotin acid esters. Ethical veterinary formulations containing dibutyltin dilaurate and dibutyltin maleate as active ingredients are commercially available in this country. Other types of organotin compounds also may have anthel-

mintic properties (1, 187, 279, 288, 289, 396, 740, 741, 742, 873a, 875a),

D. FUNGICIDES

The elegant research of van der Kerk and Luijten (378, 379, 381, 530) has shown that trialkyltin compounds of the type R_3SnX (where R may be the same group or different groups and X is halogen, hydroxyl, carboxyl, or oxygen) are active antifungal agents. That this activity is limited to the R_3SnX series is shown in table 26 (530). In addition, van der Kerk and Luijten have shown that variation of X in the series R_3SnX has no great influence on the antifungal activity of the organotin compound and that among tri-n-alkyltin compounds maximum fungitoxicity is associated with a total number of nine to twelve carbon atoms in the alkyl groups, regardless of the nature of the individual groups (see tables 27 and 28) (530). Recently it was reported that triphenyltin acetate not only did not damage beet roots, celery, and potatoes but that it actually appeared to act as a strong growth factor (198).

An unusual phenomenon is encountered in connection with these organotin compounds. A number of metals, especially mercury, copper, cadmium, and zinc, are known to possess fungitoxic properties. These properties are mostly independent of the special chemical form in which the metals concerned are present. The ions are highly toxic and if organometallic compounds exist, these are toxic as well. The behavior of tin in this respect is very exceptional because this metal, which is generally accepted to be nontoxic in its inorganic forms, can be made highly toxic by bringing it into a special type of organic structure. The fact that the antifungal properties of trialkyltin compounds are not very dependent on the nature of the group X leads to the supposition that the toxicity of the compounds is due to the trialkyltin ion or, perhaps, to the undissociated trialkyltin hydroxide formed on hydrolysis in the test media (530). In discussing the investigations of Collier (147), Krause (465) came to a similar conclusion for the

TABLE 26

Influence of the number of alkyl groups directly attached to the tin atom on the antifungal properties of ethyltin compounds

Tin Compound	Botrytis allii*	Penicillium italicum*	Aspergillus niger*	Rhizopus nigricans*
	p.p.m. = mg./l.	p.p.m. = mg./l.	p.p.m. = mg./l.	p.p.m. = mg./l.
$(C_2H_5)_4Sn$.......	50	>1000	100	100
$(C_2H_5)_3SnCl$.....	0.5	2	5	2
$(C_2H_5)_2SnCl_2$....	100	100	500	200
$C_2H_5SnCl_3$.......	>1000	>1000	>1000	>1000
$SnCl_4$..........	>1000	>1000	>1000	>1000
$SnCl_2 \cdot H_2O$......	>1000	>1000	>1000	>1000

* Concentration causing complete inhibition of growth of the fungi.

TABLE 27

Influence of varying the group X on the antifungal properties of compounds with the general formula $(C_2H_5)_3SnX$

Tin Compound	Botrytis allii*	Peni- cillium italicum*	Asper- gillus niger*	Rhizopus nigricans*
	p.p.m. = mg./l.	p.p.m. = mg./l.	p.p.m. = mg./l.	p.p.m. = mg./l.
Triethyltin hydroxide...........	0.2	5	0.5	0.5
Triethyltin chloride.............	0.5	2	5	2
Triethyltin bromide.............	0.5	2	1	1
Triethyltin iodide...............	0.5	1	5	2
Bis(triethyltin) sulfide...........	0.2	1	1	1
Bis(triethyltin) sulfate...........	0.2	0.2	5	5
Triethyltin acetate.............	1	2	5	2
Triethyltin caproate............	1	5	2	2
Triethyltin laurate..............	0.2	0.2	5	5
Triethyltin benzoate............	2	10	5	5
Bis(triethyltin) malonate........	0.5	5	2	1
Bis(triethyltin) maleate.........	0.5	5	0.5	0.5
Triethyltin phenoxide...........	0.5	1	2	1
Triethyltin p-nitrophenoxide.....	0.5	2	2	2
Triethyltin p-toluenesulfonamide.	1	5	2	5
Triethyltin methanesulfonamide..	0.5	5	2	2
p-(Triethylstannylsulfonyl)toluene	1	5	2	2
N-(Triethylstannyl)saccharin.....	1	10	2	2
N-(Triethylstannyl)phthalimide..	0.2	5	1	2

* Concentration causing complete inhibition of growth of the fungi.

organolead compounds. He remarked that the triphenyllead radical behaves as a new metal, which is more toxic than lead in its inorganic compounds.

The discoveries of van der Kerk and Luijten are being applied commercially in the use of organotin compounds as fungistats in paper, textile, and polyvinyl paint manufacture; as wood preservatives; as biostats in hospital maintenance; and especially as fungicides in the field of agriculture (36, 198, 200, 201, 205, 273, 318, 320, 333, 334, 519, 663, 664, 924).

VI. INDUSTRIAL APPLICATIONS OF ORGANOTIN COMPOUNDS

A. INTRODUCTION

By far the greatest industrial use for organotin compounds has been in the stabilization of polyvinyl chloride plastics. Upwards of two million pounds of end products are used annually for this purpose. In addition to their use as stabilizers, organotin compounds are used as rubber antioxidants, as Ziegler-type catalysts in the polymerization of olefins, as agricultural fungicides, and as active ingredients in certain veterinary medicines. This last use is discussed under the physiological properties of organotin compounds.

B. STABILIZATION OF POLYVINYL CHLORIDE

In 1940 a patent issued to Carbide and Carbon Chemicals Corporation, based on work done by Yngve (904), claimed that tetraphenyltin and diphenyldipropyltin functioned as heat stabilizers in the fabrication of polyvinyl chloride plastic materials. This

TABLE 28

Influence of varying the group R on the antifungal properties of compounds $R_3SnOCOCH_3$

Tin Compound	Total Number of Alkyl Carbon Atoms	Botrytis allii*	Penicillium italicum*	Aspergillus niger*	Rhizopus nigricans*
		$p.p.m. = mg./l.$	$p.p.m. = mg./l.$	$p.p.m. = mg./l.$	$p.p.m. = mg./l.$	$p.p.m. = mg./l.$
$(CH_3)_3SnOCOCH_3$..	3	20	20	200	200
$(C_2H_5)_3SnOCOCH_3$..	6	1	2	2	2
$(CH_3)_2(C_4H_9)SnOCOCH_3$..	6	1	2	5	5
$(C_2H_5)_2(C_4H_9)SnOCOCH_3$......................................	8	0.1	1	0.5	0.5
$(C_3H_7)_3SnOCOCH_3$..	9	0.1	0.1	1	1
$(iso-C_3H_7)_3SnOCOCH_3$...	9	0.1	0.1	1	0.5
$(CH_3)_2(C_8H_{17})SnOCOCH_3$......................................	10	0.5	0.5	0.2	2
$(C_2H_5)_2(C_6H_{13})SnOCOCH_3$....................................	10	0.5	0.5	0.1	0.1
$(C_4H_9)_3SnOCOCH_3$..	12	0.1	0.1	0.5	0.5
$(C_2H_5)_2(C_8H_{17})SnOCOCH_3$....................................	12	0.02	0.5	0.1	>5
$(C_5H_{11})_2(C_2H_5)SnOCOCH_3$...................................	12	0.2	1	1	0.5
$(CH_3)_2(C_{12}H_{25})SnOCOCH_3$...................................	14	0.2	1	0.2	10
$(C_5H_{11})_3SnOCOCH_3$...	15	0.2	5	5	10
$C_2H_5)_2(C_{12}H_{25})SnOCOCH_3$..................................	16	0.2	5	0.5	50
$(C_6H_{13})_3SnOCOCH_3$...	18	1	10	20	100
$(C_8H_{17})_3SnOCOCH_3$...	24	>100	>100	>100	>100
$(Cyclo-C_6H_{11})_3SnOCOCH_3$.....................................	18	0.5	0.5	5	20
$(C_6H_5)_3SnOCOCH_3$...	18	2	1	0.5	10
C_6H_5HgBr..		0.1	0.1	0.1	2
$C_6H_5HgOCOCH_3$..		0.5	0.5	0.5	5

* Concentration causing complete inhibition of growth of the fungi.

patent was extended further in the next few years by Yngve (905, 906) and Quattlebaum (681, 733) to show that many other organotin compounds, e.g., dibutyltin oxide, dibutyltin dilaurate, dibutyltin maleate, and dibutyltin diacetate, function as excellent heat and weathering stabilizers for polyvinyl chloride plastics. It was shown that, of the many possible types of organotin compounds that could be used, the best stabilizers resulted from the $(C_4H_9)_2SnX_2$ structure (or $(C_4H_9)_2SnX$, where X is difunctional). This early work has been followed by many other patents suggesting various X groups, e.g., esters (263, 266, 267, 425, 426, 532, 552, 576, 680, 690, 731, 735, 774, 791, 792, 798, 801, 876, 886, 894), mercapto esters (316, 496, 798, 877), mercaptides (28, 69, 113, 213, 214, 353, 497, 498, 500, 501, 503, 504, 505, 506, 507, 582, 814, 815, 816, 817, 819, 863, 871, 874, 878, 880), sulfides (799, 881), acetals (132, 133, 352), phosphates (136), polyols (540, 544, 550, 870), oxides (3, 134, 164, 274, 551, 629, 630, 703, 869, 872), mercapto alcohols (686, 689), sulfonamides (542, 750), xanthates (29, 33, 499), and isodithiocarbamates (580); various R_4Sn (5, 209, 494, 547) and R_3SnX (536) compounds also have been suggested as stabilizers for polyvinyl chloride. Dibutyltin compounds which contain a tin–sulfur bond are the most powerful stabilizers known at present (538).

Despite the extensive work done on the mechanism of the degradation of polyvinyl chloride, very little has been reported on its stabilization. In the case of the metallic stabilizers, there seems to be some evidence that they function by preventing color formation rather than by inhibiting the formation of hydro-

gen chloride (179, 217). The precise explanation for this action is still clouded, but recent research indicates that these stabilizers may act as oxidation catalysts and disrupt the chromophoric polyene groups. Not only the type of metal used in the stabilizer but also the manner in which the metal is combined in the stabilizer can have an important effect on the properties which the stabilizer will impart to the vinyl compound. In order for a good stabilizer against heat and light to function properly, it should have certain of the following characteristics:

(1) It should prevent the split-off of hydrogen chloride or be an acceptor for hydrogen chloride.
(2) It should function as an antioxidant.
(3) It should react with double bonds, i.e., be a reactive dienophilic molecule.
(4) It should act as a screener of ultraviolet light.

Organotin stabilizers most closely approach the requirements of an ideal stabilizer. All classes of organotin stabilizers give outstanding clarity to flexible and rigid vinyl compounds (537). They also have excellent light stability, they are known to function as antioxidants (see below), and they have been shown to be the only group of stabilizers that can block the formation of carbonyl groups (217). There is also a possibility that organotin stabilizers may function as dienophiles.

A mechanism through which organotin stabilizers may function has been suggested by Kenyon (373). It is postulated that a butyl group from a dibutyltin diacetate stabilizer acts as a chain repairer by adding to the polymer. Presumably, the butyl group could

add on to the unsaturated portion formed during the extraction of hydrogen chloride, thus blocking further action such as cross-linking and oxidation at that particular point in the polymer chain. A similar free-radical mechanism has been proposed by Winkler (893). However, such a free-radical mechanism does not appear to be the complete answer since, in some cases, the stabilizer contains active groups which can disrupt a radical-chain process (538). Kenyon (373) further suggested that the organotin stabilizer acts as a scavenger for hydrogen chloride.

C. ANTIOXIDANTS FOR RUBBER

In 1949 a patent issued to the United States Rubber Company, based on work done by Hart (308), claimed that unsymmetrical tribenzyltin compounds of the type $(C_6H_5CH_2)_3SnR$ (R = ethyl or another alkyl group) were useful as anticracking agents in rubber. Recently this work was greatly extended by Weinberg, Tomka, and Ramsden (575, 577, 580, 688, 704, 851, 882, 883, 884) of the Metal & Thermit Corporation. Such organotin compounds as mercapto acid esters, sulfides, mercaptides, esters, oxides, alcoholates, and chlorides of the types R_2SnX_2 and R_2SnX were claimed as rubber antioxidants. Note that these compounds are very similar to, or identical with, the organotin compounds used as polyvinyl chloride stabilizers. This fact strongly suggests that the mode of stabilization is the same in each application.

D. ZIEGLER-TYPE CATALYSTS

The recent discovery by Ziegler and Natta that organoaluminum compounds, coupled with titanium halides, form excellent catalysts for the low-pressure polymerization of olefins has prompted exploration of the potential use of other organometallic compounds in similar catalyst systems. Such companies as Phillips Petroleum (662), Montecatini (589), Goodrich-Gulf (276), Solvay & Cie (804), and Union Carbide & Carbon Corporation (67, 854) have been issued patents covering the use of organotin compounds as catalysts for the polymerization of olefins. A combination of titanium(IV) chloride (0.6g.), tetrabutyltin (2.6 g.), and aluminum chloride (1.0 g.) is an example of one of these catalyst combinations (804).

E. MISCELLANEOUS APPLICATIONS

Organotin halides have been suggested in the treatment of glass to form an electrically conductive film on the surface (533). Several patents (521, 535, 688) have been issued on the use of organotin compounds as additives for lubricating oils. Such compounds as tetrapropyltin (809), tetrabenzyltin (521), tetraphenyltin (401), diphenyltin (521), dibutyltin sulfide (22), dibutyltin dithiophosphorate (535), dibutyltin

dithioxanthate (197, 535), dibutyltin dithiocarbamates (535), and dibutyltin mercaptides (878) have been suggested as beneficial additives. Several dibutyltin compounds have been claimed as catalysts in the formation of polyesters (108) and silicone elastomers (18), as craze-prevention agents in polystyrene plastics (137, 138), and as corrosion inhibitors in organosilicon polymers (729). Tetraphenyltin is used as a scavenger in chlorinated dielectric fluids (317, 326, 684) and dibutyltin salts are used as stabilizers for chlorinated rubber paints (924).

Recently, a variety of organotin compounds have been shown to possess outstanding catalytic activity in the reaction of isocyanates with several types of compounds containing active hydrogen (109, 151). For example, the relative activity of dibutyltin dilaurate is about 37,000 as compared with an activity of 11 for the widely used triethylamine in the reaction between phenyl isocyanate and methanol at 30°C. (20). Thus it appears that organotin compounds may find extensive application in the preparation of polyurethans.

Today, widespread research is under way to investigate the possibility of obtaining useful organotin polymers (18, 42, 152, 199, 427a, 591, 592, 632); it is quite possible that a new, large-scale application for organotin compounds may develop in this area. Recently, a polymer derived from tributyltin methacrylate was announced (18, 592); the preparation of polyorganotinsiloxanes also has been reported (15, 152). Dialkyltin dihydrides and phenylacetylene, p-divinylbenzene, or other dienic compounds can react to give organotin polymers (375, 386, 632) and R_2SnNa_2 compounds react with $R_2'CCl_2$ compounds to give polymeric substances (199).

The development of a successful crop fungicide containing 20 per cent triphenyltin acetate has been reported by Farbwerke Hoechst (309). The product, which is marketed under the name Brestan, has proven to be very effective in the control of leaf-spot in celery (*Septoria apii*) and sugar beets (*Cercospora beticola*) and of potato blight (*Phytophthora infestans*). Several other researchers have reported in this area (63, 166, 751, 758). Trialkytin-based compounds have been suggested as preservatives for manila and sisal ropes (84), as fungistats for paints (36), as fungicides in paper production and preservation (148, 813), as agents for rendering fabrics resistant to mildew and the development of bacterial odors (813), as preservatives for timber (83, 201, 329, 330), and as insecticides (71).

generous assistance. In addition, the partial surveys of Arntzen (37), Gist (259), Krause and von Grosse (467), Luijten and van der Kerk (530), and Rosenberg (723) have been especially helpful in the preparation of this review.

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