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Dealkylation of Di-*n*-amyldimethyltin, Di-*n*-butyldimethyltin, and Tetraethyltin with Perfluoroacids, Inorganic Halides, and Carboxylates

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Certain inorganic halides such as SnX_2, CuX_2, HgX_2, and PdX_2 remove one ethyl group from tetraethyltin to give the triethyltin halide in approximately 60% yield; however, silver chloride and silver trifluoroacetate convert tetraethyltin into diethyltin dichloride and diethyltin bis-(trifluoroacetate), respectively. Tetraethyltin and stannous halides or acetates furnish triethyltin derivatives without contamination by detectable amounts of diethyltin dihalides or diacetates. Reactions of individual perfluoroacids with di-*n*-amyldimethyltin or di-*n*-butyldimethyltin furnish mixtures of trialkyltin derivatives which often are difficult to separate.

Previous investigations demonstrate some typical dealkylations of tetraethyltin as follows: with iodine or hydrogen chloride[1] or with ferric chloride in chloroform[2] to obtain the corresponding triethyltin halide; with mercuric chloride in ethanol or with bismuth trichloride in chloroform to obtain a mixture of triethyltin chloride and diethyltin dichloride[2]; with phosphorus tribromide to obtain triethyltin bromide and ethyldibromophosphine[3]; also, with trifluoroacetic acid to form triethyltin trifluoroacetate.[4]

Earlier publications also show typical dealkylations of mixed alkyltin compounds. Iodine and *n*-amyltrimethyltin react in ether to produce a 93% yield of *n*-amyldimethyltin iodide.[5] Iodine and di-*n*-butyldimethyltin in refluxing benzene give mainly di-*n*-butylmethyltin iodide, but also some *n*-butyldimethyltin iodide.[6] However, dimethyldi-*n*-octyltin and bromine in carbon tetrachloride at 0° react to furnish an 86% yield of dimethyl-*n*-octyltin bromide.[7] The relative decreasing order of ease of cleavage of different organic groups from tin[8] predicts the loss of one methyl group instead of one *n*-octyl group in the last reaction; thus the predicted product is methyldi-*n*-octyltin bromide.

Triethyltin hydride[9] reacts approximately 70 times as fast, on the average, as tetraethyltin does with silver bromide, mercuric chloride, stannous chloride, or palladium(II) chloride. In turn, tetraethyltin reacts approximately 2 to 4 times as fast, on the average, as di-*n*-butyldimethyltin or di-*n*-amyldimethyltin does with the same reagent. This relative order of reactivity is consistent with a shielding effect; the comparatively small hydride hydrogen offers a minimum of shielding. Moreover, the reactions of triethyltin hydride do not furnish complicated mixtures of products. In the partial dealkylation of di-*n*-butyldimethyltin with perfluoroacids (Table II of the present publication) the lower the molecular weight of the perfluoroacid, the more satisfactory the reaction is.

When the appropriate organotin halide is available, the best method[10,11] for preparing the corresponding organotin carboxylate should involve the reaction of the organotin halide $R_2R'SnBr$ or $R_2R'SnI$ and the silver salt of the carboxylic acid. A two-step procedure converts $R_2R'SnBr$ into the corresponding organotin oxide and then gives a high yield of $R_2R'SnOCOCH_3$ from this oxide[7] and glacial acetic acid; however, there is some risk of dealkylation in the latter step. Both of these methods have some advantages over the direct, partial dealkylation of $R_3R'Sn$ or $R_2R'_2Sn$ with a carboxylic acid.

The optimum partial and selective dealkylation of substituted tetraalkyltins, $R_2R'Sn$ or $R_3R'Sn$, apparently involves the following: very slow, gradual addition of a deficiency of bromine, iodine, or perfluoroacid with constant stirring;

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TABLE I

REACTIONS OF TETRAETHYLTIN, 3.5 G./RUN, WITH INORGANIC HALIDES AND CARBOXYLATES

Halide			Reaction products				
Compound	Wt., g.	Reflux, hr.	Chief product	B.p.	Wt., g.	Yield, %	Other products
$SnCl_2$	1.22	4	$(C_2H_5)_3SnCl$[a]	207	2.77	78	Sn
$SnBr_2$	1.94	2	$(C_2H_5)_3SnBr$[a]	222	3.04	71	Sn
SnI_2	2.52	1	$(C_2H_5)_3SnI$[a]	229	3.26	66	Sn[b]
$Sn(OCOCH_3)_2$	1.76	1	$(C_2H_5)_3SnOCOCH_3$	. . .[c]	2.10	53	Sn
$Sn(OCOCF_3)_2$	2.22	0.3	$(C_2H_5)_3SnOCOCF_3$[d]	215	2.64	56	Sn
$CuBr_2$[e]	3.50	0.1	$(C_2H_5)_3SnBr$	223	1.95	46	CuBr, C_2H_5Br[f]
AgCl	17.5	3.3	$(C_2H_5)_2SnCl_2$[g]	223	1.6	45	Ag, $(C_2H_5)_3SnCl$[h]
AgBr	16.1	2.5	$(C_2H_5)_3SnBr$	223	3.0	70	Ag, C_2H_5Br[f]
$AgOCOCF_3$	8.52	0.3	$(C_2H_5)_2Sn(OCOCF_3)_2$[i]	213	3.1	52	Ag
$KAuCl_4$	2.10	0.1	$(C_2H_5)_3SnCl$	210	1.8	50	KCl, Au, $(C_2H_5)_2SnCl_2$[h]
$HgCl_2$	1.56	16	$(C_2H_5)_3SnCl$	209	2.8	78	Hg
$HgBr_2$	2.10	19	$(C_2H_5)_3SnBr$	222	3.1	73	Hg
HgI_2	2.65	23	$(C_2H_5)_3SnI$	231	3.38	68	Hg
$TiCl_4$	2.07	0.1	$(C_2H_5)_3SnCl$	210	1.5	42	$TiCl_2$
$VOCl_3$	1.65	0.1	$(C_2H_5)_3SnCl$	210	1.92	54	$VOCl_2$
$TaCl_5$	2.06	0.1	$(C_2H_5)_3SnCl$	210	2.14	60	$TaCl_3$
$PdCl_2$	1.00	2	$(C_2H_5)_3SnCl$	210	2.55	71	Pd
PdI_2	3.30	0.5	$(C_2H_5)_3SnI$	230	2.04	41	Pd, C_2H_5I[j]

[a] No diethyltin dichloride, dibromide, or diiodide apparently formed. [b] Some inflammable gas, probably mainly butane, formed during reaction. [c] Double crystallization from carbon tetrachloride gave solid of m.p. 132–133° containing 22.2% acetate. [d] Double crystallization from carbon tetrachloride gave solid of m.p. 120–121°. [e] Gradual addition of this reagent. [f] Accounts for 10% of the bromine available in the starting bromide. [g] Double crystallization from carbon tetrachloride gave solid melting at 82°. [h] Present in small amount. [i] New compound described in Table III; after double crystallization from carbon tetrachloride the solid melted at 153°. [j] Weight, 194 g.; b.p., 72°. Accounts for 60% of iodine in starting iodide. Approximately 0.3 g. of butane gas also formed.

TABLE II

PREPARATIONS OF NEW COMPOUNDS WITH TWO DIFFERENT ALKYL GROUPS

Starting materials				Organotin reaction products[a]		
Compound	Wt., g.	Compound	Wt., g.	Compound	Wt., g.	Yield, %
$(CH_3)_2SnCl_2$	220	$n\text{-}C_5H_{11}MgCl$[b]	195	$(n\text{-}C_5H_{11})_2(CH_3)_2Sn$	272	95
$(n\text{-}C_5H_{11})_2(CH_3)_2Sn$	27	CF_3COOH[c]	8.6	$(n\text{-}C_5H_{11})_2(CH_3)SnOCOCF_3$[d]	7.2	39
$(n\text{-}C_5H_{11})_2(CH_3)_2Sn$	27.5	C_2F_5COOH[c]	13.5	$(n\text{-}C_5H_{11})_2(CH_3)SnOCOC_2F_5$	14	34
				$n\text{-}C_5H_{11}(CH_3)_2SnOCOC_2F_5$[e]	11	30
				$(n\text{-}C_5H_{11})_3SnOCOC_2F_5$[f]	4	9
$(n\text{-}C_5H_{11})_2(CH_3)_2Sn$	30	I_2[g]	24	$(n\text{-}C_5H_{11})_2(CH_3)SnI$	23	56
				$n\text{-}C_5H_{11}(CH_3)_2SnI$[h]	12.5	30
$(n\text{-}C_5H_{11})_2(CH_3)SnI$	9.2	NaOH[i]	2.9	$[(n\text{-}C_5H_{11})_2(CH_3)Sn]_2O$	5.6	85
$n\text{-}C_5H_{11}(CH_3)_2SnI$	12.5	NaOH[j]	3.9	$[n\text{-}C_5H_{11}(CH_3)_2Sn]_2O$	6.1	86
$(n\text{-}C_4H_9)_2(CH_3)_2Sn$	15.6	CF_3COOH[c]	7.3	$n\text{-}C_4H_9(CH_3)_2SnOCOCF_3$[k]	13.4	70
$(n\text{-}C_4H_9)_2(CH_3)_2Sn$	15.6	C_2F_5COOH[c]	9.7	$n\text{-}C_4H_9(CH_3)_2SnOCOC_2F_5$[k]	11.1	50
$(n\text{-}C_4H_9)_2(CH_3)_2Sn$	29	$n\text{-}C_3F_7COOH$[c]	27	$n\text{-}C_4H_9(CH_3)_2SnOCO\text{-}n\text{-}C_3F_7$[k]	14	30
$(n\text{-}C_4H_9)_2(CH_3)_2Sn$	42	Br_2[l]	20	$(n\text{-}C_4H_9)_2(CH_3)SnBr$	37	70
$(n\text{-}C_4H_9)_2(CH_3)SnBr$	10.8	NaOH[i]	2.9	$[(n\text{-}C_4H_9)_2(CH_3)Sn]_2O$	8.4	99

[a] Table III lists distillation ranges and properties. [b] Use of 1.1 l. of 1.3 *M* Grignard reagent, an excess. Later processing included shaking with excess sodium hydroxide solution. [c] Gradual addition of perfluoroacid over 3 hr. at 45–50°. [d] Reaction also furnished higher and lower boiling liquid fractions. [e] See Experimental for later treatment with 1.6 g. more of perfluoroacid. [f] Experimental section lists further purification. [g] Gradual addition of iodine over 40 min. at 50–60° on a hot plate, with agitation but no solvent. [h] A known compound—see ref. 5—not obtained pure, but later converted to the corresponding organotin oxide. The crude iodide boiled at 70–75° under 1 mm. pressure and had 32.5% iodine. [i] One hr. of shaking with 12 ml. of 6 *M* aqueous sodium hydroxide, then centrifuging, washing with a little bromoethane, and finally distillation. [j] Same process as previous sentence, with 16 ml. of base. [k] Some higher boiling liquid and solid accompanied each preparation. [l] Constant agitation at 0°. Two hr. constant, slow addition of bromine dissolved in 18 g. of bromoethane. Some dark colored solid formed. Reaction in very weak daylight.

TABLE III

PROPERTIES OF NEW COMPOUNDS

Compound	B.p.	d^{20}_4	n^{20}[a]	Mol. refr.		Tin[b]		OCOR or Halogen,[c] %		Distilled at	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	B.p.	mm.
$(n\text{-}C_5H_{11})_2(CH_3)SnI$	289[d]	1.502	1.5295	82.67	82.81	29.5	29.6	31.5	31.5	112–114	1
$(n\text{-}C_5H_{11})_2(CH_3)SnOCOCF_3$	265	1.324	1.4551	80.33	79.55	30.5	30.4	29.1	29.0	106–108	1
$(n\text{-}C_5H_{11})_2(CH_3)SnOCOC_2F_5$	268	1.360	1.4376	85.33	84.68	27.0	27.0	37.1	37.2	109–111	1
$n\text{-}C_5H_{11}(CH_3)_2SnOCOC_2F_5$	229	1.485	1.4281	66.74	66.36	31.0	30.7	42.6	42.6	85–86	1
$(n\text{-}C_5H_{11})_3SnOCOC_2F_5$	291[d,e]	...	...	103.92	...	24.0	24.0	32.9	33.1	143–147[e]	1
$[(n\text{-}C_5H_{11})_2(CH_3)Sn]_2O$	340[d]	1.193	1.4855	137.18	136.31	41.8	41.6	...[f]	...	170–172	1
$[n\text{-}C_5H_{11}(CH_3)_2Sn]_2O$	277[d]	1.317	1.4867	99.99	99.49	52.1	52.0	...[g]	...	107–109	1
$(n\text{-}C_5H_{11})_2(CH_3)_2Sn$	242	1.098	1.4676	73.30	73.66	40.8	40.9	...[h]	...	68–70	1
$(n\text{-}C_4H_9)_2(CH_3)SnBr$	257	1.447	1.5083	67.45	67.58	36.2	36.0	24.4	24.5	102–103	1
$n\text{-}C_4H_9(CH_3)_2SnOCOCF_3$	219	1.487	1.4465	57.10	57.25	37.2	37.0	35.4	35.2	78–79	1
$n\text{-}C_4H_9(CH_3)_2SnOCOC_2F_5$	224	1.520	1.4257	62.10	62.15	32.2	32.3	44.2	44.3	82–83	1
$n\text{-}C_4H_9(CH_3)_2SnOCO\text{-}n\text{-}C_3H_7$	230	1.552	1.4125	67.09	67.28	28.3	28.1	50.9	50.8	89–91	1
$[(n\text{-}C_4H_9)_2(CH_3)Sn]_2O$	321[d]	1.251	1.4868	118.54	117.65	46.4	46.5	...[i]	...	135–137	1
$(C_2H_5)_2Sn(OCOCF_3)_2$	213[j]	...	...	...	...	...	...	56.2[k]	55.6	...	..

[a] In white light, ±0.0010. [b] Conversion to stannic oxide using fuming nitric and sulfuric acids. [c] Halogen or acid titrating with sodium hydroxide in absolute ethanol, using cresol red indicator. [d] Decomposed during measurement of normal b.p. Some white solids formed with Sn–O–Sn compounds. [e] M.p. of tri-*n*-amyltin pentafluoropropionate was 49°; Experimental describes purification. [f] Also, Calcd.: mol. wt., 568.0. Found: mol. wt. (camphor), 500. [g] Also, Calcd.: mol. wt., 455.8. Found: mol. wt. (camphor), 430. [h] Also, Calcd.: mol. wt., 291.1; C, 49.52; H, 9.70. Found: mol. wt. (camphor), 303; C, 49.73; H 10.05. [i] Also, Calcd.: mol. wt., 511.9. Found: mol. wt. (camphor), 470. [j] M.p. of diethyltin bis-(trifluoroacetate) was 153°. [k] Also, Calcd.: mol. wt., 402.9. Found: mol. wt. (camphor), 380.

a high concentration of the excess of substituted tetraalkyltin; as low a temperature as feasible; also, a relatively small attacking element or compound—bromine preferable to iodine and trifluoroacetic acid preferable to pentafluoropropionic acid or much preferable to heptafluoro-*n*-butyric acid.

Partial dealkylation of tetraethyltin requires precautions comparable to those in the paragraph above, except the last. Table I includes the nontypical replacement of two ethyl groups in tetraethyltin using the vigorous ionic reagents silver chloride or silver trifluoroacetate, while much less ionic trifluoroacetic acid replaces only one ethyl group.

A new modification in the first five reactions listed in Table I involves the reaction between tetraethyltin and SnX_2, in which X is halogen or carboxylate, instead of the well known reaction between tetraethyltin and tin(IV) chloride. All five reactions furnish triethyltin derivatives without diethyltin derivatives, typically $2(C_2H_5)_4Sn$ (reducing agent) + $SnCl_2$ (oxidizing agent) = $2(C_2H_5)_3SnCl + Sn + C_4H_{10}$. This reaction does not form the compound diethyltin dichloride, in which the electron attraction of the chlorine is much stronger than the electron release of the ethyl group; thus the electronic structure of diethyltin dichloride corresponds closely to that of tin(II) chloride. Moreover, the formation of $(C_2H_5)_3Sn^{\delta+}Cl^{\delta-}$ involves only the first ionization potential of tin, while the unobserved formation of $(C_2H_5)_2Sn^{\delta+2}Cl^{\delta-2}$ would involve the considerably higher second ionization potential of tin.[9] An equivalent conductivity—with pure, undiluted compound at[12] the melting point—of only 21.9 for tin(II) chloride compared with 133.5 for sodium chloride justified only a partial charge on tin(II) chloride, such as $Sn^{\delta+2}Cl_2^{\delta-2}$ or possibly $ClSn^+Cl^-$. Numerous reactions of the related dimethyltin dichloride in aqueous solution suggest that the compound resembles tin(II) chloride rather than tin(IV) chloride.[13] Partial hydrolysis of di-*n*-butyltin dichloride gives the compound[14] $(n\text{-}C_4H_9)_2(Cl)SnOSn(Cl)(n\text{-}C_4H_9)_2$ and hydrochloric acid, with indication of an intermediate $(n\text{-}C_4H_9)_2Sn(Cl)OH$. For these reasons tin(II) chloride should convert tetraethyltin into triethyltin chloride, as observed, and not into the undetected diethyltin dichloride, which is comparable with tin(II) chloride itself.

Calculated molar refractions[11,15] involve an average error of 0.48%. The bond refraction Sn–O may be a little high at 3.84.[15]

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Table II shows a 9% yield of tri-*n*-amyltin pentafluoropropionate from di-*n*-amyldimethyltin and pentafluoropropionic acid; possible explanations include a free radical mechanism or a redistribution reaction.[16]

Experimental

Table I lists 18 reactions of tetraethyltin and a median yield of 60%, in reflux through electrical heating. Purifications of organotin products included several fractional distillations in small or very small equipment, or four double crystallizations from carbon tetrachloride. Tetraethyltin reacted not at all or very slowly with tin(II) fluoride or benzoate, acetyl chloride, ethyltrichlorosilane, phosphorus trichloride, mercuric oxide, copper(I) iodide, thallium(I) formate, silver oxide, silver thiocyanate, or silver iodide.

Known boiling points for the chief organotin products in Table I include[17]: triethyltin chloride, 210°; triethyltin bromide, 224°; triethyltin iodide, 234°; triethyltin acetate, 224° (m.p., 132–134°)[8]; triethyltin trifluoroacetate, 218° (m.p., 122–123°)[8]; diethyltin dichloride, 220° (m.p., 84°).

Seven dealkylations in Table II involve difficult purifications for four reasons: simultaneous removal of one methyl group and either one *n*-amyl or one *n*-butyl group; persistent retention of a little perfluoroacid or hydrogen halide, later removed by vigorous shaking once or twice with a double volume of water for 1 hr.; some free radical reaction or redistribution reaction at least in the formation of tri-*n*-amyltin pentafluoropropionate; also, the presence of dark solid residues.

Gradual addition of pentafluoropropionic acid to di-*n*-amyldimethyltin required a temperature of 45–50° to obtain a single phase. After the reaction, fractional distillation under 1 mm. pressure furnished the following: 11 g. of *n*-amyldimethyltin pentafluoropropionate, with some unchanged di-*n*-amyldimethyltin, mainly at 90° (found: $OCOC_2F_5$, 34.0); 14 g. of di-*n*-amylmethyltin pentafluoropropionate, b.p. mainly 112°, later extracted with water and redistilled to get a 5-g. pure center cut; 10 g. of high cut, b.p. approximately 140°; also, 2 g. of residue later discarded. Two hr. storage of the 11-g. low cut with an extra 1.6 g. of pentafluoropropionic acid at 50°, next extraction with water, and finally two distillations furnished 3.6 g. of center cut *n*-amyldimethyltin pentafluoropropionate. Repeated distillation of the high cut at 1 mm. furnished 4 g. of solid admixed with a little liquid, later pipetted off. Then followed four careful fractional freezings, next crystallization from *n*-butyl chloride, then pressing dry on filter paper, and finally storage in a desiccator; 1.1 g.of solid tri-*n*-amyltin pentafluoropropionate resulted. Determinations of both m.p. and b.p. were in capillaries.

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The Reaction of Carbon Disulfide with Organotin Oxides and Related Substances

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When bis-(triphenyltin) oxide is heated with carbon disulfide or carbon oxysulfide, the oxygen is quantitatively replaced by sulfur, yielding pure bis-(triphenyltin) sulfide and carbon oxysulfide and/or carbon dioxide. Similar tin, lead, mercury, and arsenic metalorganic compounds having metal–oxygen–metal or metal–hydroxide bonds also undergo this reaction with carbon disulfide to yield sulfides. Analogous phosphorus, germanium, silicon, and boron compounds do not exchange oxygen for sulfur when heated with carbon disulfide.

Introduction

It has been observed that the largely insoluble polydialkyltin oxides[1] dissolve in hot carbon disulfide to yield clear solutions. A closer examination of these solutions showed that the organotin oxygen atoms had been quantitatively replaced by sulfur atoms.

$$[R_2SnO]_n + CS_2 \longrightarrow COS + [R_2SnS]_3$$

Since the yields and product purities appeared high and the reaction conditions fairly mild, it was decided to examine the scope of this reaction using other oxygen-containing metalorganic compounds. These sulfur-containing products have been prepared previously by other methods.

Results

Table I gives the products and yields of twelve organometallic compounds which were found to

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