[Contribution from the Department of Chemistry, Drexel Institule of Technology]

REACTIONS OF TETRAETHYLTIN WITH ORGANIC ACIDS

RICHARD SASIN and GEORGE S. SASIN

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This paper reports the cleavage of ethyl groups from tetraethyltin by organic acids whose ionization constants range between 10^{-1} and 10^{-10}.

Previous to this study, cleavage reactions of tetraethyltin were reported with halogens, halogen acids, and alkyl halides (1), stannic chloride (2), sodium in liquid ammonia (3), aluminum and ferric chloride (4), bismuth trichloride (5), and trichloroacetic acid (6). Cleavage of tetraphenyltin was effected by acyl halides (7). No systematic study, however, of cleavage reactions of tetraethyltin has been made with a series of organic acids of different strengths.

One ethyl group was cleaved from tetraethyltin by heating tetraethyltin under reflux with the gradual addition of organic acids for a period of time ranging between one-half hour to six hours. Tetraethyltin reacted with monochloro-, dichloro-, and trifluoro-acetic and -benzoic acids to form triethyltin esters, with mercaptans to form triethyltin mercaptides, and with phenol and *p*-cresol to form triethyltin phenoxides. Reaction times, products formed, and the yields obtained are given in Table I. Tetraethyltin reacts most readily with halo acids and least readily with phenols. Aryl mercaptans cleave the ethyl group from tetraethyltin more readily than aliphatic mercaptans. Tetraethyltin reacted with acetic, propionic, and butyric acids, but the yields were low, and insufficient quantities of products were obtained for their purification. Gilman and Nelson (8) obtained similar results with triphenylbismuth.

The yields of products in all cases, with the exception of halo esters were low, and in general, the cleavage of an alkyl group from tetralkyltin cannot be recommended as a preparative method for trialkyltin derivatives of weak organic acids. A further study of trialkyltin halo esters is being conducted in this laboratory.

EXPERIMENTAL

Tetraethyltin. To 250 g. (0.95 mole) of stannic chloride dissolved in 500 ml. of dry benzene immersed in an ice-water bath were added over a period of three hours, with occasional shaking, 2.75 liters of 1.7 *molar* ethylmagnesium bromide. The reaction mixture was allowed to stand overnight. After gradual aqueous decomposition of the unchanged ethylmagnesium bromide, the organotin layer was separated and shaken with 400 ml. of 3 *molar* 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 then were dried over sodium sulfate and the solvent was removed by distillation. Distillation under atmospheric pressure yielded 64 g. of crude tetraethyltin at 170 to 200°. Redistillation of this fraction under atmospheric pressure yielded 52 g. of tetraethyltin boiling at 181–182°. The reported boiling point under atmospheric pressure is 175° (9).

CLEAVAGE REACTIONS

Triethyltin trifluoroacetate, monochloroacetate, dichloroacetate. To 4.7 g. (0.02 mole) of tetraethyltin was added a one *molar* proportion of the appropriate acid in approximately

TABLE I

CLEAVAGE REACTIONS OF TETRAETHYLTIN

Reagent	Product	Time Hours	Yield, %
$CHCl_2CO_2H$	$(C_2H_5)_3Sn(CHCl_2COO)$[a]	0.5	60
CF_3CO_2H	$(C_2H_5)_3Sn(CF_3COO)$	.5	59
CH_2ClCO_2H	$(C_2H_5)_3Sn(CH_2ClCOO)$[a]	.5	55
β-$C_{10}H_7SH$	$(C_2H_5)_3Sn(\beta\text{-}C_{10}H_7S)$[a]	1.5	40
p-$CH_3C_6H_4SH$	$(C_2H_5)_3Sn(p\text{-}CH_3C_6H_4S)$	1.5	40
$C_6H_5CH_2SH$	$(C_2H_5)_3Sn(C_6H_5CH_2S)$	1.5	39
C_6H_5SH	$(C_2H_5)_3Sn(C_6H_5S)$[a]	1.5	38
o-$CH_3C_6H_4SH$	$(C_2H_5)_3Sn(o\text{-}CH_3C_6H_4S)$	1.5	30
$C_6H_5CO_2H$	$(C_2H_5)_3Sn(C_6H_5COO)$	3.0	18
$CH_3(CH_2)_6SH$	$(C_2H_5)_3Sn[CH_3(CH_2)_6S]$[a]	5.0	19
$CH_3(CH_2)_5SH$	$(C_2H_5)_3Sn[CH_3(CH_2)_5S]$[a]	5.0	8
C_6H_5OH	$(C_2H_5)_3Sn(C_6H_5O)$	6.0	8
p-$CH_3C_6H_4OH$	$(C_2H_5)_3Sn(p\text{-}CH_3C_6H_4O)$	6.0	8

[a] Previously unreported compound.

three equal portions over a period of 15 minutes. The mixture was boiled under gentle reflux for an additional 15 minutes. The unchanged reactants were removed by distillation under diminished pressure, and the esters then were distilled under diminished pressure.

Triethyltin trifluoroacetate. Tetraethyltin and trifluoroacetic acid yielded 3.7 g. (59%) of triethyltin trifluoroacetate boiling at 218° at 760 mm. and melting at 112°. By repeated recrystallization from petroleum ether, the melting point was raised to 122–123°. The reported melting point is 107° and the reported boiling point is 218° (10).

Anal. Calc'd for $C_8H_{15}F_3O_2Sn$: Sn, 37.2. Found: Sn, 37.0.

Triethyltin monochloroacetate. Tetraethyltin and chloroacetic acid yielded 3.3 g. or 55% of triethyltin monochloroacetate, boiling at 118–119° under 1 mm. pressure and melting at 106–107°. By repeated recrystallization from petroleum ether, the melting point was raised to 111–112°.

Anal. Calc'd for $C_8H_{17}ClO_2Sn$: Sn, 39.7; Mol. wt., 299.4.
Found: Sn, 40.1; Mol. wt., 304.

Triethyltin dichloroacetate. Tetraethyltin and dichloroacetic acid yielded 4 g. or 60% of triethyltin dichloroacetate boiling at 121–123° at 1 mm. and melting at 121–122°. By repeated recrystallization from petroleum ether, the melting point was raised to 132–133°.

Anal. Calc'd for $C_8H_{16}Cl_2O_2Sn$: Sn, 35.5; Mol. wt., 333.9.
Found: Sn. 35.8; Mol. wt., 326.

Triethyltin phenyl mercaptide, benzyl mercaptide, o-tolyl mercaptide, p-tolyl mercaptide and β-naphthyl mercaptide. To 4.7 g. (0.02 mole) of tetraethyltin was added a one *molar* proportion of the mercaptan in approximately three equal portions over a period of one hour with intermittent reflux. The reaction mixture then was boiled under gentle reflux for an additional one-half hour. After removal of the unchanged reactants by distillation, the mercaptides were distilled under diminished pressure.

Triethyltin phenyl mercaptide. Tetraethyltin and phenyl mercaptan yielded 2.4 g. or 38% of triethyltin phenyl mercaptide boiling at 138–140° under 1 mm. pressure. The refractive index at 20° was found to be 1.5828 and d_4^{20} 1.3163.

Anal. Calc'd for $C_{12}H_{20}SSn$: S, 10.15; Mol. wt., 315.
Found: S, 10.10, 10.16; Mol. wt., 334.

Triethyltin benzyl mercaptide. Tetraethyltin and benzyl mercaptan yielded 1.2 g. or 39% of triethyltin benzyl mercaptide boiling at 138–140° at 1 mm. pressure. The index of refraction was found to be 1.5675 at 20°. The reported boiling point at 1 mm. and the index of refraction for this compound are 136–138° and 1.5682 respectively (10).

Anal. Calc'd for $C_{13}H_{22}SSn$: S, 9.73. Found: S, 9.47.

Triethyltin p-tolyl mercaptide. Tetraethyltin and *p*-tolyl mercaptan yielded 2.6 g. or 40% of triethyltin *p*-tolyl mercaptide boiling at 129–132° at 1 mm. The reported boiling point for this compound is 128–130° at 1 mm. (10).

Anal. Calc'd for $C_{13}H_{22}SSn$: S, 9.73. Found: S, 9.77.

Triethyltin o-tolyl mercaptide. Tetraethyltin and *o*-tolyl mercaptan yielded 2.0 g. or 30% of triethyltin *o*-tolyl mercaptide boiling at 132–136° at 1 mm. The index of refraction was found to be 1.5720 at 20°. The reported boiling point at 1 mm. and the index of refraction for this compound are 132–135° and 1.5740 respectively (10).

Anal. Calc'd for $C_{13}H_{22}SSn$: S, 9.73. Found: S, 9.58.

Triethyltin β-naphthyl mercaptide. Tetraethyltin and β-naphthyl mercaptan yielded 2.93 g. or 40% of triethyltin β-naphthyl mercaptide boiling at 189–190° under 1 mm. pressure. The density of this compound was found to be 1.3231 and the index of refraction was 1.5308, both of which were measured at 20°.

Anal. Calc'd for $C_{16}H_{22}SSn$: S, 8.77; Mol. wt., 365.1.
Found: S, 8.75, 8.81; Mol. wt., 361.

Triethyltin heptyl mercaptide and hexyl mercaptide. A one *molar* proportion of the appropriate mercaptan was added to 11.75 g. (0.05 mole) of tetraethyltin in approximately three equal portions over a period of two hours with intermittent reflux. The reaction mixture was boiled under reflux for an additional 3 hours. After removal of the unchanged reactants by distillation, the mercaptides were distilled under diminished pressure.

Triethyltin n-hexyl mercaptide. Tetraethyltin and *n*-hexyl mercaptan yielded 1.2 g. or 8% of triethyltin *n*-hexyl mercaptide boiling at 126–127° under 1 mm. pressure. The index of refraction was found to be 1.5032 and the density was found to be 1.1668, both being measured at 20°.

Anal. Calc'd for $C_{12}H_{28}SSn$: S, 9.88; Mol. wt., 324.1.
Found: S, 10.09, 10.17; Mol. wt., 329.

Triethyltin n-heptyl mercaptide. Tetraethyltin and *n*-heptyl mercaptan yielded 3.2 g. or 19% of triethyltin *n*-heptyl mercaptide boiling at 134–135° at 1 mm. d_4^{20} 1.1473; n^{20} 1.5006.

Anal. Calc'd for $C_{13}H_{30}SSn$: S, 9.47; Mol. wt., 338.1.
Found: S, 9.65, 9.68; Mol. wt., 329.

Triethyltin benzoate. To 4.7 g. (0.02 mole) of tetraethyltin was added in approximately three equal portions over a period of 1½ hours with intermittent reflux 2.44 g. (0.02 mole) of benzoic acid. The reaction mixture then was boiled under gentle reflux for an additional 1½ hours. The yield of product boiling at 133–134° at 1 mm. was 1.2 g. or 18%. The melting point was found to be 72°. By repeated recrystallization from petroleum ether, the melting point was raised to 80°. The reported constants for this compound are: boiling point at 1 mm., 132–134°; (10) melting point, 80° (11).

Triethyltin phenoxide and p-cresoxide. To 4.7 g. (0.02 mole) of tetraethyltin was added a one *molar* proportion of the appropriate phenol in approximately three equal portions over a period of three hours with intermittent reflux. The reaction mixture then was boiled under gentle reflux for an additional three hours. After removal of the unchanged reactants by distillation, the phenoxides were distilled under diminished pressure.

Triethyltin phenoxide. Tetraethyltin and phenol yielded 0.5 g. or 8% of triethyltin phenoxide boiling at 115° at 1 mm. The index of refraction was found to be 1.5415 at 20°. The reported constants for this compound are: boiling point at 1 mm., 115–116°; n^{20} 1.5422 (10).

Triethyltin p-cresoxide. Tetraethyltin and *p*-cresol yielded 0.5 g. or 8% of triethyltin *p*-cresoxide boiling at 124–126° at 1 mm. The index of refraction was found to be 1.5360 at 20°. The reported constants for this compound are: boiling point at 1 mm., 124–127°; n^{20} 1.5365 (10).

SUMMARY

1. Cleavage reactions of tetraethyltin were studied.

2. The following previously unreported compounds were prepared: triethyltin monochloroacetate, dichloroacetate, β-naphthyl mercaptide, phenyl mercaptide, *n*-heptyl mercaptide, and *n*-hexyl mercaptide.

PHILADELPHIA 4, PENNSYLVANIA

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