[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DREXEL INSTITUTE OF TECHNOLOGY]

Reactions of Tetra-*n*-propyltin and Tetraisopropyltin with Organic Acids[1]

GEORGE S. SASIN, ALAN L. BORROR, AND RICHARD SASIN

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The cleavage of tetra-*n*-propyltin and tetraisopropyltin by halo acids and mercaptans was studied. With tetra-*n*-propyltin one alkyl group was cleaved and the corresponding trialkyltin ester or mercaptide was formed. Mercaptans also cleaved one alkyl group from tetraisopropyltin, but with the halo acids two alkyl groups were cleaved and the corresponding dialkyl diesters were formed. The relative rate of cleavage of tetraalkyltin by acidic compounds is in the order: halo acids > arylthiols > alkane thiols. Eleven previously unreported organotin compounds were prepared.

This paper reports the cleavage of *n*-propyl and isopropyl groups from the tetra-*n*-propyltin and tetraisopropyltin by organic acids whose ionization constants range between 10^{-1} and 10^{-10}. This investigation is a continuation of work previously carried out in this laboratory.[2]

Previous to this study, a cleavage reaction of tetra-*n*-propyltin was reported with stannic chloride.[3] Apparently no cleavage reactions of tetraisopropyltin have been reported in the literature.

One propyl group was cleaved from tetra-*n*-propyltin and tetraisopropyltin with the gradual addition of mercaptans to form the corresponding tripropyltin mercaptides. As in the case of tetraethyltin, aryl mercaptans reacted more readily than aliphatic mercaptans. Reaction of tetra-*n*-propyltin with chloroacetic and dichloroacetic acids also cleaved one propyl group and formed the corresponding tri-*n*-propyltin ester. The halo acids reacted more readily than the mercaptan probably because they are stronger acids.

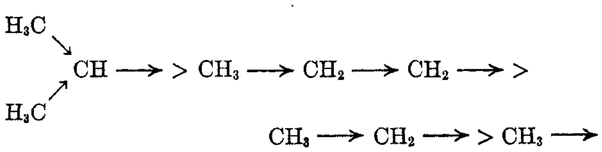
$$(C_3H_7)_4Sn + RSH \longrightarrow (C_3H_7)_3SnSR + C_3H_8\uparrow$$

$$(n\text{-}C_3H_7)_4Sn + ClCH_2COOH \longrightarrow (n\text{-}C_3H_7)_3SnO_2CCH_2Cl + C_3H_8\uparrow$$

A comparison of the yields (Table I) shows that the halo acids reacted most readily, followed by the aryl mercaptans, and the aliphatic mercaptans gave the lowest yields. Actually, the results obtained cannot be used in an absolute sense, but must be used as comparative values.

Chloroacetic and dichloroacetic acids cleaved two propyl groups from tetraisopropyltin to form the corresponding diisopropyltin diesters. A possible explanation for the cleavage of two propyl groups lies in the difference in the inductive effects of the alkyl groups. It is generally agreed that the inductive effects of alkyl groups decrease in the following order:

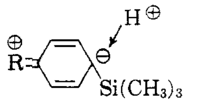
$$(i\text{-}C_3H_7)_4Sn + ClCH_2COOH \longrightarrow (i\text{-}C_3H_7)_2Sn(O_2CCH_2Cl)_2 + 2C_3H_6\uparrow$$



$$(H_3C)_2CH \longrightarrow\ > CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow\ > CH_3 \longrightarrow CH_2 \longrightarrow\ > CH_3 \longrightarrow$$

Since the isopropyl groups exert a stronger inductive effect than the *n*-propyl groups, there is a higher electron density on the carbon atom of the carbon-tin bond in tetraisopropyltin than in tetra-*n*-propyltin. Only one propyl group is cleaved by halo acids in the tetra-*n*-propyltin because the electron release effect of the three remaining *n*-propyl groups is balanced by the electron withdrawing effect of the haloacyloxy group. On the other hand, the isopropyl groups exert a stronger electron release effect than the *n*-propyl groups and two haloacyloxy groups are necessary to prevent further cleavage in tetraisopropyltin.

A very similar reaction scheme was proposed by Benkeser and Krysiak[4] for the hydrogen chloride cleavage of a series of trimethylarylsilanes. They assumed a proton attack on the carbon atom of the carbon-silicon bond and concluded that the cleavage of an aryl group from silicon is facilitated by the introduction of a substituent capable of furnishing a high electron density at the aromatic carbon-silicon bond.



A similar electrophilic attack has been proposed for the cleavage of trialkylphenyltin compounds with silver nitrate.[5] In this case, the inductive effect of the alkyl groups exerts a high electron density on the carbon atom of the phenyl group which is attached to the tin atom and thus promotes the approach of the silver ion.

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[1] From a thesis submitted by Alan L. Borror to the Department of Chemistry of the Drexel Institute of Technology in partial fulfillment of the requirements for the degree of Bachelor of Science.

[2] R. Sasin and G. S. Sasin, *J. Org. Chem.*, 20, 770 (1955).

[3] J. G. A. Luijten and G. J. M. Van Der Kerk, *Investigations in the Field of Organotin Chemistry*, Tin Research Institute, Middlesex, England, 1955, page 104.

[4] R. A. Benkeser and J. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 4528 (1953).

[5] M. Lesbre, R. Buisson, J. G. S. Luijten, and G. J. M. Van Der Kerk, *Rec. trav. chim.*, **74**, 1056 (1955).

TABLE I
CLEAVAGE REACTIONS

Reagent	Product	Time, Hr.	Yield, %
	Tetra-*n*-Propyltin		
CH_2ClCO_2H	*n*-$Pr_3SnO_2CCH_2Cl$	0.5	35
$CHCl_2CO_2H$	*n*-$Pr_3SnO_2CCHCl_2$	0.5	39
C_6H_5SH	*n*-$Pr_3SnSC_6H_5$	3	30
p-$CH_3C_6H_4SH$	*n*-Pr_3SnS(*p*-$C_6H_4CH_3$)	3	34
o-$CH_3C_6H_4SH$	*n*-Pr_3SnS(*o*-$C_6H_4CH_3$)	3	30
$C_6H_5CH_2SH$	*n*-$Pr_3SnSCH_2C_6H_5$	3	22
$CH_3(CH_2)_6SH$	*n*-$Pr_3SnS(CH_2)_6CH_3$	4	13
$CH_3(CH_2)_9SH$	*n*-$Pr_3SnS(CH_2)_9CH_3$	4	12
	Tetra-*i*-Propyltin		
CH_2ClCO_2H	*i*-$Pr_2Sn(O_2CCH_2Cl)_2$	0.5	47
$CHCl_2CO_2H$	*i*-$Pr_2Sn(O_2CCHCl_2)_2$	0.5	51
C_6H_5SH	*i*-$Pr_3SnSC_6H_5$	3	31
p-$CH_3C_6H_4SH$	*i*-Pr_3SnS(*p*-$C_6H_4CH_3$)	3	45
$C_6H_5CH_2SH$	*i*-$Pr_3SnSCH_2C_6H_5$	3	33
$CH_3(CH_2)_6SH$	*i*-$Pr_3SnS(CH_2)_6CH_3$	4	16
$CH_3(CH_2)_9SH$	*i*-$Pr_3SnS(CH_2)_9CH_3$	4	12

The cleavage reactions of tetra-*n*-propyltin and tetraisopropyltin, the yields obtained, and the length of time of heating are listed in Table I. The physical constants and analyses of the trialkyltin esters and mercaptides and the dialkyltin diesters are summarized in Table II.

TABLE II

Compound	B.P. (1 Mm.)	M.P., °C.	d_4^{20}	n^{20}	Analyses Mol. Wt.[a] Calcd.	Analyses Mol. Wt.[a] Found	Analyses Sulfur Calcd.	Analyses Sulfur Found	Analyses Tin Calcd.	Analyses Tin Found
				n-Propyltin Esters and Mercaptides						
n-$Pr_3SnO_2CCH_2Cl^b$	135–140	78–79	—	—	341	326	—	—	34.7	34.8
n-$Pr_3SnO_2CCHCl_2{}^c$	—	83–84	—	—	375	357	—	—	31.6	31.3
n-$Pr_3SnS(pC_6H_4CH_3)$	159–160	—	1.2127	1.5602	371	394	8.64	8.52	—	—
n-$Pr_3SnSCH_2C_6H_5$	165–167	—	1.2318	1.5558	371	364	8.64	8.68	—	—
n-$Pr_3SnS(CH_2)_6CH_3$	158–160	—	1.1033	1.4981	379	368	8.46	8.52	—	—
n-$Pr_3SnS(CH_2)_9CH_3$	180–183	—	1.0688	1.4998	421	436	7.61	7.39	—	—
				iso-Propyltin Esters and Mercaptides						
i-$Pr_2Sn(O_2CCH_2Cl)_2$	—	54–55	—	—	389	396	—	—	30.4	30.0
i-$Pr_2Sn(O_2CCHCl_2)_2$	—	69–71	—	—	461	467	—	—	25.4	26.6
i-$Pr_3SnSC_6H_5$	138–139	—	1.2327	1.5676	357	366	8.96	8.85	—	—
i-$Pr_3SnS(pC_6H_4CH_3)$	157–158	—	1.2191	1.5648	371	363	8.64	8.76	—	—
i-$Pr_3SnSCH_2C_6H_5$	167–170	—	1.2053	1.5497	371	386	8.64	8.58	—	—
i-$Pr_3SnS(CH_2)_6CH_3$	155–157	—	1.0940	1.5045	379	388	8.46	8.37	—	—
i-$Pr_3SnS(CH_2)_9CH_3$	192–195	—	1.0494	1.5010	421	452	7.61	7.58	—	—

[a] Molecular weights in camphor solution. [b,c] Ref. [6] reports m.p. 78–80° and 84–85°, respectively.

EXPERIMENTAL

All melting points are uncorrected.

Tetra-n-propyltin and tetraisopropyltin. To 390 g. (1.5 moles) of stannic chloride dissolved in 500 ml. of dry benzene immersed in an ice water bath were added over a period of 3 hr., with occasional shaking, 3 liters of 1.5 *molar* *n*-propyl– or isopropyl–magnesium chloride. The reaction mixture was allowed to stand overnight and the unchanged Grignard reagent was decomposed by the gradual addition of water. The organotin layer was separated and shaken with 400 ml. of 3*M* sodium hydroxide solution. The ether-benzene layer was separated from the aqueous layer, and the aqueous layer was extracted with 400 ml. of hexane. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed by distillation. The residue on distillation under diminished pressure yielded 104 g. (24%) of tetra-*n*-propyltin boiling at 110–111° at 10 mm. Luijten and Van Der Kerk report a boiling point of 108–109° at 11 mm.[5] The yield of tetraisopropyltin, boiling at 103–104° at 10 mm. was 98 g. or 22.6% of the theoretical amount. The reported boiling point of this compound is 106° at 12 mm.[5]

Cleavage reactions. Tri-n-propyltin phenyl mercaptide, benzyl mercaptide, p-tolyl mercaptide, heptyl mercaptide, and decyl mercaptide. Triisopropyltin phenyl mercaptide, benzyl mercaptide, p-tolyl mercaptide, heptyl mercaptide, and decyl mercaptide. A *one-molar* proportion of the appropriate mercaptan was added to 5.8 g. (0.02 mole) of tetra-*n*-propyltin or tetraisopropyltin in approximately three equal portions over a period of 2 hr. with intermittent reflux. The reaction mixture then was boiled under gentle reflux for an additional 1 or 2 hr. (Table I). After removal of the unchanged reactants by distillation, the mercaptides were distilled under diminished pressure.

Tri-n-propyltin monochloroacetate. To 5.8 g. (0.02 mole) of tetra-*n*-propyltin was added 1.71 g. (0.02 mole) chloroacetic acid in approximately three equal portions over a period of 15 min. The unchanged reactants were removed by distillation under diminished pressure and the ester then was distilled under diminished pressure. The resulting solid was found to melt at 69–70°. By repeated recrystallization from petroleum ether, the melting point was raised to 69.5–70.5°.

Tri-n-propyltin dichloroacetate, diisopropyltin di-monochloroacetate, and diisopropyltin di-dichloroacetate. To 5.8 g (0.02 mole) of tetra-*n*-propyltin or tetraisopropyltin was added a one-*molar* proportion of the appropriate acid in approximately three equal portions over a period of 15 min. with intermittent reflux. The reaction mixture then was boiled under gentle reflux for an additional 15 min. The solid which resulted on cooling was crystallized repeatedly from petroleum ether until there was no increase in the melting point.

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(6) A. Saitow, E. G. Rochow, and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).